# RAW MATERIALS

## RESEARCH AND DEVELOPMENT

DOSSIERS, no. II

# II. LEAD AND ZINC

## VOLUME ONE and two

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MAIN CONTENTS OF THE DOSSIER

# DOSSIER ON LEAD AND ZINC

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# F O R E W O R D

This "dossier" on lead and zinc is part of a series of tech-
nico-economic studies that have been prepared under the sponsorship of
the "Commission of the European Communities" (Directorate-General for
Research, Science and Education) on some of the most critical mineral
commodities.

The decision to carry out those studies, as well as other
work to be published under the general heading "Raw Materials
Research and Development", results from current concern about prospects
of supplying the European Community with raw materials in sufficient
quantities and at acceptable costs in the mid- to long-term.
An essential part in defining the purpose and scope of the dossiers was
played by a Sub-Committee of CREST[1] established to investigate on-
going activities in the member states, both in the areas of primary
and secondary raw materials, in order to determine what R & D actions,
if any, should be undertaken by the Community to alleviate its supply
problems.

The dossier was prepared under contracts signed between the
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1) Service géologique de Belgique, Brussels. Contract n° 262-76-ECI-B.

2) Bureau de Recherches géologiques et minières (B.R.G.M.), Paris.
   Contract n° 265-76-ECI-F.

3) Institute for Industrial Research and Standards (I.I.R.S.), Dublin.
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[1]
   Set up by the Resolution of the Council of Ministers of the European
   Communities of 14 January 1974, the Scientific and Technical Research
   Committee (CREST) is responsible for assisting the Community
   Institutions in the field of scientific research and technological
   development.

4) ITALMINIERE S.p.A. (now A.M.M.I. S.p.A.), Rome.
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# I

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Paul BARTHOLOME est décédé le 14 mars 1978, des suites d'une cruelle maladie supportée avec un courage admirable.

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# S U M M A R Y

Drafted by the Commission Services

Does not include the chapter óf Recommendations for R and D actions

# VI

## PART ONE : STRUCTURE OF SUPPLY

### 1.1 GEOLOGY AND PROSPECTING

The introductory chapter (11.1) provides a detailed review of lead-zinc ores, including data on associated minerals and by-products (fluorite, barite,...) and a list of currently mined grades in EC countries.

Chapter 11.2 ,by far the largest in the whole dossier, describes the deposits of the EC. Along with the descriptions, data are provided whenever available on past and present output of individual mines, composition of concentrates, grades, reserves ...

### 1) Denmark (Greenland)

Two lead-zinc districts should be mentioned. One is the Marmorilik district, about half-way up the west coast, with several high-grade ore bodies. Of these, two (Black Angel and Cover Zone) are known to contain considerable tonnages. They appear to be essentially stratabound in "metamorphosed" sediments (predominantly limestones). At the end of 1976, reserves of the Black Angel mine were estimated at 3 500 000 tons of ore (5 % Pb, 14 % Zn).

Several orebodies and prospects have been discovered in Central East Greenland, North of Scoresby Sund. Most of them are stratiform in Permian limestones and Triassic sandstones ("red beds"). Furthermore, veins exist in the pre-permian basement (Mesters Vig area). It seems safe to assume that some of these orebodies will be minable in the future.

### 2) Ireland

Important discoveries have been made in Ireland during the past 20 years : among them, Tynagh, first major deposit to be found (1961), and Navan, largest future producer of zinc in Europe and one of the largest in the world, for many years to come.

Most deposits occur in the Central Plain. Some emphasis is given in the report to geological controls of ore deposition and to guides for mineral prospecting. The major deposits are located in the vicinity of steep faults, some of which have been traced for more than 50 km and thus represent major structural features. They are bound to sedimentary strata of Lower Carboniferous age; other controls, much more speculative, have also been suggested.

The Navan deposit totals about 7 Mt Zn and 1.4 Mt Pb of proved + probable + possible reserves at one mine and 1.5 Mt combined metal at another. Production has started in June 1977 on the largest site.

The other two main deposits of the Central Plain are Silvermines (5.3 Mt of reserves, grading about 9 % metal) and Tynagh.

Entirely different types of deposits occur in the Lower Paleozoic of South-Eastern Ireland. Avoca is a volcanogenic deposit of copper-lead-zinc (mainly copper), with considerable reserves. Veins are hardly worth mentioning, owing to lack of economic importance under present conditions.

### 3) United Kingdom

Lead and zinc deposits are known in rocks of highly varied age and nature, and over a large part of the country. However, most of the production comes from districts such as the Northern Pennines, North Wales or Derbyshire, which are underlain by the Carboniferous Limestone. Although none of these known deposits happens to be very large, taken together they have supplied about 5 Mt of metal and significant amounts of associated minerals (fluorspar, barite ...). Orebodies consist in fracture-filling veins and in replacement "flats" adjoining feeding fissures. Large scale controls are partly hypothetical; local controls (faults, strata, wall-rock alteration) appear to be well understood.

Within the Lower Paleozoic of England and Wales, several districts were formerly producing lead and zinc, and occasionnally copper. Most ore bodies were veins, but the Parys Mountain deposit on the island of Anglesey belongs to the volcanogenic type and resembles Avoca in S.E. Ireland.

Finally, lead and zinc occur in the external parts of <u>tin-tungsten</u> veins connected with the Upper Paleozoic granites of Devon and Cornwall.

4) <u>France</u>

Of the four currently operated mines, two (St Salvy and Les Farges) were opened on new findings. This does suggest considerable potential in the country, still untapped.

The deposits are noteworthy for their diversity of types and for their wide range of geological settings. A selected list would include :

a) stratabound deposits in the Paleozoic of Brittany (Bodennec, La Porte aux Moines ...), of the Pyrenees and of the Montagne Noire area.

b) deposits in Mesozoic carbonates, in particular those of the Cevennes (800 000 t metal of past production + reserves, at Les Malines).

c) veins in areas of pre-Mesozoic terrane (St Salvy, about 500 000 t Zn; Les Farges, about 100 000 t Pb).

d) deposits in Permian and Triassic sandstones.

5) <u>Benelux countries</u>

All the important deposits of Belgium and most of the small ones are located in the <u>Carboniferous limestone</u>. Their geological controls resemble those of the English deposits in the Northern Pennine district. Moresnet, largest among those deposits, provides the unique instance of an entirely oxidized ore-body.

A recent discovery of stratiform barite in the Devonian of the Ardennes Massif suggests that metalliferous deposits may have remained undetected even in such an actively prospected district.

Small quantities of Zn and Pb minerals have been detected in the Dutch coal mines East of Maestricht and also at several localities in northern Luxemburg.

6) <u>German Federal Republic</u>

a) Stratabound deposits in the Paleozoic. Two of them are currently mined:at Meggen (Sauerland), reserves amount to several Mt of ore grading 12 % combined metal; at Rammelsberg (Harz), corresponding figures are 5 Mt and 20 %.

b) Mineralized veins in the Paleozoic. Two districts are specially worth mentioning :
 - N.W. Harz. Mining still goes on actively at Grund (8 Mt reserves of ore at about 10 % combined metal);
 - The Bensberg district, East of Köln, with the Lüderich mine (closed in 1978).

Other vein-type deposits and districts in the Paleozoic should be cited, despite recent closure of mines : Ramsbeck, in the Sauerland; the Ruhr area, where veins were discovered as a consequence of development work undertaken in the coal mines.

c) Miscellaneous : The Mechernich deposit in the Northern Eifel, with still considerable (100 Mt) reserves of low grade ore contained in Triassic sandstones; the Aachen-Stolberg district, notable for being the only one in the country where lead-zinc deposits are related to carbonates.

7) <u>Italy</u>

Nowadays, lead and zinc are mined in two major districts : the Southern Calcareous Alps with 3 active mines, and Sardinia with 15 active mines. In addition, some ore comes from Monteneve in the Axial metamorphic zone of the Alps and from Fenice Capanne in Tuscany.

a) <u>Mineralisation of the Southern Alps</u> is found in the Triassic limestone and dolomites, as partly stratiform, partly columnar/or vein-type ore-bodies. Largest deposits are Raibl (reserves = 4.75 Mt proven ore), and Salafossa (10 Mt of reserves).

b) <u>Sardinia</u>, a lead-zinc province of considerable past and present importance, contains several types of deposits :

Area of greatest output and potential is the _Iglesiente_ in the South-West of the island. Many deposits are associated with the Cambrian "Calcare Metallifero"; although essentially stratabound, they appear in detail as lenses, columns or shapeless masses, often controlled by folding and faulting. Oxidized ore prevails near the surface.

In the deposits of the Monteponi group (Monteponi, Campo Pisano ...), total reserves, proven and probable, approximate 10 Mt ore.

Another group, headed by the modern Masua mine, totals about 10 Mt proven ore. The San Giovani mine is also worth mentioning.

Montevacchio is a large vein-type deposit with reserves approximating 5 Mt proven + probable ore.

Finally, the Iglesiente contains a number of "complex deposits", termed as such because of mixed, intermediate typology : Buggerru, Arenas ...

Sardinian deposits other than those of the Iglesiente include veins (Sarabbus Silius in S.E. Sardinia : reserves = 10 Mt proven and probable ore) and, above all, the so-called skarn mineralization of Funtana Raminosa in Central Sardinia (reserves of Cu-Pb-Zn ore, grading a little more than 5 % combined metal : 243 000 t proven, 924 000 t probable).

c) The Alps and Tuscany are less important producers but appear to deserve further study. Both areas have vein-type deposits. Present reserves at Fenice Capanne are 900 000 t of mixed sulfides, predominantly Pb-Zn, above the water table, and significantly more below. At Campiano in Tuscany, deep drilling has recently found promising mineralization.

In conclusion to the description of deposits in the EC countries, it appears that two types of geological environments deserve special study :

- extensive sedimentary successions where limestones and dolomites prevail (carbonate sequences).

- thick and extensive marine detrital successions with locally large volcanic contributions (volcano-detrital sequences).

Each of these major geological settings is widely distributed. The former includes the Carboniferous Limestone of North-Western Europe, the Triassic and Jurassic carbonate succession of France and Italy, the Marmorilik succession in Greenland, the Cambrian carbonate succession of Sardinia ... Economic potential of this environment is illustrated by the fact that almost 20 Mt of metal have been mined or identified in the Carboniferous Limestone alone.

As regards volcano-detrital sequences, they may contain a considerable potential, largely undiscovered as yet. Particularly promising are areas in South Eastern Ireland, Brittany, Belgium, Central Germany and the Pyrenees mountains.

Chapter 11.3 deals with the use of geophysics and geochemistry in prospecting for lead and zinc. The introduction to geophysical methods provides an enlarged background to the study by listing data on worldwide expenditures according to survey type (airborne, land ...), objective (petroleum, minerals ...), area and method.

As regards lead and zinc deposits, the direct use of geophysics is seriously restricted by unfavorable properties of sphalerite, the major Zn-bearing mineral. Moreover, specific difficulties arise in carbonate environments. Rather than actually detecting ore, geophysics can help to outline promising geological structures; such an indirect approach is, however, expensive and time-consuming.

The case with geophysical methods is summarized in the report as follows : "With regard to EEC countries ... improvements of surface methods in view of detecting orebodies at greater depths ... will bring only temporary help. Improvements of surface methods in view of detecting favorable structures and environments are more promising avenues of research ... It is also recommended that a major research effort be undertaken in the field of borehole techniques".

Highlight of the report on geochemical methods is an account of exploration practice in Ireland. The statement that geochemistry is considered "mainly responsible" for the discovery of ten Irish deposits, including Navan, is worth remembering. It is suggested that, of all geochemical methods, rock geochemistry will contribute most to deep discoveries.

Future prospecting will be looking for deeper and deeper orebodies. Bearing 'this in mind, the authors of the report have found it useful to present two case histories dealing with the discovery of very large North-American deposits. It appears that the role of repeated and extensive drilling has been essential. However, the report also insists on two preliminary conditions for discovery at depth :

1) Availability of reliable models of orebodies;

2) Three-dimensional knowledge of lithology and structure of potentially promising areas.

A detailed presentation of discovery costs illustrates the need for improved and cheaper drilling methods. Finally, it is pointed out that the best use must be made of every drilled hole by borehole geophysical and geochemical techniques.

Chapter 11.4 lists reserves and resources, both in the world and in the EC. Identified Zn and Pb resources (excluding low grade resources) in the Community are summarized as follows :

| | million tons of metal | | |
|---|---|---|---|
| | Zn | Pb | Zn + Pb |
| Denmark | 0.5 | 0.175 | |
| Ireland | 7.6 | 1.8 | |
| France | | | 1.0 |
| Germany (excluding data on Meggen) | 1.2 | 1.0 | |
| Italy | 3.0 | 1.1 | |
| TOTAL : | 12.3 | 4.1 | 1.0 |

## .2 TECHNOLOGY OF CONCENTRATES PRODUCTION

The first pages of the chapter provide an introduction to the three basic steps of concentrates production : comminution, gravimetric concentration and above all flotation. An average flowsheet is outlined, despite the fact that variations in ore characteristics make it impossible to describe a standard procedure.

Processes and plants are then reviewed in detail. Data is thus available for each operating mine in the Community.

The conclusions for mineral processing are repeated hereafter, somewhat abridged :

### a) Common Sulfide ores

"Common lead-zinc ores are floated by the direct method of successive differential flotation ... It seems that French mills favor flotation in rather long circuits with a great number of cells; it may be interesting to check how this system compares with the new circuits at Salafossa or Bad Grund which use a few very large cells. Moreover, some innovations at Greenex (Black Angel mine) and St Salvy should be examined in detail.

When the minerals are not too finely disseminated in the gangue or in another sulfide such as pyrite, well-crystallized clean galena and sphalerite ores can generally be treated in a preconcentrating stage in order to eliminate part of the calcareous or siliceous gangue. It appears that heavy-media separation is only used for that stage and there is no example in the EEC countries of gravimetric concentration by another process.

The so-called "static sink-float separation" operates only on particle sizes not under about 5 mm, and ores sufficiently liberated at coarser sizes are not common.

It is possible to go finer with a dynamic system; it may be worthwhile to intensify the studies on such processes in order to determine conditions for working at ever decreasing sizes.

### b) Pyritic Sulfide Ores

Some large orebodies in Europe contain pyritic ores with finely disseminated sulfides (Meggen, Rammelsberg); the selective flotation of galena and sphalerite offers a challenge to the metallurgical engineer : beneficiation requires a very fine grind to particle sizes for which flotation is difficult. A balance has to be found between selectivity and recovery of the minerals.

There now seem to be various fields of research needing exploration in order to make the best use of this type of ore, which could represent a significant part of the lead and zinc reserves in Europe.

c) Oxidized Ores

Oxidized ores are mainly treated in Tynagh (Ireland) and Sardinia (Italy). Although cerusite, and in one plant pyromorphite, are floated without much problem, this is not true for the zinc oxidized minerals. Generally called "calamines", these ores have a variable composition. It is not fully known yet why some calamines can float with a relatively good recovery and why others cannot ...

... It can be said that the present method of treating these ores is still questionable and that many more improvements are needed before balanced use can be made of the oxidized zinc ores."

1.3 METALLURGY

This chapter comprises three main headings :

- a review of metallurgical processes (lead pyrometallurgy, zinc pyrometallurgy, zinc hydrometallurgy and treatment of mixed lead-zinc concentrates);

- a detailed account of practice and plants in EC countries;

- a review of by-products recovery and uses (sulfur, cadmium, copper, tin, arsenic, antimony, bismuth, precious metals, rare metals).

Extracts from the conclusion on practice in the EC are given hereafter :

a) Lead production

"In the EEC countries, primary lead capacity (about 700 000 t/y) is divided into two types of plants : the blast furnace, where lead bullion is the principal product (50 % of capacity), and the Imperial Smelting furnace (I.S.P.), where lead bullion is co-produced with zinc (20 % of capacity).

Four I.S.P. furnaces exist in these countries : Avonmouth in the U.K. (Commonwealth Smelting Ltd), Berzelius Metallhütten in Duisburg-Wanheim, Germany (Metallgesellschaft), Noyelles-Godault in France (Penarroya), and Porto Vesme in Sardinia, Italy (AMMI Sarda).

Most of the lead production comes from the blast furnace, a very versatile tool that can accept varying charges with good metallurgical results.

Many plants are fed with combined charges, sulfide and oxide ores being mixed before or after roasting; they are sometimes combined with a significant proportion of scraps and/or wastes (such as used batteries).

In any case, lead bullion is always very impure and must undergo thorough refining, in which many by-products of high value are recovered ...".

b) Zinc Production

In the EEC countries, primary zinc production is mainly obtained in electrolytic plants, with an installed capacity of 1 070 000 t/y.

I.S.P. capacity in comparison is 380 000 t/y; other processes represent a total capacity of 120 000 t/y.

The large capacity of zinc and lead production in the I.S.P. is supported by a number of advantages claimed for this process :

a. treatment of mixed or separate lead and zinc concentrates (either sulfides or oxides), and secondary materials (other than metal scraps);

b. recycling of materials produced by smelting;

c. potential for energy conservation : energy use is slightly less than in electrolytic plants, with lead production as a bonus;

d. adaptation to environmental and emission standards."

c) <u>By-products recovery</u>. On this topic, the report concludes as follows : '

"... the highly technicized lead-zinc plants of the European Community are able to recover with a high efficiency the by-products that have a high commercial value, either by the amount (like S or Cu), either by the intrinsic value (like cadmium or the precious metals).

However, some by-products which are present in low amounts in lead and zinc concentrates, like mercury, selenium, nickel or cobalt, are still left in the residues or badly recovered.

In order to attain a better economical recovery of these by-products, it is felt that some kind of collaboration should be set up among lead and zinc producers."

## 1.4 TECHNICAL ASPECTS OF SUPPLY BY WASTE

This chapter comprises 1) a presentation of secondary sources and secondary production processes of lead and zinc; 2) details pertaining to each EC country.

It is claimed that about 50 % of the lead and 20 % of the zinc consumed are produced from secondary sources. Thus, the recovery of scrapped batteries accounts at present for 44 % of the secondary production of lead.

Most of the metallic zinc is used for galvanizing steel, and the problem of recovery in the dusts and fumes of steel mills is still more or less open.

The next important use of zinc is die-casting, the major part of which is employed in automobile production; these die-castings already represent a major source of secondary zinc, as more and more cars are dismantled for metal recovery. Expansion of zinc die-casting recovery seems to depend partly on advance in collecting and sorting of municipal waste.

In a few countries (Ireland, the U.K.), there are dumps containing beneficiation tailings or metallurgical slags; the recovery of lead and zinc from these dumps cannot be neglected.

France and Italy have provided for the report abundant details on available residues from metallurgy, on the availability of scrap and on present and potential uses of the various types of scrap. The chapter on France also includes a paragraph on lead-zinc recovery from urban refuse.

The chapter on Italy describes a typical company, and provides comparative data with other parts of the world.

PART TWO : STATISTICS OF PRODUCTION, CONSUMPTION AND TRADE

## 2.1 STRUCTURE OF PRODUCTION

### Producers of ore, concentrates and metal. Production statistics and costs

World-wide data are tabulated for mine production of lead and of zinc in metal contents (per annum 1967 to 1976), and for growth in mine production of both metals (percentage per annum over two periods : 1972/1963 and 1976/1972). As regards the EC, a decline over recent years is clearly apparent.

Similarly, tables are provided for world data on refined lead and slab zinc production, on plant capacities, and on growth in production of refined lead and slab zinc (percentages per annum over the periods 1972/1963 and 1976/1972). A table lists the capacities of zinc smelters in the EC. Detailed data on production costs in the USA are also provided.

### Scrap availability

1) Recycling

Scrap trading appears to be a complex and highly fragmented affair, because traders operate on a great variety of levels, from base collection upwards. One notes a strong tendency to carry out the whole chain of operations (collection, separation, upgrading, packaging and shipping) within integrated companies; the report gives examples ("classes") of such companies which perform more than one operation of the chain.

Detailed tables also provide analyses of the successive scrap processing operations, of smelters operations (sizing, refining, melting, alloying), and of scrap processing equipments.

2) The importance of lead and zinc scrap in industry, worldwide and in the EC

In order to assess this importance, tables have been compiled on production and on consumption of both metals, as well as on scrap arising from domestic sources, for each member state and for the EC as a whole during the period 1967 to 1976. Other tables present secondary production, and secondary production as a percentage of total production.

Some statements are extracted hereafter from the bulk of data and comments provided by the dossier.

Lead

Secondary lead production in EC countries accounts for 47 to 49 % of total lead consumption.

"Recycling of scrap lead materials accounts for 30 to 48 % of total lead demand in the main industrialized areas ... The largest contribution to the recycling lead industry comes from the lead-acid battery sector, which accounts for 40 to 50 % in the EC of total recycled material. The amount of battery scraps, and its percentage on total recycled scrap, is expected to grow; as a consequence of this, an increasing proportion of total lead consumption will be met by the recycling industry. The need for primary lead from mines could level out and in the long run even decline."

Zinc

Recycling of scrap zinc materials accounts for 23 % of the total zinc demand in the main industrialized areas... In the four main countries, secondary zinc production makes up 28 % of total consumption.

The proportion of recycled zinc in total consumption is lower than that of other main non-ferrous metals - aluminium, copper, lead - for two basic reasons :

i) the large extent to which zinc is employed in dissipative uses;

ii) the wide dispersion of old scrap and the consequent problem of economic retrieval.

3) Secondary_flow_in_industry

Lead

Depending on its composition, scrap can be treated by smelting, refining, or remelting ... The report summarizes the situation as follows : "The utilisation of lead scrap tends to follow a fairly well defined pattern. Soft lead scrap arisings including ashes and residues, are recycled as secondary refined lead or remelted low purity lead. Whenever possible alloy scrap is recycled as an alloy, making full use of the contained alloying elements. Antimonial battery lead scrap, cable alloy and printing metals scrap are frequently recycled for use in the same industry while excess printing metal, whitemetal bearings are recycled as Pb-Sn-Sb alloys in solder production."

Zinc

"Secondary zinc flow in industry may be summarized as follows : The major user of zinc scrap is the chemical industry which produces four main products : zinc dust, zinc oxide, sulphate and chloride. Galvanizing scrap and waste represent the basic raw material for the chemical industry.

Non-metallic residues are utilized for chemical products. Metallic residues constitute the basic feed for zinc dust production. Dross is also utilized for zinc oxide production.

The amount of scrap residues is insufficient to cope with the demand of converters.

Brass scrap, whether new or old scrap, is used to make new articles, closely allied to the original composition, with virgin zinc only added to make up final tonnages in conjunction with additions of secondary refined copper. Old brass scrap constitutes the major part of zinc old scrap.

Old rolled zinc scrap is remelted and used as metallic residues, mainly for zinc dust production."

4) Scrap_availability_in_EC_countries_and_future_availability

Detailed data are provided for scrap availability (on the average 550 000 tons/year of lead and 450 000 tons/year of zinc in the EC) and for the recycling rate by sector of use (the rate for lead is generally high). Forecasts are given for 1985 and 1990.

5) Conclusions

The recycling rate is considerably lower than the rate deemed theoretically achievable. A number of recommendations, apart from those listed after this summary, are put forward in the dossier to improve the situation. Some deal with general policy (improving the image of the recycling industry, introducing incentives ...). Others are specific to the technology of lead or zinc scrap recycling.

2.2  STRUCTURE OF CONSUMPTION

Lead

Present and past trends of refined lead consumption are examined in the report for the main economic areas of the world. There are clear indications of differential evolution within the EC.

For total consumption of lead, data exist only concerning the EC, the USA and Japan.

A review is made of total metal consumption,by uses (batteries; semi-finished products; sheets, strips and pipes; cable sheathing; alloys; antiknock ...).

In many of these uses, trends of consumption vary somewhat from EC country to country. The dossier presents detailed figures from 1967 to 1976, for the EC countries, Japan and the USA.

Alternative_products

The possibilities of substitution are described and briefly discussed in the cases of batteries and of alkyl-lead compounds (antiknock). For other uses, a list is given, from which it appears that the most serious competition derives from plastics, aluminium, titanium and from technology innovations in the printing industry.

Zinc

The report discusses present and past trends of <u>slab zinc consumption</u> for the main economic areas of the world. As with lead, evolution of demand varied somewhat within the EC.

For <u>total consumption of zinc</u>, as in the case of lead, data are only available for the EC, Japan and the USA.

A review is made of <u>total metal consumption by uses</u> (galvanizing, brass, zinc die-casting, zinc semis, zinc oxide ...).

The dossier presents tonnages corresponding to these various applications, from 1967 to 1976 and for the EC countries, Japan and the USA.

Alternative products

In galvanizing, potential substitutes are the corrosion - resistant steels and other coating materials such as paints and aluminium. In zinc die-casting, aluminium and plastics are the competitors to zinc. These possible substitutions are briefly discussed.

There are also various substitutes to brass applications.


2.3 INTERNATIONAL TRADE

Based on detailed figures, this part of the dossier describes international trade of concentrates, refined metals and scraps, and outlines the structure of world market. The initial statement, out of which the whole presentation grows, is that with the exception of the USA, major users of lead and of zinc are not major producers and most trade takes place among the industrially developed countries of the western world.

The USSR, China and the Eastern European countries are important producers and consumers of lead, but they are not major importers or exporters of the metal as a group. Tables show that the USA, Western Europe and Japan are net importers of lead and of zinc, while Canada, Australia and some others are net exporters. In particular, the EC is a net importer of both metals in their various forms.


2.4 FORECAST OF CONSUMPTION

Forecasts on consumption, both worldwide and concerning the Community, were formulated on a long term basis, thus covering a period sufficient to consolidate some existing trends in some specific sectors (batteries, cables, alkyl lead, galvanized sheets, zinc oxydes) as well as to care for intensified scrap recycling.

On the whole, demand in the Western world should increase at average annual rates lower than those registered in the past, and reserves in the Western world are such as not to create problems for the satisfaction of future concentrate demand.

Mine production in the EC is expected to climb from 135 000 tons of lead (metal) in 1976 to 230 000 tons in 1985; the corresponding figures for zinc are 332 000 tons and 700 000 tons. Figures are also provided for metal production in 1985.

a) Lead (metal consumption)

This part of the dossier mainly consists in a review of available forecasts :

1) U.S. Bureau of Mines; Mineral Facts and Problems, 1975 edition.

2) Stanford Research Institute : World minerals availability, 1975-2000, April 1976.

3) Conference "Lead and zinc in the 80's", June 1977.

4) U.S. Dept. of Commerce : U.S. Industrial outlook 1977.

These forecasts are based on somewhat different growth rates (from 2 to almost 4 % per annum for the whole world). It is therefore not surprising that projected consumption figures should vary.

The future of present uses and new uses is discussed. "New uses", i.e. these that are already known but not yet developed, include in particular lead composites for electric vehicles. This has led the authors of the dossier to give an account of the potentialities of electric car development in the USA.

b) Zinc (metal consumption)

Available forecasts come from the same sources as for lead. Again, they differ to some extent in being based on various growth rates (between 1.4 and 3.1 % for the whole world). The dossier supplements these data with a brief review of "new uses", summarized from the "Research Programmes of the International Lead and Zinc Research Organization Inc.".

For lead and for zinc, the dossier gives and comments forecasts of total metal consumption in the EC (including metal from scrap), by uses, for the years 1985 and 1980, and outlines the degree of foreign dependence of EEC countries.

# SYNTHESIS, GENERAL CONCLUSIONS
# AND
# RECOMMENDATIONS FOR R AND D ACTIONS

SYNTHESIS, GENERAL CONCLUSIONS AND RECOMMENDATIONS :

# C O N T E N T S

# INTRODUCTION

Zinc and lead balances for the Community, borrowed from part 2.4 of this report, are presented in the following tables. They show that in 1976 mine production accounted for about 20 % of the total zinc consumption and 10 % of the total lead consumption.

Proposals presented in this chapter aim at increasing the degree of self sufficiency of the Community. They belong to four fields : geological exploration, mining technology, mineral processing and metallurgy. The last three fields have already reached a high degree of scientific development. In comparison the first one is in its infancy : although some very elaborate techniques are used, there is no well established scientific method allowing a systematic search for orebodies concealed at depths of more than 50 or 100 m.
As a result, proposals concerning geological exploration aim at developing new strategies. Proposals concerning the other fields are more technical.

ZINC BALANCE IN THE COMMUNITY

(unit : a thousand metric tonnes of contained metal)

|  | 1972 | 1976 |
|---|---|---|
| Mine production | 363,7 | 332,3 |
| Net import of ore | 764,5 | 918,7 |
| Total slab production | 1 153,4 | 1 130,4 |
| Net import of slab | 133,5 | 8,6 |
| Slab consumption | 1 352,6 | 1 207,4 |
| Direct use of scrap | 285,7 | 379,2 |
| Total consumption | 1 661,2 | 1 611,1 |

LEAD BALANCE IN THE COMMUNITY

(unit : a thousand metric tonnes of contained metal)

|  | 1972 | 1976 |
|---|---|---|
| Mine production | 169,2 | 135,3 |
| Net import of ore | 251,2 | 195,5 |
| Net import of lead bullion | 201,9 | 234,9 |
| Production of primary refined lead | 610,3 | 600,4 |
| Net import of refined lead | 145,4 | 113,9 |
| Secondary production | 607,3 | 623,6 |
| Total consumption | 1 301,1 | 1 308,3 |

## R1    EXPLORATION

### R1.1.  OLD MINES. PRODUCTION AND RESERVES

Many thousands of zinc and lead deposits have been discovered and mined within the territory of the EEC countries over several centuries. Together they yielded enormous amounts of metal : about 6.5 Mt (million metric tonnes) in the United Kingdom, 3.3 Mt in France, 2 Mt in Belgium, perhaps 10 Mt in Italy and more in the Federal Republic of Germany.

All but a few of these old deposits were abandoned at the end of the 19th or during the first half of the 20th century. Most were of very small size and many are now depleted. Some were, however, abandoned with substantial quantities of unmined ore, either because mining was not economic at depth, or because the remaining ore was not amenable to treatment, with the technology available at the time.

In order to exploit such resources again, however, one needs to re-open a mine, which requires proving a minimum reserve at a minimum grade; this may be very difficult, especially where the underground workings are no longer accessible.

Of the few deposits that are still mined at the present time, some have reserves sufficient to keep them in production for a number of years. For example Rammelsberg in F.D.R. has been operating for more than 1000 years; according to Friedensburg (1971), this deposit produced 3 Mt of metal during the period before 1965 and at that time contained enough ore to yield another 1.12 Mt of metal; Rammelsberg is now said to have about 10 years of reserves at the current production rate.

Presumably further investigation will prove additional reserves in some of these old mining areas.

### R1.2.  NEW MINES. THE RATE OF DISCOVERY

Substantial unexploited zinc and lead (Zn and Pb) reserves are known to exist at the present time in Greenland, Ireland, France,

Germany and Italy. They amount to a total of at least 17.5 Mt of contained metal. It is remarkable that a large part of these reserves are found in orebodies that have been discovered in the last 20 years. These orebodies are :

- Black Angel in Greenland
- Tynagh, Silvermines and Navan in Ireland
- Les Farges and Saint-Salvy in France
- Salafossa and Masua in Italy.

Similarly a sizeable part of the current production comes from newly discovered orebodies. This part will increase dramatically with the opening of Tara mine at Navan, Ireland, which will contribute more than 200 000 t Zn and 40 000 t Pb per year.

Although there has been a high rate of discovery of new reserves in several EEC countries, the highest rate is observed in the Republic of Ireland. This is due in part to a favorable geological environment but undoubtedly also to an intense exploration programme, maintained over a long period of time. During the last few years, 75 to 150 km of exploration holes [1] have been drilled per year for Zn and Pb in the Republic of Ireland, which is much more than in all other EEC countries.

If exploration was more intense in all EEC countries, a more acceptable degree of self sufficiency would be reached.

R1.3. THE NEED FOR CONTINUED EXPLORATION

At the planned mining rate of 2.5 Mt of ore per year, the very large reserves known in the newly discovered deposits at Navan will be depleted in less than 30 years. Most probably additional reserves will have been found in the meantime in these deposits.

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[1]
These figures do not include development drilling taking place around operating mines nor auger drilling used for deep geochemical sampling.

The figures show, however, that because of the high outputs that must be obtained nowadays to ensure economical operation by amortizing the original capital investment as quickly as possible, few Zn and Pb mines can live for more than a few decades. On a world as well as on an EEC scale the supply of metal cannot possibly be maintained unless new orebodies are discovered at an adequate rate.

It must also be emphasized that considerable lead times are involved in each phase of development of the mining industry. It takes years to design, test and apply a strategy of exploration; several more years to delineate an orebody and prove reserves; several years of development work are again needed before production starts. It is therefore essential that exploration projects are undertaken in due time.

An additional complication is that some of the deposits that are or will be discovered are likely to remain unexploited because of environmental regulations or non-amenability of the ore to treatment or for some other technical, financial, or political reason. This makes it desirable to maintain a high rate of discovery.


R1.4. THE CHANCES OF EXPLORATION SUCCESS IN EEC COUNTRIES

New orebodies have recently been discovered by surface mapping in East Central Greenland. If further investigation shows that they are minable economically, this area would become a new mining district for non ferrous metals.

New orebodies have also been discovered in the Central Plain of Ireland and in old mining districts such as the Armorican Massif and the Pyrenees in France. It remains to be seen whether they are large enough to make them minable assuming economic and other conditions are suitable in the next few decades. A few other deposits are known in Ireland, France, Germany and Italy where drilling has failed, until now, to prove reserves or a grade that is quite high enough to warrant mining. Further study, i.e. in most cases further drilling, may reveal that some of these deposits are minable, and could support new mines within a few years.

Furthermore, most experts agree that in a number of areas in Greenland, Ireland, the United Kingdom, France, the Benelux countries, Germany and Italy, minable deposits of Zn and Pb are concealed at shallow or moderate depth, awaiting discovery. The search made in the previous centuries and up to 1950 was thorough, but for the most part limited to deposits with surface outcrops and tending in each area to be directed to a particular type of orebody, the geological features of which were locally well known.

Comparative studies of orebodies in different areas are beginning to suggest the value of renewed exploration even in old mining areas or areas otherwise dismissed as unpromising. From that point of view an exchange of information and experience between experts belonging to different countries is essential.

Questions arise therefore, not about the existence of undiscovered deposits, but about the techniques to be used to discover them and about the cost of their discovery. With regard to the latter, the common belief that ore deposits are easier to find in Canada or in Australia is no longer well-founded. According to Derry (1975, in Downes and Burton, 1977) : "In Ireland to 1973, 14.8 million pounds spent resulted in 4 previously unknown orebodies, whereas in Canada, the cost of discovering an orebody averages 6.12 million pounds and in Australia the cost is still higher".

In fact exploration in Canada in recent decades has been so intensive that L.S. Collett, a well-known expert, has recently written : "It is doubtful that any major new deposit within 30-60 m of the surface will be found, at least in Canada, by the present exploration methods since most favourable areas have been covered at least once by geophysical methods". (In Govett and Govett, 1976).

R1.5. AREAS IN THE COMMUNITY TO BE PROSPECTED IN THE FUTURE

As shown in chapter 11.2, there are many districts in Greenland, Ireland, the United Kingdom, France, Belgium and Luxemburg, Germany and Italy where Zn and Pb are or were mined.

Most of these districts have been explored for centuries. None of them however has been explored so thoroughly and so deeply that new discoveries are ruled out.

On the other hand there are areas which for geological reasons are considered favorable to the occurrence of Zn and Pb deposits and which have not yet produced ore.

From a geological point of view, "favorable" districts include all the Variscan massifs and the lower part of the post-Variscan sedimentary succession. In the following, an effort has been made to select areas which, on the basis of currently available information, appear especially promising. In these "highly favorable" areas, discoveries can be expected at a lower cost and within a shorter time than in the others. The selection is not intended to mean that other "favorable" districts have no potential at all.

On the other hand, "unfavorable" districts are those underlain by a few hundred meters of strata younger than the Triassic in most of the Community, younger than the Jurassic in the areas surrounding the French Massif Central. Yet these are considered "unfavorable" on the basis of purely empirical observation. There is no scientific law which prohibits the presence of Zn and Pb deposits in these younger strata.

Within the territory of EEC countries, several districts are considered "highly favorable" from the point of view of Zn and Pb exploration. All of them should be explored actively. They belong mostly to two broad geological environments : the carbonate sequences and the volcano-detrital sequences.

## 1. The Marmorilik District, Greenland, Denmark

It is reasonably likely that additional reserves can be found in the Marmorilik district (section 11.22.C) where a mine is already active.

## 2. The Central East Greenland District

It is also reasonably likely that reserves can be proven in the
Central East Greenland District where orebodies and mineralized outcrops
have been found by surface mapping. This district is the only one in
the Community which is practically virgin while displaying so many
favorable features.

## 3. The Central Plain of Ireland

According to Derry (1975, in Downes and Burton 1977), an average
of 84 t of Pb and 235 t of Zn has been identified per square kilometer
of land surface in the Lower Carboniferous strata of Ireland. Compara-
tive figures for North American Palaeozoic carbonate strata are 38 t
of Pb and 43 t of Zn.

In spite of the several major discoveries made in the last
twenty years, the Central Plain of Ireland is still considered an area
with much potential, where deeper exploration will result in new disco-
veries.

## 4. The volcano-detrital belts of the Southern Caledonides in Ireland

The volcano-detrital succession of the Caledonides of Ireland
(section 11.23.I), which has not been prospected as intensely as the
Lower Palaeozoic strata, is also considered attractive.

## 5. The eastern continuation of the Northern and Southern Pennines, in Great Britain

Particularly interesting areas for future exploration are the
eastward continuations of two districts which were very productive :
the Northern Pennines and the Southern Pennines (sections 11.24.C and
E).

The following is borrowed from a report prepared by I.G.S.
(1977) for the present dossier :

"Northern Pennines -

Targets might include the continuation of the Carboniferous
Limestone eastwards below younger strata. The greatest concentration
of mines occur in the Alston Block whose structural characteristics
appear to extend at least 12 miles offshore. Mineralized Carboniferous
Limestone may therefore extend eastwards below the Durham coalfield
along the Stockdale monocline, or along the continuation of the Craven
faults. The eastern edge of the Askrigg Block is probably near
Darlington with the Cleveland Basin beyond. Mineral values associated
with the Craven reef limestones on the Yorkshire/Lancashire border
have been encouraging.

"Southern Pennines -

One of the most interesting target areas for lead-zinc minera-
lization in the U.K. is probably the continuation of the Carboniferous
Limestone eastwards below the Permo-Triassic in the Eakring-Newark area.
Lower Carboniferous rocks of block facies with fluorite and barytes
mineralization have been proved during oilfield exploration drilling
in this area. The limestone is overlain by shales and contains volcanic
horizons, making it worthy of further study. The southeastern end of
the Eakring-Foston High is the most promising part of the anticlinal
structure. Another favorable structure, the Kiveton-Egmanton Anticline
may represent Lower Palaeozoic sediments and granite host rocks for
channelways feeding solutions to the Lower Carboniferous - Millstone
Grit boundary".

6. The Armorican Massif, France, (section 11.25.C), where several
interesting discoveries have been made recently and where more can
reasonably be expected as a result of increasing experience. No mining
takes place at the present time in this area.

7. The Axial zone of the Pyrénées, France, (section 11.25.D), where
geological models are being developed which will make exploration
more efficient.

8. The Bordure Sous-Cevenole, France, (section 11.25.G), where two mines are presently active. This area has been much explored but remains attractive. Deeper exploration might reveal favorable structures which have not been observed at the surface.

9. The belt between Namur, Belgium, and Aachen, Germany, extending northward to Maastricht in the Netherlands.

The Northern District of Belgium, which has already yielded much metal, remains the most favorable one, in particular because of the new vistas opened by the recent discovery of Chaudfontaine. This district extends north of Liège towards Maastricht in the Netherlands under a cover of flat lying sediments. The Carboniferous Limestone present below this cover is an attractive target.

10. Large districts underlain by Middle and Upper Devonian strata in Germany

Much of the Variscides in Germany remains favorable land. Because the large deposits of Meggen and Rammelsberg are located near the boundary between Middle and Upper Devonian strata, it is rather natural that exploration is focused on that particular stratigraphic interval.

The three-year programme of exploration which was recently completed must have delineated particularly favorable districts within the rather large area where Middle and Upper Devonian strata are observed in Germany.

11. South and Central Sardinia, the Southern Calcareous Alps, and Tuscany, Italy

The large producing districts of Sardinia and the Southern Calcareous Alps (sections 11.28.E and H) remain especially favorable land where new discoveries can reasonably be expected as a result of renewed exploration.

Tuscany (11.28.G) is another highly favorable area where the orebearing Triassic strata should be explored in depth more systematically.

## R1.6. NEW MINING DISTRICTS

Except for Central East Greenland, all the "highly favorable" areas just mentioned are old mining districts. They will be described in chapter 11.2 of this report, with the types of orebodies and their geological controls.

The possibility of entirely new mining districts in the British Isles or in continental Europe should also be entertained. As mentioned above, there are areas which for geological reasons are considered favorable although they have not yet produced ore. In these areas, little or no information is available about the type of orebodies which can be expected, so that only reconnaissance work can be recommended at this stage.

Among these new possibilities, the following are noteworthy :

1) Margins of the Southern Caledonides in Ireland, Wales and Scotland.
   Zn and Pb deposits are known in quartzites of Lower Cambrian age along the south-eastern margin of the Caledonides in Scandinavia. Among them, Laisvall with 40 Mt of ore at 4.5 % Pb and 0.5 % Zn. Similar deposits are found in somewhat younger strata along the western margin of the Caledonides in Newfoundland. The basal formations of the Lower Palaeozoic succession in the British Isles should therefore be explored (Scott, 1976).

2) Northern France and western Belgium.
   The Carboniferous Limestone is known to occur from the English Channel to beyond the Belgian border under a rather thin cover of horizontal strata of Mesozoic and Cainozoic age. Since the same Carboniferous Limestone has proven so fertile both to the east and to the north-west, this area is worth a preliminary study.

3) Calabria.
   Geochemical anomalies have been found in an 10 000 km2 area underlain by Triassic dolomites in Calabria. A stream sediment survey has already been carried out. Further work will show which of the anomalies deserve more study.

## R1.7. DIFFICULTIES OF EXPLORATION

Against this background of undoubted potential it must be recognized that exploring for concealed deposits even at shallow depths is difficult, costly and slow. No geological, geophysical or geochemical method can be expected to detect all concealed deposits with certainty. All methods may give rise to spurious results.

The information obtained must therefore be carefully analyzed and the conclusions constantly reviewed as each new piece of evidence is added.

The difficulty of exploration and the need for persistence is illustrated by the deposits at Navan, which the first surveys failed to detect and which were eventually discovered in 1970, many years after the beginning of the post-war period of intense exploration in Ireland.

Since in the future, deposits will have to be found at increasing depths or under more opaque overburdens, exploration will become correspondingly more difficult, costly and slow unless new strategies and new technologies are developed. The appropriate research into these new methods needs to be commissioned now.

## R1.8. SELECTING TARGET AREAS

In much of Western Europe, there are indications of Zn and Pb mineralization, so that some kind of reconnaissance work can be recommended (see chapter 11.5). The surface to be explored is very large and methods are needed to select areas where the probability of a discovery is high, or to discard areas which are considered less favorable.

One method of selecting target areas is to use broad geophysical and geochemical reconnaissance surveys. These surveys use a variety of geochemical and geophysical techniques which share the common objective of locating some kind of anomaly relative to the general background characteristics of the region. In order to ensure a statistically objective survey, measurements are made along traverse lines or on a pre-determined grid pattern which bear no relationship to the geological nature of the ground in the region under examination. Since the measurements must be made in great numbers, they must be quick and inexpensive, which generally rules out those made in boreholes.

Geological methods are also used : they consist in identifying large-scale geological features, such a large faults or high-rank stratigraphic units, which are thought to control the emplacement of orebodies and with which the orebodies are spatially associated.

In practice several methods are often used simultaneously to select target areas. But with regard to exploration for Zn and Pb deposits in Western Europe, it seems that research is most needed, and can be undertaken at a reasonable cost, into the geological environment in which such deposits occur. With this in mind, the following suggestions are made :

a) A major drawback of geological methods has often been that geological features fortuitously associated with an orebody were erroneously

thought to have controlled its emplacement. To avoid repetition of
such mistakes, often related to ill-considered or premature accep-
tance of one particular scientific theory, a comprehensive study of
deposits considered representative of each important type should be
undertaken (or completed if it is already in progress).
Detailed proposals are presented in section 11.29 of this report.
They aim primarily at unravelling the processes of ore deposition.
If these processes were better known, more models of orebodies
could be designed which would be more reliable and would fit better
the geological features of each particular area. It would also
become possible to inventorize the traps where, in each area, ore
might have deposited. The search would become more systematic.

Laboratories belonging to different schools should contribute
to these studies in order to avoid bias in favor of the locally
accepted theories and to allow a systematic search for characters
fitting the various theories. All the laboratory and field methods
available at present should be used to determine which geological
features are causally associated with the deposits. Only deposits
which have been extensively drilled should be considered for such
studies.

b) Geological methods can be used only if the regional geology is well
known. This condition is fulfilled for most areas within the EEC
countries. However much of the information useful to the exploration
geologist is not readily available to him because it is scattered
through a multitude of papers and reports written by specialists for
specialists of some other geological discipline. An effort should
be made to collect and screen all the useful information relative
to each favorable area and to publish it under a suitable form.

No doubt progress is also possible and desirable in reconnais-
sance geophysics and geochemistry, if only because for some types of
deposits (vein-type for example) geological controls are likely to
remain rather indefinite. It is particularly desirable that techniques
should be designed that are capable of revealing anomalies originating
at greater depths or which can discard spurious anomalies more efficiently;

the development of such techniques would in any case benefit greatly from
an improved knowledge of geological controls of orebodies. This is one
more reason to emphasize the need for progress in geological methods as
a first priority.


R1.9. FOCUSING ON THE OREBODY

Once an area has been selected for detailed exploration, more
refined geophysical, geochemical and geological methods are needed to
select drilling sites and focus progressively on the orebody. At that
stage as the area to be covered is smaller, samples can be collected
and measurements can be made at narrow intervals, not only at the sur-
face but also at depth.

With regard to this stage of exploration also, some progress can
be expected from the improvement of surface geophysical and geophysical
techniques which should become capable of deeper penetration.

However most importantly, methods have to be developed which make
better use of the many holes drilled during exploration campaigns and
of the samples obtained from them. It is quite remarkable that these
holes and drill core samples are often so little used. All geophysical,
geochemical, petrological and geological techniques should be marshalled
in order that one may determine whether a drill-hole has passed close
to an orebody and at what approximate distance. This will require the
development of down-the-hole measurement methods on one hand and on the
other identification of haloes of all types, shapes and dimensions
which may exist around each type or orebody. Research concerning down-
the-hole measurement methods should aim at decreasing cost as well as
at increasing performances.


R1.10. DRILLING

At all phases of exploration and development of an orebody,
drilling is necessary and comprises much of the cost. There is no doubt
that in the future more and more of it will be needed.

Any improvement in drilling techniques which can make it cheaper will therefore help greatly in discovering new orebodies.

However the cost of drilling depends on many factors in addition to technology. From a preliminary survey which has recently been made, it appears that a four-fold variation is observed between different EEC countries although the same technologies are available in all of them. It is suggested that a special study group examines how drilling could be made cheaper in all EEC countries.

## R1.11. SUMMARY OF MAIN CONCLUSIONS AND RECOMMENDATIONS

The main conclusion of this report is that it is possible to maintain a high rate of discovery of Zn and Pb reserves in EEC countries during the next decades and hence increase the supply of locally-produced metals in those countries.

The main recommendation is that new R and D projects should be commissioned without delay along the following lines :

a) a comprehensive study of deposits representative of each important type should be undertaken so as to identify their geological controls and genetic processes with all possible certainty.

b) a comprehensive study should be undertaken of each favorable area with the purpose of collecting all information concerning geological features of interest.

c) down-the-hole geophysical methods capable of determining whether a drill-hole has passed close to an orebody should be developed and tested.

d) a major effort should be undertaken to identify rock-geochemical and other primary haloes around each type of orebody.

It is recommended that under the auspices of the commission a permanent working group supervise the work suggested above.

Other recommendations are the following :

a) all "highly favorable districts" mentioned in section R1.5 should be actively explored;

b) reconnaissance work should be carried out in many other districts (see chapter 11.5 of this report);

c) the collection, critical examination and publication of significant information about zinc and lead deposits in the Community should be improved and accelerated.

## R1.12. ADDITIONAL RECOMMENDATION

Underground mines afford good opportunities from the point of view considered in this report : by drilling from deep workings, it may be possible to explore volumes of rock which could not be reached from the surface except at much greater expense. Before a mine closes down, the possibility should therefore be examined to use it as a base for deep exploration.

This is not only true of Zn and Pb mines. Many coal mines have been closed in North-Western Europe during the last twenty five years. Some of them could have been used advantageously to explore the Carboniferous limestone which underlies the coal-bearing formations and is known as a favorable host rock for Zn and Pb, or to explore faults suspected to be guides to ores. Many such opportunities have however been lost.

## R1.13. MINERAL RIGHTS

Even if powerful techniques are available and if prospects are good from the geological and economic points of view, exploration may be hindered by legal restrictions.

In several European countries it may be difficult or impossible to obtain mineral rights over an area which is large enough for modern methods to be used. Sometimes it is even difficult to know who owns the mineral rights over a particular area. The mining law may be such that

owners of mineral rights are allowed to keep them indefinitely even if
they do not proceed to any exploration work.

Such inhibiting factors must be removed and a system of incenti-
ves has to be designed instead, if exploration is to become more active.

## R1.14. ENVIRONMENTAL CONSIDERATIONS

In many parts of Europe, public opinion has been so much impressed
by the environmental damage caused by the old quarries and mines that it
has become very suspicious towards all forms of mining. However with
the advent of modern techniques, environmental damage can be controlled
to a very large extent in favorable cases.

The threat that local authorities or public opinion would oppose
mining projects even if all safeguards are obtained, may also greatly
inhibit exploration. It seems essential that guarantees are given con-
cerning the permission to mine a prospective deposit before the very
large expenses required for proving reserves and delineating the orebo-
dies are made.

## R1.15. REFERENCES FOR SECTION R1.

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> Chapter I, Part I (Draft form) of the CREST dossier on
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GOVETT G.V.S. and GOVETT H.M. (1976) :
> World Mineral Supplies (Amsterdam, Elsevier).

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> Zinc and Lead mineralization along the margins of the Caledonian
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## R2. MINING TECHNOLOGY

R2.1. Few problems of mining technology are specific to Zn and Pb. However with regard to the supply of these metals from mines within EEC countries, it would obviously be advantageous to encourage the use of methods by which orebodies are completely removed, without pillars being left behind. Research on such methods would be worth the expense in the case of large orebodies.

It would also be advantageous to lower the cut-off grades as much as it is economically feasible. In fact the degree of recovery is determined in each mine according to various geological, technological and economical criteria which may not guarantee a maximum recovery.

R2.2. Untapped Zn and Pb resources (Chapter 11.4) consist of :

- Low grade deposits. These resources include :

  a) A large deposit at Mechernich, Germany, estimated at 2 or 3 Mt of metal;

  b) Other deposits in Sardinia, Italy, in the southern part of the French Massif Central, and in the northern part of the Vosges Mountains in France. These low grade resources are recoverable only in part. If however they could be mined economically, they would contribute significantly to the supply of Zn and Pb within the Community.

- High grade- low tonnage deposits. These resources include several identified orebodies in Ireland and Germany, amounting together to 1 Mt of metal. In addition they include the downward continuation of many vein type deposits, the shallower parts of which have been mined out. The amount of metal contained in the latter group could be significant.

- Concealed and deep seated deposits. The largest untapped resources are thought to lie in undiscovered orebodies of adequate tonnage and grade.

As shown earlier in this report, it has now become possible to locate orebodies at depths of several hundred meters, at least under favorable circumstances. The technology required for mining at such depths is already available.

R2.3. An effort should be made to refine and systematize the gathering of resources and reserves data so that a running inventory of the metal available in the Community can be kept. Simultaneously, future production rates should be calculated according to the various scenarios which appear likely.

R2.4. Often in the past it proved advantageous to re-open Zn and Pb underground mines which had been abandoned several decades earlier during a period of low metal prices.

Because metal prices keep fluctuating widely, it may be again necessary in the future to abandon a deposit which is not depleted but has become uneconomical and appears likely to remain so in the foreseeable future. In such a case, it would be worth studying the most economical way to keep the workings accessible or at least to prevent them from being damaged excessively by underground waters and other destructive agents.

Among other measures of conservation, it should also be recommended that tailings are kept in places where they can be retrieved if for some reason they contain an unusually high amount of some useful mineral or metal.

## R3.    RESEARCH AND DEVELOPMENT RECOMMENDATIONS FOR MINERAL PROCESSING

### R3.1. EXCHANGE OF INFORMATION

We first recommend frequent meetings of scientists and technicians in the field, in order to :

- get acquainted with the other's practice;
- compare various solutions to the same problem;
- compare various innovations and check their possibilities of applications in one's own field;
- share with others the practical experience in the control and automatization of beneficiation systems, in order to collect enough data for modelling and integrated command by computer.

It may be worthwhile to survey scientific societies, academic departments, and public organizations that could help in the initiation of such meetings, under the sponsorship of the EEC Commission.

### R3.2. OPTIMIZATION OF PRESENT MILLS AND APPLICATION OF ADVANCED TECHNOLOGY TO SMALL PLANTS

Much remains to be done before a beneficiation plant can be completely controlled for constant optimization of metallurgical performance. If it is true that scaling-up of milling operations has often been the result of the drive towards improved efficiency, it is also true that the large producers have had the greatest incentive and means for developing and introducing new methods and equipment.

There is probably now room for a systematic effort to make more of such progress applicable to smaller unexpandable operations, whose exploitation is one of the possible ways of expanding mineral reserves. For example, automation, which has greatly contributed to the exploitation of large deposits, cannot yet be applied to those plants that need the greatest help from technology (on account of their size or ore grade).

A technical and economical inquiry could be made into the possibility of evaluating presently existing models, and extensively automating

small grinding-classification circuits or flotation processes. This could be done with a minimum number of extremely reliable sensing elements and measuring devices; a small computer would control the operation on the basis of simple mathematical models. For flotation processes, flotation kinetics is still in question, and a deeper look into the theories and applications in the field would be most valuable.

In this respect, it must be strongly emphasized that a rigorous scientific treatment can take years before being translated in practice. A more experimental approach might be very useful if results, even though not perfectly reliable, can be applied immediately.

The research program should thus aim not so much for perfection as for simplicity and low investment and operating costs. It could be carried out as follows :

- investigation on already-adopted or proposed mathematical models, and research on new ones for general or specific mineral processing applications;

- inquiry into existing equipment, and involvement of manufacturers in the development of simpler, more reliable, and more easily repairable devices;

- study of better psychological approaches to the training of operators, in order to obtain their willing and intelligent integration into the system;

- research on the rather high zinc content of many sulfide tailings, either old ponds or newly produced ones, and on remedies which can be applied : stronger collectors, regrinding, longer flotation time, etc...

## R3.3. FINELY DISSEMINATED SULFIDE ORES

The treatment of the finely disseminated ores, generally with a pyritic matrix, has been only partially solved. It is unlikely that flotation alone can provide high selectivity and recovery, in comparison with common Pb-Zn ore (coarsely-grained and particularly clean). However, several approaches can be taken to improve on the present results, notwithstanding the fact that a complex sequence of metallurgical and mineral beneficiation processes might turn out to be the most economical from all points of view.

Mineral processing research could be aimed at :

- the production of a bulk sulfide concentrate at a not-too-fine particle
  size, the very fine regrinding of this concentrate, and the selective
  flotation of galena and sphalerite;

- the production of a mixed lead-zinc concentrate at very high recovery
  to feed metallurgical processes such as the I.S.P. furnace;

- the development of very selective reagents, working specifically on
  fine sizes, either in selective flocculation of one of the sulfide
  minerals, or in selective flotation.

## R3.4. PRE-CONCENTRATION STEPS

As already pointed out, only the sink-float process is used in
the EEC countries for the pre-concentration of sulfide ores and for the
beneficiation of bulk oxidized ores.

After a detailed survey of present applications and the results
obtained, it should be interesting to promote research to improve the
operation of dynamic cyclone-type machines, checking the results by a
systematic use of the Tromp curve.

Gravimetric concentration in hydrocyclones should be thoroughly
investigated in many different systems, to ascertain its limits and to
obtain the greatest efficiency in present applications.

Since several ores contain various amounts of iron oxides, it
could be interesting to check the possibility of preconcentration in high-
intensity wet magnetic separators which could remove some of the slimy
materials that can impede the correct flotation of oxidized zinc minerals.

## R3.5. FLOTATION OF FINE OXIDIZED ZINC ORES

In the treatment of finely ground ores, flotation still retains
the most important role. Its replacement by other processes is not fore-
seen for the near future. The use of flotation for the beneficiation of
oxidized zinc ores (and therefore the possibility of exploiting them
with good recoveries and low costs) has so far been hindered by two facts :

- the unselective and weak collecting effect of ordinary amine promoters on the extremely fine smithsonite and hemimorphite;

- the detrimental influence of the slimes on selectivity and recovery of the coarser sizes, when the above-mentioned promoters are used.

A complete solution of the problem would require the discovery or development of reagents that retain their selectivity in the presence of slimes, and have a strong collecting action on the extremely fine oxidized zinc minerals. These effects can be sought either directly by straight flotation or indirectly through selective flocculation.

The development of a reverse flotation process to float the gangue instead of the metallic minerals may also be proposed.

A partial solution, which would accept the loss of finest fractions, may be found among existing methods of obtaining low-cost separation and elimination of the finest fractions. Energy consumption, wear, cost of equipment and difficulties of operation oppose this solution for the moment. It is possible, however, that research will improve the desliming step by cutting at finer sizes and obtaining a sharper classification. The possibility of improvements, especially as far as energy is concerned, may be found in the combined effects of centrifugal force and physical chemistry.

The reserves of ores whose recoveries and treatment results could be improved are :

- in Sardinia, about 15 million tons assaying 1.5 % lead and 7 % zinc;
- in France, upper zones of sulfide deposits, such as Saint-Salvy;
- in Ireland, 1-2 million tons assaying 1.5 % lead and 7-20 % zinc.

R3.6. BULK FLOTATION OF SULFIDE AND OXIDE LEAD AND ZINC MINERALS

At present, a complex, partially-oxidized lead-zinc ore must often be subjected to 4 or 5 flotation steps, and requires considerably high grades in order to be economical.

The availability of an Imperial Smelting furnace does not change the situation substantially, because the mineral dressing process cannot take full advantage of the possibilities offered by metallurgy, such as the treatment of mixed lead-zinc charges with separate production of lead bullion and zinc vapor.

In fact, mineral processing can make neither a bulk of the oxidized lead and zinc minerals nor a bulk of these with sulfides.

This problem is not completely unrelated to that of R 3.5 and properly aimed research may even find a solution for both.

In Sardinia, which has an I.S.P. furnace, the amount of presently recognized reserves that would benefit from new possibilities for bulk flotation is no less than 10 million tons, and some possibilities may exist in Southern France.

R3.7. <u>SELECTIVE FLOTATION OF VERY POOR MIDDLINGS (WITH RESPECT TO PURE GANGUE)</u>

So far, preconcentration by gravity has been considered the most important means of lowering treatment costs by discarding part of the material at an early treatment stage.

Increased labor costs, the introduction of larger grinding and flotation equipment, and concern for the need of increasingly high recoveries have considerably reduced the interest in this type of treatment.

Furthermore, lower-grade ores, for which preconcentration is more desirable, seldom display satisfactory liberation at sizes for which the cheapest and more precise gravity preconcentration methods are effective.

The existence of collectors (or combinations thereof) more powerful and selective than the present anionic types would enable the elimination (by flotation) of some free gangue after a comparatively coarse grind; this would limit the amount of fine grinding often necessary to liberate valuable minerals.

Such a procedure is generally not possible with present reagents, because a substantial amount of mineral-gangue middlings cannot be floated, and would thus be discarded with the gangue.

With normal ores (particularly if low-grade) and with the help of cells for coarse feed, the introduction of a flotation step between rod and ball milling could be considered. The new reagents would enable the reduction of grinding in favor of cheaper regrinding. The treatment of ores heretofore considered too low-grade may thus become possible.

## R4. RESEARCH AND DEVELOPMENT RECOMMENDATIONS FOR METALLURGY

### R4.1 PRIMARY PRODUCTION

### R4.11. LEAD SMELTING

Lead smelting in blast furnaces still has a long way to go before being entirely satisfactory. Despite the progress already made after years of research, it seems that several investigation fields can still be proposed.

First of all, it is clear that the blast furnace should be considered as obsolete. It requires a perfectly dead-roasted charge (of uniform composition and particle size), the use of coke as reducing agent and furnace fuel, a limited amount of low-melting materials in the charge, the collection of many impurities in the bullion (resulting in a long refining procedure), and so on. But this unit offers a very high versatility, accepts mixed charges with recycled materials, scraps or residues, and provides an economic means of recovering small quantities of valuable metals (precious metals, for instance) from various sources. Bulk lead recovery is about 96-98 %. Significant improvement has been shown in sintering practice when an updraft is applied to roast high-lead charges; it may be worthwhile to transform most of the lead directly into metallic form during sintering, thus increasing the next furnace's capacity. It may also be useful to look further into the behavior of the minor elements, into their volatilization possibilities, and into the production of a gas richer in $SO_2$ for $H_2SO_4$ production.

Research may also carried out on the sintering of pelletized charges, leading to increased production rates on the same machine.

Blast furnace smelting should be investigated thoroughly, in order to build a sufficiently elaborated model which could predict, control, and design the furnace's operation. This research appears to be urgently needed, as we still don't really know what happens when the blast is oxigen-enriched, when fuel or gas are injected through the tuyeres, and so on. There is a need for a mathematical model of the furnace as such, and another one for the metallurgy of the smelting operation.

Coupled with direct and automatic chemical analysis, this model could lead to the immediate control of the furnace, resulting in a steady-state operation under the best economical operating conditions at all times.

One of the disadvantages of the blast furnace lies in the treatment of fine flotation concentrates rich in lead. For this type of metallurgical feed, a number of new processes have been proposed in the past 20 years, and some of them are now in operation; examples are the Boliden electric furnace and the Lurgi short rotary furnace used in Yugoslavia. There are other proposals, such as the KIVCET cyclone furnace (designed in the USSR) and the direct-smelting of sulfide charges in some type of converter or flash furnace. It is suggested that all these processes be thoroughly and critically evaluated, and that the most promising systems be piloted through a common study group.

However, the evaluation of hydrometallurgical processes cannot be neglected; lead is soluble in aqueous solutions only in nitrate or hot chloride systems, and these solvents are expensive. Nevertheless, it would certainly be worthwhile to look at some proposals already made and concerned by the use of organic reagents for selective extraction.

These hydrometallurgical processes could be the answer for the treatment of difficult ores in small orebodies, or of lean ores (not amenable to mechanical concentration) in big orebodies.

## R4.12. LEAD REFINING

It does not seem advisable to suggest a research program aimed primarily towards the adaptation of a continuous refining process to the conditions of the European lead smelters and refineries.

Lack of clean ores from European orebodies results in the smelting of foreign concentrates containing a number of by-products. Since lead is a powerful solvent for many metallic and semi-metallic elements, flexibility is needed in the flowsheet and in the lead refining capacity.

Through recycling, the commonly used Harris process gives a high lead recovery and produces a very pure metal.

Its operations are complex, and a lot of by-products must be treated to recover the valuable metallics or to eliminate the noxious ones.

A number of excellent papers, describing theoretical as well as practical research, have thrown some light on the different steps of pyro-metallurgical refining; this work must be pursued in order to get a better understanding of the mechanisms leading to improved industrial methods. It would also be useful to obtain a better selectivity, leading to higher by-product concentrations in the phases where they are recovered. Research might first be directed towards the improvement of the decopperizing step and of precious metal and bismuth removal.

There seems to be no expansion of the electrolytic refining process, which is based on a lead fluosilicate-fluosilicic acid electrolyte. A sulfamate-based refining process was introduced, but it was soon dropped in favor of the classical one. The problem here is the discovery of a better electrolyte, enabling a decrease of energy, reagent, and labor costs.

## R4.13. ZINC PYROMETALLURGICAL SMELTING

In the E.E.C. countries, zinc pyrometallurgy is restricted almost entirely to the Imperial Smelting furnace, the remaining horizontal retort furnaces, if any, being converted to zinc powder production. Vertical retort and electrothermic furnaces are exceptions which might not to be repeated.

Imperial Smelting furnaces still suffer from a number of disadvantages : consumption of expensive coke as a reducing agent, high content of zinc in the slag (but slag quantity is moderate), dross, dust and fumes in the condenser, high rotor wear, low quality of zinc produced, etc ...

However, taking into account its advantages, it is certainly worthwhile to increase our knowledge of the intrinsic processes and thus better control the operations. Research could therefore be developed in the following fields :

- elaboration of a mathematical model of the furnace, first considered as a chemical reactor (vertical tubular reactor with moving porous bed, comprising heat and mass transfers), then considered as a metallurgical tool treating complex charges with numerous components distributed in many products (gases, fumes, slag, lead bullion, matte and/or speiss). It could perhaps be linked with the elaboration of similar models for the lead blast furnace; a single working group could work on both subjects, with possibly two sub-groups;

- research on the decrease of coke consumption, either by the use of an oxygen-enriched blast, or by fuel-oil or natural-gas injection through the tuyeres;

- research on the behavior of the slagging components, for better control of the slag and a decrease in its zinc content;

- improvement of the condenser operation, in order to reduce the amount of dusts and drosses produced during zinc cooling.

Zinc refining is best operated by selective distillation in columns. The original New Jersey design has been perfected by Overpelt, and most units sold in Europe are produced by Mechim.

A recent improvement has been made on the three-column refining unit by eliminating the intermediate condensation step and carrying out the operation in one column.

## R4.14    ZINC HYDROMETALLURGY

### R4.14.A. CURRENT ELECTROLYTIC PROCESSES

#### I. INTRODUCTION

The most important breakthrough in zinc production technology in the past 25 years is, undoubtedly, the development of new processes in most sections of the zinc electrolysis flowsheet. Sixty-five per cent of the present capacity of zinc production is due to the hydrometallurgical process. This is not surprising when one knows of the important progress made successively or simultaneously in fluidized-bed roasting (Vieille Montagne- LURGI reactor), hot leaching of residues, iron precipitation by the jarosite process (Electrolytic Zinc of Australia - Asturiana de Zinc - Norske Zink) or by the goethite process (V.M.),

continuous reverse purification (V.M.), and automatic stripping of the cathodes (MITSUI - PORTO MARGHERA - V.M.).

It is clear that many points remain to be explained and many new techniques to be discovered and applied, but it is these improvements that permit the electrolytic process to be so successful (figure).

## 2. ROASTING

Overpelt and Prayon (partly) excepted, all the zinc hydrometallurgical plants in the E.E.C. use the V.M.-LURGI fluidized-bed reactor. This unit has achieved a high degree of safety; it still must achieve better control of the sulfate sulfur amount, although iron precipitation processes can help to discard the excess of $SO_4$ ions. It would also be interesting to better correlate the leaching results with the roasting conditions, and to investigate calcine with modern characterization techniques so as to discriminate its different components (ferrites, for instance) and to observe their behavior. Comparison should be made with Overpelt fluidized-bed reactor, fed with a prepared charge, which gives very good metallurgical results.

## 3. LEACHING

All the newest plants recently built in Europe include the hot leaching of residues in strongly acidified spent electrolyte. While zinc is practically entirely dissolved in this way, iron is simultaneously brought into solution and must be subsequently removed.

The new leaching process, with its ability to dissolve the zinc ferrites, has permitted the increase of zinc dissolution from 88-90 % to 96-98 %. Only a very small proportion of soluble zinc is drawn along with precipitated iron.

It seems that not much can be done to further improve the leaching step, and that progress will be limited to minor developments. However, it could be rewarding to collect information on the different leaching procedures, still of variable complexity, and to evaluate the different flowsheets for zinc recovery, ease of iron precipitation, maintenance, corrosion, etc ...
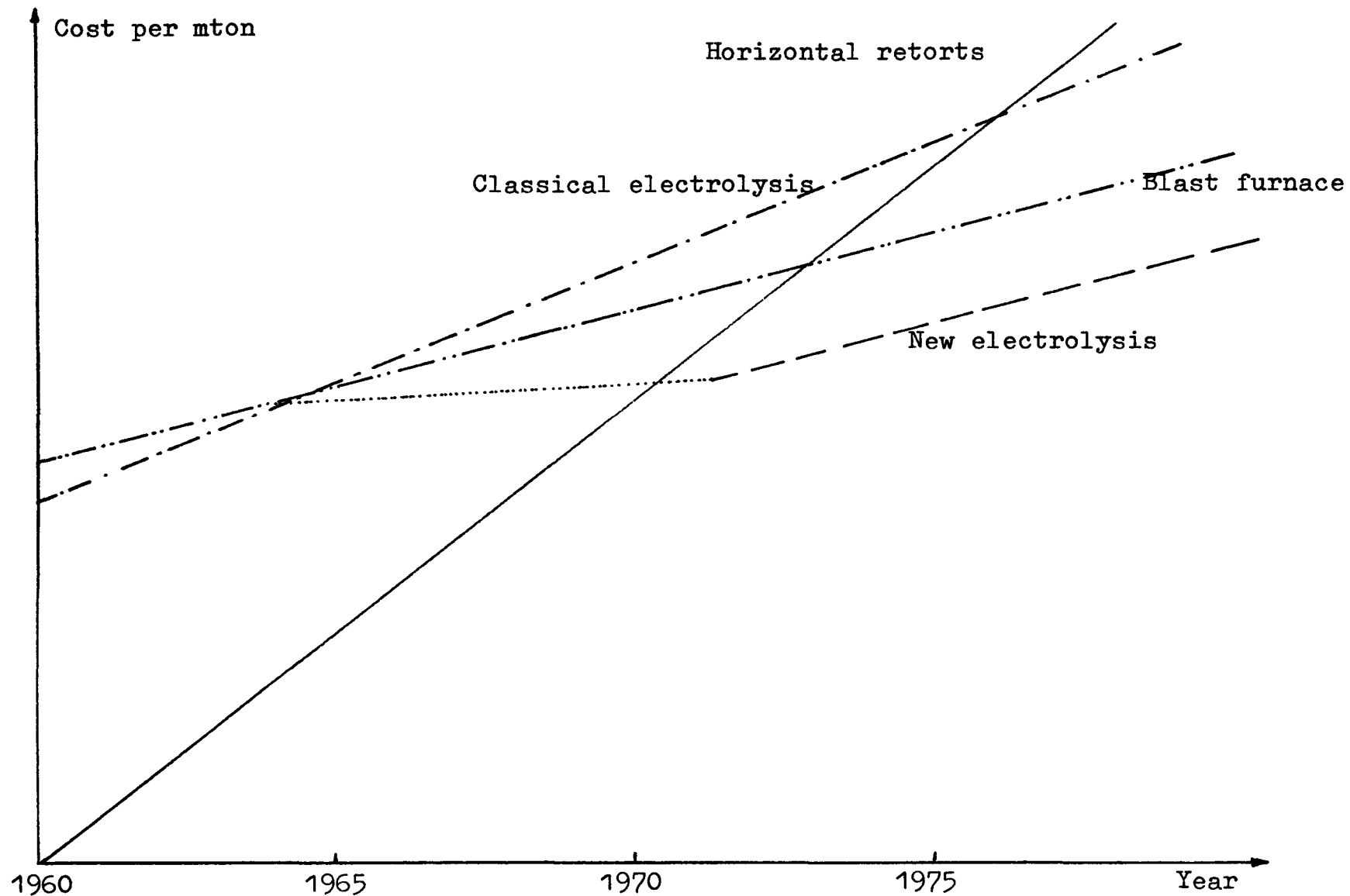
Cost evolution of zinc smelting

(from C. EK, Compléments d'Hydrométallurgie)

## 4. LEACHING RESIDUES

Improvements in the leaching process have resulted in the appearance of new problems related to the disposal of residues or to the recovery of contained values.

Hot leach residue contains the gangue, with lead and silver as the principal valuable metals; iron precipitate (either jarosite or goethite) is very bulky, wet, and not chemically stabilized.

It appears, therefore, that research must be conducted as follows :

- to find a process to transform the jarosite or goethite, either in solid product that can be disposed of without any environmental risk (or, at best, used in some way), or in a series of valuable metallic compounds (mainly iron-based), leaving a harmless final residue;

- to find a separation method able to concentrate silver and lead in a product which can be profitably sold to a lead smelter, or to find a metallurgical process giving the metals directly.

## 5. SOLUTION PURIFICATION

Significant progress has resulted from the application of the new V.M. continuous reverse purification. Further improvements can be expected in that field, but it may be wise to look at processes other than the older chemical treatment.

Investigations on zinc electrolyte purification may thus be carried out by techniques like ion-exchange, solvent extraction, or combined physico-chemical methods.

## 6. ELECTROLYSIS

As zinc electrolysis is highly sensitive to the presence of many impurities in the electrolyte, it should be worthwhile to continue the research on the influence of foreign ions on zinc deposition.

Research could also be done to further investigate the role of the lead anode which is responsible for a 0.6-0.8 V overpotential,

and which also, at high current densities, introduces lead into the cathode.

It would also be fruitful to share practical experience in the design and control of automatic stripping machines, which represent a major economical breakthrough but can still be perfected.

R4.14.B. OTHER PROPOSED PROCESSES

A number of metallurgical processes have been proposed for the extraction of zinc.

There seems to be two areas of useful research :

- treatment of silicate ores in a circuit parallel to the present zinc leach-electrolysis cycle. Problems arise since the silica is partly dissolved by the spent electrolyte. It must therefore be precipitated in some way without carrying too much zinc. Processes now operated in several countries may be usefully compared.

- direct treatment of the sphalerite (by leaching at high temperatures and pressures) to get rid of the sulfur as the element and not as $SO_2$. In many places production of $H_2SO_4$ is a heavy burden on zinc metallurgy; it is suggested that a complete survey be made of all the processes proposed for the treatment of sphalerite concentrates without evolution of $SO_2$, either by hydrometallurgical or pyrometallurgical processes (fused-salt electrolysis, for instance).

R4.15.  TREATMENT OF ZINCIFEROUS SLAGS

Most of the zinc contained in lead concentrates smelted in a blast furnace passes to the slag.

For years, these slags have been treated in some plants by a fuming process in the so-called "slag-fuming furnace".

Even though it is not yet clear whether this fuming process is of a thermodynamic or kinetic nature, hundreds of thousand tons of slag are fumed every year to produce a zinc-rich oxide most suitable for hydrometallurgical extraction.

It appears that this process is not used in E.E.C. countries (Crotone, in Italy, is fuming the leach residues in a "cubilot" blast furnace); slags, containing a significant amount of metal, are disposed of mainly as building materials. When zinc prices are as low as at present, recovery from the slags is economically questionnable, but anticipation of the future needs can induce a modification of the present operations.

Current practice is to fume the slag with the addition of fine coal to the blast. The use of fuel oil for coal has been successfully developed by Bulgarians. This has no bearing, however, on either the principles of process, or the use of costly reducers in an energy-consuming operation. It has been suggested to make use of new fuming designs to save fuel; one of the proposals is the cyclone furnace, as pioneered in Australia. However, it must be concluded that without specific incentive, such as Governmental legislation, there is at present little prospect for better metallurgical use of zinciferous slag.

## R4.16. LEAD AND ZINC RECOVERY FROM MINING AND METALLURGICAL RESIDUES

Residues generated in the lead and zinc primary metallurgy, during ore beneficiation and concentrate transformation into metal, are generally stored at zero value. Technological improvements result in the successive recycling of these residues with the double view of recovering the metal contained and increasing the smelter productivity. The energy crisis, together with a changing world structure in relation with raw material supply, accentuated the need for their optimum use so as to preserve unrenewable resources and, as far as European countries are concerned, to minimize their dependance from abroad as well as to improve their commercial balance. Moreover, processes which, although widely used, are characterized by a high energy consumption are affected by the price increase of fuels.

Residues previously neglected may be profitably treated in the future if improved technology can be found which saves fuel through new reagents or procedures.

Available residues consist of :

- fractions of lead-zinc oxidized ores which, due to their chemical and

physical characteristics, are not susceptible of being immediately be-
neficiated through conventional gravimetric and flotation processes;

- slags from primary metallurgy of lead and zinc concentrates.

Recycling of part of these residues is carried out on an industrial
scale by rotary furnace volatilization of lead and zinc and production
of a mixed metallurgical concentrate. This process is becoming increa-
singly too expensive as far as fuel and reducer prices are also increasing.

Several countries of the E.E.C. are faced with the problem of
recovery of lead and zinc from such residues, which in Sardinia only
contain about 350 000 t zinc and 65 000 t lead. Taking into account the
fact that some residues are still continuously produced, economic inte-
rest cannot be disputed.

It is recommended to carry out a research following three phases :

- residue characterization through sampling of stocks, general chemical
  analysis (by-products included); morphological and structural analysis
  to develop research methodologies and to facilitate the choice of :

  a) physical separation techniques;
  b) alternative metallurgical techniques (chlorine or sulfur metallurgy);
  c) alternative slag formation techniques.

- laboratory testing of the techniques developed above.

- pilot-plant scaling-up to develop the industrial processes.

R4.17. TREATMENT OF LEAN ORES AND MATERIALS

There are several ores and/or materials with a low lead and/or
zinc content, that could prove a valuable source of these metals
("valuable" here is used metallurgically, not economically).

1. Sulfide ores will not be discussed; fine grinding methods and flotation
   schemes capable of good beneficiation results will hopefully be found.

2. There are several European orebodies with some lead and zinc present
   mainly in oxidized minerals, very often finely disseminated in an
   oxide gangue (limestone, dolomite, iron oxides). Unfortunately an
   acid leaching process is, at present, out of the question.

Research could therefore be proposed on the possibility of applying an alkaline leach or, more generally, a hydrometallurgical process that would not attack the calcium and magnesium carbonates. Such a process could, in many cases, become a complete or partial alternative to flotation of oxidized ores. The possibility of applying fluid-bed leaching could be considered as a possible low-cost alternative to other more common methods. Since it seems possible to electrolyze zinc in caustic soda solution, a complete flowsheet of the process should be evaluated.

3. In situ leaching has been suggested for the treatment of lean subsurface ores; this proposal cannot be rejected, but it appears that several conditions must be fulfilled before such a system could be viable. The main problem is the development of a rather cheap solvent, and the recovery of the metal from very dilute streams.

4. Lead and zinc are present in minute quantities in iron ores and concentrates, and in galvanized recycled materials. Thus, they appear in blast furnace dusts in recoverable amounts. Iron metallurgists are presently sponsoring, through CECAS's specialized committees, several studies on the beneficiation of these dusts by various procedures (some not yet disclosed or published). It may be useful for iron and non-ferrous metallurgists to work together in order to attain their goals more rapidly and/or more safely.

R4.18. PARTICULAR RESIDUES

It is worthwhile to mention that cadmium is only found in zinc ores, and is produced by the metallurgical treatment of several products arising during the production of metallic zinc.

All the proposals cited above cannot be tested without taking into account the recovery of cadmium.

Moreover, all the effluents from the metallurgical plants of either type will probably contain heavy metals such as lead, zinc, cadmium, etc ..., which must be recovered.

Here again, all the proposals for new or improved metallurgical processes cannot neglect environmental aspects as far as gases, fumes, and liquid effluents are concerned.

## R4.19. CONCLUSION

Despite years of research on improving the extractive metallurgy of lead and zinc, it remains a field open to much investigation.

It does not appear that a single academic laboratory or company can have such a broad spectrum of skill and facilities to successfully tackle the various problems cited above.

If the European countries want to get a much better position in the resource pattern for lead and zinc, there is a need for serious collective work, based on a systematic survey of the interested bodies in either universities, research laboratories, or industrial companies.

May it be suggested that such a common enterprise be undertaken without delay, even on a minor or marginal subject, in order to test the running of this type of project.

## R4.2   SECONDARY PRODUCTION

## R4.21. SECONDARY LEAD

Recovery of lead from scrap, wastes and residues seems to be rather complete at present. A stricter control could be applied to the collection of lead sheathed power and communication cables, for which present recycling rate is low.

Since lead in tetraethyl-compounds is not recoverable as long as automobiles are not constructed with "in place" recovery systems, most lead used in other applications will be recovered after more or less time.

A study can, however, be recommended to survey the relative merits of the different processes used now for scrapped batteries. Ideal capacity and safe control of pollution may thus be determined.

A general survey of the used batteries business should be initiated to determine the best collection methods, advantages of treating wet or dry batteries, right way to separate the different parts (made of various materials), etc ...

It may also be worthwhile to look into the behavior of lead in several hydrometallurgical processes which are proposed to recover completely the metals contained in a variety of scrap, wastes and residues.

No Research and Development actions are to be considered for lead recovery from obsolete products.

R4.22. SECONDARY ZINC

Zinc scrap, wastes, and residues are much more diversified than the corresponding lead materials. Most scrap and wastes collected and sold by dealers must be carefully sorted before retreatment. This operation can be tedious and expensive, especially when other materials such as plastics, rubber, grease, contaminate the metallic parts.

Wastes and residues in which zinc metal is mixed with other components are often treated by a preliminary mechanical separation. A new milling process using an Aerofall grinding unit has recently been proposed.

Zinc recyclable from flue dust in iron and steel mills in the E.E.C. countries is estimated of the order of 80 000-90 000 tpy. Facilities must be provided to recover zinc (and lead) from these dusts.

Fabrication of galvanized sheet and strip gives trimmings that are scrapped. Since it is recycled with zinc still on it, the metal is lost out the stack of the steel furnace or is collected by air pollution control equipment and dumped. None of the clippings are recycled for their zinc content, although they contain 4 - 5 % zinc.

An economic method for separating the zinc from the steel would increase their value and would reduce corrosion of steel furnace refractories and make air pollution control easier. Sixty to sixty-five thousand tons of zinc may be recyclable in clippings in 1985-1990. Research and development action should be undertaken to develop an economical process for the direct recovery of zinc from galvanized clippings.

Nearly all zinc-base alloy scrap is in the form of die-castings, which vary in size from grams to a few pounds. They often contain inserts of steel, brass, or other materials; 30-35 % of the die-castings are in autos and the remainder are attached to large amounts of other materials in home appliances, machinery, or farm equipment. Inserts of other metals can be easily removed; larger easily-accessible die-castings can be removed by hand; smaller non-accessible die-castings can be removed by disintegration and separation equipment such as auto hulk shredders; separation from ferrous metals is easily made magnetically. Fragmented scrap, non-magnetic auto-shredder reject, in its worst form (a mixed package with rubber, plastics, fabric, glass) does not make suitable feed. The product must be cleansed of non-metallics. Integrated processes are proposed for the treatment and separation of the non-ferrous metals contained in shredders concentrates. Research may be undertaken to look in the low recycling rate of die-castings scrap, and to develop better equipment for selective and mechanized separation of zinc, aluminium, and copper.

Brass mill and all brass foundry products are generally considered as copper scrap and treated in copper recovery plants.

Close to half of zinc oxides are scrapped as constituents of rubber products. Economical recovery of zinc oxides from scrap rubber products might be possible if economical recycle of rubber is carried out, or zinc can be recovered as flue dust if scrapped rubber can be burned as fuel. Research may be proposed to develop processes for the recovery of materials from tires and other rubber products.

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# DOSSIER ON LEAD AND ZINC

## PART ONE

## STRUCTURE OF SUPPLY:
## GEOLOGY, MINERAL PROCESSING, METALLURGY,
## TECHNICAL ASPECTS OF SUPPLY BY WASTE

*Main authors: P. Bartholomé (+) and C. Ek*

## CONTENTS OF PART ONE

### Note on presentation of the bibliography

It was found convenient to give a short bibliography at the end of each section rather than to gather it as a separate chapter at the end of the volume.

This bibliography includes :

a)   the works to which reference is made in the text

b)   a few recent books and papers dealing with the subject in a general way.

A more extensive bibliography can be found in these books and papers.

# PART 1.1.

# GEOLOGY AND PROSPECTING

*UNITS :*

*The only units of mass used in this report are the gramme (g), the kilogramme (kg), the metric tonne (t) and the megatonne or million of metric tonnes (Mt). In quotations, however, other units appear (short or long tons, ounces etc...).*

*The only units of concentration are the percent (%) and the ppm (part per million or gramme per tonne).*

*When quantities were originally expressed in other units, conversion factors were applied. In some cases we found that in the original source the units used were not specified with precision ; errors may have resulted, which are, however, thought to be few and minor.*

*QUOTATIONS :*

*Text between brackets are our own translation if the original source was in French, German or Italian.*

CHAPTER 11.1 - ORES


11.11 - MAIN FEATURES OF LEAD-ZINC ORES


11.11.A - GRADE


Many common rocks contain a few ppm or a few tens of ppm of zinc and lead (1 ppm = 1 gram per ton). The winning of the metals from such raw materials would be so expensive that it is never undertaken or even contemplated. Only rocks of quite abnormal composition can be used as ore.


In the past, ores have been mined, which contained more than 50 % combined metal (Zn + Pb). Very limited amounts of them could however be found so that, progressively, ores of lesser and lesser grades came to be used. This evolution required new technologies in the fields of mining, beneficiation and metallurgy. But it happened that roughly speaking, on a global scale, the improvement of technologies kept pace with the depletion of the richest ores.


Nowadays, with a 33 % average grade, the Kabwe mine in Zambia stands as an exception. A 10 % average grade is considered quite attractive. And mines are opened to produce ores containing 4 % combined metal[1] although occasionnally rich orebodies are still found.


Data concerning grade in European Pb-Zn deposits mined at the present time are summarized in table 11.11.1.

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[1] For example the Elmwood Mine in Central Tennessee with 4.5 to 5 % Zn and no Pb; or the Viburnum n° 27 Mine with 0.23 % Zn, 2.9 % Pb and 0.17 % Cu (Kyle, Econ. Geol., 1976, p. 892 and Grundmann, Econ. Geol., 1977, p. 349). Both are underground mines.

*TABLE 11.11.1.* - Grade of some Zn and Pb deposits currently mined in the E.E.C.

| | Zn (%) | Pb (%) | Ag (ppm) | Cu (%) | |
|---|---|---|---|---|---|
| Black Angel, Greenland | 14.7 | 5.2 | 28 | | 800 ppm Cd |
| Tara, | 11,43 | 2,35 | | | |
| Silvermines | | | | | |
| upper G | 9,2 | 2.4 | 22 | | |
| lower G | 3.4 | 4.5 | 34 | | |
| B | 6.07 | 3.5 | ? | | |
| Tynagh, | | | | | |
| zone II | 3.23 | 4.06 | 46 | 0.29 | |
| zone III | 4.45 | 2.44 | 14 | 0.05 | |
| Les Farges, | - | 5.7 | 105 | | barite |
| Noilhac - Saint-Salvy, | 6 to 15 | | 50 to 120 | | germanium |
| Rammelsberg | 12 to 13 | 6 to 7 | 100 | 0.5 | |
| Grund | 4 to 5 | 3 to 4 | 100 | 0.1 | |
| Meggen | 11 | 1.2 | | | |
| Lüderich | 7 | 1.5 | | | |
| Monteponi | 2.95 | 2.20 | | | |
| Campo Pisano- Funtanaperda | 7.11 | 0.20 | | | |
| Seddas Moddizzis | 5.92 | 0.85 | | | |
| Acquaresi, Montecani Masua and Nebida | 4.95 | 1.64 | 4 | | |
| San Benedetto | 3.70 | 1.80 | 5 | | |
| Rosas | 2.01 | 0.10 | 3 | 0.28 | |
| San Giovanni | 6.85 | 1.5 | 7 | | |
| Montevecchio | 3.5 | 1.7 | 13 | 0.04 | |
| Funtana Raminosa | 3.0 | 1.4 | | 1.0 | |
| Buggeru - Su Zurfuru | 8.0 | 1.1 | 5 | | |
| Fenice Capanne | 5.2 | 1.1 | | 0.3 | |
| Raibl | | | | | |
| (sulfide ore) | 4.4 | 0.5 | | | |
| (oxyde ore) | 7.6 | 1.1 | | | |
| Gorno | 4.4 | 0.85 | | | |
| Salafossa | 4.0 | 0.7 | | | |

## 11.11.B - MIXED ORES

It is well known (and clearly displayed in table 1) that lead and zinc are often associated in ores. One can hardly overemphasize the technical and economical importance of this fact, which has recently been underlined by Mr. Tom Borresen at the recent meeting in London (Mining Journal, June 24, 1977) :

"Out of a total mined lead output of around 2.6 million tons some 1.6 million was recovered from mixed ore which as defined by the Lead-Zinc Study Group are those in which the proportion of lead to zinc is in the range of 1 to 4 and 4 to 1. Considering zinc, mined output from mixed ore accounted for nearly 2.6 million tons of the world total of 4.3 million tons of primary zinc output".

## 11.11.C - MINERALOGY OF ZN AND PB

Zn-Pb ores are heterogeneous mixtures of minerals. Some of these are Zn and Pb compounds, which can be conveniently classified as sulfides and as oxidized ores, the latter group including carbonates, silicates, sulfates, etc ...

Most Zn and Pb ores currently mined are sulfide ores. Oxide ores occur mostly at the surface or at shallow depths so that many of their deposits are mined out. Ores where sulfides and oxides occur together are also found.

A few interesting properties of major Zn and Pb minerals are summarized below (see Palache et al., 1944, and Wedepohl, 1969, for more detailed information).

Galena, which is the most widespread Pb mineral and the only common sulfide of Pb, corresponds rather closely to the formula PbS (86 % Pb). As impurities, it contains small amounts (less than 50 ppm) of Mn, Ni, Tl, Sn and Cd, and larger ones (up to a few thousands ppm) of Ag, Sb, Bi and As. Of these impurities, Ag is the most important economically. Ag-bearing sulfides such as acanthite-argentite ($Ag_2S$) or mathildite ($AgBiS_2$) form limited solid solution with PbS.

In addition Ag-bearing minerals such as native silver, acanthite and tetra-hedrite are often found as minute inclusions in galena.

Other Pb-bearing sulfides, much less common than galena, are :

| Name | Formula | Pb content | Impurities |
|---|---|---|---|
| jamesonite | $Pb_4FeSb_6S_{14}$ | 40 % | up to 3 % Cu, 6 % Zn |
| boulangerite | $Pb_5Sb_4S_{11}$ | 55 % | traces of Zn, Ag, As |
| bournonite | $PbCuSbS_3$ | 42 % | much As, some Ag and Zn |

Cerusite ($PbCO_3$) contains about 77 % Pb with small amounts of Zn, Ca and Mg as impurities. Anglesite ($PbSO_4$) contains about 68 % Pb.

Sphalerite, which is the most widespread Zn mineral and the only common sulfide of Zn, corresponds approximately to the formula ZnS. Usually the Zn content is however significantly below the 67 % suggested by the formula, because sphalerite contains many impurities, some of which are quite abundant :

| | |
|---|---|
| Fe | up to 25 % |
| Cd, Mn | 5 000 ppm |
| Ga, Ge, In | 100 ppm |
| Sb, As, Se, Hg | 30 ppm |
| Au, Ag | traces |

The main oxide minerals of Zn are :

smithsonite ($ZnCO_3$) with about 52 % Zn and various impurities (up to 10 % Fe, 1 % Mn, Ca and Cu)

hemimorphite : $Zn_4 (OH)_2 Si_2O_7 H_2O$

hydrozincite : $Zn_5 (CO_3)_2 (OH)_2$

## 11.11.D - <u>OTHER MINERALS PRESENT IN ZN AND PB ORES</u>

Many minerals occur in Zn and Pb ores. Those mentioned in this report are listed in table 11.11.2. Among them, a few may be recovered for the production of some other metal (Cu, Ag, Bi for example); others can be used as minerals (barite and fluorite for example). Most are waste material. Common gangue minerals found in Zn and Pb ores are calcite $(CaCO_3)$, dolomite $(CaMgC_2O_6)$, quartz $(SiO_2)$, and various silicates.

Among the useful minerals occurring in Zn and Pb ores, the following are noteworthy :

> Native silver
> Argentite-Acanthite
> Pyrargyrite
> Proustite
> Chalcopyrite
> Tetrahedrite
> Tennantite

TABLE 11.11.2

Minerals mentioned in this report

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(the figures between brackets are the Zn and Pb contents)

## 1. SULFIDES

| | | |
|---|---|---|
| Arsenopyrite | : | FeAsS (mon., -, -) |
| Bismuthinite | : | $Bi_2S_3$ (orth., -, -) |
| Boulangerite | : | $Pb_5Sb_4S_{11}$ (-, 55) |
| Bournonite | : | $PbCuSbS_3$ (-, 42) |
| Chalcopyrite | : | $CuFeS_2$ (tetr., -, -) |
| Covellite | : | CuS (hex., -, -) |
| Galena | : | PbS (cub., -, 87) |
| Greenockite | : | CdS (-, -) |
| Jamesonite | : | $Pb_4FeSb_6S_{14}$ (-, 40) |
| Marcasite | : | $FeS_2$ (-, -) |
| Mispickel | = | arsenopyrite |
| Polybasite | : | $(Ag, Cu)_{16} Sb_2 S_{11}$ (-, -) |
| Pyrite | : | $FeS_2$ (cub., -, -) |
| Pyrrhotite | : | $Fe_{1-x}$ S (-, -) |
| Sphalerite | : | ZnS (cub., 67, -) |
| Stannite | : | $Cu_2FeSnS_4$ (tetr., -, -) |
| Stibnite | : | $Sb_2S_3$ |
| Tennantite | : | $(Cu, Fe)_{12} As_4 S_{13}$ |
| Tetrahedrite | : | $(Cu, Fe)_{12} Sb_4 S_{13}$ |

## 2. CARBONATES

| | | |
|---|---|---|
| Ankerite | : | Ca (Fe, Mg, Mn) $(CO_3)_2$ (trig., -, -) |
| Azurite | : | $Cu_3 (CO_3)_2 (OH)_2$ (mon., -, -) |
| Calcite | : | $CaCO_3$ (trig., -, -) |
| Cerusite | : | $PbCO_3$ (orth., -, 77,5) |
| Chalybite | = | Siderite |
| Dolomite | : | CaMg $(CO_3)_2$ (trig., -, -) |
| Leadhillite | | (see sulfates) |
| Malachite | : | $Cu_2CO_3 (OH)_2$ (mon., -, -) |
| Otavite | : | $CdCO_3$ |
| Siderite | : | $FeCO_3$ (trig., -, -) |
| Smithsonite | : | $ZnCO_3$ (trig., 52,1, -) |
| Witherite | : | $BaCO_3$ (orth.) |

## 3. SULFATES

| | | |
|---|---|---|
| Anglesite | : | $PbSO_4$ (orth., -, 68,3) |
| Barite (Baryte) | | $BaSO_4$ (orth., -, -) |
| Gypsum | : | $CaSO_4 \cdot 2H_2O$ (mon., -, -) |
| Lanarkite | : | $Pb_2O$ $(SO_4)$ (mon., -, 78,7) |
| Leadhillite | ; | $Pb_4$ $(SO_4)$ $(CO_3)_2$ $(OH)_2$ (mon., -, 76,8) |

## 4. PHOSPHATES

| | | |
|---|---|---|
| Pyromorphite | : | $Pb_5$ (Cl) $(PO_4)_3$ (hex., -, 76,2) |

## 5.

| | | |
|---|---|---|
| Cryolithe | : | $Na_3AlF_6$ (mon., -, -) |
| Fluorite (fluorspar) | : | $CaF_2$ (cub., -, -) |

## 6. SILICATES

| | | |
|---|---|---|
| Calamine | ▪ | hemimorphite |
| | ▪ | sometimes hemimorph. + smithsonite |
| Chalcedony | = | fine-grained variety of quartz |
| Hemimorphite | : | $Zn_4Si_2O_7$ $(OH)_2 \cdot H_2O$ (orth., 54,3, -) |
| Kyanite | : | $Al_2SiO_5$ (tricl., -, -) |
| Pyrophyllite | : | $Al_2Si_4O_{10}$ $(OH)_2$ (mon., -, -) |
| Quartz | : | $SiO_2$ (trig., -, -) |
| Sericite | = | a fine grained member of the Mica group |
| Staurolite | : | (Fe, Mg, Zn) $Al_9$ $Si_4$ $O_{23}$ (OH) (orth., -, -) |
| Tremolite | : | $Ca_2Mg_5Si_8O_{22}$ $(OH)_2$ (amphibole) |

## 7. OXIDES

| | | |
|---|---|---|
| Hematite | : | alpha-$Fe_2O_3$ (trig., -, -) |
| Psilomelane | : | a general term for massive, not specifically identified, hard manganese oxides |
| Rutile | : | $TiO_2$ (tet.) |

## 8. HYDROUS OXIDES

| | | |
|---|---|---|
| Goethite | : | alpha-FeO (OH) (orth.) |
| Limonite | : | a general term for hydrous iron oxides, mostly goethite |

Native silver does not as a rule consist of pure silver. This element is alloyed with variable (often small) quantities of mercury and gold. It is often found associated with galena or oxyde minerals of Pb.

Argentite-Acanthite ($Ag_2S$), Pyrargyrite ($Ag_3SbS_3$) and Proustite ($Ag_3AsS_3$) are rare minerals, the value of which results of their high silver content.

Chalcopyrite ($CuFeS_2$) is a major source of copper.

Tetrahedrite ($CuSb_4S_{13}$) and Tennantite ($CuAs_4S_{13}$) are copper minerals but they may contain

| | | | |
|---|---|---|---|
| Ag | up to 18 and | 14 | % respectively |
| Zn | 8 | 9 | % |
| Bi | 4 | 13 | % |
| Co | 4 | 1 | % |
| Ni | 4 | | |
| Hg | generally less than 1 % | | |
| Pb | generally less than 2 % | | |

## 11.11.E - COMPOSITION OF CONCENTRATES

There is no common sulfide or oxyde mineral which is rich in both Zn and Pb. As a result it is in principle possible to obtain separate concentrates of Zn and Pb after crushing and grinding the ore. In practice however this operation may be very difficult if the mineral grains are too small or too complexely interlocked with each other. The technology of concentrate production is dealt with in part 1.2 of this report. The composition of the various concentrates obtained from the Navan, Ireland, and Black Angel, Greenland, deposits are shown in tables 11.11.3 and 4 respectively.

TABLE 11.11.3

Concentrates obtained at Navan, Ireland

(by courtesy of Tara Mines Limited)

Monthly composite analysis

| | LEAD FLOT. CONC. | ZINC FLOT. CONC. | ZINC LEACH CONC. | MILL FEED | FINAL TAILINGS |
|---|---|---|---|---|---|
| Zn % | 7.18 | 57.06 | 55.57 | 9.52 | 1.09 |
| Pb % | 62.87 | 2.22 | 2.23 | 2.04 | 0.36 |
| Fe % | 4.09 | 0.32 | 0.84 | 4.10 | 1.59 |
| MgO % | 0.13 | 0.48 | 0.29 | | |
| Ba % | 0.51 | 2.04 | 1.12 | | |
| Hg p.p.m. | 16 | 62 | 56 | 16 | <1 |
| Ni % | 0.029 | 0.010 | 0.010 | | |
| Sb | 1.08 | 0.11 | 0.10 | | |
| As | 0.326 | 0.139 | 0.086 | 0.060 | 0.067 |
| Ag g/t | 210 | 67 | 64 | 19 | 6 |
| Mn % | 0.012 | 0.016 | 0.014 | | |
| Cu | 0.05 | 0.10 | 0.11 | | |
| Cd | 0.032 | 0.210 | 0.210 | | |
| F | <0.02 | <0.02 | <0.02 | | |

TABLE 11.11.4

Concentrates obtained at Black Angel, Greenland

(by courtesy of Greenex A/S)

| ELEMENT | MILL FEED | LEAD CONC. | ZINC CONC. |
|---|---|---|---|
| Pb | 4.5 % | 69.0 % | 1.9 % |
| Zn | 15.0 % | 7.0 % | 58.8 % |
| Fe | 16.0 % | 2.1 % | 4.8 % |
| Ag | 28.8 g/t | 36.16 g/t | - |
| S | - | 16.2 % | 33.5 % |
| Bi | - | 0.002 % | - |
| As | - | - | 0,002 % |
| Cd | 0.08 % | 0.04 % | 0.32 % |
| Hg | - | - | 0.007 % |

| ELEMENT | ZINC CONC. | LEAD CONC. |
|---|---|---|
| Cl | - | 0.051 % |
| Au | 0.03 g/t | 0.16 g/t |
| Ag | 12.8 g/t | 387 g/t |
| Cu | 0.16 % | 0.43 % |
| Sb | - | 0.065 % |
| As | - | 0.052 % |
| Hg | - | 0.00085 % |
| Sn | 0.003 % | 0.006 % |
| Bi | - | 0.01 % |
| Tl | 0.0001 % | 0.0001 % |
| Se | 0.0001 % | 0.0007 % |
| Te | <0.0001 % | 0.0003 % |
| F | - | 0.002 % |
| $Al_2O_3$ | 0.08 % | 0.08 % |
| Mn | 0.02 % | - |
| CaO | 0.6 % | 0.5 % |
| MgO | - | 0.16 % |
| $SiO_2$ | 0.4 % | 3.1 % |

As illustrated by these tables, and for the reasons mentioned above, Cd tends to be associated with Zn and Ag, Ag and Sb with Pb in the concentrates.

The commercial value of concentrates is strongly dependent on the nature and amounts of impurities. For example Cd, Ag and Au increase the value while Hg, As and Sb tend to decrease it. Mg is undesirable in concentrates to be treated in electrolytic plants. Few definite and permanent rules can however be given in this matter. Each smelter has its own requirements. These requirements may change with changing technology. In addition small quantities of rather impure concentrates can be accepted by a particular smelter if they can be mixed with purer concentrates.

At the present time, because of more severe environmental regulations, Cd is becoming less desirable and Hg more undesirable than they were in the past.

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## 11.12 - BY-PRODUCTS AND CO-PRODUCTS OF ZN AND PB

## 11.12.A - METALS AND MINERALS

Barite ($BaSO_4$), witherite ($BaCO_3$), fluorite ($CaF_2$), chalcopyrite ($CuFeS_2$), pyrite and marcasite ($FeS_2$), are minerals commonly associated with galena and sphalerite in Zn-Pb ores, and are recovered as distinct concentrates in some mines.

On the other hand, some valuable chemical elements are recovered as by-products from the Zn and Pb concentrates themselves. The following data, which refer to the U.S.A., are very informative in this regard, although equivalent figures for EEC countries must be somewhat different.

TABLE 11.12.1

Zinc by-product and co-product relationship   U.S.A.   1973

| | Unit | Quantity | % of total output |
|---|---|---|---|
| Cadmium | t | 3 370 | 100 |
| Germanium | t | 12.25 | 100 |
| Indium | kg | w | 100 |
| Thallium | kg | w | 100 |
| Gallium | kg | w | w |
| Lead | t | 65 300 | 11.9 |
| Silver | t | 120 | 10.3 |
| Gold | kg | 1 800 | 5.2 |
| Copper | t | 4 535 | 0.3 |
| Sulfur | t | 263 000 | 2.2 |
| Zinc | t | 325 600 | 74.9 |

w : withheld to avoid disclosing company confidential data.

(Mineral Facts and Problems, 1975)

TABLE 11.12.2

Lead by-product and co-product relationship  U.S.A.  1973

| | Unit | Quantity | % of total output |
|---|---|---|---|
| Bismuth | t | w | 100 |
| Antimony | t | 665 | 57.3 |
| Zinc | t | 91 600 | 21.1 |
| Silver | t | 190 | 16.6 |
| Tellurium | kg | w | w |
| Copper | t | 9 977 | 0.6 |
| Sulfur | t | w | w |
| Gold | kg | 60 | 0.2 |
| Lead | t | 478 000 | 87.4 |

w : withheld to avoid disclosing company confidential data.

(Mineral Facts and Problems, 1975)

## 11.12.B - SOME CHEMICAL ELEMENTS ASSOCIATED WITH ZN AND PB

Cadmium is a rare element, present in common rocks at concentrations lower than 1 ppm. It is closely associated with Zn, the Zn/Cd ratio usually ranging from 500 to 900. Cadmium minerals such as greenockite (CdS) or otavite ($CdCO_3$) are very uncommon and cannot be mined for themselves.

In sphalerite, the Cd content is often between 1 000 and 5 000 ppm, reaching exceptionally 1 or 2 %. As a rule, it is higher in deposits of the Mississipi Valley type (see chapter 11.2).

Germanium is also a rather rare element with an average concentration of 1.5 ppm in the earth crust. However there are a few ore deposits in the world where germanium minerals can be recovered. On the other hand a number of common sulfides contain small proportions of germanium :

| | | |
|---|---|---|
| sphalerite | up to 2 000 ppm | (commonly 100) |
| enargite | 5 000 ppm | |
| galena | 10 ppm | |
| tennantite | 5 000 ppm. | |

Indium, Gallium and Thallium are other rare elements, which do not form minerals of their own except in very special circumstances and very small amounts. Therefore they can be recovered only as by-products from a more common mineral in which they are concentrated : sphalerite or cassiterite for indium, sphalerite or galena for thallium, sphalerite again for gallium.

Bismuth forms several sulfide minerals, which occur locally in large amounts. There is a deposit in Bolivia where bismuth is mined independently of any other metal. However large amounts of bismuth are also obtained from the smelting of Pb, Cu, Mo, Sn, Ag and Au ores.

Antimony, although a rare element, is a major component of two not unfrequently found minerals : stibnite ($Sb_2S_3$) and tetrahedrite ($Cu_8Sb_2S_7$). Many antimony deposits are known in Bolivia, China, South Africa. Most of them are however very small. Considerable amounts of this element are obtained from the smelting of Pb ores.

Silver, although a rare element with an average concentration of 0.2 ppm in the earth crust, is a major component of some 50 minerals, among which several sulfides. Much silver is obtained as a by-product of Cu, Pb or Zn smelting.

## 11.12.C - SOME USEFUL MINERALS ASSOCIATED WITH GALENA AND SPHALERITE

Fluorite and barite are important industrial minerals which are often found in association with galena and sphalerite. Fluorite is the only major source of the chemical element fluorine. Barite is the major source of the chemical element barium. Another barium mineral, witherite, which is much less abundant than barite, was mined in England until 1969 and also belongs to the same association.

In ore deposits, fluorite and barite are mixed with Zn and Pb sulfides and gangue minerals in various proportions so that any one of these minerals can locally be recovered as a by-product of another.

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CHAPTER 11.2 - DEPOSITS OF THE EUROPEAN COMMUNITY.

## 11.21  CLASSIFICATION OF Zn AND Pb DEPOSITS

Several authors have attempted to classify Zn and Pb deposits into types or families but no classification has gained general acceptance. There is no agreement concerning the number of types or the criteria to be used to distinguish among them. Further disagreement may arise with regard to the type or family a particular deposit belongs to.

Four examples of classifications in current usage are given below.

Bouladon (1969) classifies Zn and Pb deposits into four major classes on the basis of the geological environment where they are found :

1. deposits emplaced in sedimentary covers without associated volcanism and plutonism,

2. deposits emplaced during sedimentation in volcano-sedimentary successions of orogenic belts,

3. silver-bearing deposits emplaced in orogenic belts and associated with late-orogenic plutonism and volcanism,

4. other deposits.

The economic importance of the first three major classes is shown by the following table :

| | % of the world production in 1969 | | % of the world reserves | | size of orefield | size of district |
|---|---|---|---|---|---|---|
| | Zn | Pb | Zn | Pb | Mt metal | Mt metal |
| 1. | 24 | 25 | 23 | 25 | up to 2 | up to 15 |
| 2. | 27 | 13 | 41 | 27 | up to 6 | up to 10 |
| 3. | 27 | 35 | 21 | 22 | | up to 5 |

At the present time, the second class is becoming economically more important while the third one is becoming less so.

Bauchau (1971) distinguishes between several types of Zn and Pb deposits on the basis of both geochemical and geological criteria. In his classification, the most important types are the following :

type  1. : Pb-, Zn-, and Cu-bearing pyritic orebodies associated with volcanic rocks,

type  2. : stratiform disseminations, poor in pyrite, associated with volcanic rocks (kuroko),

type  4. : stratiform deposits of disseminated ore in sulfur-poor and iron-poor sediments (Kupferschiefer),

type  5. : tin deposits with Pb, Zn, and Cu,

type  6. : veins and other orebodies associated with subvolcanic intrusions and containing Cu, Mo, Pb, Zn, Ag,

type  7. : veins and other orebodies associated with subvolcanic intrusions and containing Cu, Pb, Zn, Ag as well as large amounts of As and Sb,

type 11. : Cu + Pb + Zn deposits with siderite,

type 13. : Cu + Pb + Zn tennantite deposits in carbonate environment,

type 14. : silver-poor Zn + Pb deposits, sometimes with pyrite, in sedimentary covers (Mississipi Valley type),

type 15. : fluorite bearing stratiform or vein-type Zn + Pb deposits associated with mafic rocks.

On a world scale, the abundance of the different types is shown by the following figures where the amounts of Pb, Zn and Ag correspond to the original metal content of the deposits (past production + reserves) :

| type | Pb | | Zn | | Ag | |
|------|----|----|----|----|----|----|
| | Mt | % | Mt | % | x100t | % |
| 1 | 53 | 25 | 95 | 34 | 127 | 16 |
| 2 | 0.7 | 0.3 | 2 | 0.7 | 2 | 0.3 |
| 4 | 0.8 | 0.4 | 1.9 | 0.7 | 16 | 2 |
| 5 | 0.4 | 0.2 | 0.5 | 0.2 | 47 | 6 |
| 6 | 44 | 21 | 39 | 14 | 383 | 47 |
| 7 | 28 | 13 | 28 | 10 | 193 | 24 |
| 11 | 7 | 3.5 | 7 | 2.6 | 21 | 2.5 |
| 13 | 2.7 | 1.3 | 4 | 1.4 | 5 | 0.6 |
| 14 | 66 | 31 | 88 | 32 | 13 | 1.6 |
| 15 | 4 | 2 | 0.4 | 0.2 | 0.5 | |
| others | | 2.3 | | 4.2 | | |
| | | 100 | | 100 | | 100 |

According to Bauchau, the relative abundance of the different types on the European continent (the U.S.S.R. not being taken into account) is as follows :

| Type | Pb % | Zn % |
|------|------|------|
| 1 | 7.15 | 25.01 |
| 4 | 1.26 | 2.37 |
| 5 | 0.47 | 0.05 |
| 6 | 25.25 | 12.62 |
| 7 | 4.75 | 2.55 |
| 11 | 8.01 | 4.92 |
| 14 | 46.47 | 52.08 |
| 15 | 6.32 | 0.25 |
| others | 0.30 | 0.15 |
| | 100 | 100 |

Wedow and others (1973) classified the zinc deposits "by broad geological environments" as :

1. contact-metamorphic deposits

2. irregular replacement deposits and associated fissure fillings

3. vein deposits

4. stratabound deposits in metamorphic rocks

5. stratabound deposits in carbonate rocks

6. stratiform deposits

7. deposits formed by supergene enrichment or laterization.


Finally Smirnov and Gorzhevsky (in Smirnov, 1977) propose the following classification :

1. skarn deposits

2. metasomatic deposits in carbonate rocks

3. vein deposits

4. pyritic deposits

5. stratiform deposits

6. metamorphosed deposits.


Because of the lack of agreement between the different authors, it seems appropriate to examine in some detail what kind of deposit has actually been found in Europe and in what geological environment.

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## 11.22 - DENMARK

## 11.22.A - INTRODUCTION

There are two lead-zinc areas in the Kingdom of Denmark. Both are situated in Greenland (fig. 11.22.1). One, on the West coast, will be called the Mârmorilik district (A on fig. 11.22.1 and 2) in this report. The other, on the East coast, will be called the Central East Greenland district (B on fig. 11.22.1).

Small amounts of zinc and lead sulphides were recovered from the cryolite mine at Ivigtut (C on fig. 11.22.1) when it was in operation. This deposit must have contained initially about 122 000 t of Zn and 10 000 t of Pb (Pauly, 1974). The unmined iron sulfide deposit at Lersletten near Egedesminde (D on fig. 11.22.1) should also be mentioned here since it contains 3.5 Mt probable ore and 12 Mt possible ore with 2 % Zn.
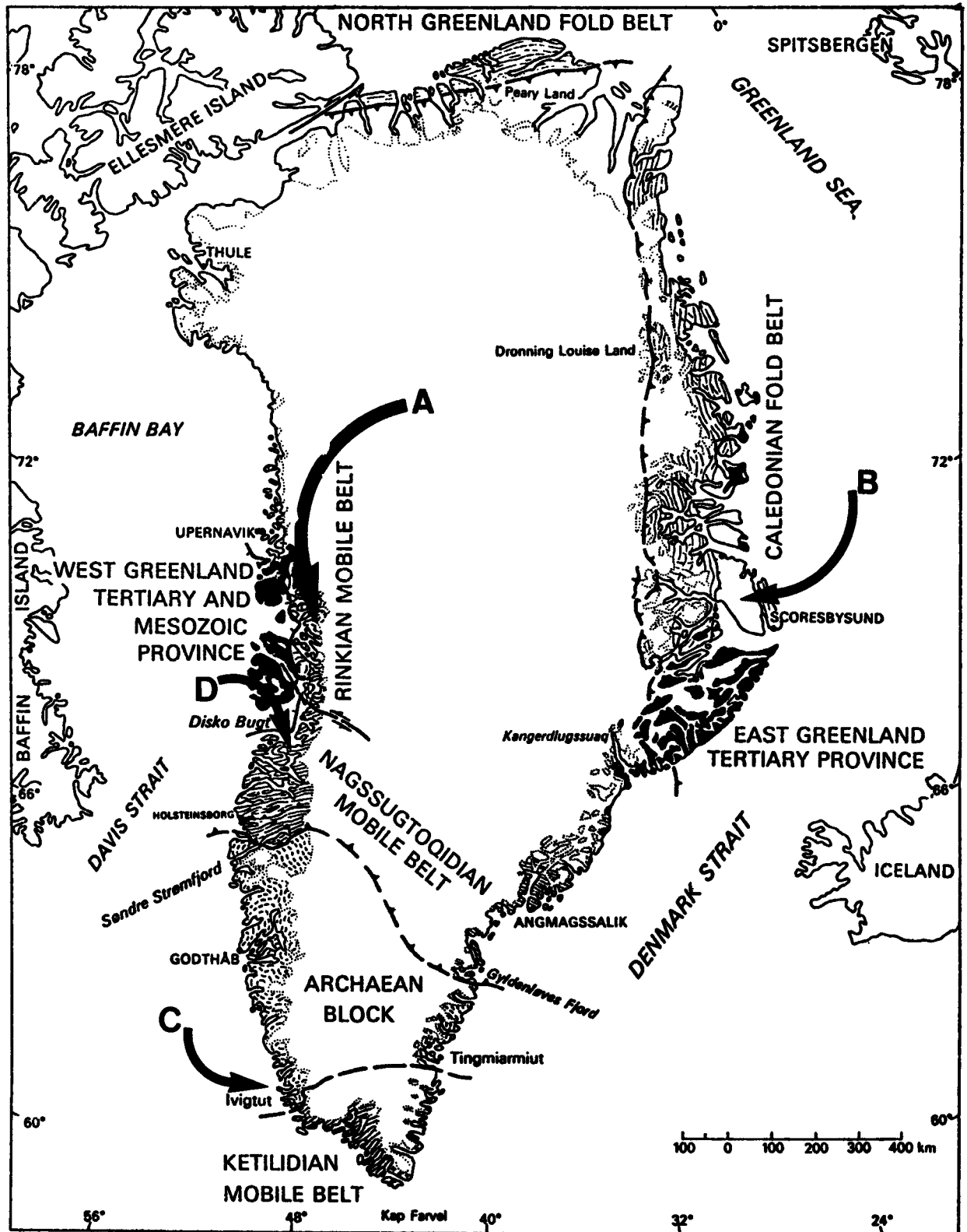
Fig. 11.22.1 - The main geological provinces of Greenland
(from Escher and Watt, 1976)

A : Mårmorilik District. See fig. 11.22.2 for precise location.

B : Central East Greenland district.

C : Ivigtut cryolite deposit.

D : Lersletten.
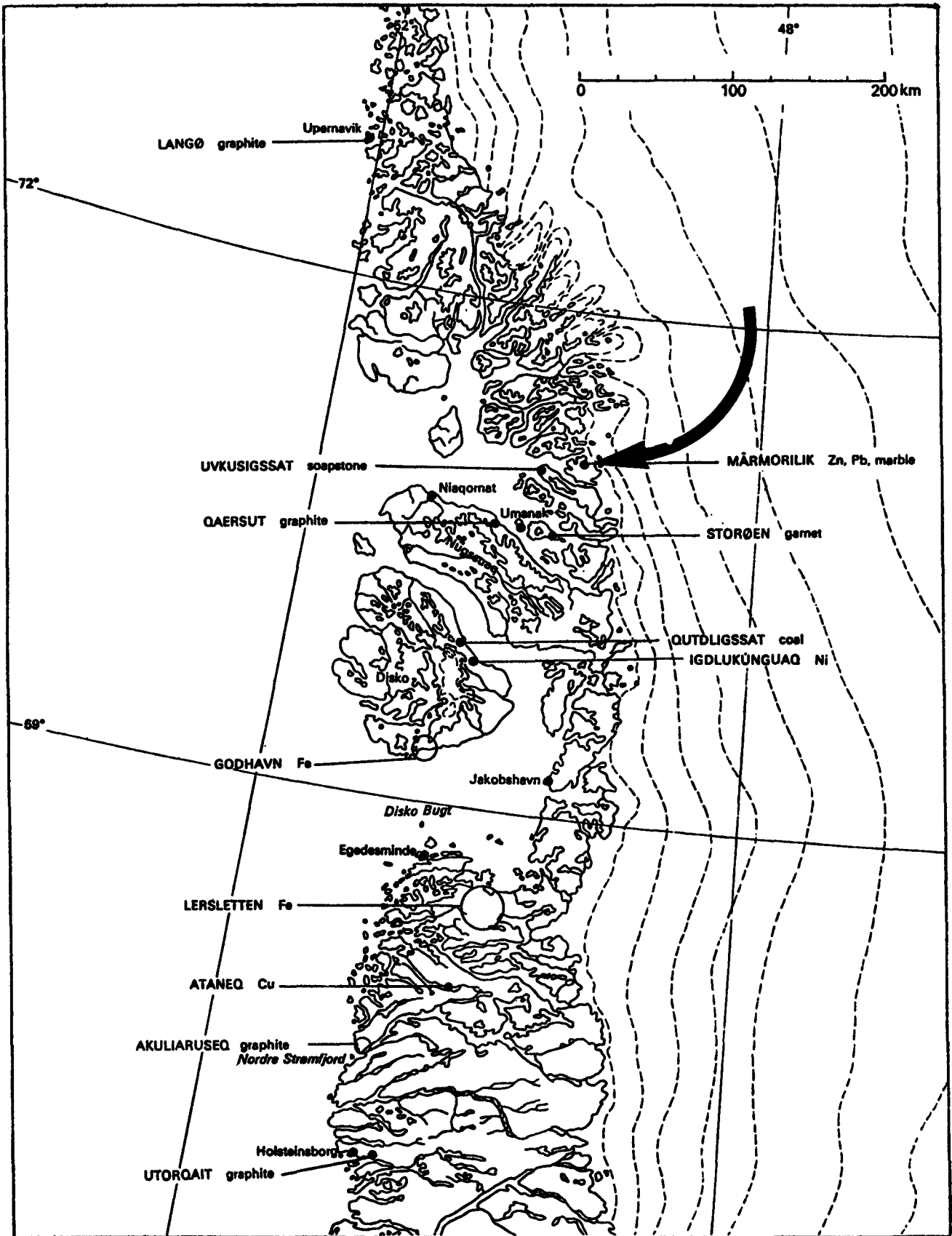
Fig. 11.22.2 - Location of the M&rmorilik District (after Nielsen, in Escher and Watt, 1976)

## 11.22.B - REGIONAL GEOLOGY

The geology of Greenland has recently been described in a book edited by Escher and Watt (1976), to which the reader is referred. Fig. 11.22.3, summarizing the geological history of the island is taken from that book.

We shall be concerned here with only two of the geological provinces constituting Greenland : the Rinkian Mobile Belt and the Caledonian Fold Belt (fig. 11.22.1 again).

The former lies to the North of the Archaean Block and of the Nagssugtogidian Mobile Belt. According to Escher and Watt (p. 12-13) :

"It is considered as a separate structural province because it presents a striking contrast in tectonic style to the Nagssugtoqidian. The Rinkian is characterised by large-scale recumbent isoclinal folds and nappes, and large open gneiss domes which are often surrounded by rim synclines of metamorphosed supracrustal rocks. Corresponding structures and supracrustal successions are known from Baffin Island.

"The supracrustal sequences overlie earlier gneisses and are particularly well developed in the Umanak region where a succession over 5 km thick of quartz-ites, pelites and flysch-like metasediments is preserved. These were meta-morphosed together with remobilised basement gneisses under upper greenschist-amphibolite facies conditions during the formation of the dome structures.

"To the north, near Upernavik, the supracrustal sequences are cut by a major igneous body, the Prøven granite, which locally resembles the Ketilidian rapakivi granites of South Greenland. The northern part of the granite and the adjacent gneisses contain granulite facies mineral assemblages.

"K-Ar mineral ages from the Rinkian mobile belt range from 1870 to 1650 m.y.".

The Caledonian Fold Belt of East Greenland is described as follows by the same authors (p. 14 and 15).

"The East Greenland fold belt is part of a major Caledonian orogenic belt which occurs on both sides of the North Atlantic Ocean. In North-East Greenland the Caledonian fold belt is superimposed on the traces of a Caroli-nidian fold belt which may have formed about 1000 m.y. ago.

| | South Greenland | southern West and South-East Greenld | south central West Greenland | north central West Greenland | central East Greenland | North-East and eastern N. Greenld | North Greenland | North-West Greenland |
|---|---|---|---|---|---|---|---|---|
| PHANEROZOIC | | | | | | | | |
| 600 | | | | | Caledonian 395 - c. 455 m.y. | Caledonian 320 - c. 410 m.y. | North Greenland fold belt | |
| Late 900 | | | | | Eleonore Bay Gp. ? | Hagen Fjord Gp. ? | | |
| PROTEROZOIC Middle | Gardar magmatism 1130 - 1330 m y | | | | c. 1160 m.y. Krummedal | Carolinidian c. 1000 m.y. | Carolinidian | c. 1200 m.y. Thule Group |
| 1600 | Ketilidian mobile belt 1830 - 1850 m.y. | | Nagssugtoqidian mobile belt ? | 1680 - 1870 m.y. Rinkian mobile belt | c. 1900 m.y. Charcot Land | | | c. 1880 m.y |
| Early 2500 | | c. 2550 m.y. c. 2750 m.y. Development of Archaean c. 3000 m.y gneiss complex | c 2830 m.y. Basement | Basement | c 3000 m.y. Basement | c 3000 m.y. Basement | | Basement |
| ARCHAEAN 3700 | | c. 3750 m.y | | | | | | |

Divisions in the Precambrian are used informally

——— End of thermal activity (K - Ar and Rb - Sr mineral ages)

——— Major magmatic/metamorphic event (Rb - Sr whole rocks and U - Pb zircon ages)

▢ Deposition

▨ Orogeny

▨ Cratogenic igneous activity

**Fig. 11.22.3** - Schematic chronology of the major events in the Geological history of Greenland (after Escher and Watt, 1976).

"The Caledonian fold belt contains extensive areas of Archaean and Protero-
zoic gneisses, and at least two groups of early Proterozoic metasediments.
Geosynclinal conditions were established in late Proterozoic time and sedi-
mentation was almost continuous through the Cambrian and Ordovician until
the onset of the Caledonian orogeny. The youngest sediments affected by the
orogeny are carbonate sequences of Middle Ordovician age in central East
Greenland, and Middle to Upper Silurian age in North-East Greenland. The
older metamorphic complexes and younger geosynclinal sediments are variously
involved in the Caledonian folding, thrusting and regional metamorphism, and
are locally cut by late granites.

"Devonian to early Permian continental sediments (molasse), periodically
disturbed by minor movements, accumulated east of the fold belt and preserve
a celebrated fish and tetrapod fauna.

"In East Greenland the Caledonian molasse deposits were followed by an Upper
Permian transgression with deposition of limestone, gypsum and shale on
down-faulted and tilted blocks along the eastern border of the fold belt.
Triassic sediments mostly comprise marine and continental clastic rocks
whereas the succeeding Jurassic clastic sequence mostly accumulated in a
shallow marine shelf environment and is highly fossiliferous. Cretaceous
sediments are marine and predominantly clastic, consisting of conglomerates,
sandstones and shales. The composite thickness of the whole sequence approa-
ches 7000 m. Cretaceous and early Tertiary sandstones are known further
south at Kangerdlugssuaq (68° N) immediately below the Tertiary basalts.

"The Jurassic rocks provide one of the most complete sequences bordering
the North Atlantic Ocean and are thus of special interest for studies of
the evolution of the early Atlantic Ocean. Faulting was active throughout
the Mesozoic and into the Tertiary, and has been related to crustal widening;
the intense faulting in the late Jurassic may be related to the initial
spreading between the North American and European continents".

## 11.22.C - THE MARMORILIK DISTRICT

An important deposit, named Sorte Engel (Black Angel) has been mined
for several years in this district. It is briefly described by Nielsen (in
Escher and Watt, 1976, pp. 470-472). We are indebted to Mr. Erik Sprunk-
Jansen, Managing Director of Greenex A/S in Copenhagen and to Dr. F.D. Pedersen,
geologist with the same company, for additional and more recent information.

The Black Angel deposit is found in a succession of marbles named
the Mârmorilik Formation, the precise stratigraphic position of which is un-
certain. According to Pedersen, it overlies unconformably the Umanak gneiss,
which constitutes the basement of this complexely and repeatedly folded
metamorphic province.

The following is borrowed from the same author :

- The marbles of the Mârmorilik Formation extend over an area of approxima-
  tely 200 km2, which is entirely included within the perimeter conceded to
  Greenex A/S. Their maximum exposed thickness reaches 1300 m. Quartzites
  occur at the base of the formation, resting unconformably on the Umanak
  Gneiss. They are overlain by dolomitic marbles followed by calcitic marbles.
  The sequence also contains pelitic units.

- Sulfide mineralization has been observed at at least four distinct strati-
  graphic levels within the marbles. This mineralization occurs as massive
  or semi-massive sulfide lenses lying parallel to the bedding, measuring
  up to several hundred meters in length and up to 35 m in thickness. Two
  major lenses and a number of small ones are known.

- One of these lenses, the Black Angel Zone, contained 3.4 Mt ore before
  mining started. Another one, the Cover Zone, has not yet been entirely
  delineated.

- The main sulfides present in the ore are pyrite, sphalerite and galena.
  Minor minerals are tennantite, stannite, polybasite (?), arsenopyrite,
  gold and rutile. The gangue is made of calcite, dolomite, quartz, tremolite
  and pyrophyllite. Abundant fluorite is found in the adjacent marble.

- The ore is fine-grained in the limbs of folds where it is almost undeformed;
  it is coarse-grained in the axial part of the folds.

Numerical data about the Black Angel mine are given in table 11.22.4.

Table   11.22.4

---

Black Angel mine
Production and reserves (in metric tons)

| PRODUCTION | 1973 | 1974 | 1975 | 1976 |
|---|---|---|---|---|
| - Ore | 158 589 | 575 299 | 590 148 | 601 774 |
| % Pb | 4.3 | 5.1 | 4.8 | 5.2 |
| % Zn | 18.6 | 18.3 | 15.4 | 14.7 |
| - Lead conc. | 8 350 | 36 870 | 34 047 | 38 258 |
| % Pb | 68.7 | 69.1 | 69.9 | 70.7 |
| % Zn | 6.6 | 6.6 | 6.0 | 5.7 |
| ppm Ag | | | 374 | 379 |
| - Zinc conc. | 46 128 | 167 820 | 145 238 | 139 199 |
| % Pb | 1.5 | 1.6 | 1.7 | 1.8 |
| % Zn | 58.4 | 58.5 | 58.3 | 58.2 |
| % Cd | | | 0.31 | 0.30 |
| - % Zn recovery | 91.6 | 93.1 | 92.6 | 91.7 |
| % Pb recovery | 83.5 | 86.2 | 85.0 | 85.9 |

| RESERVES AT YEAR-END (November 1 for 1974) | | | | |
|---|---|---|---|---|
| - Total | 4 230 364 | 3 573 667 | 4 877 100 | 4 535 451 |
| % Pb | 5.0 | 5.1 | 4.9 | 4.8 |
| % Zn | 16.1 | 15.5 | 14.6 | 14.1 |
| - Non-extractable | 820 966 | 781 143 | 892 200 | 963 700 |
| % Pb | 5.0 | 5.1 | 5.0 | 4.9 |
| % Zn | 16.1 | 13.7 | 15.3 | 14.6 |
| - Extractable | 3 409 398 | 2 792 524 | 3 994 880 | 3 571 751 |
| % Pb | 5.0 | 5.1 | 4.9 | 4.9 |
| % Zn | 16.1 | 15.6 | 14.1 | 13.9 |

## 11.22.D - THE CENTRAL EAST GREENLAND DISTRICT

Several quartz veins carrying Pb and Zn are known in the Mesters Vig
area (fig. 11.22.5). One of them, at Blyklippen, which has been described by
Bondam and Brown (1955), was mined from 1956 to 1963. According to Nielsen
(in Escher and Watts, 1976), 58 000 t  of galena concentrates and 75 000 t
of sphalerite concentrates were recovered from it. The ore was high-grade :
12 % Pb and 10 % Zn. However, apart from these quartz veins which are related
to alkaline intrusives of Tertiary age, a number of discoveries have been
made in Central East Greenland. We are indebted to Mr. Roberto Kayser,
Managing Director, and to the staff of Nordisk Mineselskab A/S (The Northern
Mining Company Ltd) in Copenhagen for the following information about them.
Nordisk Mineselskab A/S owns a large concession in that area.

As far as is known, Pb-Zn mineralization has been emplaced after the
Caledonian folding. Some of it is found in sedimentary beds of Upper Permian
and Triassic age. Some of it is found in quartz veins as mentioned above.

The Upper Permian beds are marine limestones and shales (Birkelund
and Perch-Nielsen, in Escher and Watts, 1976, 304ff). They occur within a
basin extending over a distance of 400 km along the coast (fig. 11.22.6).
Their thickness reaches 300 m but is actually quite variable, in part because
of the bioherms found in the Limestone-Dolomite Member (fig. 11.22.6 again)
of the Foldvik Creek Formation.

Within the Upper Permian limestone, two types of mineralization can
be distinguished on the basis of mineralogy :

1 : Galena + barite + ankerite + (sphalerite)
2 : Galena + barite + chalcopyrite + tennantite + sphalerite + (fluorite)

Both types are stratiform. The first one is found in rocks which are rhythmi-
cally banded on a centimeter scale with alternating layers of barite and
ankerite.

Type 1 occurs mainly in the western part of the basin. One major
occurrence is the 1.8 km-long outcrop of the Bredehorn  mineralization. The
maximum thickness measured in outcrop is 10 m but the orebody is mostly
barite and ankerite at that location.

Type 2 occurs in the Eastern part of the basin, more particularly in the Wegener Halvø (fig. 11.22.6), where it is found mainly at the top of a bioherm. A major occurrence of it is known to be outcropping over a distance of 3 km on Quensel Bjerg.

Other minor occurrences of both types are known south of Kong Oscars Fjord. The area north of this fjord has not yet been investigated. Some Pb and Zn mineralization is also known in the black shales of the Upper Permian Foldvik Creek Formation.

Triassic sediments are somewhat more extensive than Permian ones in Central East Greenland (fig. 11.22.7). They are also much thicker, reaching 1500 m in places and have been subdivided as follows :

|  |  | FORMATION | MEMBER |
|---|---|---|---|
|  |  |  |  |
| TRIASSIC RED BEDS | | FLEMING FJORD | ØRSTED DAL |
| | | | MALMROS KLINT |
| | | | EDDERFUGLEDAL |
| | | GIPSDALEN | KAP SEAFORTH |
| | | | SOLFALDSDAL |
| | | PINGO DAL | KLITDAL |
| MARINE TRIASSIC | | WORDIE CREEK | |

A number of mineralized horizons have been discovered in the upper three of these formations, i.e. the red bed ones, which are known only south of Kong Oscars Fjord. Of these horizons, two are presently considered of some economic significance : one with Cu + Pb + (Ag) in the upper Klitdal Member and one with only Cu at the top of the Edderfugledal Member. We are interested here in the first one, on which rock-geochemical studies have been carried out, delineating a favorable area of about 100 km2.
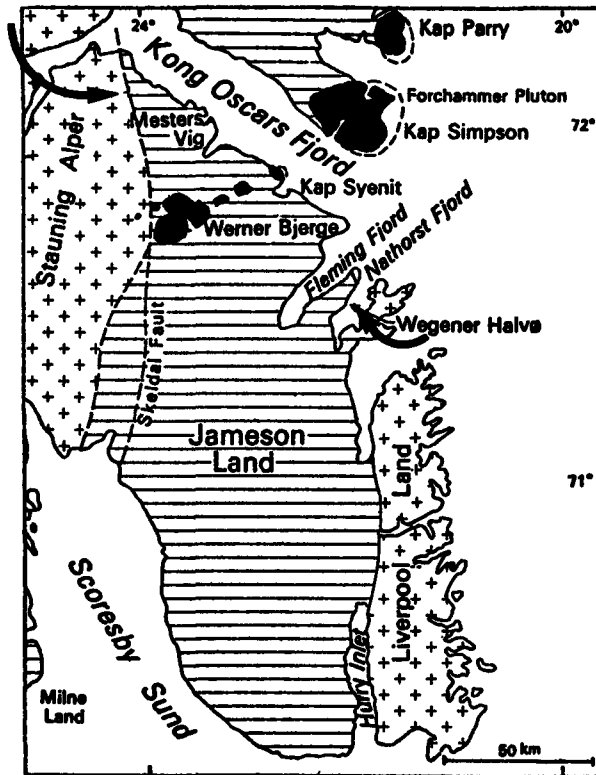
Fig. 11.22.5 - Map showing the location of
              Mesters Vig with its vein-type
deposits and of the Wegener Halvø with its
stratiform deposits   (From Escher and Watt, 1976).
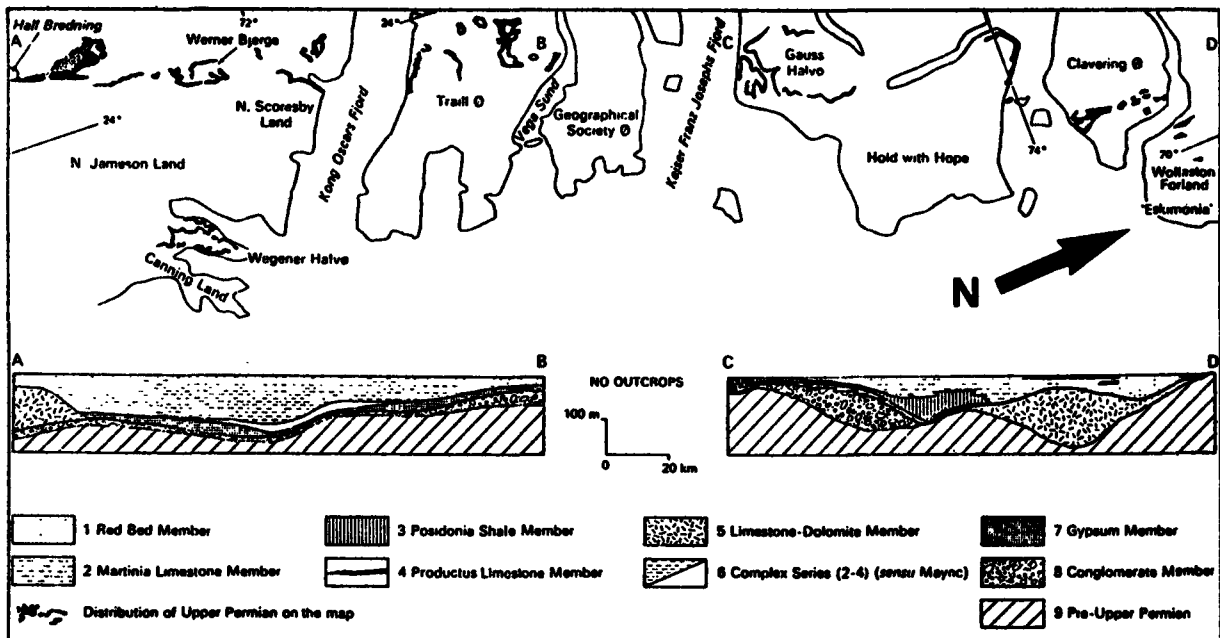


Fig. 11.22.6. - Geographical distribution of outcrops and facies
                distribution of the marine Upper Permian Foldvik Creek
Formations in Central East Greenland (after Birkelund and Perch-Nielsen,
in Escher and Watt, 1976).
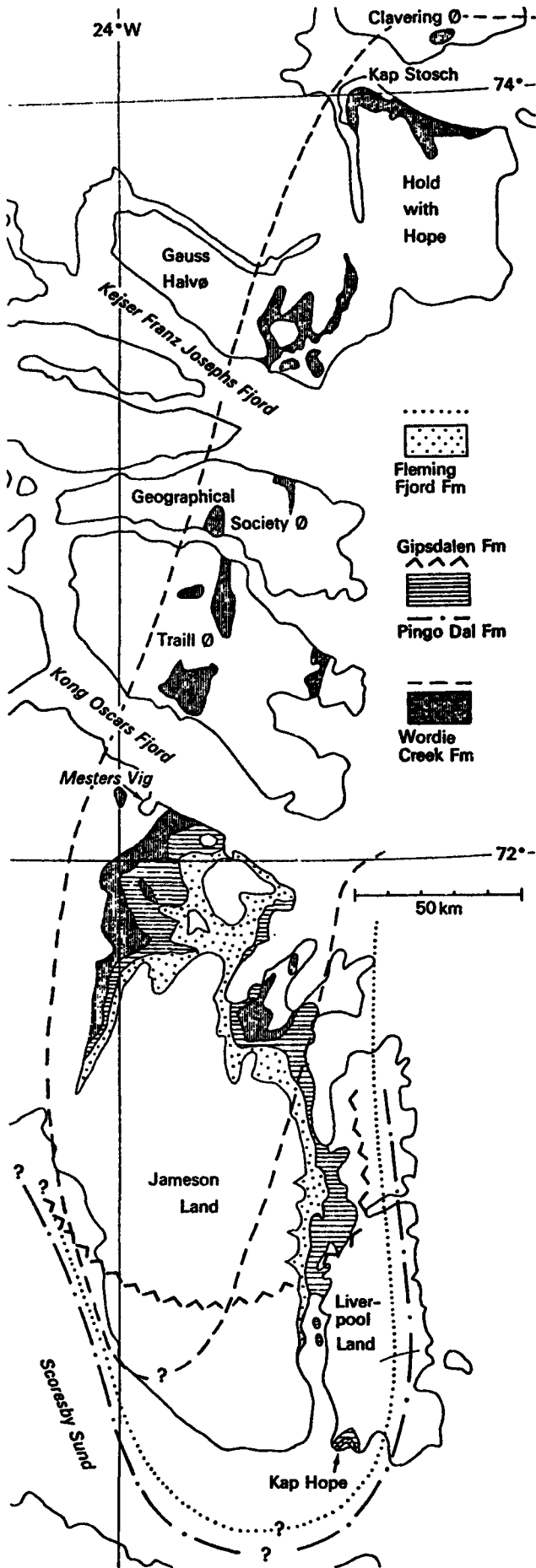
Fig. 11.22.7 - Geographical distribution of outcropping Triassic sediments and estimated areal extent of the Triassic Formations in Central East Greenland (ibidem).

## 11.22.E - SUMMARY

High grade orebodies have been discovered in the Mârmorilik
district. Two of them have so far been proven to contain considerable tonnage.
They are included in a (metamorphosed) sedimentary succession where carbonates
are prevailing. They are essentially controlled by stratigraphy; but folding
is severe, which on one hand increases the potential per unit area and on the
other makes exploration more difficult. As of December 1, 1976, one of these
orebodies had already supplied about 500 000 t of zinc concentrates at 58 %
and 125 000 t of lead concentrates at 69 or 70 %, plus some silver.

Several orebodies and prospects have been discovered in the Central
East Greenland district. Some of them are stratiform and occur in a sedimen-
tary succession of Permian age which is mainly limestone; they may be asso-
ciated in some way with bioherms. Others, which are also stratiform, occur
in a sedimentary succession of Triassic age where detritals are prevailing;
the control seems to be stratigraphic only. Finally veins are known in the
pre-Upper Permian basement of the district; they are supposed to be related
to alkaline intrusives of Tertiary age. One may reasonably hope on the basis
of outcrop examination that grade, tonnage, and associated metals and minerals
will make some of these orebodies minable.

## 11.22.F - BIBLIOGRAPHY

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## 11.23 - THE REPUBLIC OF IRELAND

### 11.23.A - INTRODUCTION

Important discoveries have been made in Ireland during the last twenty years; among them the zinc and lead deposit at Navan, County Meath, which will be the largest producer of zinc in Europe, and one of the largest in the world, for many years to come.

Navan, as well as most other deposits of zinc and lead in Ireland, occur in sedimentary strata of Lower Carboniferous age. Younger rocks seem to be barren. Older rocks on the other hand do contain prospects and have some potential (fig. 11.23.1).

### 11.23.B - REGIONAL GEOLOGY

The geology of Ireland is described in detail by Charlesworth (1963). It is also dealt with more briefly in books by D.H. Rayner (1967) and Bennison and Wright (1969). The following summary emphasizes some of the features that are important to the understanding of the Irish Zn and Pb deposits, and focalizes on the area where most of these deposits have been found, i.e. the Central Plain. This summary is borrowed almost literally from Morrissey, Davis and Steed (1971) but includes additions suggested by Downes and Burton (1977). The geological structure of Ireland is schematically illustrated by figures 11.23.1 and 2.

The Central Plain encompasses about two-thirds of the surface area of the Republic of Ireland, the extensive low-lying parts of the region being mantled by glacial deposits and peat. The bedrock geology is dominated by a diachronous succession of gently dipping Lower Carboniferous sediments, mainly limestones, which attain a maximum thickness of about 1 000 m.
The lowermost Carboniferous succession is composed of sandstones, siltstones, shales and shaly limestones deposited in fluviatile, estuarine, tidal and shelf sea conditions during the transition from a continental to a marine environment. A thick sequence of bedded bioclastic limestones follows. Above these, and to some extent interfingering with them, are pale, chemically pure limestones (micrites, biomicrites, encrinites; etc ...) that belong to a complex of reefs and associated rocks.

This complex known as the Waulsortian Reef Complex covers extensive areas of the Central Plain; it is overlaid by and passes laterally into dark, bedded, compact limestones known as Calp.

The Lower Carboniferous sediments rest conformably in the south of the region, but unconformably farther north, on unmetamorphosed sandstones and red beds of Upper Devonian age. These are separated by a pronounced unconformity from the underlying Lower Palaeozoic rocks, which comprise metamorphosed shales, sandstones and volcanics of Silurian and Ordovician age. The structural grain of the folded Lower Palaeozoic rocks in large areas of exposure to the northeast and southeast of the Central Plain is northeasterly. Within the Central Plain pre-Carboniferous rocks are exposed in a number of tectonic inliers that are elongated and folded about axes trending between east-northeast and northeast. Some of the inliers are partially bounded and transected by major faults with the same trend. Although these structures are generally considered to be Variscan in age, it is possible that both folds and faults are geometrically related to structures in the Caledonian foundation of the Central Plain and that the faults have a long history of activity, possibly lasting into the Tertiary. Some of the faults may have been active during Lower Carboniferous sedimentation.

Thus the Carboniferous, Old Red Sandstone and Lower Palaeozoic strata of Central and Southern Ireland show the combined effects of the Variscan and Caledonian orogenies, which have, through the superposition of NS forces (Variscan) on the NE-SW Caledonian structures, resulted in a distinctive ENE-WSW trend. The effect of the Variscan movements is more evident in the SW part of Ireland where there is extensive tight folding and thrust faulting. Many of the structural features developed during this period are displaced by North-South faulting.

No post-Devonian plutonic rocks are known in Ireland, but sporadic vulcanicity occured at several places in central Ireland during Lower Carboniferous times. The location of known centers of Carboniferous volcanic activity is shown in fig. 11.23.1. Volcanic rocks of Lower Carboniferous (chiefly or entirely Visean) age include lavas, pyroclastics and intrusives of basic to intermediate composition.
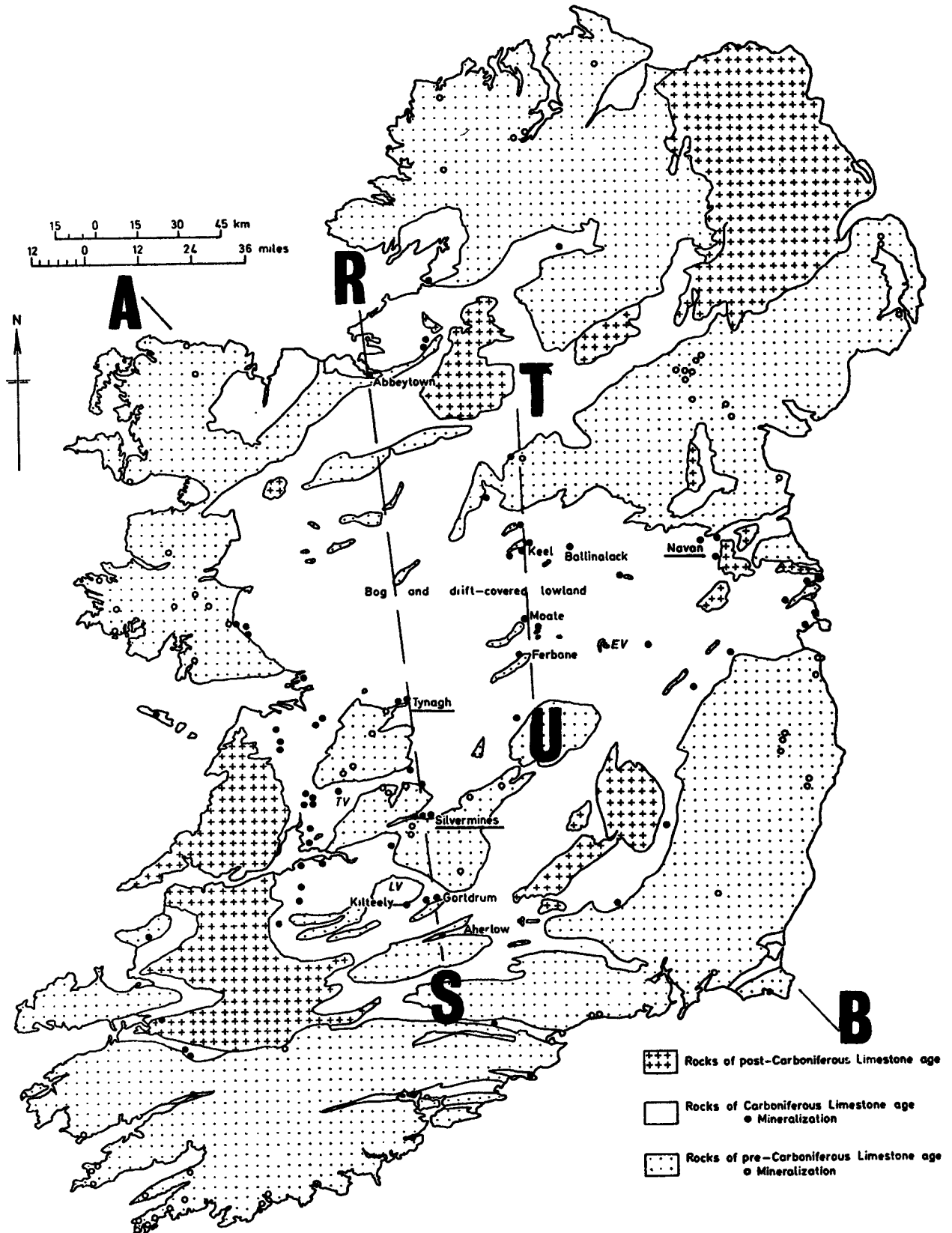
**Fig. 11.23.1** - Known Pb-Zn-Cu mineralization in Ireland (after Morissey et al.). The cross-section in fig. 11.23.2 is drawn along line AB. The deep N-S fractures of Russel (1975) are located along RS and TU. LV : Limerick volcanics ; EV : Edenderry volcanics ; TV : Tulla volcanics.
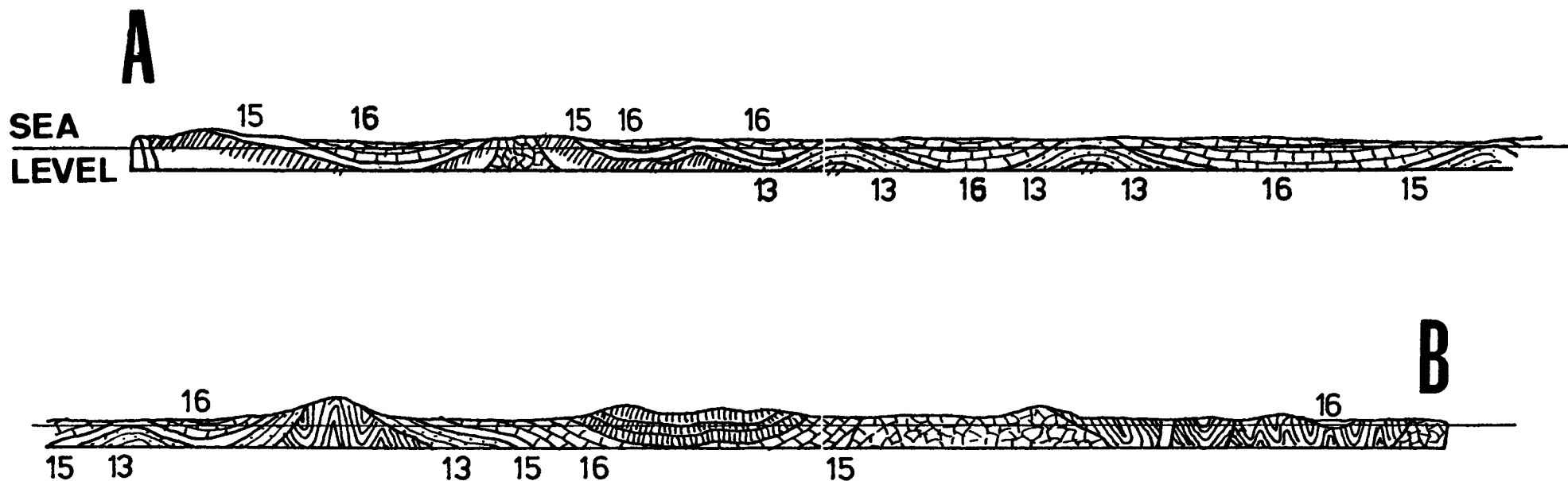
Fig. 11.23.2 - Diagrammatic section across Ireland along line AB of fig. 11.23.1 (Adapted from the Geological Map of Ireland at the scale of 1 : 750 000. 3d edition 1962)

16 : Carboniferous Limestone

15 : Basal Carboniferous Shales and Sandstones

13 : Old Red Sandstones.

## 11.23.C - THE NAVAN DEPOSIT

The major Zn + Pb sulfides deposit at Navan is owned by two companies, Tara Mines Ltd. and Bula Mines Ltd., whose mines are, respectively, at Navan and Nevinstown. Peripheral to the major orebody are the Tatestown and Sabina prospects, for which no geological information is available at present.

The size of the Navan deposit is shown by the following figures (Downes and Burton, 1977)

- Tara Mines Ltd.

  proven and probable reserves : 31 Mt at 2.35 % Pb and 11.43 % Zn

  possible reserves : 30 Mt at about the same grade

  which corresponds to a total of about 7.0 Mt of Zn and 1.4 Mt of Pb.

- Bula Mines

  proven reserves : 13 Mt at 9.2 % combined metal

  probable reserves : 6 Mt at 5.2 % combined metal

  which corresponds to a total of about 1.5 Mt of metal.

Tara Mines Ltd. has been milling ore since June 1977. By late 1978, when the mine and concentrator will operate at full capacity, the mining rate will be 2.25 Mt of ore per year; annual production will reach 360 000 t Zn concentrate (corresponding to 200 000 t of contained Zn) and 70 000 t Pb concentrate (corresponding to 42 000 t of contained Pb) (World Mining, Aug. 1977).

Bula Ltd. on the other hand hopes to start production in mid-1978 at the annual rate of 0.9 Mt of ore.

The following description of the Navan deposit, a cross-section of which is shown in fig. 11.23.3, is due to Downes and Burton (1977) :

"The orebody occurs near the base of the Lower Carboniferous succession. It is stratabound and facies controlled within a 30 m-150 m thick series of pale limestones and dolomites termed the Pale Beds, which are of Tournaisian age and which dip south west at about 20°.

It is overlain by a thick series of thin bedded limestones and intercalated black shaley mudstones, over 120 m thick in the south west part of the area, known as the Upper Dark Limestone. It is underlain by a mixed series or argillites and calcareous sandstones up to 60 m thick (the Muddy Limestones and Laminated Beds), that in turn overlie a red sandstone and conglomerate facies, the Red Beds.

"The orebody consists of series of stacked lenses dipping SW at 20° and lying along a NE/SW axis. Maximum mineral development is to the NE where the lenses merge into a continuous vertical thickness in excess of 60 m.

"It is located on either side, but primarily on the west side of a north east striking fault, the B. Fault (pre-Visean age) with a throw of about 75 m, which is situated on the west flank of a Lower Palaeozoic anticline that plunges to the southwest at Navan with a mantle of younger Carboniferous rocks draped over it.

"Dolomite is the preferred host lithology to the mineralization and occurs as a clearly defined horizon only within the Pale Beds. It forms an irregular envelope around the orebody, thickening and thinning in conjunction, suggesting a secondary origin.
The mineralization consists entirely of primary sulphides with sphalerite and galena having a zinc to lead ratio of approximately 5 : 1. Lesser amounts of pyrite and barytes and rare traces of fluorspar also occur. Silver is present in association with galena. The mineralization is fine grained and in style it varies from massive to finely disseminated. Lithology exerts a strong controlling influence on individual massive ore shoots which can be traced along the bedding over distances of about 100 m. Banded light tan and dark sphalerite with galena and colloform textures are frequent in massive sections with several phases of sulphide brecciation and recementing by sphalerite. In sections with disseminated sulphides fracture control is evident with fine ramifying veinlets infilled by sphalerite that extends laterally out from fracture walls into host dolomite. Pyrite is generally present in only minor amounts in massive sections and with frequent indications of replacement by sphalerite, it is very rare in disseminated sections. It reaches its maximum development in the area of greatest ore development, adjacent to the fault, where it forms a cap up to 12 m thick at the top of the ore section. Sphalerite-pyrite-baryte associations are common in ore sections east of the fault, and west of the fault near the north margin of the ore body. (Byrne, Downing and Romer, 1971; Anon., 1975)".

**LEGEND**

**VISEAN**
Upper Dark Limestone

**TOURNAISIAN**
Conglomerate Group
Pale Beds
Muddy Limestone
Laminated Beds

**DEVONIAN / CARBONIFEROUS**
Red Beds

☐ —— Ore

▨ —— Marker Beds

SURFACE

Upper Dark Limestone

Pale Beds

Conglomerate Group

Pale Beds

Muddy Limestone

Laminated Beds

Muddy Limestone

Laminated Beds

'B' Fault

Red Beds

Red Beds

TARA MINES LIMITED

NAVAN MINE NW/SE SECTION FACING NE

**SCALE**

Metres

0  20  40  60  80  100

— 42 —

Fig. 11.23.3   Section across the Navan deposit showing the reverse B fault

## 11.23.0 - THE SILVERMINES DEPOSIT

A map of the Silvermines deposit with its several zones named G, B and Magcobar is shown in fig. 11.23.4. Cross-sections through the orebodies will be found in figs. 11.23.5 and 6.

This other major deposit consists of two separate orebodies called the G zone and the B zone. The former is divided into an upper part (originally 8.4 Mt of sulphide ore at 9.2 % Zn, 2.4 % Pb and 22 ppm Ag) and a lower one (originally 1.9 Mt of ore at 3.4 % Zn, 4.5 % Pb and 34 ppm Ag). The B zone orebody consisted originally of 2.4 Mt of ore at 6.07 % Zn and 3.5 % Pb.

The reserves are at present given as follows (Downes and Burton, 1977) :

| Zone | Mt of ore | % Pb | % Zn | % Combined |
|---|---|---|---|---|
| Upper G | 2.5 | 1.77 | 7.67 | 9.44 |
| Lower G | 0.3 | 3.34 | 4.52 | 7.86 |
| Total G | 2.8 | 1.95 | 7.31 | 9.26 |
| B | 2.5 | 3.18 | 5.29 | 8.47 |
| Total B + G | 5.3 | 2.53 | 6.36 | 8.89 |

The following description is due to Downes and Burton (1977) :

"The orebodies occur in Carboniferous limestones on the down-faulted northern flank (Silvermines fault) of a large Old Red Sandstone and Silurian inlier. The limestones extend northward into a gently folded ENE-WSW major syncline which pitches gently ENE. The low lying ground to the north of the inlier is blanketed by deep drift and alluvium.

"The zig-zag Silvermines fault system has been traced for over 25 miles east-west and has a downthrow to the north of about 200 m in the vicinity of the mine. The limestone beds in the vicinity of the fault have been subjected to drag which as increased their dip to 45-65° near the fault compared with a dip of around 20° further away from the fault.

"Two separate orebodies stretched along the fault - the G (composed of an upper and lower orebody) and B - are now being mined. An undeveloped K zone lies further east of the B zone and is adjacent to the mine fault. An undeveloped C zone lies further to the east of the K zone, while promising results have been encountered in the S zone 200 m west of the main shaft. The nearby Macobar barite deposit, discovered in 1959, occurs at the same stratigraphic level as the upper G zone.

"The G. orebodies are located in a Tournaisian succession of cherty limestones, dolomites or dolomitised limestones, poorly developed Waulsortian reef limestones and a basal mixed assemblage of carbonaceous limestones, shales and subordinate sandstones.

"The Upper G. zone is a concordant pyrite, sphalerite, galena stratabound fine grained sulphide body extending along the base of a dolomite formation (about 750 m east-west, up to 550 m north south, with an average thickness of 10 m and a dip of about 18° north). The lower G. zone consists of fracture filling and replacement sulphides (galena, sphalerite and pyrite and subordinate chalcopyrite, tennantite - tetrahedrite and arsenopyrite) on the Silvermines fault and partly on adjoining hanging wall limestones. Pb : Zn ratios decrease upwards in the lower G zone and copper is concentrated in the lower and western parts.

"An important ESE normal fault defines the south boundary of the B zone. This fault is probably a tension fracture of the complex 'en-echelon' Silvermines system of faults. The bulk of the mineralization located north of the fault thins slightly against it and dips gently away, thickening to the north. A secondary tensional fracture is observed 30 m south of the main fault. It runs parallel to it but is confined to the west of the orebody.

"The reef limestone, which is also the ore host rock, underlies a large portion of the sulphides in the B as well as a zinc-rich barite horizon. South of the main fault the sulphides are underlain by black shales, whereas in the extreme north portion of the orebody a thin horizon of cherty argillite separates the sulphides from the reef limestone. Locally fine grained pyritic muds are associated with penecontemporaneous slump features (fore reef ?) and patchy pyrite-galena-sphalerite mineralization is found in bands of muddy dolomitic breccia.
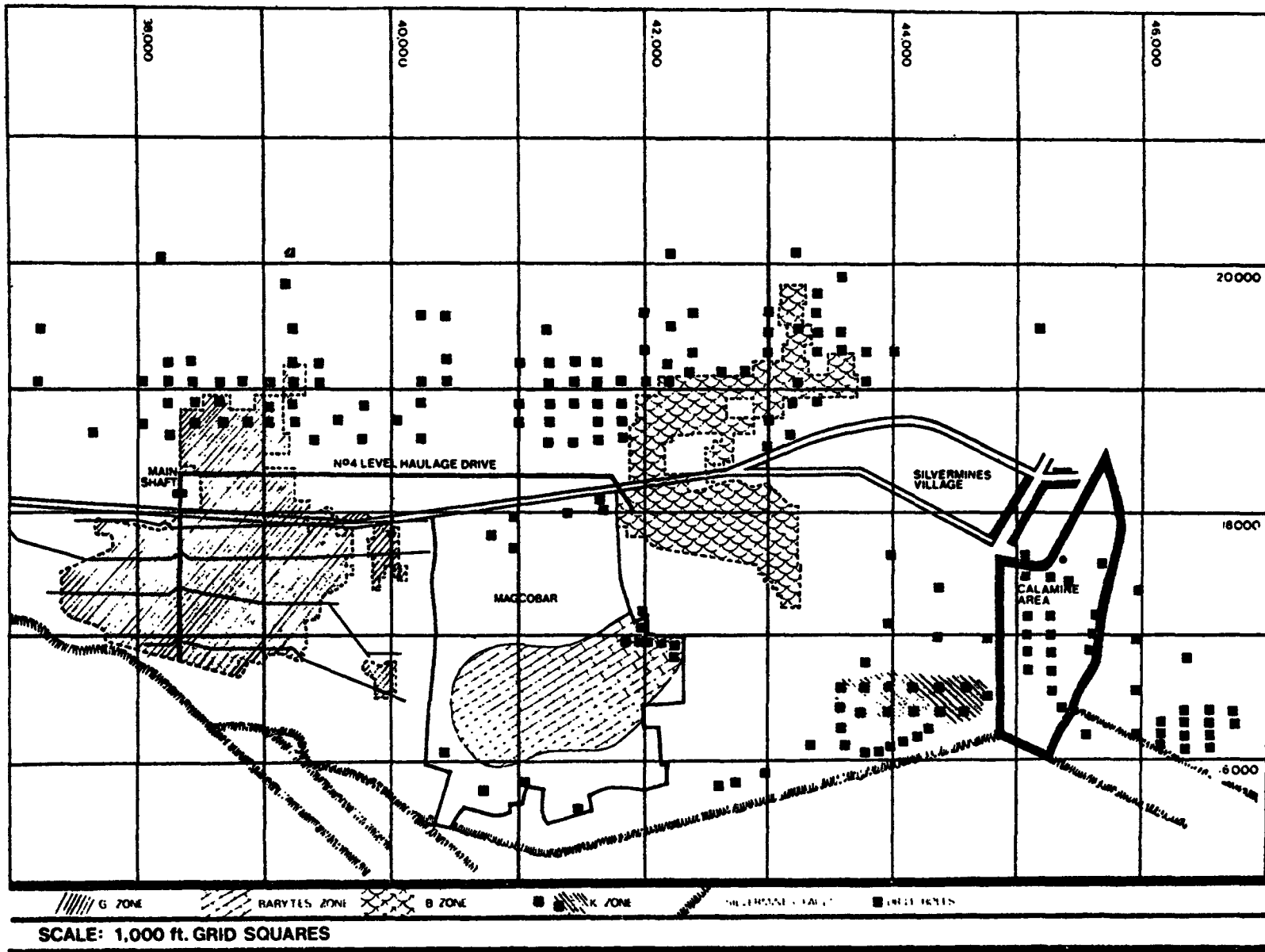
Fig. 11.23.4 - Map of the Silvermines orebodies (Silvermines Ltd., Annual Report 1976, by kind permission)
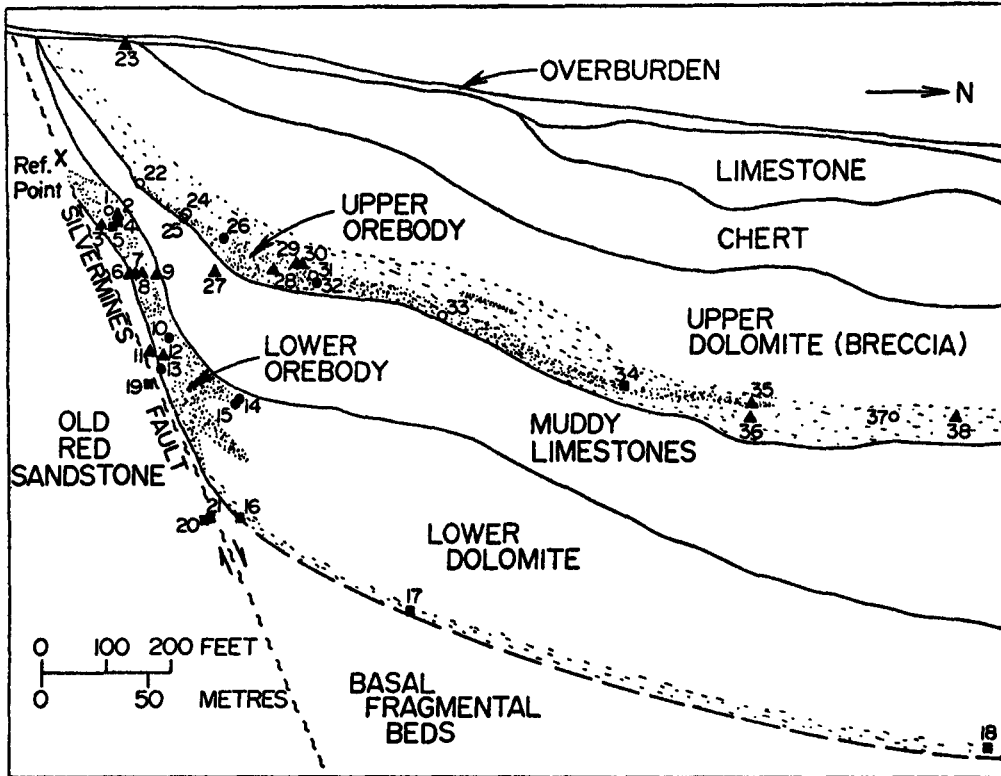
**Fig. 11.23.5** - Simplified section of Silvermines

G orebody (Coomer and Robinson, 1976).

Symbols and numbers refer to samples studied by these

authors.

OVERBURDEN

LIMESTONE AND CHERT

DOL. & L.S BRECCIA 53

MUDDY 54

LIMESTONES 55

56

41-52

MUDDY
LIMESTONES

57

58

59

60

Feet above footwall

-70 • 41
• 42
-60 • 43
-50 • 44
-40 • 45
HANGING WALL
-30 • 46
• 47
-20 • 48
PYRITE 49
ORE
-10 • 50
FeCO₃ 51
ORE 52
FOOTWALL

N

OVERBURDEN

REEF
AND MUDDY REEF

LIMESTONE AND CHERT

DOLOMITE AND
LIMESTONE BRECCIA

0          500          1000          1500          2000 FEET (north of 17,700N)

- 47 -
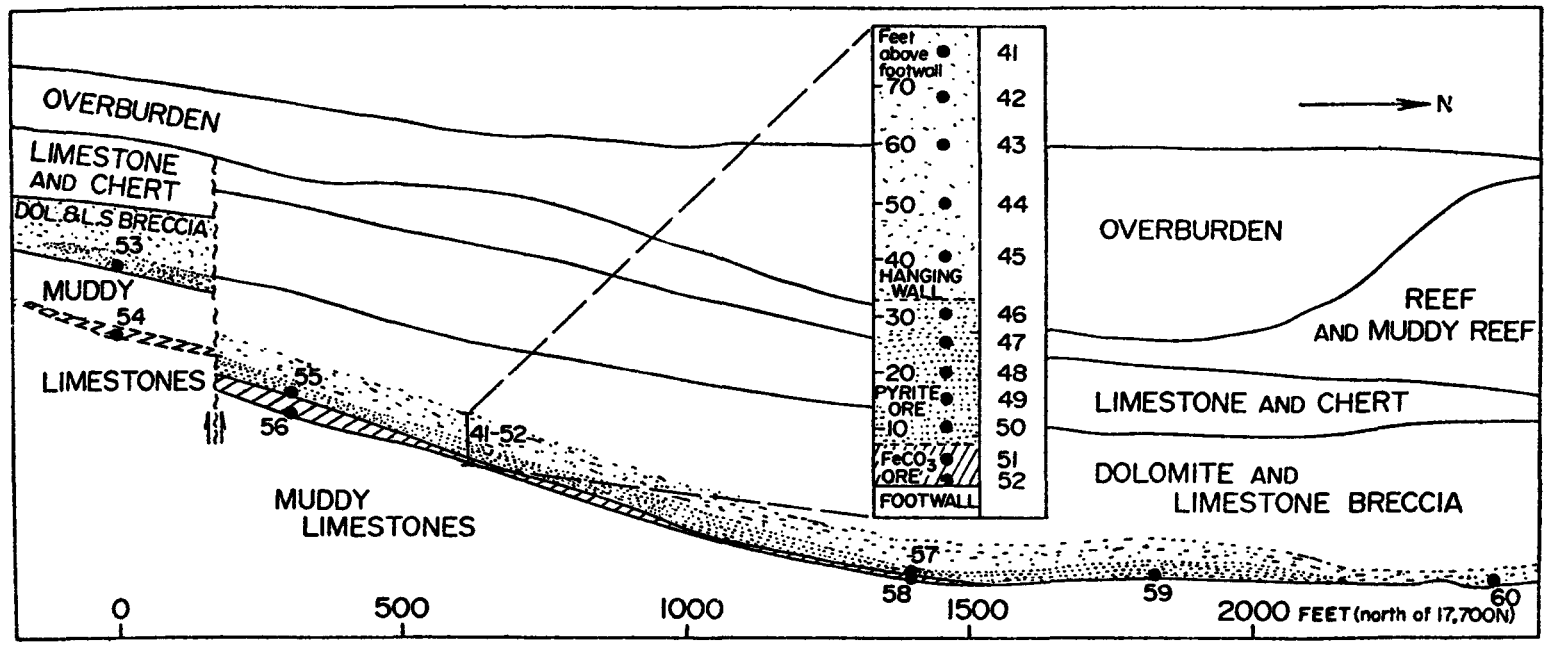
Fig. 11.23.6 - Simplified section of Silvermines B orebody (Coomer and Robinson, 1976).
Symbols and numbers refer to samples studied by these authors.

Above the known limits of the sulphide zone a 65 m thick Dolomite Breccia extends over the entire B zone and interfingers in a complex fashion with the reef limestone at the periphery of the orebody indicating rapid lateral facies change. The lower half of the Dolomite Breccia is strongly recrystallised and disseminated pyrite is common. The top section changes into moderately recrystallised limestone or a brecciated limestone with a muddy carbonaceous matrix.

"The B zone is a tabular galena-sphalerite bearing pyrite zone changing gradually from massive at the bottom to disseminated high above the Muddy Reef Limestone. The massive section varies from 3-11 m and the disseminated ore can be as thick as 30 m. The pyrite content can be as high as 20 % and the lead and zinc content as high as 4.0 % and 6.0 % respectively. The base of the sulphide zone in the extreme east is a thin layer 0.5-3 m thick of pale buff coloured ferruginous fine grained carbonaceous barite, locally finely fragmented, which is transitional to the reef limestone. Its zinc content is typically higher (6.1 % Zn) than the lead content (2.15 % Pb) as commonly occurs in B zone.

"A 6-8 m thick horizontal sulphide zone underlies the Dolomite Breccia south of the fault but as a higher topographic level (fig.). The vertical throw averages 60 m and no evidence of lateral displacement has yet been found.

"Extensive dolomitisation preceded ore formation throughout".

11.23.E - THE TYNAGH DEPOSIT

Tynagh was the first major deposit to be discovered in Ireland as a result of post-war exploration. Discovery actually took place in 1961 and mining was begun in 1965 by Irish Base Metals, Ltd. The deposit comprised several orebodies. Between 1965 and 1974 an open pit operation mined a 4.5 Mt orebody consisting of residual or secondary, partly ox de, ore containing 9.2 % Pb, 7.5 % Zn, 100 ppm Ag, as well as some Cu and barite. A deeper sulfide orebody was originally estimated at 3.4 Mt of ore with 4.8 % Pb, 4.3 % Zn and 66 ppm Ag (O'Brien, 1966) and has been mined since 1973.

At the present time, reserves consist entirely of sulfide ore.
They are given as follows :

|  | | Pb | Zn | Cu | Ag· |
|---|---|---|---|---|---|
| Proven ore : | (includes 5 % dilution) | | | | |
| Zone II | 1.5 Mt | 4.06 % | 3.23 % | 0.29 % | 46 ppm |
| Zone III | 0.7 Mt | 2.44 % | 4.45 % | 0.05 % | 14 ppm |
| Probable ore : | includes 10 % dilution) | | | | |
| Zone III | 1 Mt | 4.41 % | 4.50 % | 0.31 % | 23 ppm |

The metal contained initially in the deposit must have amounted to
approximately 0.5 Mt Pb, 0.4 Mt Zn and 600 t Ag, plus some copper and con-
siderable amounts of barite.

A section through the Tynagh deposit is shown as fig. 11.23.7. The
following description is due to Downes and Burton (1977) :

"The orebodies occur in Carboniferous limestones on the north of a steeply
dipping east-west fault - the Tynagh Fault - which has a vertical displace-
ment of about 600 m and which bounds the northern flank of a small anticli-
nal Old Red Sandstone inlier. The limestones are folded about approximately
north-south axes. Drift of between 2-12 m thickness, the result of two
phases of glaciation, covered the deposit.

"The main host rocks are micrites and biomicrites of Waulsortian Reef facies,
which are of upper Tournaisian and Lower Visean age and which in the vicinity
of Tynagh are up to 180 m thick. However, mineralisation also occurs in
shaley limestones below the reef and there is widespread minor mineralisation
in various rock types at various stratigraphic levels including some sand-
stones in the footwall block. Within the Waulsortian Reef the ores occur in
rough bands, layers or lenses approximately conformable to the bedding and
also as disseminated lower grade ores. Replacement of bedded limestones has
in places been highly selective giving stratiform ore concentrations bounded
top and bottom by bedding plates.

"The original orebody, as discovered, consisted of two parts : (a) a boat
shaped mass of residual or secondary ore measuring 700 m east-west, up to
150 m north-south and up to 75 m in depth, bounded at its southern edge by

SOUTH                                                                                          NORTH
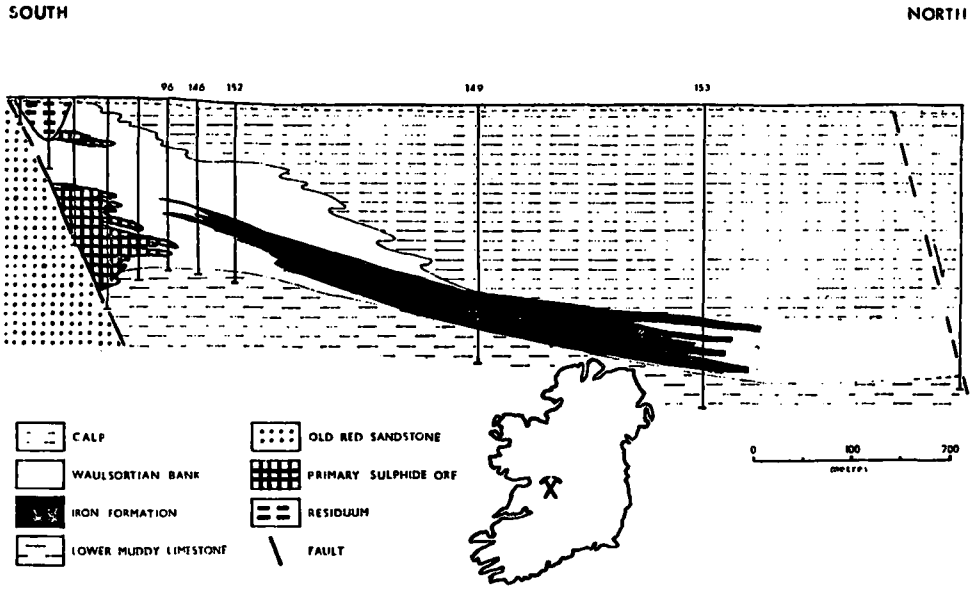
Fig. 11.23.7 - Section across the Tynagh deposit showing
              the funnel-shape residual orebody overlying
the primary orebody (Derry, Clark and Gillatt 1965)

the main fault and elsewhere by unweathered limestones; and (b) underlying
primary ore largely confined to Waulsortian Reef Limestone. The primary
ore consists of galena, sphalerite, pyrite, tennantite - tetrahedrite and
barite. The residual ore consisted of galena, pyrite, sphalerite, barite
and oxides and carbonates of lead, zinc and copper, together with iron
oxide in grey or black mud.

"A bedded iron formation associated with minor tuffs lies to the north of
the sulphide deposit at about the same stratigraphic level (fig. ).
It is composed essentially of haematite and chert in sedimentary layers
that range in thickness from a few centimeters to a metre or more. Maxi-
mum thickness is about 45 m but about 60 % of this is made up of interve-
ning limestone layers. The overall dimensions of the iron formation are
at least 550 m north-south and 1 650 m east-west. Green tuff bands
interbedded with the iron formation point to coeval volcanic activity at
as yet unidentified centres. Thinning of the formations towards the fault
indicates continued fault movement throughout the period of formation of
the sediments and ore formation".

## 11.23.F - OTHER Zn + Pb DEPOSITS IN THE CENTRAL PLAIN OF IRELAND

Apart from the three major Zn + Pb deposits just described, a number
of less important discoveries have been made in Ireland (fig. 11.23.1) but
they have not as yet given rise to mining operations because of small size
and/or low grade or other unfavorable features.

Downes and Burton (1977) give the following indications about some
of these minor deposits :

Abbeytown (reserves unknown)

"The deposit lies between two major east-west faults, separated by 0.8 km,
in lower Visaan limestones with interbanded sandstones and grits. Minera-
lisation consists of sulphide (sphalerite, galena and pyrite) replacements
in and near the top of a 4 m thick calcareous grit and sandstone member.
Ore grade mineralisation also occurs in limestones above and below the
main ore zinc, mainly associated with small flexures  and related fractures.
The limestones are dolomitised near ore".

Ballinalack (2 Mt of ore at 0.66 % Pb + 4.35 % Zn)

"The deposit occurs principally in Tournaisian limestones of Waulsortian reef facies but also in shales and sandstones. There is evidence of faulting in a NNE-SSW direction but the detailed structural setting is unknown.

"The mineralisation, which consists of sphalerite, galena, pyrite and subordinate barite, occurs as fracture fillings and replacements in the reef limestones - the style of mineralisation is similar to that of the primary Tynagh ore. Lesser sulphide mineralisation, apparently fracture controlled, occurs in argillaceous limestones beneath the Waulsortian reef, and locally in the underlying sandstones.

"Dolomite gangue suggests that dolomitisation, in association with mineralisation, has occurred".

Keel (1.8 Mt of ore at 4.0 % Pb + 3.0 % Zn)

"The deposit occurs in Lower Carboniferous (Tournaisian) clastic sediments on the down faulted southern flank (east-west normal fault) of an NE-SW trending Lower Palaeozoic anticlinal inlier.
The rocks comprise a series of interbedded sandstones and conglomerates overlain by mixed mudstones, sandstones an dolomitised limestones, with various calcareous limestones at the top of the sequence, and underlain by basal mudstones of Silurian age. Green mudstones, possibly tuffs, occur in the lower part of the Tournaisian sequence. The main east-west fault is accompanied by several lesser parallel faults in the hanging-wall block.

"The mineralisation consists of sphalerite (cadmium rich), galena (argentiferous), barite and pyrite, and occurs as sulphide oreshoots localised mainly in the dolomitic sandstones, sandstones and conglomerates where they are intersected by the main and subsidiary faults. The orebodies display replacement characteristics with the mineralisation occurring as breccia and fracture fillings spreading and weakening away from the faults which appear to have acted as feeders. Locally dolomitisation and silicification have affected the mixed beds.

"There is a marked increase in lead concentration (1) with depth and (2) towards the east end of the orebody.

A mercury halo surrounds the deposit but there is little correlation between the total mercury content of the rocks and proximity to the sulphide ore. However, analyses of the distribution of mercury compounds about the deposit has shown up a distinctive halo in which mercuric sulphides occur nearest the mineralisation and mercuric chloride occurs farthest away from the mineralisation. There is also a transitional zone in which the two overlap".

Moate (0.125 Mt of ore at 1.0 % Pb + 6.4 % Zn)

"The deposit occurs in a succession of Tournaisian limestones, basal shales and sandstones which outcrop under about 3.5 m of glacial drift.

"The mineralisation consists of sphalerite, galena and pyrite with some barite and occurs as infillings in closely spaced, narrow, steeply dipping faults, fissures and joint-like fractures in the limestones which are in part sandy and oolitic".

## 11.23.G - GEOLOGICAL CONTROLS OF THE Zn + Pb DEPOSITS

As shown by the above descriptions, the major Zn and Pb deposits of Ireland, as well as the Cu deposit at Gortdrum, are located in the vicinity of steeply dipping faults striking about ENE. Some of these faults are major geological features, which have been traced for more than 50 km. Their relationship with the mineralization is described as follows :

"The greatest concentration of mineralisation occurs adjacent to the faults. Fractured rocks within fault planes are also preferentially mineralised and some mineralisation may occur along the fault planes. In some localities pre-Carboniferous rocks in the footwall of major faults contain mineralisation. The orebodies extend for short distances into the rocks adjacent to the faults and their strike lengths are short in comparison with the strike lengths of the faults"

(Downes and Burton, 1977). Several students of Irish geology have reached the conclusion that these faults were active during Lower Carboniferous times; this feature may be a very important link between the theory of ore deposition and the particular features of the orebodies.
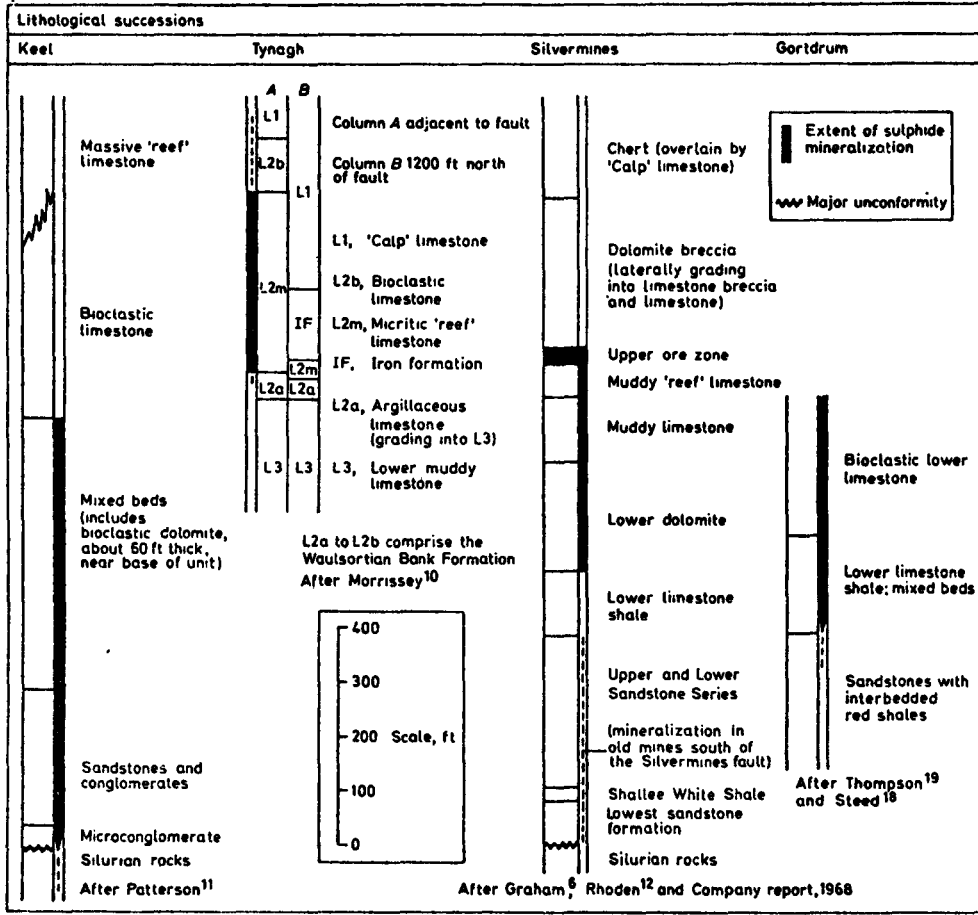
Fig. 11.23.8 - Stratigraphic control of mineralization
in some deposits of the Central Plain
(after Morissey et al., 1971)

A relationship between the deposits and deep, hidden N-S fractures has also been suggested (Russel, 1968). These hypothetical fractures may have been formed in Lower Carboniferous times in response to incipient continental splitting. One of them is traced from Aherlow to Abbeytown (fig. 11.23.1). Tynagh, Silvermines and Gortdrum are located at the intersection of ENE faults with this N-S fracture.

Horne (1975) has suggested that Ireland's ore deposits are controlled by another set of deep fractures, generated during the spreading phase of an ocean much older than the Atlantic.

Evans and Maroof (1976) have drawn attention to the fact that the same ore deposits seem to be spatially related to buried Caledonian granites, as would be the Pb and Zn deposits of Great Britain (in particular those of the Northern Pennines where such a relationship has actually been observed).

Apart from these controls which remain hypothetical although certainly worth keeping in mind, there is an obvious relationship between ore deposits and stratigraphy in the Central Plain of Ireland since all the deposits are located within the lower part of the Lower Carboniferous succession (fig. 11.23.8). This stratigraphic control is, however, not precise :

"The host rocks vary greatly in grain size and nature from non-calcareous sandstones to a most diverse collection of carbonate rocks. There is no single lithological feature common to all the host rocks. When the sedimentological milieu is considered then a common feature becomes apparent-that sedimentation was nearly always in shallow seas. It is clear that at any given locality certain lithologies have been extensively mineralized, e.g. the Waulsortian Mudbank Complex at Tynagh, but shallow water sedimentation appears to be the only common factor as far as general setting is concerned". (Evans, 1976).

## 11.23.H - OTHER GUIDES TO ORES

As shown again by the above descriptions, dolomitization is commonly - and silicification is occasionally - associated with mineralization :

"Dolomitization is the only important form of wall rock alteration. However, its time relationship to mineralization is difficult to establish and the usual combinations of possibilities crop up.

At Tynagh, Schultz (1968) recognized three periods of dolomitization, ore being associated with one of them. Dolomitization forms a halo around the ore at Navan which is developed in a dolomite horizon. The halo thickens and thins in sympathy with the ore body suggesting a secondary origin. The lower G ore body at Silvermines occurs in a thick dolomite which may be of primary origin. At Abbeytown the limestones are always dolomitized in the presence of ore. Recrystallization of limestone and dolomitization are widespread at Gortdrum, but in the nearly and similar deposit at Aherlow dolomitization is only extensive in one part of the sulphide zone. A little silicification is present at both localities". (Evans, 1976).

It should also be mentioned here that beds rich in iron oxydes or sulfides are found in the vicinity of the Zn and Pb deposits at Tynagh, Keel and Ballinalack (fig. 11.23.7).

An aureole of a different nature has been discovered at Tynagh by Russel (1975), who gives the following description and interpretation :

"The Waulsortian mud bank complex, which serves as the principal host rock to the sulphide orebody, and of which the iron formation is a lateral equi-valent, contains anomalous concentrations of manganese centred on the iron deposit and extending from it up to a distance of about 7 km. The zinc con-tent of this limestone is also unusually high up to 1 km or so from the mine. The dimensions of these anomalies indicate that they are syngenetic and that mineralizing solutions were escaping into the mid Lower Carbonife-rous sea in the vicinity of the Tynagh orebody. Presumably, most of the load was deposited from these solutions prior to their escape into the sea, so explaining the epigenetic (non-conformable) nature of the orebody itself. The patterns of the anomalies indicate that the Tynagh fault was in motion in Waulsortian times".

Finally it should be mentioned that volcanics of Carboniferous age are found in the vicinity of some deposits.

## 11.23.I - DEPOSITS IN LOWER PALAEOZOIC ROCKS

Lower Palaeozoic rocks of Ireland belong to an old mountain range known as the Southern Caledonides. They include granites and volcanics in addition to rocks of sedimentary origin (fig. 11.22.9).
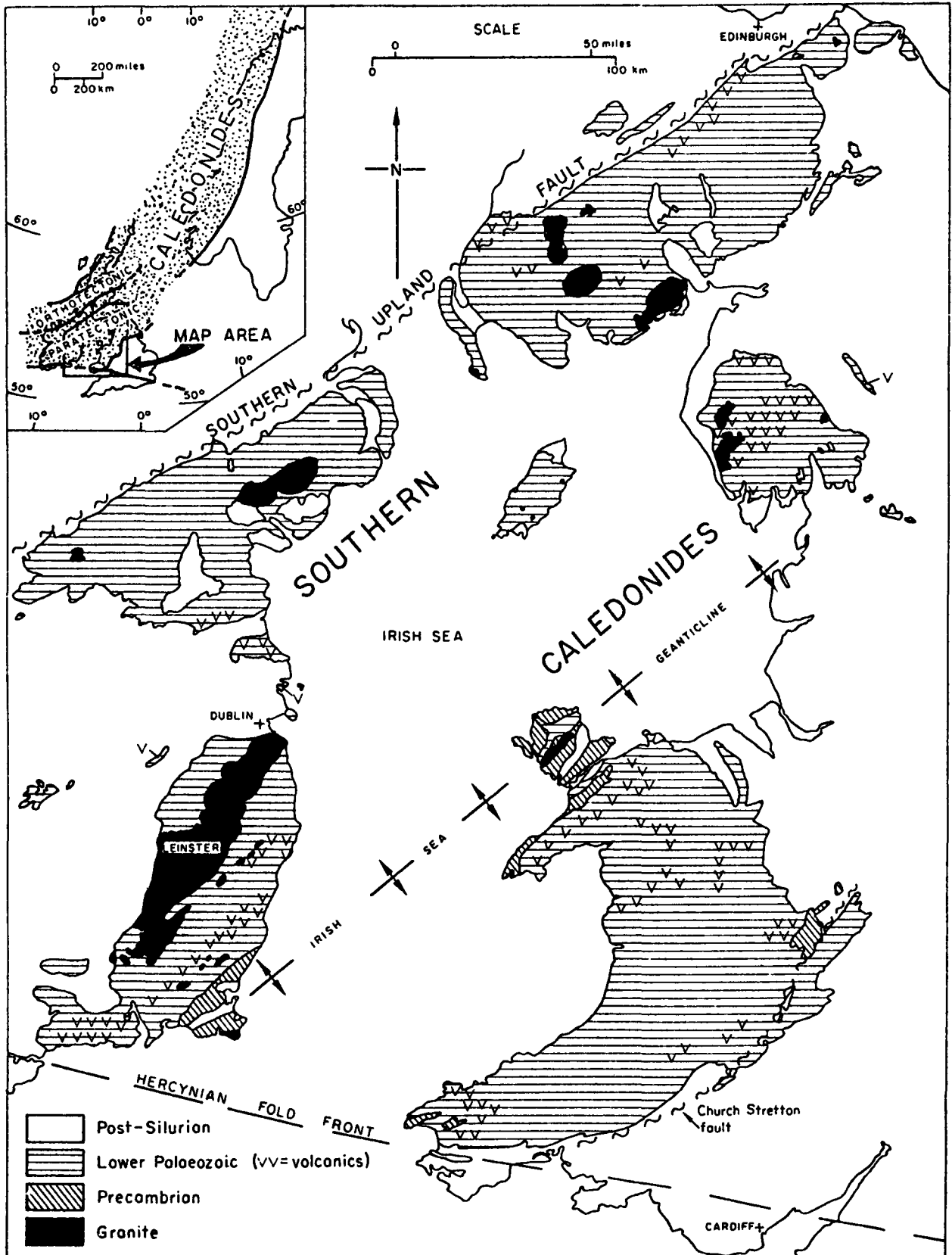
Fig. 11.23.9 - Geological framework of the Southern Caledonides
(Wheatley, 1971)

Two types of ore deposits containing Zn and Pb are known in the Southern Caledonides : veins and volcanogenic deposits.

Veins are numerous in Ireland as well as in England and Wales (fig. 11.23.10). Many of them were mined during the past centuries and the first part of this century. None is known to contain reserves sufficient to sustain a modern mining operation.

On the other hand, volcanogenic deposits are being mined at the present time. They are located at Avoca Co. Wicklow, and while copper is their main product, zinc and lead are also found in some areas.

The very short description that follows is due to Downes and Burton (see figs. 11.23.11 and 12) :

"The Avoca deposits are the only known representatives of this type in Ireland. Features of the Avoca deposits are :

"They occur within a calc-alkaline acid volcanic pile of Upper Ordovician age.

" They comprise a low grade stockwork ore (sulphides of Cu, Pb and Zn) stratigraphically overlain by bedded, stratiform sulphide ore which is typically zoned, having a copper rich base and a lead-zinc rich top. These two zones may be separated from one another by a layer of sediment. The stockwork ore is characterised by strong chloritisation and silicification. Mineralisation consists of disseminations and veinlets of base metal sulphides, frequently in association with quartz veins. It is interpreted as a feeder zone (exhalative zone) for the stratiform massive ores. The bedded sulphide ore is interpreted as having formed as a chemical sediment, consequent on being exhaled onto the sea floor.

"They are spatially related to brecciated, pyrite cemented, rhyolite domes.

"Magnesium metasomatism characterises the stockwork ore while potash metasomatism typifies the brecciated rhyolite domes and much of the volcanic pile outside the stockwork ore.

"They are spatially related to zones of crystal weakness which frequently acted as loci for rhyolite eruptive centres and which had high geothermal gradients associated with them.

HARLECH — Mineral field, with major metals (minor metals in parentheses)

AVOCA — Locality disscussed in text

320±50 — Mineralization, with lead isotope age, m.y.

560±30 — B-type lead

(-20) — J-type lead

SCALE

0 ... 50 miles
0 ... 100 km

—N—

EDINBURGH

310±60
LEADHILLS
Pb Zn(Cu)
320±50

NEWTON STEWART
Pb Zn(Ni,Cu)
320±80

420±70
DOWN
Pb Zn
280±60

ISLE OF MAN
Pb Zn(Cu)
220±60
220±40

220±40
210±70
260±90
340±70
300±80
330±90
310±80
170±80
470±50
310±80
210±70
LAKE DISTRICT
Pb Zn Cu
CONISTON

280±60
370±40

MONAGHAN
Pb Zn (Cu)

PARYS MOUNTAIN

ANGLESEY
Cu Pb Zn
300±40

LLANRWST
Pb Zn (Cu)
340±70
430±80

200±50
DUBLIN
150±60
300±30
280±90
220±50
240±70
430±40
210±40
AVOCA

SOUTH EAST IRELAND
Cu Pb Zn (Au)

ISG

HARLECH
Cu Pb Zn Au
470±60
420±50

BERWYN
Pb Zn
280±70

SHROPSHIRE
Pb Zn (Cu)

450±50
430±80
450±60
360±60
PLYNLIMON
Pb Zn(Cu)

390±40
560±30

280±80
310±50  250±60
(-20)  BUNMAHON

Major mineral fields and lead isotope age determinations in the Southern Caledonides. Data from Moorbath[29] and Pockley.[34] ISG, Irish Sea geanticline

CARDIFF

Fig. 11.23.10 - Vein type deposits in the Southern Caledonides after Wheatley (1971)

GEOLOGICAL PLAN WEST AVOCA MINE

North lode

Weaver lode

Pond lode

South lode

55°

North

Great fault

☐ Massive sulfide (banded)

☐ Quartz-chlorite ore (disseminated)

☐ Rhyolite-andesite

▨ Sericite

▨ Quartz-eye schist (porphyry)

▨ Sericitic phyllites

▨ Dolomite series

0                              500

FEET

CROSS SECTION OF THE WEST AVOCA OREBODIES
(LOOKING SOUTHWEST)

South lode
open cast

North lode
open cast

NW

500

SE

Sea level

1000

Pond lode

0        500

Feet

South lode

1500

Geological legend

Elev. ft.
2000

☐ Massive sulfides

☐ Quartz-chlorite ore (disseminated)

▨ Sericite

Fig. 11.23.11. Structure of the West Avoca deposit, (after Tinsley,1973)
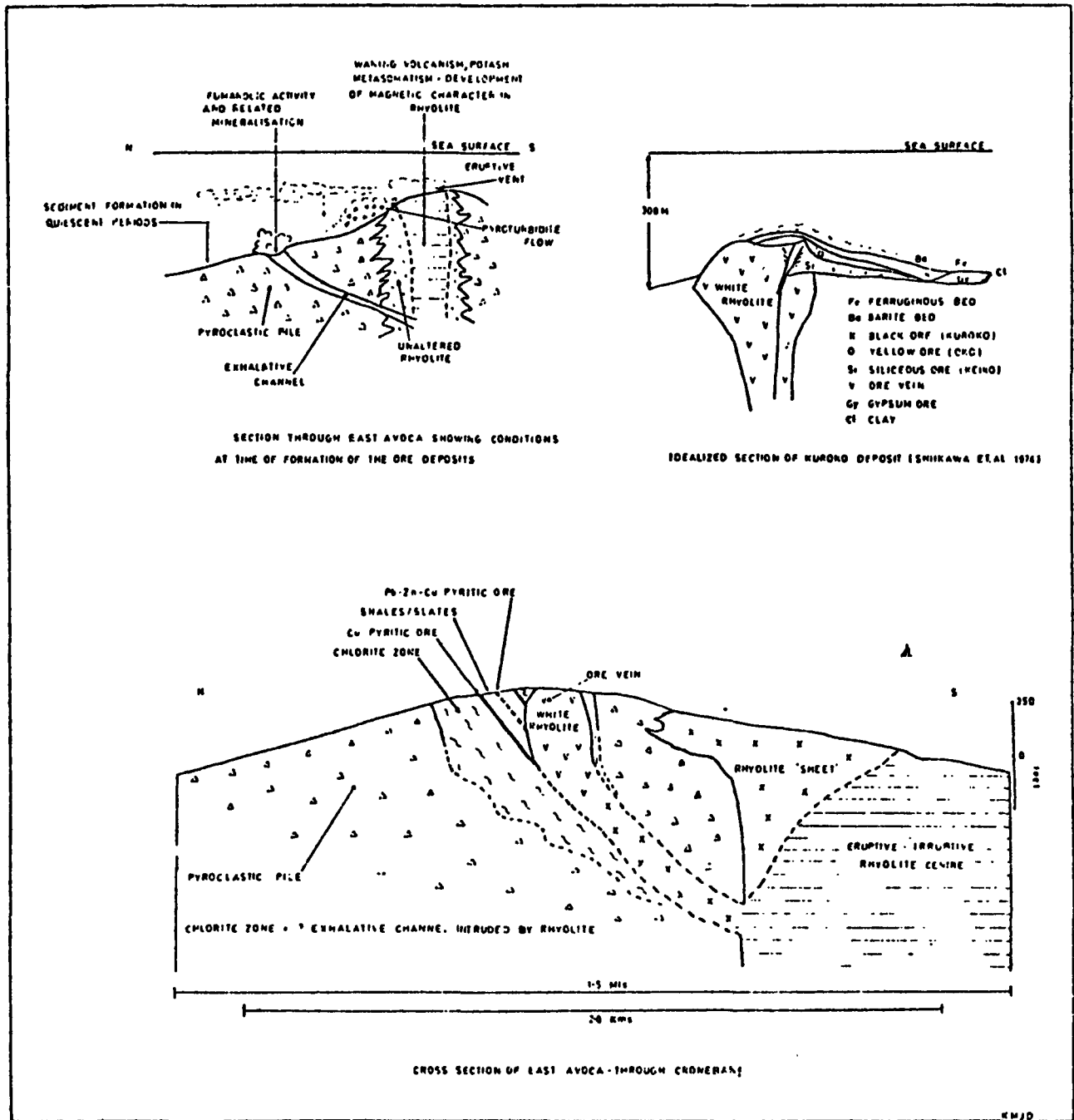
**Fig. 11.23.12** - Genesis of the Avoca deposits. The structure of the deposit is interpreted as due to submarine volcanic and hydrothermal events such as those responsible for the formation of the Kuroko deposits of Japan (from Downes and Burton, 1977, quoting Downes, 1976)

"The ore minerals are chalcopyrite, galena and sphalerite with accessory
gold and silver".

According to the same source, 200 000 t of ore at 8 or 9 % Pb + Zn
have been found at West Avoca.

## 11.23.J - SUMMARY

A number of Zn and Pb deposits have been discovered in Ireland during
the last 20 years as a result of an intense and persistent exploration effort.
Three of these are mined at the present time; the total amount of metal con-
tained in them (past production plus reserves) exceeds 10 Mt of zinc, 2 Mt of
lead, 900 t of silver plus a little copper. In addition, they have produced
large amounts of barite. The orebodies are located in strata of Lower Carboni-
ferous age in the vicinity of ENE-trending faults. Other geological features
such as deep fractures or Caledonian granites may also have contributed in
controlling their localization.

A quite different type of deposit is known in the Lower Palaeozoic
basement of Ireland. Volcanism played a major part in its genesis.

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## 11.24 - UNITED KINGDOM

## 11.24.A - INTRODUCTION

Lead has been mined in Great Britain since pre-Roman times. Thousands of deposits, mostly of very small size, were found. Total production is estimated at 8.7 Mt of concentrate or about 6.5 Mt of metal (I.G.S., 1977). The last deposit mined for lead was abandoned in 1961 but small amounts of concentrates are still recovered at the rate of 4 000 or 5 000 t per year as a by-product of fluorite mining.

Zinc was also found and mined in many localities. Total production is estimated at 1.2 Mt of concentrates or about 0.6 Mt of metal.

The following table gives the estimated order of Pb and Zn production in Great Britain per district in tons of concentrates (I.G.S., 1977) :

|  | Pb | Zn |
|---|---|---|
| 1. Northern Pennines | 4 000 000 | 267 000 |
| 2. North Wales (Halkyn-Minera) | 1 870 000 | 290 000 |
| 3. Derbyshire-Southern Pennines | 678 000 | 91 000 |
| 4. Central Wales | 479 000 | 151 000 |
| 5. Cornwall and South Devon | 317 000 | 89 000 |
| 6. Isle of Man | 268 000 | 256 000 |
| 7. Leadhills-Wanlockhead | 317 000 | 14 000 |
| 8. West Shropshire | 237 000 | 21 000 |
| 9. Lake District | 226 000 | 34 000 |
| 10. Mendips | < 200 000 (?) | ? |
| 11. South Wales | 66 000 | 500 |
| 12. Newton Stewart-Minnigaff | 50 000 (?) | ? |
| 13. N.W. Wales | 47 000 | 33 000 |
| 14. N. Devon | 5 000 | ? |
| 15. Strontian | 2 000 (?) | ? |
| 16. Tyndrum | 2 000 (?) | ? |
| 17. Islay | ? | ? |

The numbers on the left-hand side of this table correspond to those in fig. 11.24.1.

Note : County names used in this chapter on the U.K. refer to those in existence before local government reorganisation in 1974. The old names are widely understood and are better for the purposes of this document.

Fig. 11.24.1 - Main Pb and Zn districts of the United Kingdom
              in relation with the geological constitution of the
British Isles (adapted from Dunning).

Black : pre-Cambrian basement.

Continuous vertical shading : metamorphic Caledonides.

Discontinuous vertical shading : non-metamorphic Caledonides.

Horizontal shading : Variscides

Stippled : Older Cover.

White : Younger Cover.
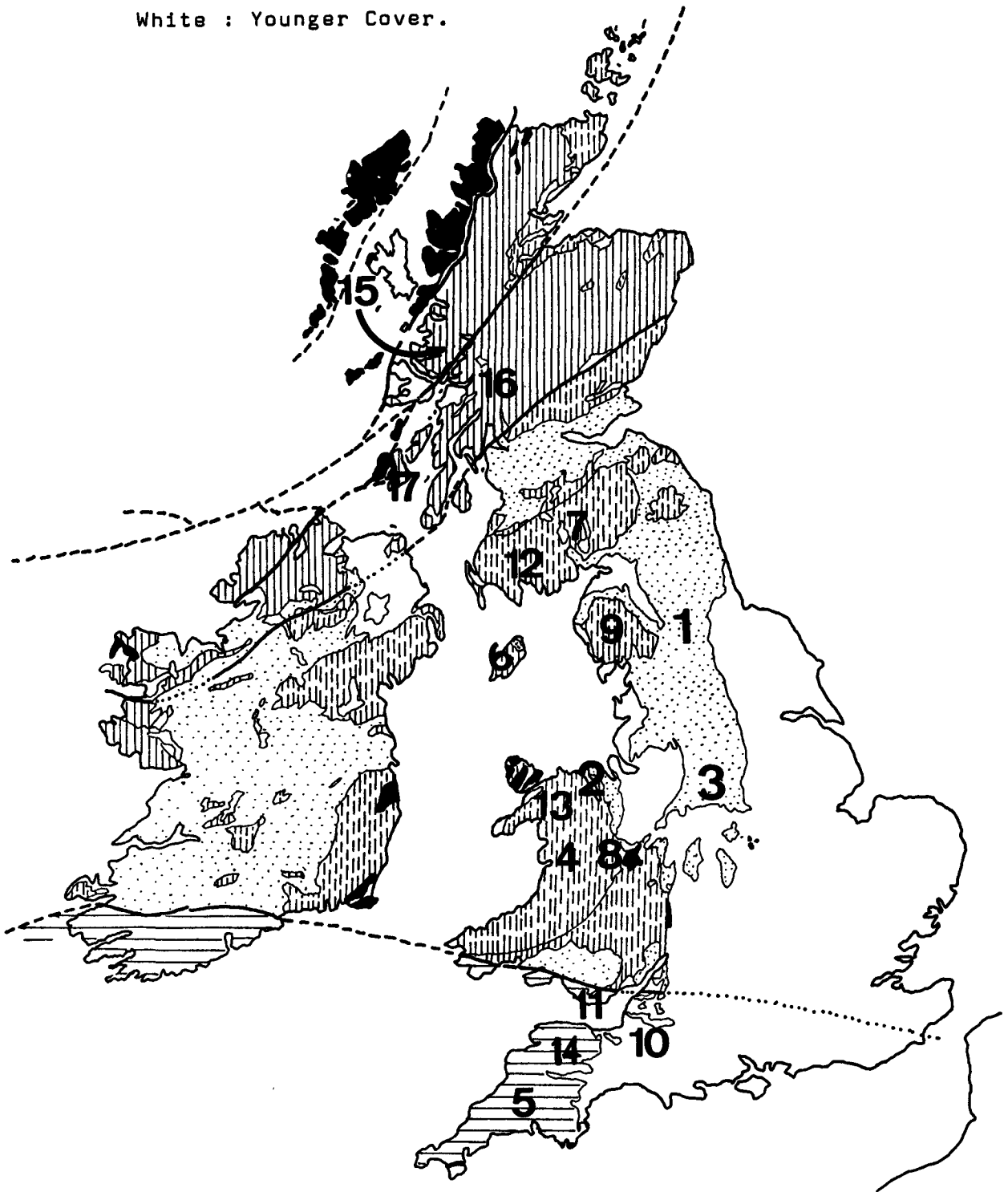
As shown by the above figures, Pb was much more abundant than Zn in all districts, except in the Isle of Man where both metals were mined in approximately equal amounts. The most important individual contributions to the tonnages per district mentioned above are the following :

| | | Tons of concentrates | |
| --- | --- | --- | --- |
| | | Pb | Zn |
| Mill Close mine | (Derbyshire) | 475 000 | |
| Allenheads mine | (N. Pennines) | 260 000 | |
| Greenside mine | (Lake district) | 200 000 | |
| Minera Mine | (North Wales) | 200 000 | 150 000 |
| Halkyn mine | (North Wales) | 200 000 | |
| Foxdale mine | (Isle of Man) | 169 000 | |
| Great Laxey mine | (Isle of Man) | 80 000 | 230 000 |

In Great Britain, Pb and Zn deposits and prospects were found in rocks of highly varied age and nature, and over a large part of the country. However, it is interesting to note that

1° most of the production, i.e. 75 % of the lead and 52 % of the zinc (I.G.S., 1977), comes from districts such as the Northern Pennines, North Wales or Derbyshire, which are underlain by Lower Carboniferous strata, and more particularly by the Carboniferous Limestone.

2° the post-Triassic strata seem to be entirely barren.

## 11.24.B - REGIONAL GEOLOGY

The geological structure of Great Britain is very complex because it results from at least ten orogenic events which took place over an interval of about 3 000 million years. It is represented very schematically by fig. 11.24.1 where only a small number of large units are shown. These are briefly described in the following pages from the youngest to the oldest. The reader is referred to a short paper by Dunning (1964) for more information, or to books by Rayner (1967) and Bennison and Wright (1969).

1. The Younger Platform Cover. This cover consists of beds of Permian, Mesozoic and Cainozoic ages deposited on a basement composed of rocks folded by pre-Cambrian, Caledonian and Variscan movements.

The surface of this basement is irregular, with troughs and plateaus so that the thickness of the cover varies greatly, exceeding 3 km in places. In Southern England this Younger Cover is affected by folding due to Alpine movements.

Small amounts of Pb and Zn mineralization have been found at the base of the Younger Cover, i.e. in the Magnesian Limestone, of Permian age, which is correlated with the rich metalliferous beds of the Zechstein in Germany, and in the Dolomitic Conglomerate of Triassic age.

2. The Older Platform Cover. Sediments of Carboniferous age with locally abundant volcanic rocks were deposited over a large part of England and Wales on a platform of folded pre-Cambrian and Caledonian rocks. This platform behaved in a rather irregular manner, subsiding in places to depths of several kilometers, and remaining stable elsewhere. The thickness of the Older Cover is therefore greatly variable.

In Great Britain, the Lower Carboniferous strata (Dinantian) are mostly marine limestones grading northwards into detrital rocks deposited under deltaic conditions.[1] They are overlain by the Millstone Grit of Namurian age, which consists of shales and sandstones of both marine and deltaic origins, and then by the Coal Measures of Westphalian age. This Older Cover is affected by Variscan folding and contains most of the Pb-Zn deposits found in the country.

3. The Variscides. "The highly folded Devonian and Carboniferous rocks of Devon and Cornwall in South-West England belong to the Variscan eugeosyncline, and form a westerly continuation of the so-called Rhenohercynikum of Middle Europe.

"The rocks are mostly slates, greywackes, shales and sandstones with a well-developed spilitic vulcanism. The geosynclinal sequence commences with the Lower Devonian and extends with few breaks into the Lower Westphalian. The main folding is of post-Westphalian (Asturic) date ... The style of folding is alpine-type in the South, where great thrusts may exist, and concertina-like with numerous minor thrusts and strike-faults elsewhere, decreasing in intensity northwards. In the extreme South of Cornwall and Devon metamorphic rocks of greenschist facies occur ...

[1] The "Culm facies" is also present in Devon and Cornwall.

"A great batholith, now known as the Cornubian Batholith has been shown to
extend from Devon to the Scilly Isles and beyond, beneath the Variscan
chain ... The post-tectonic granite intrusions of South-West England are
cupolas on this batholith". (Dunning, 1964, 97-99).

Devon and Cornwall are important metalliferous districts, which have
been mined mostly for tin and copper. However, significant quantities of Pb
and Zn have also been produced : about 6 % of all the Pb and Zn concentrates
recovered from British deposits (I.G.S., 1977).

## 4. The Caledonides

"The greater part of Highlands of Scotland and Northern Ireland, the Southern
Uplands of Scotland and their continuation in Ireland, the Lake District in
Northern England, the Isle of Man and Wales are Caledonian foldbelts which
display many variations of stratigraphy, tectonics, metamorphism and igneous
activity.

"The extraordinary asymmetry of the British Caledonides is their most striking
and obvious feature. A wide non-metamorphic zone on the south-eastern side is
flanked on the north-west by a relatively narrow metamorphic zone whose "hot"
side is in powerful tectonic juxtaposition with a "cold" basement of Lewisian
and Torridonian rocks with a Cambro-Ordovician sedimentary cover of typical
platform aspect. It is clear that the movement on the boundary thrust must
have been very large, that this movement is very likely of the nature of un-
derthrusting.

"A second significant feature is the unusual abundance of migmatites and late-
and postorogenic   granitoids, and especially the considerable quantity of
granitic magma available in Lower Old Red Sandstone times. The idea that this
might be connected with underthrusting of the Lewisian foreland and possible
melting of the underthrust Lewisian gneisses beneath the Highlands to produce
at least some of the large volumes of granitic material required may be worth
considering.

"A third feature is the truly remarkable thickness of the Late Precambrian and
Lower Palaeozoic sedimentary and volcanic accumulations in various parts of the
British Caledonides : at least 7 km of Moinian (Riphean) sediments in Scot-
land, 7.5 km of Cambrian in the Isle of Man, 10 km of Arenig (!) in western
Ireland, and 4.5 km of Upper Silurian in the Lake District, to mention but a
few.

"The total thickness of Caledonian sedimentary and volcanic rocks in the south Southern Uplands - northern Lake District region - the probable axial region of the Caledonides of Britain - could well amount to as much as 20 km. Not only was the Caledonian geosyncline of the British Isles a geosyncline on a grand scale, it also had an extremely mobile floor which led to very rapid localized downwarping on a number of occasions in its history.

"In general, the Caledonides of Great Britain may be divided into a metamorphic zone with alpinotype nappe tectonics in the Scottish Highlands and Northern Ireland, and a non-metamorphic zone in the Southern Uplands of Scotland and north-eastern Ireland, in England and in Wales, whose folding ranges from gentle-open to isoclinal with small thrusts, but is rarely alpinotype.

"The rocks of the metamorphic zone were folded and metamorphosed at least twice in most areas. The absolute ages of the last main metamorphisms are early or mid-Ordovician and late Silurian (Giletti, Moorbath, Lambert, 1961). In the non-metamorphic zone the main folding is late Silurian and in places, mid-Devonian". (Dunning, 1964).

A few significant deposits of Pb and Zn and many small ones, mostly of vein-type, have been found in the Caledonides of Great-Britain.

5. The pre-Cambrian Basement is well exposed in the N.W. Highlands of Scotland and the Hebrides. It is also found on the SE side of the Caledonides, where it is observed locally at the surface, for example in Anglesey. A few minor deposits of Pb and Zn have been found in the Basement of Great Britain.

11.24.C - THE NORTHERN PENNINE OREFIELD

This important district consists of two blocks, named Alston and Askrigg (figs. 11.24.2 and 3), which have remained stable during Carboniferous sedimentation while a trough formed between them and basins formed around them. Within the contours of these blocks, many Pb and Zn deposits were found. One of them (Allenheads) produced over 250 000 t of Pb concentrates; ten have produced 100 000 t or more. In addition to Pb and Zn concentrates, the orefield has produced 930 000 t of fluorspar ore, 910 000 t of barite, and 775 000 t of witherite (Dunham, 1959).
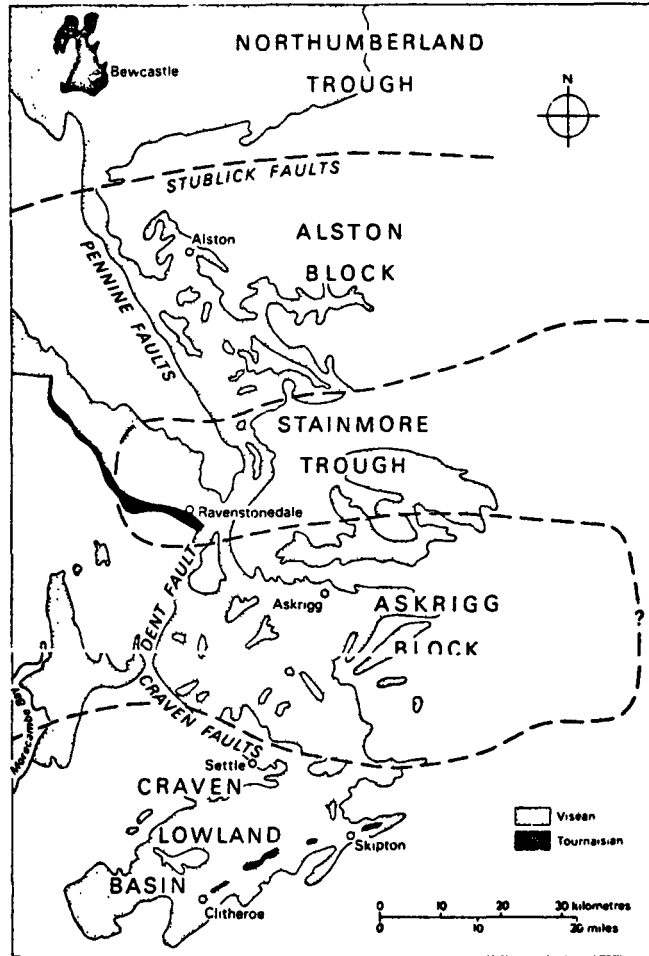
**Fig. 11.24.2** - Distribution of Lower Carboniferous rocks in the Northern Pennine region. Faults limiting the Alston and Askrigg Blocks (after Rayner, 1967)
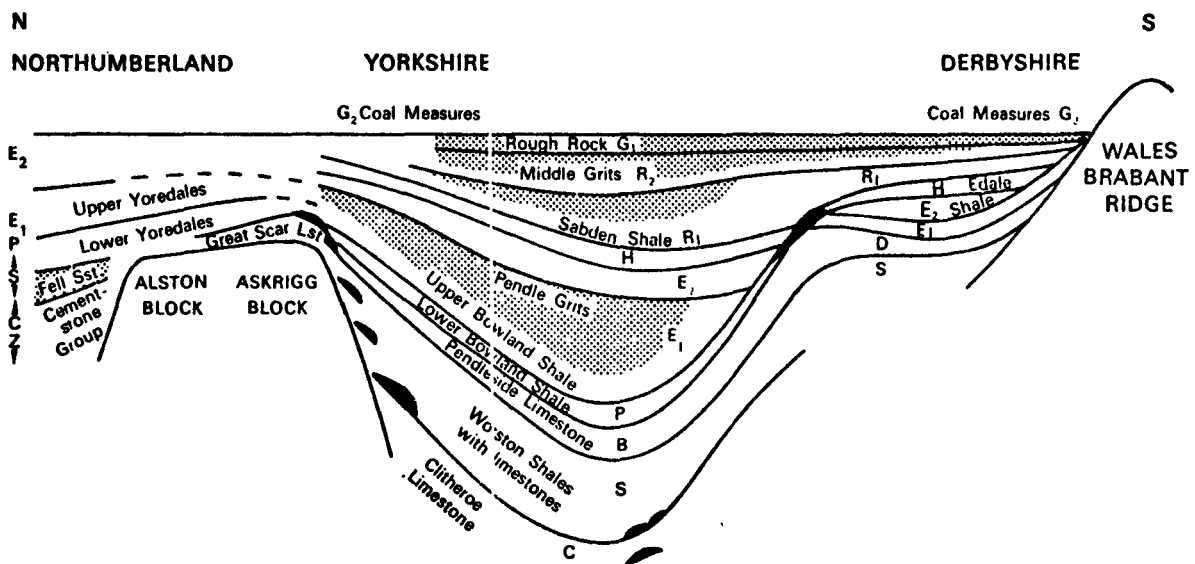


**Fig. 11.24.3** - Schematic cross-section through the Northern Pennine and adjacent regions (after Bennison and Wright, 1969)

The ore deposits of the <u>Alston Block</u> have been described in detail
by Dunham (1948). The same author (1959) and Ineson (1976) have published
shorter accounts of the economic geology of the whole orefield. The follo-
wing description is borrowed from a I.G.S. report (1977); the stratigraphy
is found in fig. 11.24.4.

"The Northern Pennine orefield covers an area of about 3 800 km2 in the coun-
ties of Northumberland, Durham, Westmoreland and Yorkshire. It is defined
by the distinct structural units of the Alston and Askrigg Blocks. The ore-
field is bounded by faults on three sides - the Stublick Faults to the North,
the Pennine and Dent Faults to the West, and the Craven Faults to the South -
and on its eastern margin it disappears below the Durham Coal Measures and
Permian. The Alston Block is separated from the Askrigg Block to the south
by the Lunedale/Stainmore trough but the sedimentary sequence is comparable
in both areas.

"The main ore-bearing horizons are the Visean and Namurian, but mineral depo-
sits also occur in strata ranging from the Ordovician and Silurian slates to
the Permian Magnesian Limestone. Greatest output in the northern block was
from the Great Limestone of the Lower Limestone Group, while in the southern
part of the Askrigg Block the host rock is the Great Scar Limestone and the
basal members of the Millstone Grit Series.

"The Carboniferous rests unconformably on highly folded Lower Palaeozoics in
which there are concealed Devonian granites and both blocks are underlain by
an elongated east-west granite. In the Askrigg Block there is also some post-
Carboniferous intrusive activity in the form of quartz-dolerite sills and
dykes of the Whin Sill. These caused induration of adjacent shales which
locally provided a host rock for ore deposition.

"Most production was however from vein fissure fills along normal faults and
was influenced by the lithology of the rhythmic sequence. Hard brittle beds
were favoured and replacement "flats" in the limestone are common at some
horizons. The major vein directions are ENE, NNW and WNW, the former being
most productive for galena.

"The main ore minerals are galena and sphalerite with occasional chalcopyrite,
pyrite, marcasite, pyrrhotite and chalybite. The matrix of most veins is
fluorite but barytes, quartz, calcite and witherite also occur.

*Recent and Pleistocene*
  peat and alluvium,
  glacial moraines and boulder clay

*Permo-Triassic*
  Keuper Marl, Bunter Sandstone,
  Permian Upper Marl, Magnesian Limestone,
  Marl Slate and Basal Yellow Sands                                    1025 m

*Carboniferous*
  Coal Measures    : Upper, Middle and Lower
    Upper          : shales and sandstones
    Middle         : productive coals
    Lower          : thin sandy coals                                   750 m
  Millstone Grit:  : sandy deltaic beds with thin limestones            370 m
  Limestone Series: Lower, Middle and Upper Groups
    Upper          : grits, sandstones, ganisters, coals,
                     limestones and shales
    Middle         : rhythmic alteration of limestones,
                     shales, sandstones and coals
    Lower          : massive limestone overlain by
                     alternating limestones, shales and
                     sandstones                                         540 m
  Basement Group : sandstones and conglomerates                       +300 m

*Devonian*                        — unconformity —
  Weardale Granite

*Ordovician*                      — unconformity —
  Skiddaw Slates   : slates and flags                                 unknown

**Fig. 11.24.4.** -   Stratigraphy of the Northern Pennine
                      region (Ineson, 1976).

"The orefield had the largest production of any area in the United Kingdom, estimated at 4 000 000 tons of lead concentrate (70-80 % lead) and 267 000 tons of zinc concentrate (40-50 % zinc). Today lead is extracted as a by-product of the fluorspar industry and sphalerite is concentrated in particular areas only (i.e. Nenthead-Alston and Greenhurth areas).

"The Weardale Lead Company reported in 1975 that diamond drilling had inferred substantial fluorspar ore on its mineral lease in County Durham as well as significant finds of lead and indications of zinc. A deep borehole has also been sunk to prove the granite underlying the Carboniferous of the northern Pennines. It showed that mineralization (not yet established as economic) continued far deeper than previously thought.

"Isotope studies on the galena have indicated a late Carboniferous - early Permian age for the mineralization and the faulting may date from a similar period of Hercynian doming associated with the Whin Sill".

Two main types of deposits are known in this orefield : veins and flats (see figs. 11.24.5 to 7). They are controlled by structure, stratigraphy and also by the mineral zoning represented in fig. 11.24.8. According to Dunham (1959) :

"(1) The fundamental structural control is the fracture-system and, except on the Swaledale-Wensleydale watershed, the favourable directions are ENE and WNW. Fractures trending NNW seldom carry major ore-shoots and seem to have been under compression during mineralization.

"(2) The refraction effect causes the ore-shoots to be related to hard beds in the wall-rock. Since such beds are thin, the shoots tend to be ribbon-shaped in longitudinal section. There are numerous cases of ore-shoots 4 000 ft long by 60 ft high.

"(3) Ore-shoots tend to terminate and commence at the intersections of cross (i.e. NNW) fractures; thus a single vein may carry several oreshoots, separated laterally by barren ground bounded by cross-veins.

"(4) Of all the hard beds, the Great or Main Limestone has proved to be by far the most favourable and has probably yielded 75 per cent of the output of the orefield. This indicates a very active lateral circulation of mineralizing fluids at this horizon.
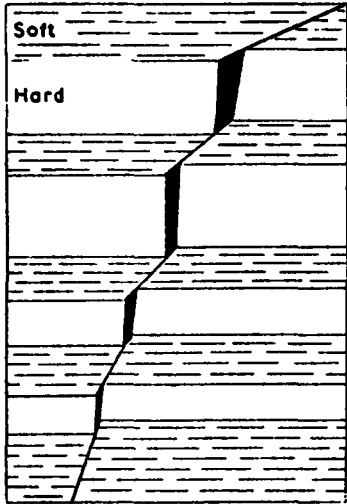
Fig. 11.24.5 - Idealized cross-section of fissure-vein (Dunham, 1948).



Great
Limestone

Tuft
Shale

Quarry
Hazle

Shale

Four Fathom
Limestone

Nattrass Gill
Hazle

Shale

TRENT LEVEL

QUARRY HAZLE
DRIFT

0                    100
FEET
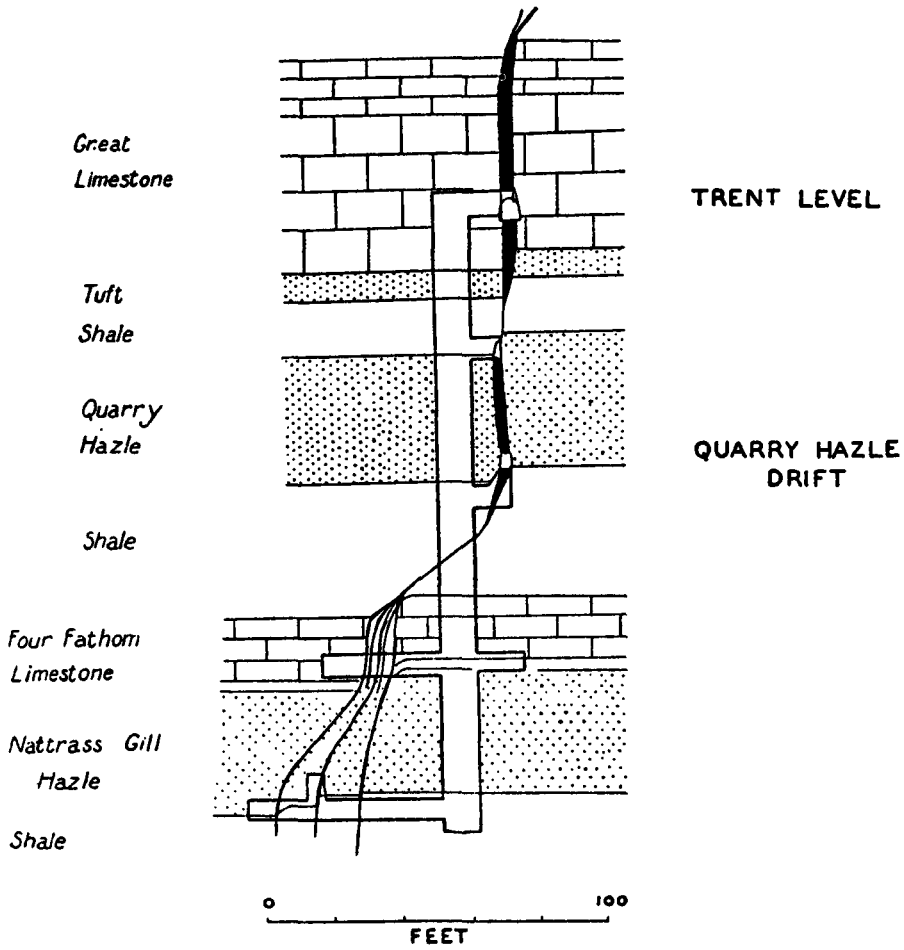
Fig. 11.24.6. - Cross-section of Killhopehead vein
(Dunham, 1948)

GEOLOGICAL MAP
OF
THE SCORDALE MINES

LIMESTONES OF MIDDLE LIMESTONE GROUP
S-Smiddy    L-Lower Little    J-Jew    T-Tynebottom

WHIN SILL

MELMERBY SCAR
LIMESTONE

FLATS

VEIN OR LEADER

LEVEL

0    100    250    500    1000

Scale of Feet
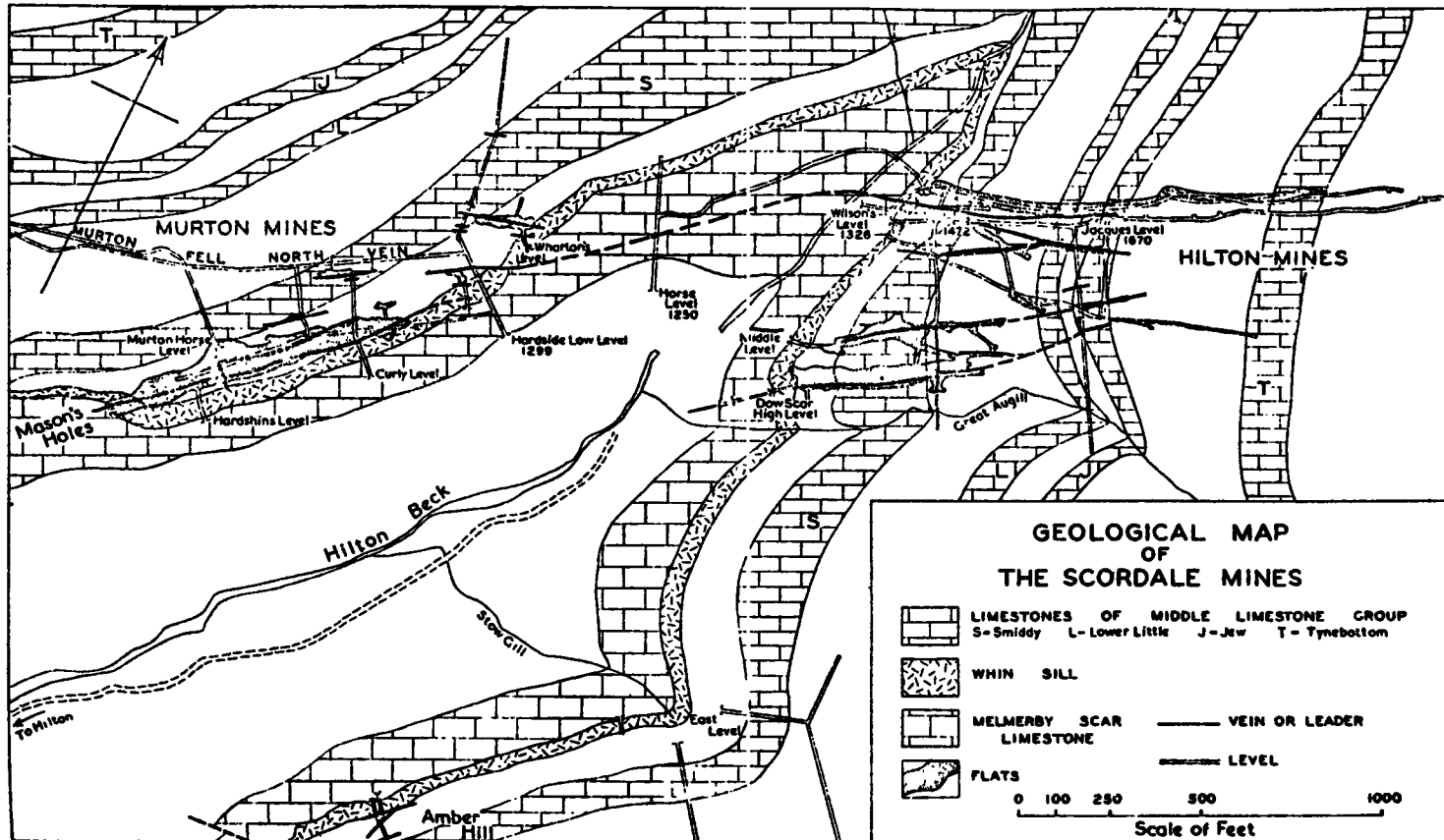
Fig. 11.24.7. - Sketch-map of Scordale mines showing the location of "flats" relative to veins (Dunham, 1948).
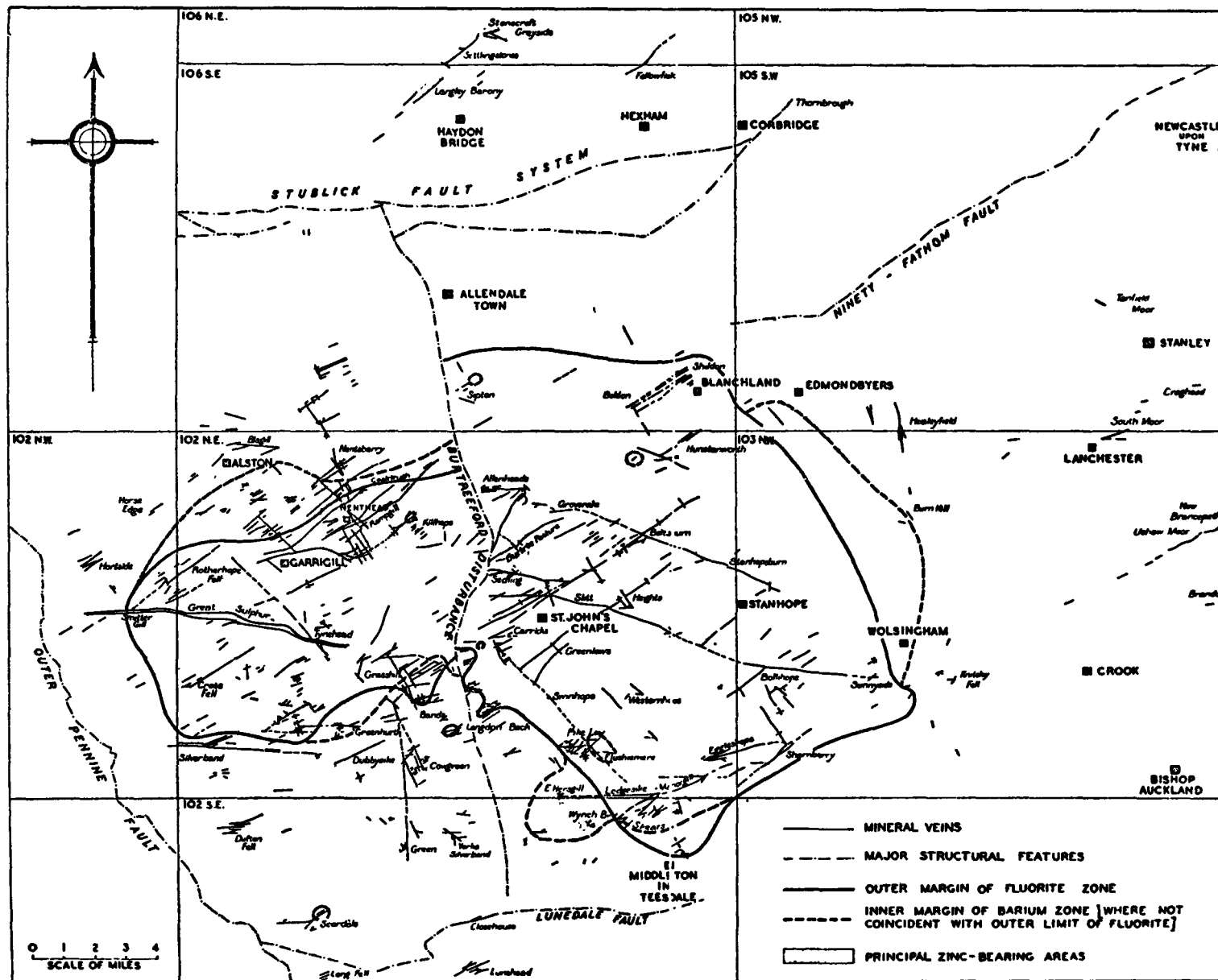
Fig. 11.24.8 - Map to illustrate the zonal distribution of minerals (Dunham, 1948)

"(5) Other hard beds are nevertheless sometimes mineralized, and several hard beds may be productive one above another, separated by barren ground corresponding with shale wall-rock.

"(6) There is a systematic zonal arrangement of the minerals, mainly evident in a lateral sense. Fluorite is the gangue of the inner zones, barium minerals of the outer. Minor concentrations of copper occur near the centres of the inner zones; the maximum deposition of galena and blende lies in the outer part of the fluoride and the inner part of the barium zone. The peripheral part of the barium zone is for practical purposes almost devoid of sulphides, but contains valuable barytes or witherite deposits. The inner part of the central zone contains the large fluorspar deposits.

"(7) Where a vertical zonal sequence exists it corresponds with the concentric lateral sequence; fluorite gives place upwards to barytes; downwards to quartz-marcasite-pyrrhotite-chalcopyrite.

"(8) In certain·limestones, metasomatism has produced valuable replacement 'flats'. These are always related to feeding veins and fissures; they never occur independent of such fissures as is apparently the case, for example, in the Mississippi Valley or Silesian orefields. The replacement may be preferential within the limestone, locally related to thin shale partings, or perhaps to peculiarities in the composition of the limestone. Thus a very widespread favourable level for 'flats' lies about 4 ft below the shaly upper part of the Great Limestone, about 40 ft above its base.

"(9) The condition for the formation of metasomatic deposits in limestone rather than vein-oreshoots is probably related to the restriction of flow of fluids in the limestone, for example by the upward sealing of the fracture by particularly impervious shale. Where sandstone rests on a limestone such a condition is not realized and 'flats' do not occur.

"(10) Replacement is also favoured by a closely-spaced complex of fractures in limestone, but this tends to produce wide vertical rather than horizontal ore-shoots. The fractures may be completely barren in shale above or below.

"(11) The usual alterations are observed in the oxidation zone; there is no evidence of secondary movement or enrichment of lead, but secondary concentration of zinc silicate or carbonate has been recorded (Raistrick, 1954).

"Cavities in limestone related to the present or perhaps to an earlier groundwater cycle are clearly post-primary mineralization in age".

The Allenheads mine, the most important mine of the Northern Pennine region, is represented in fig. 11.24.9.

## 11.24.D - THE NORTH-EAST WALES OREFIELD (Fig. 11.24.10)

The following summary is borrowed from an I.G.S. report (1977) :

"The most important of the former lead-zinc mining areas of Wales occurs in the Middle and Upper Carboniferous Limestone (Visean) and succeeding Cefn-y-Fedw Sandstone Series (Namurian) of east Denbighshire and Flintshire.

"Two main groups of mines, separated by a major fault, were active in the Halkyn-Llanarmon and Minera districts respectively, covering an area of about 40 sq. miles.

"The ore-bearing rocks are part of the belt of Lower Carboniferous strata which flanks the Lower Palaeozoic complex of North Wales. The Carboniferous is either unconformable on or faulted against the Silurian of the Clwyd Hills. As in the northern Pennines of England, the ore deposits are located on the eastern side of a graben and confined to eastward dipping strata. No mineralization has been found in the Silurian or above the Cefn-y-Fedw Sandstone.

"Most of the ore comes from veins in the top 1 500 feet of the Carboniferous Limestone. Three mineralized horizons, each overlain and controlled by a shale band and preferably with a structural constraint, or at a cross-fault and vein intersection, are particularly favourable. The most productive horizons are found in the White and Upper Grey Limestones directly below the Main Shale. However, in the Minera district stratigraphic control by the shales is less evident. Greatest production has been from the ribbon-shaped steeply-dipping ore shoots, though stratiform replacement "flats" and "pipes" also occur. The veins trend east-west in the northern part of the area, near Halkyn, but NNW-SSE further south, at Llanarmon and Minera.

"Galena is ubiquitous over the orefield, but sphalerite while present over the whole area, only becomes common in the Minera district and predominant in the southeast.
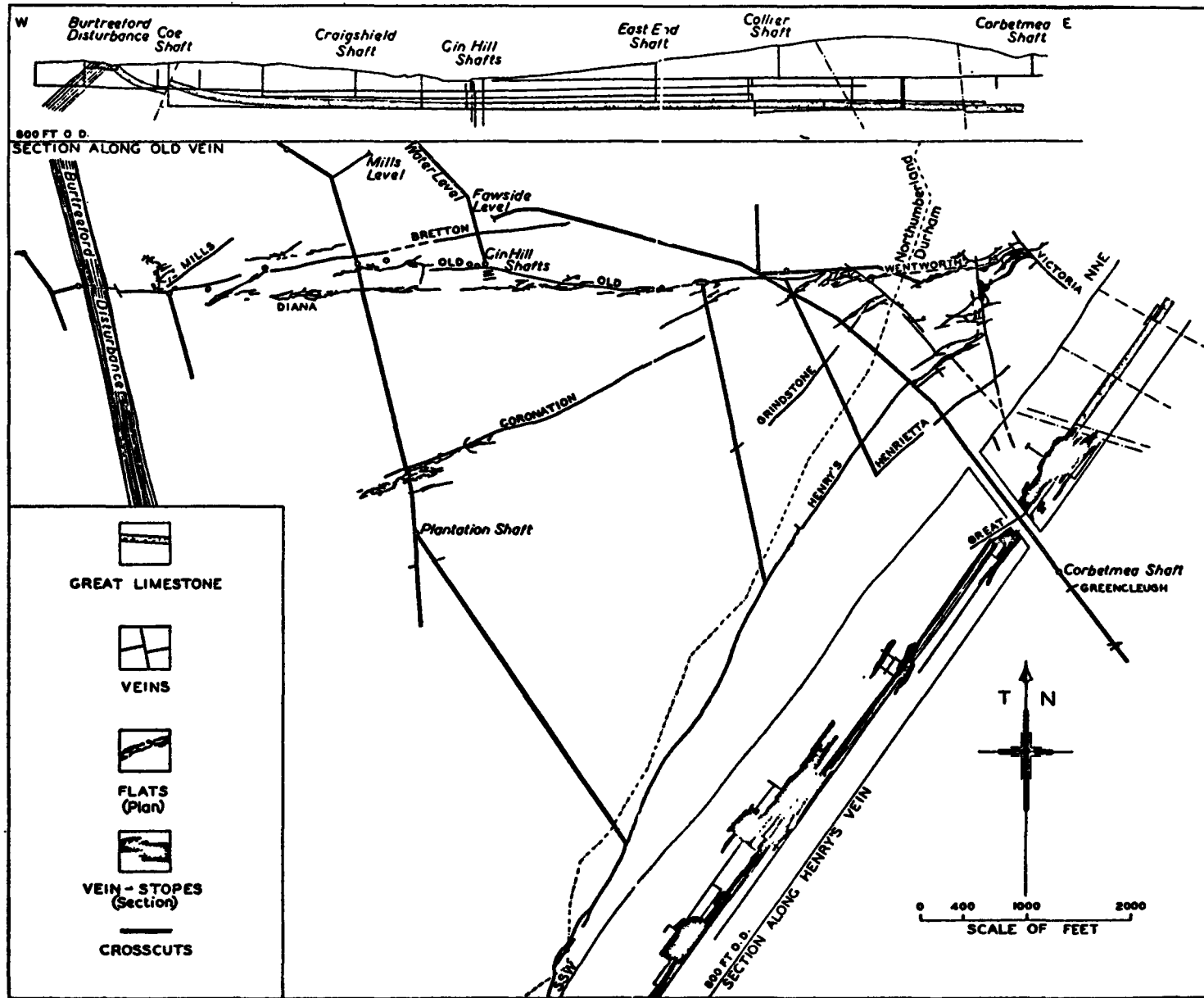
Fig. 11.24.9 - Plan and Sections of Allenheads Mine (Dunham, 1948)

*Permo-Triassic*
    Bunter sandstone of Vale of Clwyd            ?
                 — unconformity —

*Carboniferous*
    Coal Measures
        Barren Measures
        Productive Measures                         max. 600 m
    Millstone Grit
        Holywell Shales (northern outcrop)
        Cefn-y-fedw Sandstone (southern area)             max. 180 m
        (sub-divisions contemporaneous)
                   — local unconformities —
    Limestone Series
        Sandy Limestone (south Flintshire and Denbighshire)     150 m
        Black Limestone (north Flintshire)
        Upper Grey Limestone: crinoidal in upper part presence of
            quartz grains and pebbles                    240 m
        Middle White Limestone: similar to Upper Grey Limestone    450 m
        Lower Grey/Brown Limestone: limestones, pseudobreccias
            and mudstones                           290 m
        Basement Beds: mudstones, sandstones, shales and
                   conglomerates                 max.  90 m
                   — unconformity —

*Silurian*
    Ludlow: sandy shales and mudstones
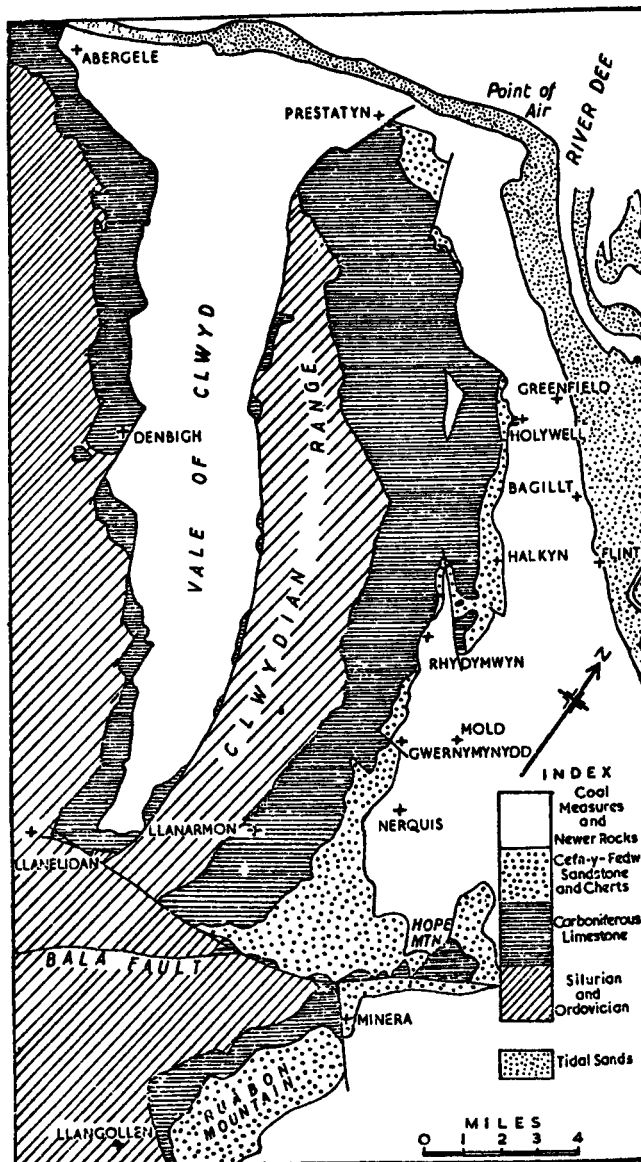


Fig. 11.24.10 - Stratigraphy (after Ineson, 1976) and geology (after Schnellmann, 1957) of the Northeast Wales orefield.

"Pyrite, chalcopyrite, cerusite, anglesite and calamine have also been exploited. Calcite is the common gangue with some quartz at Minera and fluorite-barytes at Maeshafn. The lowest level reached at Minera was 1300 feet and, in common with other British orefields, galena tends to become rarer at depth, leaving sphalerite as the main ore".

More detailed information will be found in Schnellmann (1959) and Ineson (1976).

## 11.24.E - THE DERBYSHIRE OREFIELD

The Lower Carboniferous strata, which are host to most of the Pb and Zn deposits in the Central Plain of Ireland, in the Northern Pennines and in Northeast Wales, are again observed in Derbyshire; and again large amounts of useful minerals are found in them. Fluorite, rather than Pb and Zn sulfides, is the main production of this orefield. Two major mines are still active, currently yielding 150 000 t of fluorspar and 20 000 t of barite per year with 4 000 or 5 000 t of Pb concentrate as a by-product.

There is a zonal distribution of minerals in Derbyshire (fig. 11.24.11). The orebodies are similar to those of the Northern Pennines as shown by the following (I.G.S., 1977) :

"The Carboniferous Limestone massif of Derbyshire is traversed by hundreds of mineral veins containing galena, fluorite, barytes, sphalerite and calcite. A thickness of approximately 1 500'of Carboniferous Limestone is exposed in the anticlinal structure and the base is below the deepest mine workings.

"Mineralization extends through a thickness of about 800' in the Lower Carboniferous, the Reef Knoll Limestone being very favourable for the formation of replacement ores whereas the darker limestones of the Black Beds above are less so. Volcanic horizons occur in the limestone and at Mill Close, one of the most famous Derbyshire mines, at least five lava horizons are known.

"Derbyshire lead mines have been unproductive in the Millstone Grit Series which rests unconformably upon the mineralised Lower Carboniferous. This contrasts with parts of the Northern Pennine ore field where considerable production came from these rocks.

Map of mineral veins and hydrothermal zones of Derbyshire. After Mueller

Legend:
- Lower Carboniferous limestone-shale boundary
- Hydrothermal veins and pipes
- 'Pyritic fluorite' zone
- 'Bradwell spar' zone
- 'Purple fluorite' zone
- 'Baritic' zone
- 'Pyritic calcite' zone
- 'Ecton-type' mineralization
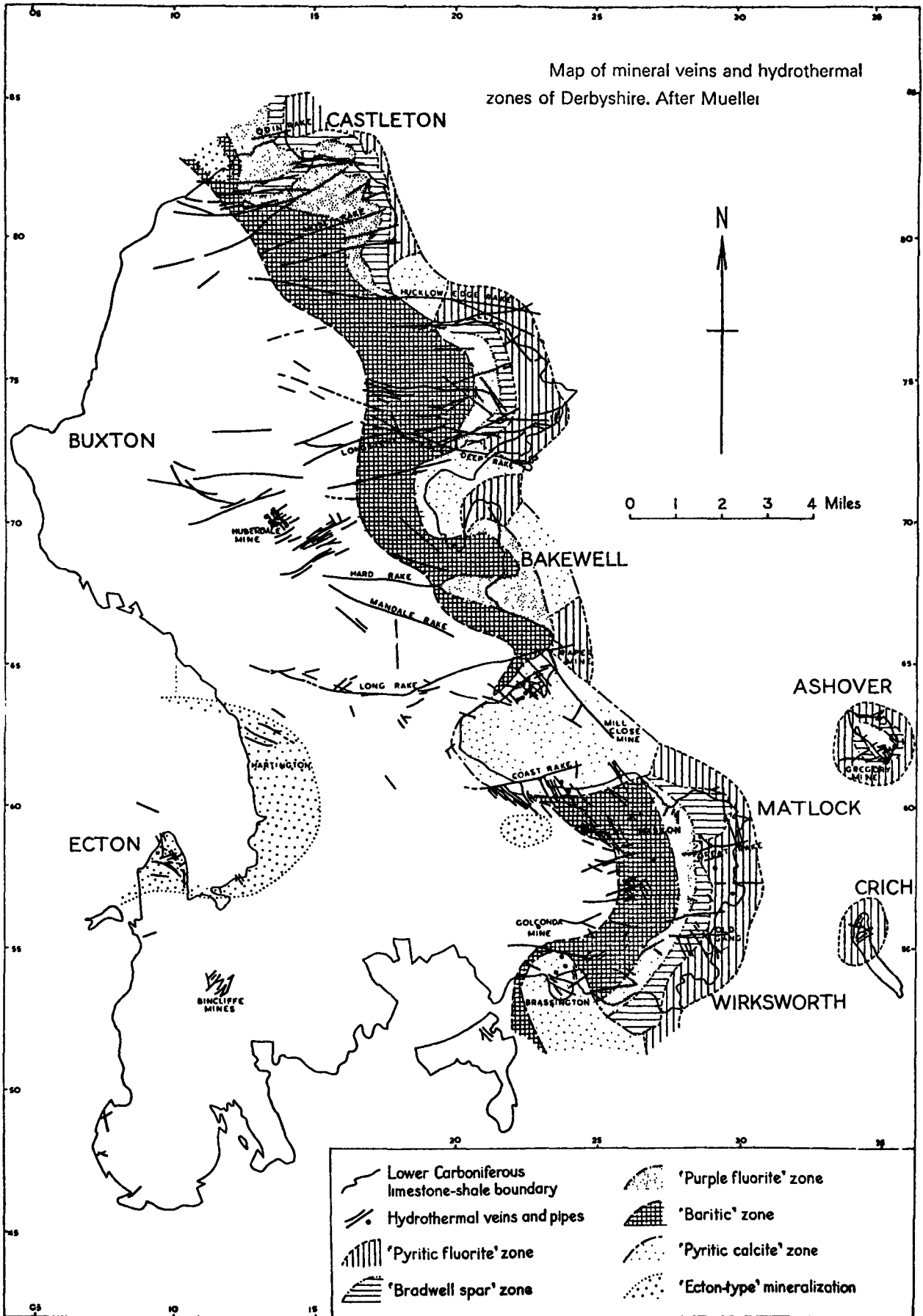
Fig. 11.24.11 - Mineral zoning in Derbyshire (Ford and Ineson, 1971)

"This may be because by the end of the L. Carboniferous the area was capped by imperme-ble Edale Shales (Namurian). Some evidence of Karst formation occurs on the erosion surface and cave development during mid-Carboniferous times may have provided channels for water or fluid migration.

"The mineralization takes the form of either veins, joint-plane fills, or stratiform "flats" and "pipes", The vein mineralization, which appears to be polyphase, is developed along steeply dipping wrench faults in the near-horizontal sequence of interbedded limestones and shales. There is a great variety of facies changes but the veins cut through the varied lithologies without apparent effect. Most of the veins trend between ENE and ESE, though the main vein at Mill Close had a north-south trend.

"The type of sedimentary environment is similar to that of the northern Pennine ore field and similar fissure filling has given rise to ore shoots limited by lithological changes (shale, tuff or lava) or by variations in dip and strike of the vein. Small anticlinal structures are also important to ore localisation.

"Stratiform "flats" and "pipes" have been produced by replacement of the limestone and are considered to be epigenetic telethermal mineralization related to palaeogeomorphological features. The deposits are interesting since they are all interconnected and have remarkable continuity. A thermal zoning of the gangue minerals has long been known. Fluorspar is commonest along the eastern margin of the limestone outcrop, barytes replaces it to the west and is followed still further west by calcite.

"Nearly all the lodes carry galena in a variable matrix of calcite, barytes and fluorspar; some cerussite is known as well as poor quality lead-silver ore. The ores are particularly rich on the northern and eastern flanks of the massif where they have in several cases been followed for miles below the overlying sandstones and shales. Sphalerite and calamine show a more sporadic and irregular distribution in the veins.

"The deepest working was to a depth of 1092 feet and in common with deposits in other parts of Great Britain the ores tend to become impoverished with depth. Unlike other areas there is no record of galena being replaced in depth by sphalerite.

"The Derbyshire or Southern Pennine orefield produced a total 678 000 tons of lead and 91 000 tons of zinc concentrates. Almost all of the zinc and 70 % of the lead came from Mill Close mine which was in major production from 1861 to 1938 and was probably the richest mine in the U.K.".

Further information on the Derbyshire orefield can be found in papers by Ford and Ineson (1971) and Ford (1976).

## 11.24.F - THE MENDIP HILLS AND SOUTH WALES

Some Pb and Zn are found in the Mendip Hills. Again most of the mineralization occurs in the Carboniferous Limestone, but in addition, the overlying Dolomitic Conglomerate of Triassic age has produced small amounts of oxide ore (Ford, 1976).

The same stratigraphic units are also observed in South Wales where they have again produced minor amounts of metal.

## 11.24.G - CONTROLS OF MINERALIZATION IN THE CARBONIFEROUS LIMESTONE AND OVERLYING SEDIMENTARY UNITS

Deposits of Pb and Zn, or prospects thereof, have been discovered in many but not all parts of Great Britain where Lower Carboniferous strata crop out. This raises the questions of why some areas are mineralized, and what controls the distribution of orebodies on a regional scale ? The following answers have been suggested :

1) Pure limestones are more favorable than shaly ones because open fissures can be maintained and therefore veins can be emplaced in them. This would explain, for example, why the Midland Valley of Scotland is barren. However, Lower Carboniferous strata around the Lake District consist in part of pure limestone and are nevertheless barren (K.C. Dunham, 1977, personal communication).

2) Domical areas and other structural highs are more favorable than basins, for a reason which may be directly related to the mechanism that formed the deposit.

3) Areas underlain by pre-Carboniferous granites are favorable because
   these granites are the channelways through which the ore solutions reach
   the Lower Palaeozoic strata. In fact a pre-Carboniferous granite was
   discovered some years ago beneath the <u>Alston Block</u>; since then indica-
   tions of geophysical and other nature have accumulated which indicate
                     granites at some depth under Derbyshire and the Mendips
   (Evans and Maroof, 1976).


   On a local scale, the orebodies are controlled by faults and stra-
tigraphy as mentioned in section 11.24.C.


## 11.24.H - <u>OTHER GUIDES TO MINERALIZATION</u>


   Unfortunately Pb and Zn deposits of the English type are not surroun-
ded by a large system of concentric aureoles of wall rock alteration such as
observed for instance around porphyry coppers. Within an orefield however,
some rules apply and may be useful.


   Ford (1976) describes wall-rock alteration in Derbyshire as follows :


"Alteration of the limestone wall-rocks adjacent to veins varies from recrys-
tallization with progressive loss of original and diagenetic textures and an
increase in microfracturing as a vein is approached, to dolomitization and
silicification (Ineson, 1969, 1970). Dolomitization is recognizable in the
northern part of the area only to a very minor degree but areas of widespread
dolomitization occur in the southern part of the orefield. Silicification is
again highly variable and is most intense in areas where volcanic horizons
are most common, particularly in limestones immediately adjacent to basaltic
ashes and lavas, suggesting leaching of silica from the basalts. These in
turn are often altered to montmorillonite and illite. Some "wayboards" are in
fact low-grade K-bentonites.

"Metasomatic replacement of wall-rocks by ore-minerals is again patchy. Fluo-
ritized limestone occurs adjacent to the pipe-veins of Treak Cliff, and
fluoritized dolomite is common in Masson Hill at Matlock.

"Dispersion aureoles of both ore - and trace - elements have been detected
adjacent to several rakes (Ineson, 1969, 1970). Pb, Ba and Zn fall off to
blackground values irregularly within about 10 m of major veins (the irregu-
larity seems to be related to the intensity of microfracturing); F remains
high through the same distance and then falls off rapidly.

"Zr has a similar distribution, but Sr and Mn remain fairly constant.

"Geochemical soil sampling on traverses across both known veins and their projections into virgin ground have shown dispersion patterns of the principal elements, but no consistent pathfinder trace-elements have been detected so far. In some veins Mo was a pathfinder for extensions, while elsewhere Ba, Mn, Zr and Co gave some indications. Regional geochemical soil sampling has confirmed the distribution of high blackground values of Pb, Zn, Cu and F in the mineralized areas, and has suggested the presence of some, as yet untested, areas of mineralization in concealed ground along the western margins of the limestone outcrop".

## 11.24.J - THE SOUTHERN CALEDONIDES. VEIN-TYPE DEPOSITS

Within the Southern Caledonides of England and Wales, several districts were formerly producing Pb and Zn, and occasionally copper (figs. 11.23.9 and 11.23.10). With few exceptions, the orebodies from which the metals were mined are veins, often steep-dipping, and often well-developed in only one or two types of country-rock. The following indications have been supplied by I.G.S. (1977). See fig. 11.24.1 for the location of the districts.

### Northwest Wales

"Lead-zinc mineralization occurs in Lower Palaeozoic sediments and volcanics in three main areas and several smaller ones in Northwest Wales around the centrally placed Harlech Dome.

"In east Caernarvonshire the Llanrwst mining district was the main Pb-Zn bearing region of Lower Palaeozoic rocks in North Wales. The majority of the workable veins occur in faults in the Crafnant Volcanic Series of the Upper Ordovician. The series consists of interbedded shales, tuffs and rhyolite lavas, and the main lode is developed in the volcanics, while the sediments are poorly mineralized.

"Two other areas, the Llanengan and Llangynog districts, were formerly also of importance. The Lower Ordovician flagstones and mudstones, that rest unconformably on the Cambrian in the Llanengan area (western Lleyn), contain mineralized fault zones. Middle and Upper Ordovician interbedded shales, mudstones slates and volcanics in the Llangynog district of the Berwyn Dome (north Montgomeryshire) have produced small quantities of galena, sphalerite and chalcopyrite.

"In all these areas the ore-bearing veins occur in steeply dipping normal
faults, and fissure-fills of suitable structural openings in favourable
lithologies accounted for most of the production. The trend of the veins
was variable but was predominantly N-S and E-W with a set varying from
ENE to ESE. As in central Wales the ore shoots usually bottomed in soft
shales (where the dip of the fault decreased). The central Harlech Dome
area is characterised by chalcopyrite mineralization in a quartz gangue,
while the lead-zinc ores occur around this area with associated calcite,
quartz and barytes".

## Central Wales

"The second most important Pb-Zn mining region in Wales comprises approxi-
mately 400 sq. miles of mid-Wales, where lodes traverse a northeasterly
trending belt of Upper Ordovician and Lower Silurian sediments. The bulk
of the ore field lies in north Cardiganshire and west Montgomeryshire
where 133 mines raised galena, sphalerite and some copper.

"The sequence consists of an alternating series of sandstones, mudstones
and shales with three dark pyritic shale horizons up to 600' thick. Ore-
producing veins follow steeply dipping faults and tension fractures in
the sandstone horizons, the most productive being the Frongoch Formation
(L. Silurian). There is evidence that the fissure filling of these struc-
tural weaknesses may have originated from the pyritic shale bands. The
gangue is quartz and brecciated country rock with some barytes and calcite,
but considerable amounts of barytes and witherite were also mined in Mont-
gomeryshire.

"Some 6 000 feet of strata were worked, though the greatest working depth
was about 1 000'. A maximum annual production of 14 000 tons of lead ore
was recorded for the area in 1876; an estimated total of 479 000 tons of
lead concentrate (probably assaing 70 % Pb) and 151 000 t of zinc concen-
trate were produced largely between 1840 and 1885".

## Shropshire

"In Shropshire lead mining was centered on a small anticlinal area lying
within a 3 miles radius of Shelve. However, in 1872 it produced from 10
mines over 10 % of Great Britain's lead ore.

"The mining area is bounded to the north, west and south by unconformably overlying Silurian strata, and to the east by a major fault.

"The veins occur in vertical normal faults and are confined to the Lower Ordovician Mytton Beds. They crop out as an inlier on the Shelve anticline and are composed of about 1 500' of flagstone and gritsone. Lithological control is evident since the mineralized Mytton Beds are capped by the Hope Shales and floored by the Stiperstones Quartzite, neither formation affording any workable ore. The Ordovician contains contemporaneous andesites and andesitic tuffs and the veins cut dolerite dykes and sills of early Silurian age.

"The greatest production came from ENE trending veins but northwesterly trending veins can also be important. Calcite is the commonest gangue with subsidiary barytes, while witherite and barytes occur in veins higher in the sequence but not accompanied by significant sulphide mineralization. Barytes veins are also found in the Pre-Cambrian to the east of the sulphide ore field.

"The greatest depth of working was 1956' at Snailbeach mine where sphalerite is reported to have increased in abundance with depth. At the peak of the 1873 boom the output of Shropshire mines was 7 600 tons of lead ore from only 5 mines. An estimated total of 237 000 t of lead concentrate and 21 000 tons of zinc concentrate were produced in the West Stropshire mining field".

Isle of Man

"The Isle of Man has long been famous for its silver-lead-zinc production, the period of greatest activity being 1823-1919. The area produced 266 000 t of lead concentrate, 93 % of which came from two mines - Foxdale and Great Laxey which was the largest single producer of zinc in the U.K.

"The mineralization occurs in the Cambrian Manx Slates and in the Manx Granite below, the whole being overlain by Carboniferous sediments. The most productive ore came from the basal part of the Manx Slates consisting of a blue-grey flaggy slate and no ore has been found in the quartz-veined grits. The veins continue down into the underlying granite (the greatest working depth was 2100') where they are equally productive, though the galena is less argentiferous.

"The main lode system at Foxdale trends E-W but at most of the other workings, including Great Laxey, the trend was NW-SE. The veins are fissure-fills of steeply dipping normal faults and all the more productive lodes occur on or near the structural axis of the Manx Slates. The sulphides occur either as disseminations or as thin lenses in the veins, with a gangue of quartz, calcite, dolomite, brecciated country rock and a little barytes and fluorspar. A late Mesozoic, probably Upper Triassic age is envisaged for the mineralization".

## Lake District

"Despite its great variety of metalliferous minerals, the Lake District veins have never been extensive enough to support more than a modest mining industry.

"The geology is complex but may be said to consist of a dome of severely folded and faulted Ordovician and Silurian rock intruded by many acid and basic masses including lava flows Visean, Namurian, Permian and Triassic rocks surround, often unconformably, the Lower Paleozoic. Almost all production came from the Lower Ordovician particularly, the Borrowdale Volcanic Series and the underlying Skiddaw Slates.

"The district may be divided into the Caldbeck Fells, the Keswick area and the Coniston area, the latter having produced only copper ore. The Caldbeck Fells exhibit the greatest diversity of rocks and minerals ranging from the Carboniferous to the Ordovician with the Carrock gabbro-granophyre complex and the Skiddaw Granite. These latter are the only intrusions in the mining district that are cut by mineralised veins. Mined ores include tungsten, copper, lead, zinc and barytes.

"The northwest of the Keswick field has yielded lead, zinc and barytes, with small amounts of copper, from folded shales, mudstones and flagstones in the Skiddaw Slates; to the south the Borrowdale Volcanics contain lead and some graphite.

"There is an upward zoning in the orefield, galena and sphalerite giving way to barytes-dolomite and then pyrite-manganese. There are no strong lithological controls in the Lower Ordovician rocks, though harder bands are better ore-bearers; although the Keswick and Caldbeck areas flank the main anticline little structural control is evident.

"Isotopic determinations suggest Upper Triassic mineralization, but more than one phase probably occurred and lower to middle Carboneferous ages have also been obtained.

"At the most important mine, Greenside, the main vein runs approximately north-south and is spatially associated with a quartz-porphyry dyke. Most of the veins are steeply or vertically dipping normal faults filled by country rock breccia. Mineralization was fissure-filling, localised in steeper dipping parts of the vein and at vein intersections.

"The chief lead ore is argentiferous galena, which, in some barytes-rich veins at Force Crag and Driggith, normally contains 30 oz per ton of silver. Sphalerite is the main zinc ore while chalcopyrite and pyrite often occur in the lead-rich veins. Cerussite, pyromorphite, calamine and psilomelane are found in the more superficial parts of the veins. Quartz is the universal gangue with small amounts of barytes and calcite.

"The peak of mining activity was in the nineteenth century when copper and lead were in demand. In the twentieth century mining has been primarly for barytes and tungsten. Up to its final closure in 1961 the Greenside mine produced 1 500 000 oz of silver at an average grade of 7 1/2 oz silver per ton of lead concentrate. It produced 90 % of the 226 000 tons of lead con- centrate and 34 000 tons of zinc concentrate recorded for the Lake District as a whole.

"Investigations in the lower levels of the Force Crag mine in 1967 with a view to the availability of lead-zinc ore proved unfeasible".

In Scotland, three districts have produced a sizable amount of metal :

Leadhills-Wanlockhead

"Leadhills and Wanlockhead are situated in the Southern Uplands of Scotland; the two villages are separated by the Dumfries shire-Lanarkshire county boundary and comprised an important lead-zinc mining district in the past, accounting for perhaps 45 % of the total lead output of Scotland.

"The mining area occurs within and area of Ordovician rocks which were intensly folded along NE-SW axes during the Caledonian orogeny. This synclinorial belt is bounded to the north and south by anticlinoria of older rocks.

"The general succession comprises Arenig volcanics, successively overlain by radiolarian cherts, Caradocian black shales and greywackes of the Lowther Group (Ashgill). A prominent structural feature of the greywacke belt is a marked NNW-SSE jointing. The mineralisation occurs in steeply dipping veins which generally parallel the main fracture direction. A minor set of veins strike WNW. The vein directions correspond to the pattern of Caledonian wrench faulting in the Lower Palaeozoic greywackes.

"All the Wanlockhead veins terminate against a low angle thrust which forms the southern margin of the anticlinal cherts and black shales. It has been suggested that the shear zone of the thrust or the thrust mass of the black shales themselves acted as an impermeable barrier and governed the localisation of the ore deposits.

"The country rock is intruded by numerous dykes of the Caledonian suite which usually parallel the mineralized fractures. As these dykes are brecciated and altered by the mineralizing fluids, the vein filling was post Caledonian dyke emplacement. A lower to middle Carboniferous isotopic age has been recorded for one lead sample.

"The veins are filled with brecciated greywacke cemented by gangue minerals, and the sulphide minerals are usually concentrated on the vein walls. Galena and sphalerite were the two widespread primary ores worked in the district, with sphalerite slightly less abundant in the extreme east. Smaller amounts of chalcopyrite, pyrite, haematite, limonite, ankerite, marcasite and witherite are found. Quartz, calcite, dolomite and barytes are widespread gangues.

"The galena and sphalerite may be either disseminated or in coarse crystalline aggregates often intergrown with each other and with pyrite and chalcopyrite.

"Secondary lead minerals produced by oxidation of the galena include
cerussite and anglesite; two secondary lead sulphates Leadhillite and
Lanarkite are characteristic of the area.

"Over seventy veins were worked of which about twelve were extensively
mined to a maximum depth of 1 440 feet. The area has an estimated produc-
tion of 317 000 tons of lead and 14 000 tons of zinc concentrates between
1785 and 1958".

## Newton Stewart-Minnigaff area

"A large number of mainly lead-zinc veins occur in west Kirkudbrightshire
near the edge of the Cairnsmore granite. The area is composed of flags,
shales and greywackes of the Llandovery-Tarannon Series (Silurian), with
underlying black Birkhill shales. Intense folding, hornfelsing by the
granite, and intrusion of numerous felsite dykes has occurred. The majori-
ty of the veins, which are preferentially associated with the greywackes,
trend WNW-ESE; a few trend NW or NNE.

"The ore is often quite complex, exhibiting an association of galena and
sphalerite with smaller amounts of pyrite, chalcopyrite and mispickel.
The common gangue minerals are calcite, dolomite, quartz and barytes.

"Initially the veins were worked for their copper and lead contents, but
later on sphalerite attracted most attention. The most important mines
were at Blackcraig but production figures are lacking".

## Islay

"The lead mines on the island of Islay were the second most productive
group in Scotland and were probably worked by the Danes or Norsemen.
Numerous old workings are known and the veins are most abundant near
Ballygrant, but mining ceased in 1880.

"The local geology is complex but broadly the Dalradian sequence from base
up comprises the basal black Esknish Phyllites, the Islay Limestone, the
Conglomerate Group and the Quartzite Group. The veins occur in the Islay
limestone and its interbedded slaty phases which is thought to be about
300-400 feet thick.

"The trend of most of the veins is across the strike of the limestone outcrops and hence the ore pockets may be of limited extent.

"Tertiary dolerite dykes cut all the older formations and the series is slightly metamorphosed and gently folded. There does not seem to be any connection between the dykes and the mineralization.

"The ore is galena with smaller amounts of copper sulphides, sphalerite and pyrite in a predominantly calcite gangue. The actual area of ore-bearing limestone as defined by the old workings is only some 12 square miles, but it is probable that undiscovered replacement deposits may exist within the limestone.

"Between 1862 and 1880, 1 919 tons of ore and 1 426 tons of lead were produced, mostly from the Mulreesh area where workings reached a depth of 240 feet.

"At least one mining group considered the prospects of central Islay in the late 1950's and although no developments resulted, it was indicated that the area remained of interest".

11.24.K - SOUTHERN CALEDONIDES. STRATIFORM DEPOSITS

One would expect that, in addition to veins, stratiform deposits associated with volcanics exist in the Caledonides of Great Britain. The island of Anglesey contains such a deposit (I.G.S., 1977) :

"A formerly important non-ferrous mining field containing copper and subsidiary lead and zinc ores occurs in the Parys Mountain - Mona area of the Isle of Anglesey, north Wales. The area was famous for its chalcopyrite ore, but the most concentrated Pb-Zn mineralization was found in lenses of mixed sulphides in silicified Silurian shales called "Bluestone".

"Mineralization is associated with a single overturned tight syncline composed of a thick acid volcanic unit set in Ordovician and Silurian shales. This belt of Lower Palaeozoics rests unconformably on schists and gneisses of the Mona Complex (late Pre-Cambrian). High angle thrusts have modified the synclinal structure and mineralization occurs primarily along the faulted contacts of the lithological units.

"The "Bluestone" ore consists mainly of sphalerite as grain aggregates and intergrowths with galena, pyrite and chalcopyrite. When pure, the ore can contain up to 30 % Zn, 10 % Pb and 1 % Cu. The common gangue is quartz with smaller amounts of sericite, siderite and carbonates.

"A syngenetic model for the mineralization has been suggested with later Caledonian and possibly Variscan remobilization. The area has been extensively drilled recently with a view to exploitation of copper, lead and zinc, but lateral extension of the higher grade ore bodies was not proved and development did not proceed any further".

## 11.24.L - THE VARISCIDES

"Devon and Cornwall are famous for their tin and copper mining but significant quantities of lead and zinc have also been produced. The area yielded about 6 % of all the lead and zinc concentrates recovered from British deposits.

"Most of it was obtained in the nineteenth century from the small mining districts of Perranzabuloe, Menheniot and the Parran Iron Lode in Cornwall, and from the Tamar and Teign Valleys in Devon.

"The region consists mainly of Palaeozoic shales and mudstones with bands of grit and conglomerate known locally as "killas". These are of Devonian age in most of the area but include the Carboniferous Culm Measures in the north. The killas is overlain by Permo-Triassic sediments in the east and numerous basic sills, dykes and lavas occur. Folding, cleavage and jointing of ENE trend was followed in the late Carboniferous early Permian by granite intrusion and the production of metamorphosed killas aureoles. Fissures opened up in the granite along lines of weakness during late stage consolidation and in these, ore minerals were deposited. Both the granites and the veins are related to the Hercynian orogeny. After emplacement of tin and copper in east-west fissures, lead-zinc, fluorspar and barytes were deposited mainly in the steeply dipping north-south cross-courses.

"Zonation of the ore minerals follows the upward and outward sequence : tin, copper, zinc, lead, iron. All the known lead-zinc lodes are in the killas, either within the metamorphic aureoles or more commonly in the unaltered mudstones and shales.

"The gangue is quartz, fluorspar, calcite and barytes.

"The period of greatest activity was between 1845 and 1886 when the average annual output was over 10 000 tons of lead concentrates. The area produced a total of 317 000 tons of lead concentrates, assaying 60-75 % Pb, from which 7 062 750 oz of silver were obtained. Zinc concentrates have totalled 89 000 tons, assaying 20-45 % Zn, 71 % of all lead production came from 9 of 200 or so mines and 63 % of all the zinc came from 3 mines. The most productive workings reached over 1 300' in depth.

"Lead and zinc are only mined in southwest England to-day as by products of the tin industry. For the year 1975 Consolidated Gold Fields Wheal Jane mine produced 2 739 tons of zinc concentrate and 2.6 tons of silver concentrate.

"About 5 000 tons of galena were produced from the tiny ore field of Combe Martin in north Devon before mining ceased in 1848. The ore was probably extracted for its high silver content (up to 168 oz. silver per ton of metallic lead). The E-W trending galena-rich veins occur in steeply dipping normal faults cutting Devonian slates, and often parallel the bedding to produce stratiform pods. Quartz, siderite, chalcopyrite and sphalerite occur with the galena, though there is no record of zinc production. Near surface secondary enrichment produced malachite, azurite, covellite and native silver, and the mineralization is probably late Devonian in age".

The geological features which control the mineralization at Wheal Jane, Cornwall have been recently studied by Rayment et al. (1971). These authors showed them to be related to the detailed structure of the area and especially to the shape and position of the intrusive dykes, which are themselves controlled by the emplacement of the granite cupolas (figs. 11.24.12 and 13).

11.24.M - SUMMARY

The many Pb and Zn deposits found in the Carboniferous strata of Great Britain belong to a quite distinctive type. They have supplied about 5 Mt of metal and large amounts of associated minerals, although none of them taken alone was found to be very large. The geological controls of these deposits are rather well known.
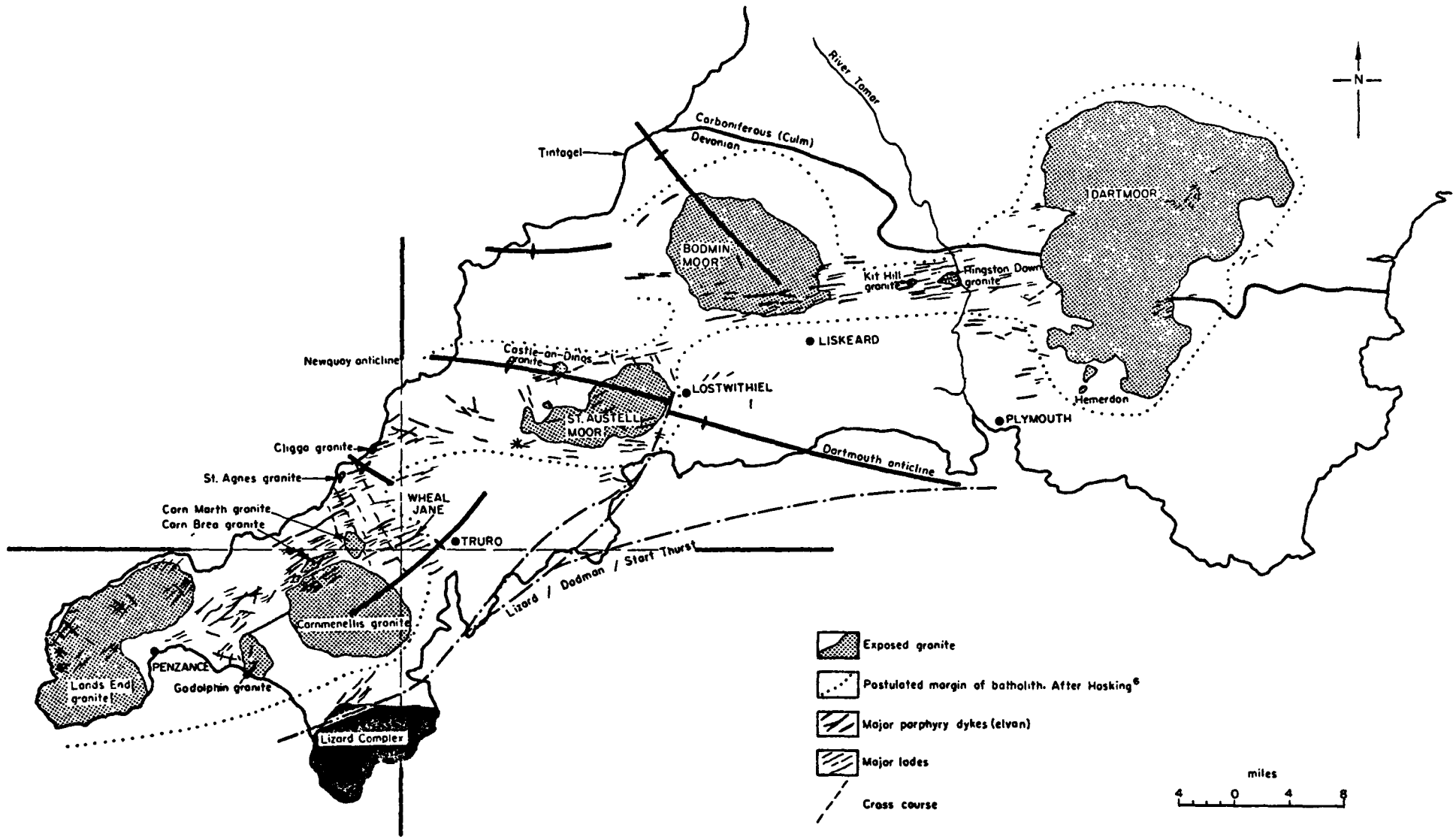
Fig. 11.24.12 - Regional map of southwest England (After Hosking in Rayment, 1971)

Lodes occur as predominantly steep dipping conjugate sets

Lodes predominantly of Wheal Jane orientation

C

North Busy

Scorrier Consuls

Boscoman Cu Zn As

East Downs Sn

Seymour Sn

Great Bay

TPb

Deniol

East Falmouth Pb:Zn

Ross Cu Sn

SCORRIER

Chance

Cu Sn As W

CHACEWATER

Great North Downs

Killifreth Sn Cu As

Penberthy

Treskerby

Unitywood Cu Sn As Pb

Derrick

West Poldice

TOLGULLOW

Creegbrawse

PROSPER

Clifton

Gorland

Unity Poldice Cu As Zn Pb W

Wheal Jane Sn Cu

D lode

Rock on Cha Sn

Trefula

Pink Cu

ST DAY

St Day United Cu Sn As Zn

Mais

TWELVE HEADS

F6

Cupid Cu

North Grambler

Taleer

Counter Bedden TPb lode

F5

Jewell Cu

Great Consolidated

F6

West Jewell Cu

Jewell Cu Sn Pb

Clifford

Andrew

Nangiles Cu Sn Zn As

Sn

Gambier

Amalgamated

Mt Wellington Sn

West Damsell

United

Great

Mt Sn

Ale and Cakes

SUNNY CORNER

Bissoe Pool Sn

F5

Ting Tang Moyle Cu

Cu

Poldory

Cu

Fortenoy

F5

EDGECUMBE

LANNER

A

B

D

F

Granite

Porphyry dyke (elvans) where known

Lodes—where known

Permo-Carboniferous

Portscatho series (cleaved silts and sandstones)

Falmouth series (cleaved sandstones and silts)

Mylor series (cleaved shales and silts)

Slaty cleavage plane commonly sub-parallel to bedding

Lower Devonian

Axial trend of fold

Cross course

Fault

Miles

1/4   1/2   3/4   0

TRURO

KEA

F2

N

Fig. 11.24.13 – Outline geology of Truro-Carn Marth area (Rayment, 1971)

- 98 -

The Pb and Zn deposits found in the Caledonides are mostly veins, a number of which yielded more than 0.1 Mt of metal. A stratiform deposit is known in Anglesey.

In the Variscides as well, substantial amounts of Pb and Zn were mined, as co-products or by-products of copper and tin. These are again vein-type or stqckwork deposits.

No Pb and Zn mine is in operation at present in the United Kingdom.

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11.25 - FRANCE


11.25.A - INTRODUCTION


Many occurrences of Zn and Pb have been discovered in France.
Among them more than 100, found in quite different provinces (fig. 11.25.1),
are large enough to be considered significant ore deposits. Past production
amounts to 3.5 Mt of metal.


Of the four mines currently producing Zn and/or Pb, two (St. Salvy
and Les Farges) have recently been opened on newly discovered deposits.
This suggests that the untapped potential of the country may be conside-
rable and shows that exploration is proceeding actively.


The Zn and Pb deposits of France belong to several different types
and are found in rocks of widely different ages. To keep consistent with
the arrangement of the previous paragraphs, we shall deal separately with
those found in the Post-Variscan Cover and those found in the underlying
Basement. However contrary to what is observed in Ireland or in Great
Britain or in Greenland, there are deposits in France which straddle the
boundary between these two major geological units. The distinction just
mentioned is therefore somewhat artificial.


11.25.B - REGIONAL GEOLOGY


The map (fig. 11.25.1) shows the contours of the Old French Massifs,
which are parts of the Variscides. We are interested here in the Armorican
Massif (n° 1 in fig. 11.25.1), the Central Massif (n° 2), the Pyrenean
Massifs (n° 3) the Massifs de Provence (n° 4), the Alpine Massifs (n° 5)
and the Vosges (n° 6).

Fig. 11.25.1   ZN AND PB DEPOSITS IN FRANCE   (B.R.G.M., 1977)

Types of deposits :

- diamonds : stratiform and other orebodies, including associated veins, in orogenic successions which are partly volcanogenic

- triangles : stratiform and other orebodies, including associated veins, in sedimentary successions deposited on the post-Variscan platform (either clay-carbonate or detrital successions)

- circles : other veins.

Size of deposits (past production + reserves, as tonnes of metal)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| - 1 | : | 1 000 | to | 10 000 t | Example | : | Argentella, Corsica |
| - 2 | : | 10 000 | | 100 000 t | | : | La Finosa, Corsica |
| - 3 | : | 100 000 | | 500 000 t | | : | Les Bormettes, Maures |
| - 4 | : | 500 000 | | 1 000 000 t | | : | Les Malines. |

The names of currently mined deposits are underlined.

Fig. 11.25.1.

Zn and Pb deposits in France

(B.R.G.M., 1977)

**7**

**1**

BODENNEC
Trémuson
POULLAGUEN
HUELGOAT
PORTE AUX MOINES ● LA TOUCHE
PLÉLAUFF
● PONTPÉAN

St Avold ▲

LA CROIX AUX MINES ● ● STE MARIE AUX MINES

**6**

GIROMAGNY ▲ St Thenn

Chitry les Mines ▲ Aillevy en Morvan

Stelle ▲

LA NUIZIÈRE

A'fires  Amberose ▲
Cherchemine ▲

PONTGIBAUD ●

ST MARTIN LA SAUVETÉ
Monthandout
Bagne
Aurelles

La Petite
Rocell
LES FARGES ●

La Vieille Voute
LA PEYPE
La Pesse ● ● Brousain

**2**

St Barthélémy le Plaon

Ste Marie de Feuilly
● B. de la Corse

PEISEY
LA PLAGNE
Nantoud
BOIS FEUILLET

Pierre Rousse ● Oultes ● Brandes
Laffrey ● ● Le Grand Clot
La Fayette ● La Pontet

▲ L ARGENTIÈRE LA BESSÉE

ST CIERGE LA SERRE  CHALIAC

FIGEAC ▲
LA VIDALE ● St Louis
LA BAUME ● La Fole
VEZIS ●
La Sirmar du Tarn ●
VILLEMAGNE
TRÈVES ▲
ST LAURENT LE MINIER ▲
Brusque ●
PEYREBRUNE ●
LA RABASSE ▲
NOAILHAC-ST SALVY
LA LOUBATIÈRE ●
LA CAUNETTE ●

LE ALEVIGNAND
Albert
Rompnerache
Meyrueis

LARGENTIÈRE
Villefort
VIALAS
▲ Landès

▲ MÉNGLON
Bretis

NORD ALES
ST SEBASTIEN D AIG PEFEUILLE
▲ LA CROIX DE PALLIÈRES
DUNFORT
St Hippolyte de Fort
LES DEUX JUMEAUX
LES AVINIÈRES
LES MALINES
Villecelle

**9**

**8**

Condazes Ligas

VALAURIA ▲

Vautron
St Daumas  Pic Martin
LE VERGER  LA MEILLE
● COGOLIN
LES BORMETTES

**4**

0    100   200   300   400 km

PIERREFITTE  HERBIOU
Tuc de Auquerfort  SENTEIN
Argut  Herran
ARRE  ARRENS  Chase
Marpineau
Crabioulou  Juite
Hospice de France  CARBOIRE
Mont Coustand
Cadeilhan
Moncaus
Pech Rhiju

**3**    **3**

Argentella ●
LA FINOSA ▲

The Old French Massifs are surrounded and overlain by a Cover con-
sisting of post-Variscan sediments. Some of them have been involved in the
Alpine orogeny along with the adjacent parts of the Cover.

Between the Old Massifs, there are two large and deep sedimentary
basins where beds have remained mostly horizontal : the Paris basin (n° 7)
to the North and the Aquitaine Basin (n° 8) to the SW. In the South, there
is a third large sedimentary basin, more or less complexely deformed
between the Central Massif and the Alps (n° 9).

The following is largely based on the recent "Geologie de la France"
edited by Debelmas (1974).

1. - The Armorican Massif consists of a fan-shaped structure opening east-
ward. A folded Palaeozoic succession occupies the synclinal parts of
the fan; remnants of a pre-Cambrian basement are found between them.
Schematically four main zones can be recognized (fig. 11.25.2) :

a) Domnonea : mostly a complex pre-Cambrian basement, affected only
locally by the Variscan orogeny.

b) Mancellia : mostly a Late Proterozoic (Brioverian) succession fol-
ded during the Cadomian orogeny and intruded by granites before
the deposition of the Palaeozoic sequence, then moderately affected
by the Variscan orogeny.

c) The Central Armorican Zone : a rather complete succession of
Brioverian and Palaeozoic sediments folded during the Variscan
orogeny and intruded by granites.

d) The South Armorican Zone or Ligeria : a thicker and monotonous
succession of sediments which was so much transformed at various
times during the Palaeozoic that the structure is not yet entirely
elucidated.

2. - The Central Massif includes parts of an old basement consisting mostly
of metamorphic and granitic rocks, which underwent various transforma-
tions until the end of the Variscan orogeny. It was then cut by major
faults, and deep trenches formed which were filled by sediments in
Late Carboniferous and Permian times. During the Alpine orogeny, it
was again fractured and a number of large volcanoes were built.
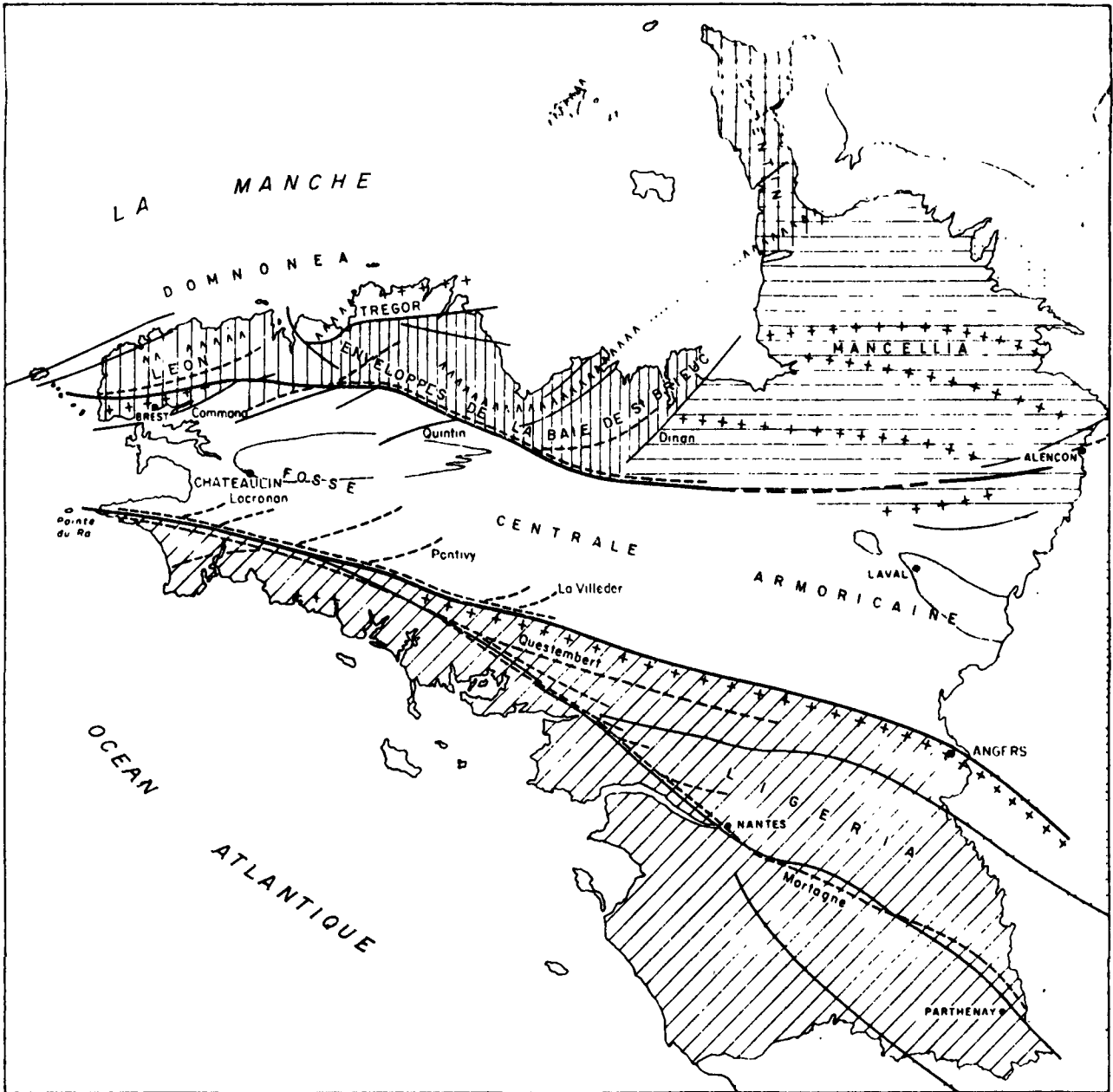
Fig. 11.25.2. Structure of the Armorican Massif after Chauris and
Guigues (1969)

_____ Major faults and lineaments

- - - - - - - - Axis of Variscan granitization

+ + + + + + + + Axis of Cadomian granitization.

A three-fold subdivision of the <u>Central Massif</u> has been suggested (fig. 11.25.3) :

- "<u>Le Noyau arverne</u>", a metamorphic complex whose history is mostly Cadomian except for fractures of Variscan and Alpine ages.

- "<u>L'Ensemble ruteno-limousin</u>", resulting largely of Variscan or perhaps Caledonian events.

- "<u>La Ceinture cévenole</u>" including <u>La Montagne Noire</u> and most of the <u>Cevennes</u> s.s.(a rather complex belt the history of which is Variscan although parts of it formed earlier).

3. - The <u>Pyrénées</u> have a rather symmetrical structure, roughly parallel zones being recognized on each side of an E-W axis (fig. 11.25.4). We are concerned here with the northern part of the range only, i.e. with three zones :

- The <u>Axial Zone</u> (<u>Zone primaire axiale</u>), which consists of a Palaeozoic succession resting on gneisses and micaschists, folded during the Variscan orogeny and intruded by granites at the end of Carboniferous times.

- The <u>North Pyrenean Zone</u>, which consists of a Mesozoic succession resting on a Variscan basement and folded during the Alpine orogeny.

- The <u>Sub-Pyrenean Zone</u>, which consists of a Cretaceous and Cainozoic succession and has undergone folding during the Alpine orogeny.

The Variscan basement is observed not only in the <u>Axial Zone</u> but also locally in the <u>North Pyrenean Zone</u> and even in the <u>Sub-Pyrenean Zone</u> (Massif du Mouthoumet).

4. - The <u>Massifs de Provence</u> consists of a cristalline basement overlain by red beds of Permian age. The cristalline basement is exposed mainly in the <u>Massif des Maures</u>, which is a continuation of the <u>Axial Zone</u> of the Pyrénées, the intervening part of the same belt having sunk under the Mediterranean Sea. Granites of Carboniferous age have been recognized in the Maures; they intrude a metamorphic complex.
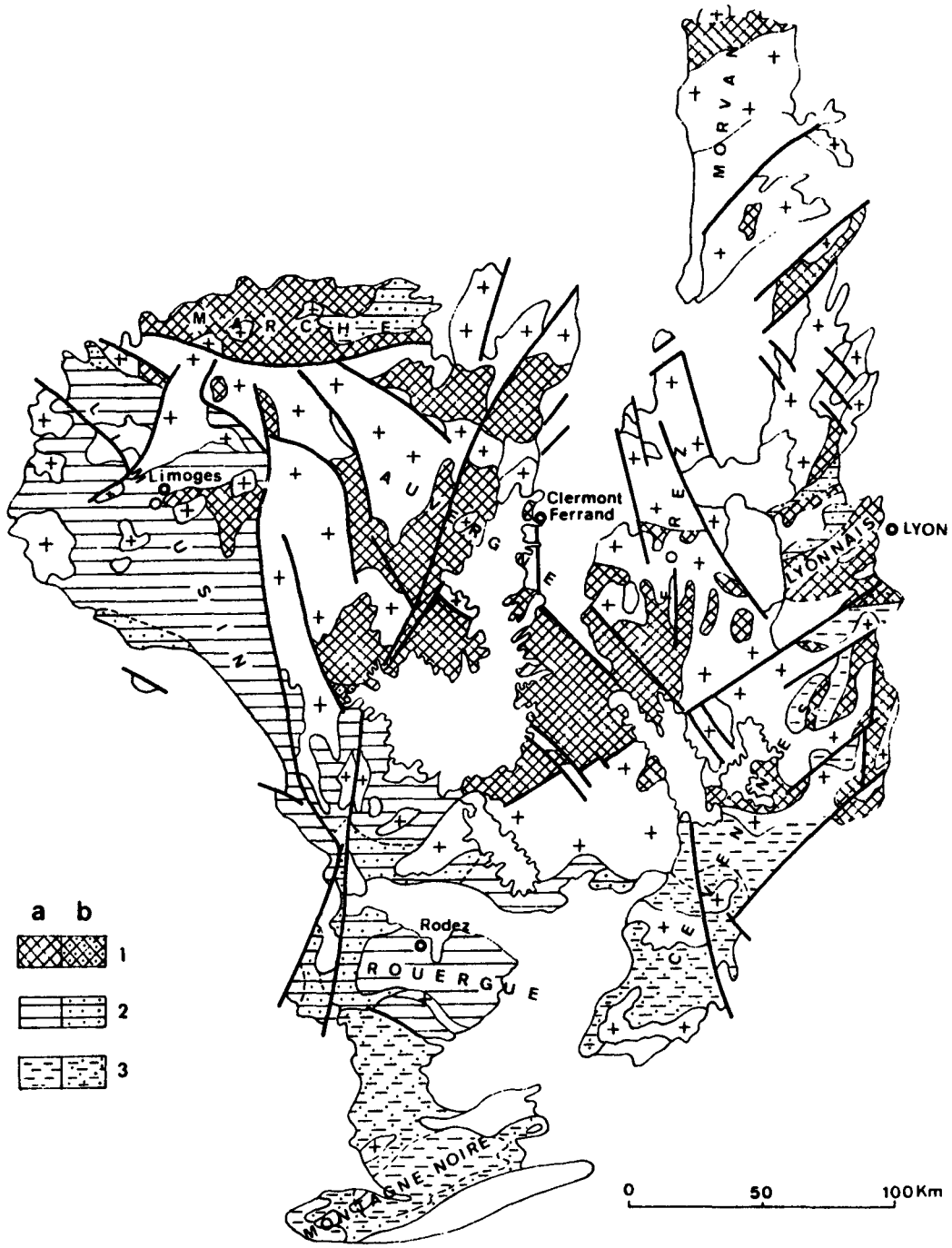
Fig. 11.25.3   Structure of the <u>Central Massif</u>   (in :

Debelmas 1974 ; after Chenevoy and Ravier, 1971)

1. Noyau Arverne

2. Ensemble ruteno-limousin

3. Ceinture cévenole

a. mesozonal and catazonal metamorphism

b. epizonal metamorphism
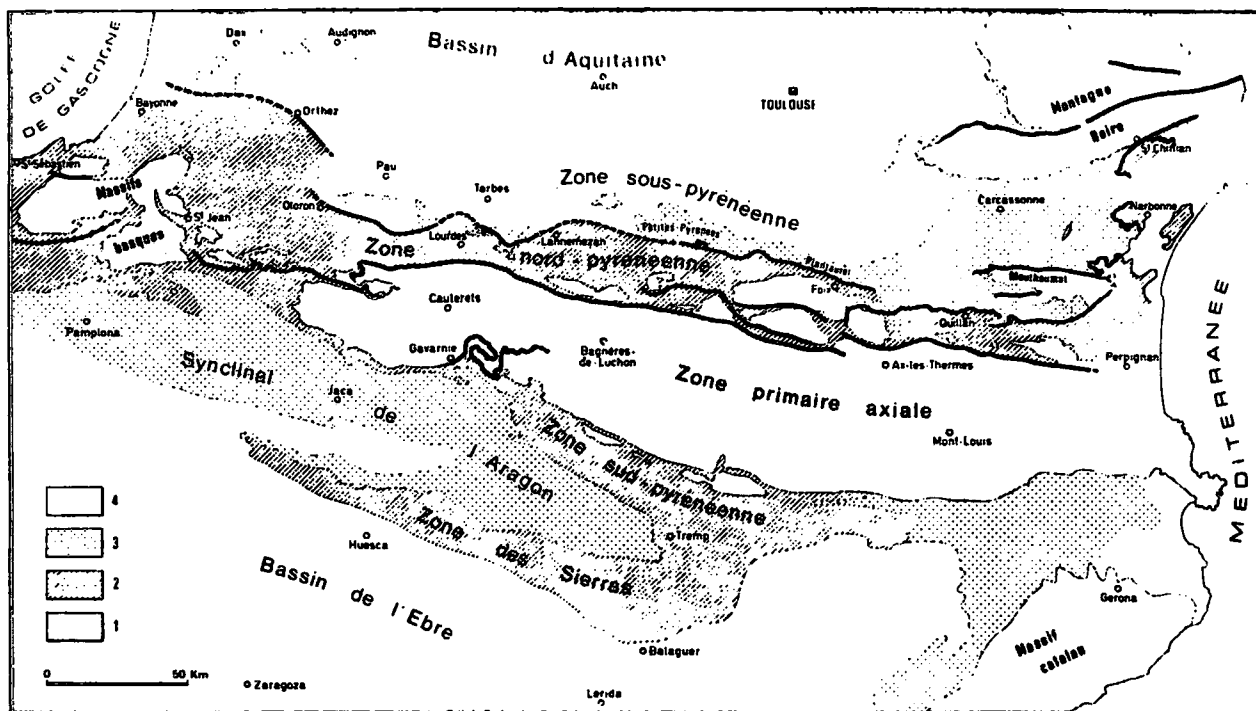
Fig. 11.25.4. Structure of the Pyrenees (Casteras, in Debelma s, 1974)

1. : Variscan basement
2. : Mesozoic succession of the North and South Pyrenean Zone
3. : Cretaceous and Cainozoic succession of the Sub-Pyrenean Zone and the Aragon Syncline.
4. : Beds of post-Eocene age.

5. - <u>The Old Alpine Massifs</u> consist of Variscan or older material, more or
    less modified by Alpine events. They belong to three belts (fig. 11.25.5) :

    - the external one with <u>Mont-Blanc-Aiguilles Rouges</u>, Belledonne-<u>Grandes
      Rousses</u>, <u>Pelvoux</u>, <u>Argentera</u>. In these massifs, a sedimentary succession
      of Late Carboniferous and Permian age overlies a metamorphic basement.

    - the middle one with the <u>Briançon Coal Zone</u>, where the basement is al-
      most entirely concealed under a thicker sedimentary succession of the
      same age as above.

    - the internal one with <u>Vanoise</u>, <u>Ambin</u>, <u>Grand Paradis</u>, where the basement
      is exposed under a metamorphic Permo-Carboniferous succession.

6. - The <u>Vosges</u> belong, with the <u>Black Forest</u> in the adjacent part of Germany,
    to a large Variscan massif, which separated into two parts when the
    Rhine Graben formed during the Alpine orogeny. The <u>Vosges</u> are subdivided
    into three zones as follows (fig. 11.25.6) :

    - a central one consisting of a metamorphic and granitic complex, the
      age of which is in part pre-Variscan.

    - a southern one where the same complex is overlain by a thick sequence
      of Carboniferous age folded during the Variscan orogeny.

    - a northern one where a succession of Silurian and Devonian age over-
      lies an old basement, the whole being intensely deformed by folding
      and faulting.

    The following description of the Zn and Pb deposits known in the
various parts of France are mostly borrowed or adapted from "Les gisements
de Pb-Zn français" (B.R.G.M., 1977).

11.25.C - <u>STRATIFORM DEPOSITS IN THE ARMORICAN MASSIF</u>
N.B. : For an updated presentation, see last reference of this section on France.

    Two stratiform deposits are known in the Gedinnian (Lower Devonian)
succession of the <u>Central Armorican</u> Zone (fig. 11.25.7).

    At Bodennec-Yeun Dong, mineralization consists of a pyrite-rich
massive sulfide bed with 30 % combined metal (Pb + Zn + Cu). The thickness
varies from a few centimeters to a few meters.
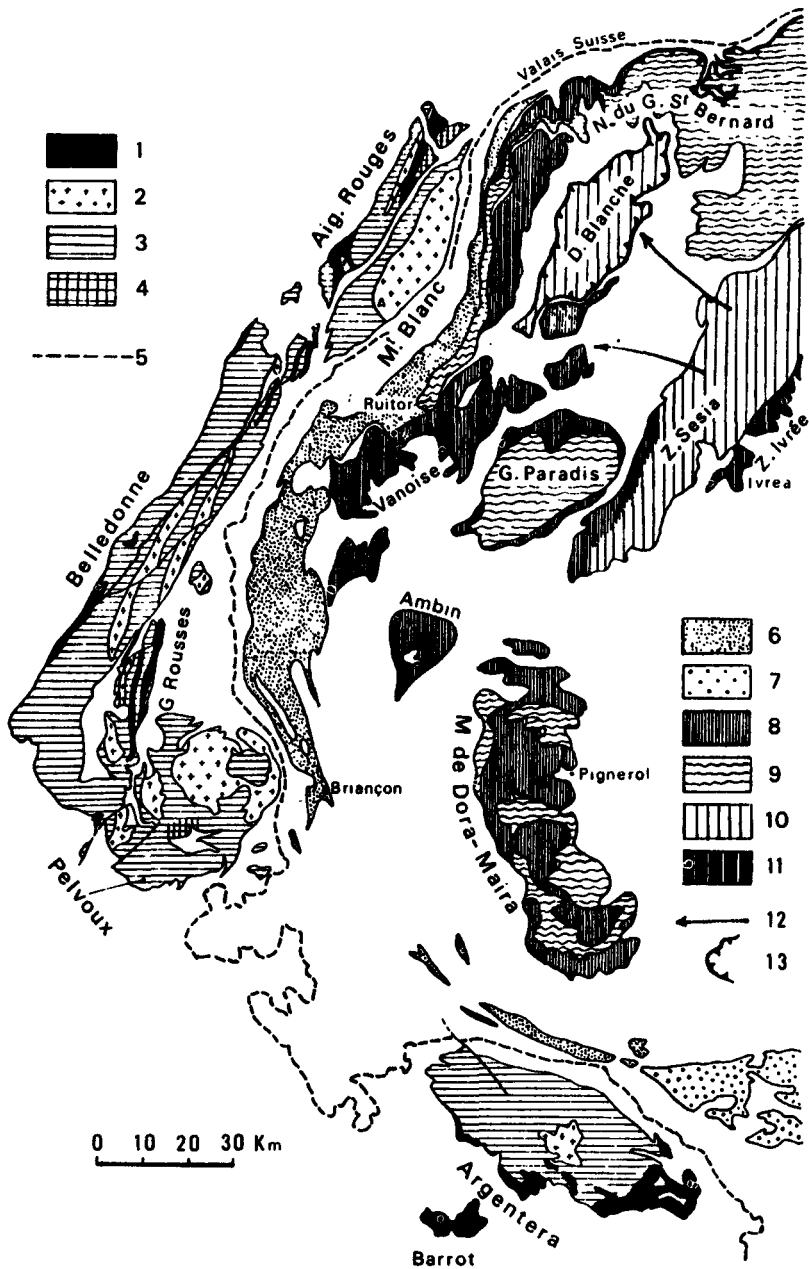
Fig. 11.25.5. Old Massifs in the French-Italian Alps

External zone : 1. Permian and Carboniferous-
2. Variscan granite intrusions- 3. Schists- 4. Pre-Cambrian

Internal zone : 5. Pennic thrust- 6. Permian
and Carboniferous- 7. Volcanics of Permian and Carboniferous
age- 8. Metamorphics of Permian and Carboniferous age -
9. Pre-Carboniferous basement- 10. Schists- 11. Pre-Cambrian
12-13 "Dent Blanche-Cervin" thrust and klippe
(Debelmas, 1974).
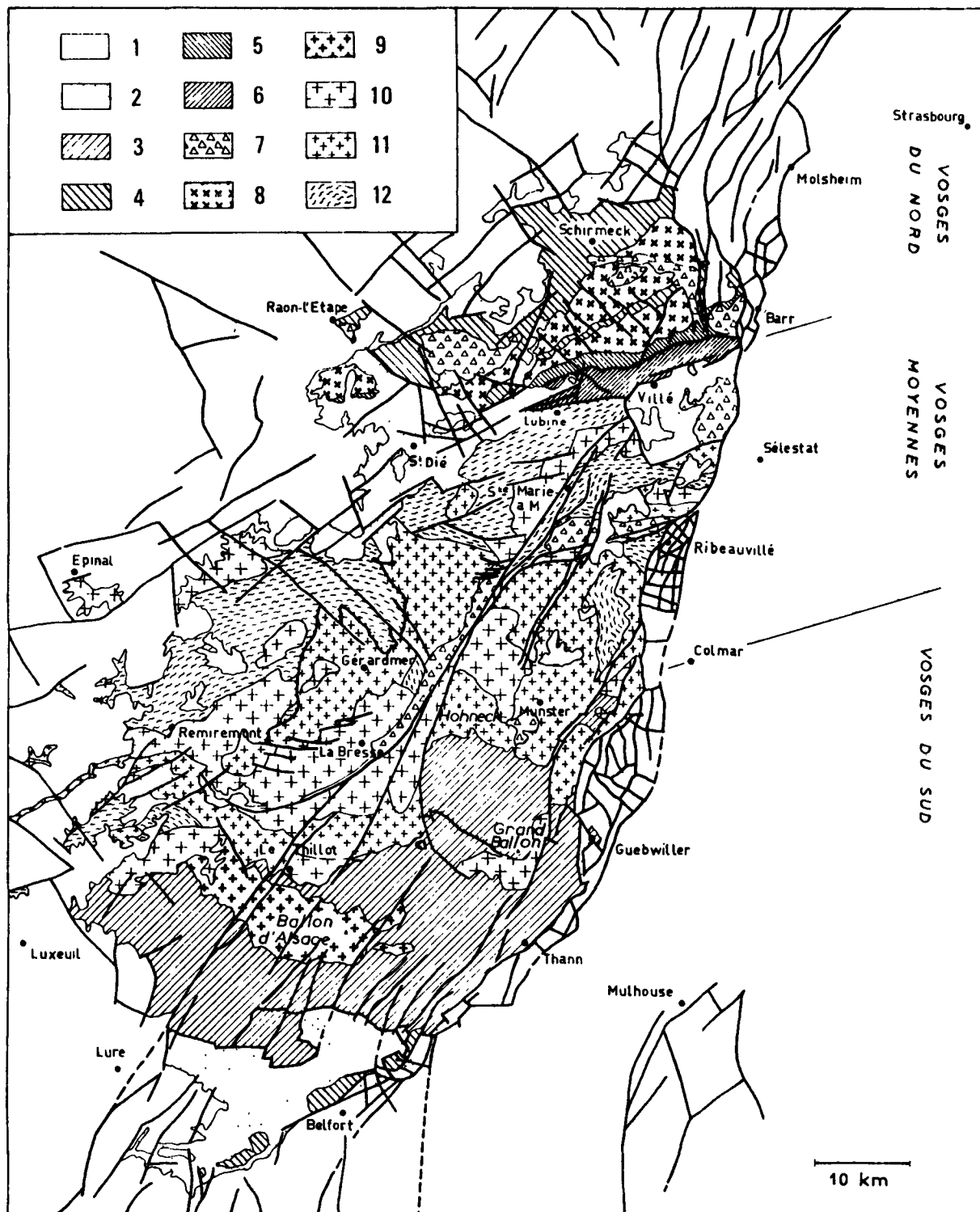
Fig. 11.25.6.    Basement geology of the Vosges (according to
von Eller and Fluck in Debelmas, 1974).

1. : Post-Permian strata

2. : Permian

3. : Visean in the Southern Vosges

4. : Devonian

5. : Silurian and Ordovician

6. : Late Variscan granite intrusions

8 to 12 : Other granites, gneisses and migmatites.

LÉGENDE

Pliocène

Carbonifère

Cambrien à Dévonien

Briovérien

Roches éruptives et cristallophylliennes

●x Pb Gisement ou indice de plomb — zinc
d'après la carte des gîtes minéraux au 1/320.000 e, feuilles Cherbourg, Brest, Rennes, Nantes

ÉCHELLE

0    25    50    75    100 Km
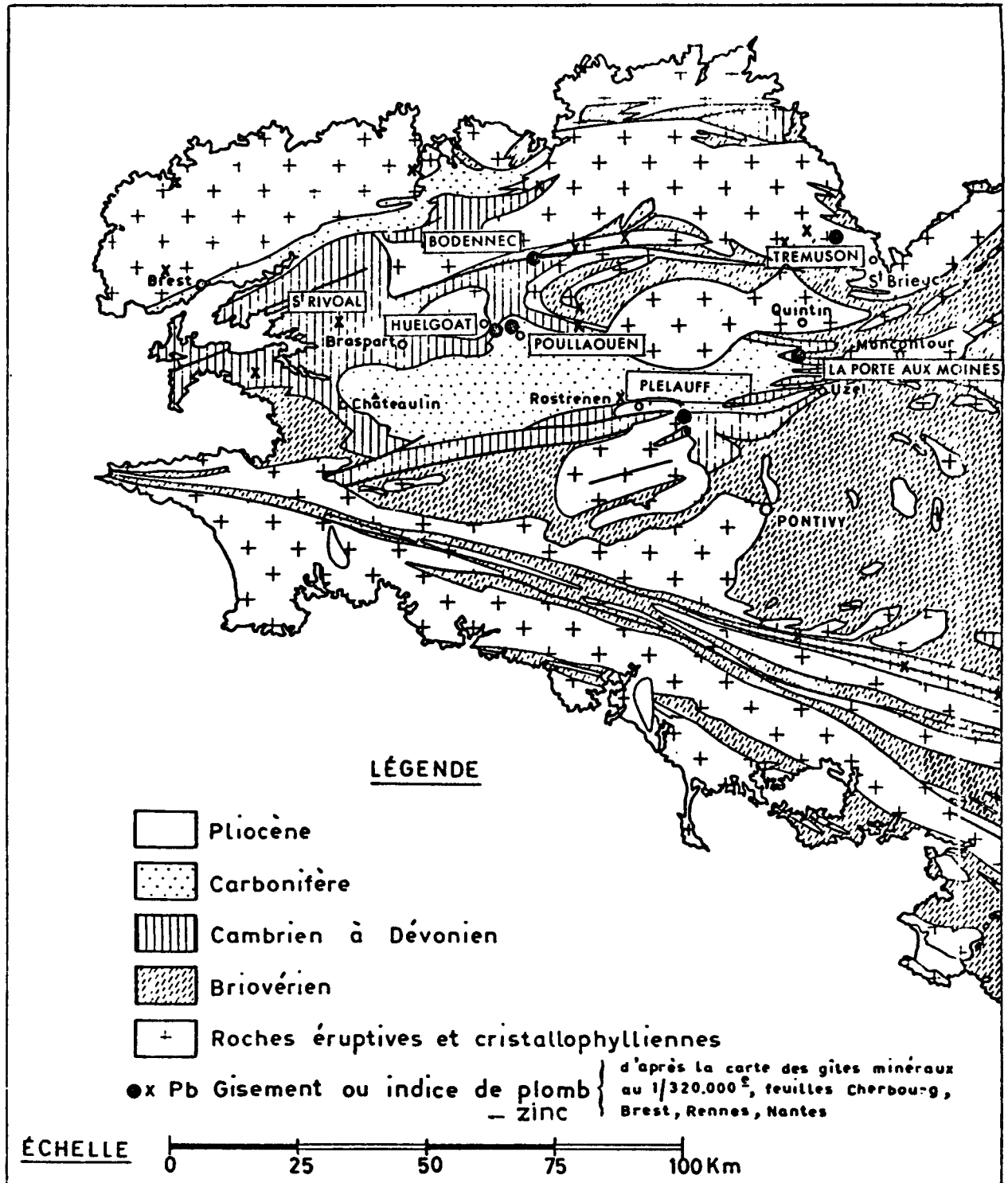
Fig. 11.25.7. Location of Zn-Pb deposits in the Armorican Massif (B.R.G.M., 1965)

This bed is locally underlain by a smaller thickness of shale containing stringers and disseminations of sulfide (mostly pyrite with occasionally considerable Cu and/or Zn). The stratigraphic succession is shown in fig. 11.25.8. The structure of the deposit results of two phases of folding, between which sills and dykes of microdiorite were intruded.

The ore consists of sphalerite, galena, chalcopyrite and pyrite (pyrrhotite) with traces of sulfosalts, in a gangue of chlorite, quartz and white mica. Some 200 000 t of metal have been identified at Bodennec.

At Porte-aux-Moines, the ore is interbedded in black chloritic shales overlain by sandstones. In places a stockwork of disseminated and stringer pyrite is observed in the hangingwall, which consist of detrital rocks mixed with ignimbrites and tuffs. Intense silicification and chloritisation are observed in the hangingwall. The structure of the deposit is synclinal.

The ore consists of pyrite, sphalerite, chalcopyrite, galena, pyrrhotite, arsenopyrite and sulfosalts in a gangue of quartz, chlorite, micas and barite. Some 300 000 t of combined metal have been identified.

In addition to Bodennec-Yeun Dong and Porte-aux-Moines, two other deposits have been found in a Brioverian detrital succession where volcanics are present : Rouez and Tremuson.

11.25.D - PARTLY STRATIFORM DEPOSITS IN THE PYRENEES (fig. 11.25.9).

Orebodies are known in both the Ordovician and the Lower Devonian successions of the Pyrenees. They have been much deformed by folding and otherwise.

The Ordovician succession consists of fine grained detritals with carbonate lenses; a few volcanic centers were active during its deposition. Some Zn and Pb deposits are associated with basic vulcanicity but most are located in fine grained detritals with an acid contribution (rhyolite pebbles). Veins and stratiform lenses, with about 10 % combined metal, constitute the deposits. The veins are found in the footwall of the lenses. Four distinct horizons were mineralized as a result of hydrothermal activity associated with faults active during sedimentation.

shales, mudstones and siltstones becoming richer and richer in sericite and organic matter.

shales, mudstones and silstones becoming richer in chlorite and quartz

dark, chloritic sandstone

massive sulfide bed

ashfall

alternating layers of white sandstone and dark shale : these layers become thinner (millimetric or centimetric) toward the top

white sandstone
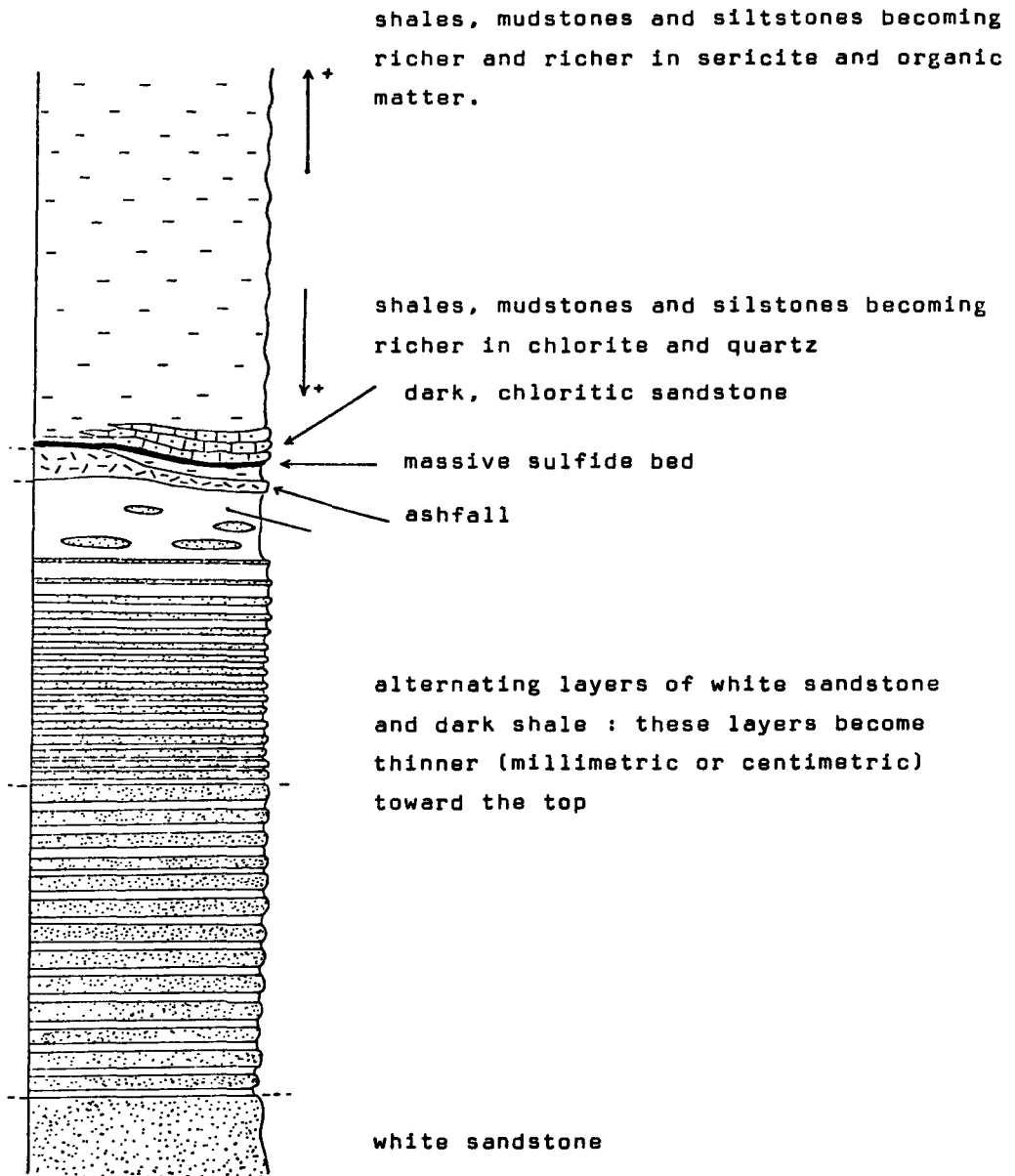
Fig. 11.25.8   Stratigraphic succession at Bodennec (Aye, 1977, in B.R.G.M., 1977).
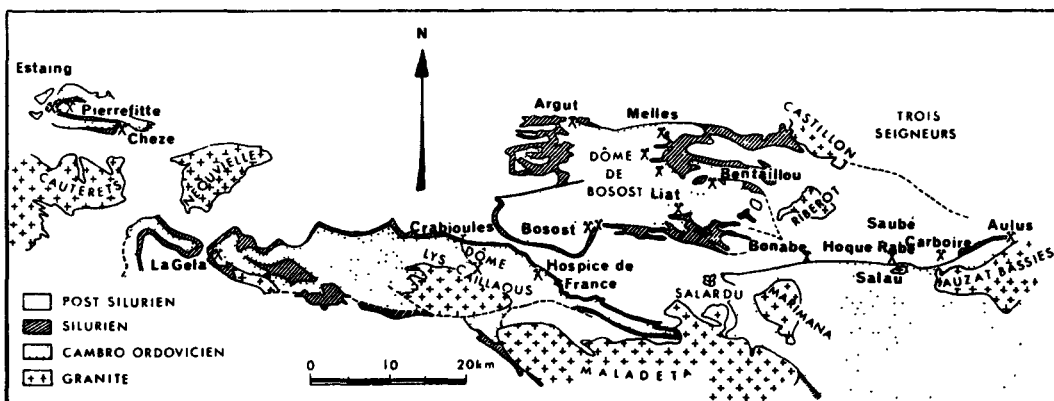


Fig. 11.25.9   Main Zn and Pb mineralizations in the Ordovician succession observed in the domes of the Pyrenean Axial Zone. (Bois, Pouit et al., 1976)

Seven deposits totalling 400 000 t combined metal were mined in the Ordo-vician : Pierrefitte, Sentein, Tuc de Roquefort, Melles, Argut, Crabioules and Hospice de France.

The Lower Devonian succession consists of both detritals and carbo-nates; albitites, possibly volcanic in origin, are present. Orebodies are low-grade (5 %) and consist of beds which can be followed over distances of several kilometers. There are several ore-bearing horizons, mineralization being lower grade but more widespread in the upper one. The Zn/Pb ratio is high. Barite is abundant while it is practically lacking in the Ordovician succession. Two deposits were mined in the past : Nerbiou and Arrens. Another one, Carboire, has been explored in some detail. A total of 250 000 t Zn has been identified in these three deposits but hypothetical resources are probably much larger.

Three types of orebodies occur together in the Pyrenees : veins, complex stockwork-disseminated bodies and beds (Bois, Pouit et al., 1976).

11.25.E – STRATA-BOUND DEPOSITS IN THE CENTRAL MASSIF

A number of deposits are known in the Georgian (Lower Cambrian) succession observed in the Montagne Noire, southern extension of the Central Massif. They are located in dolomite formations or in their vicinity. The dolomite formations themselves are interbedded with micaschists or other more or less metamorphosed detrital sediments; basic and acid volcanics are present, as well as intrusives. In addition, mineralization is observed in black shale beds, which may reach several meters in thickness and carry 1 to 3 %, rarely 5 % Zn.

The shapes of the orebodies are quite varied : veins, "columns" lying parallel to bedding at La Rabasse, beds at La Loubatière.

La Rabasse, which was the most important mine of the district, is thought to have yielded 100 000 t combined metal (Zn + Pb) and some 120 t of silver (fig. 11.25.12).

N 63°0
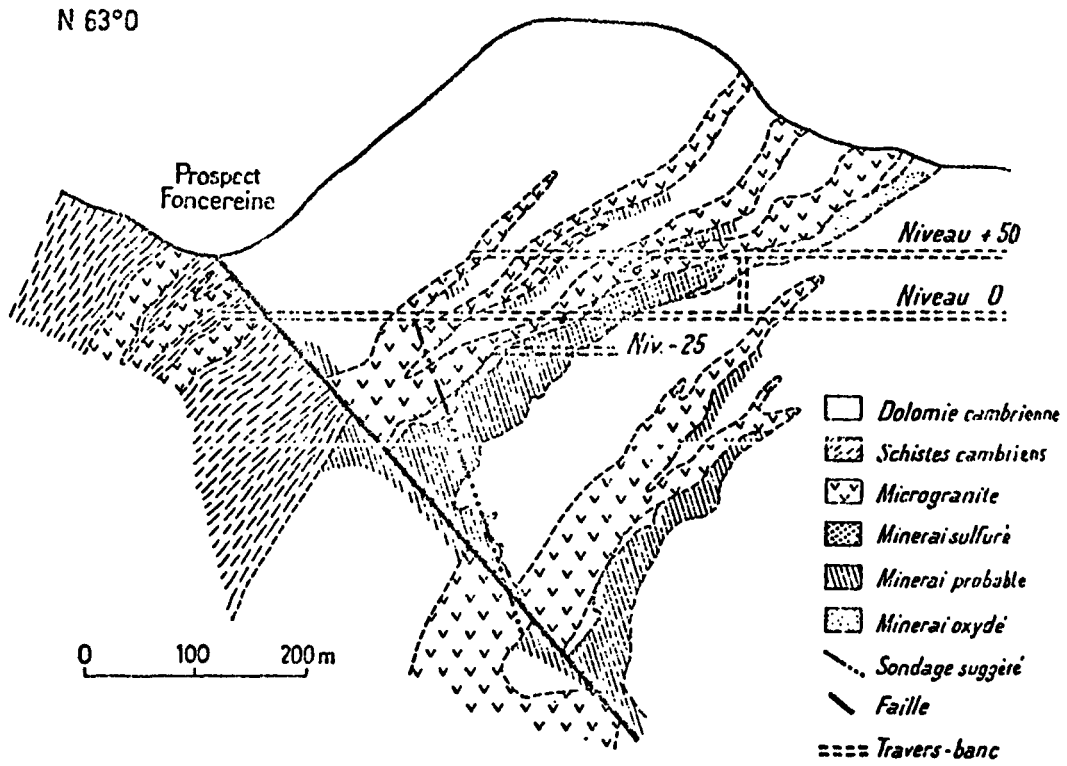


Fig. 11.25.12 - Vertical section through the La Rabasse
deposit showing sulfide orebodies and
microgranite intrusions in Cambrian dolomite (Routhier, 1963).

## 11.25.F - <u>VEINS IN THE OLD MASSIFS</u>

In addition to the veins just mentioned, which are found in the footwall of stratiform orebodies and are genetically associated with them, many other veins are known in the <u>Old Massifs</u> of France. Some have yielded considerable amounts of metal :

|  | | Pb | Zn | Ag |
|---|---|---|---|---|
| Pontpéan (Armorican Massif) | : | 150 000 t | 30 000 t | 232 t |
| Les Bormettes (Massif des Maures) | : | 9 000 t | 170 000 t | 6 t |
| Pontgibaud (Massif Central) | : | 50 000 t | - | 100 t |
| Peyrebrune (Massif Central) | : | 54 000 t | 35 000 t | 150 t |
| La Baume (Massif Central) | : | 50 000 t | 30 000 to 50 000 t | 180 t |

Les Farges and Noilhac-Saint-Salvy are recently discovered veins.
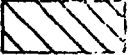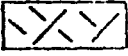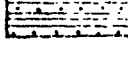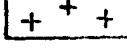
The former is emplaced within a 400 My old granite batholith and can be followed over a distance of about 7 km. Barite and quartz are predominant minerals in the upper 150 m while at greater depths Ag-bearing galena is found in a quartz gangue. In this deposit, 1.9 Mt of ore at 5.7 % Pb and 105 ppm Ag (dilution being taken into account) were identified; 350 000 t of barite is included in this figure. The Noilhac-Saint-Salvy deposit is found 2 km south of a granite batholith within a sedimentary succession, mostly pelitic, which is probably Cambrian in age. The orebody is 1 to 10 m thick, 1 900 m long, and contains 6 to 15 % Zn, 50 to 120 ppm Ag and some germanium; 500 000 t of metal were identified in it.

Two main sub-types may be recognized among the veins of the French <u>Old Massifs</u>, although in a few cases this distinction appears arbitrary (B.R.G.M., 1977) :

a) Veins consisting of sphalerite, galena, sulfosalts, barite, carbonate and quartz and always located within granites or in their vicinity. Most of these veins must be Variscan in age although some may be Caledonian.
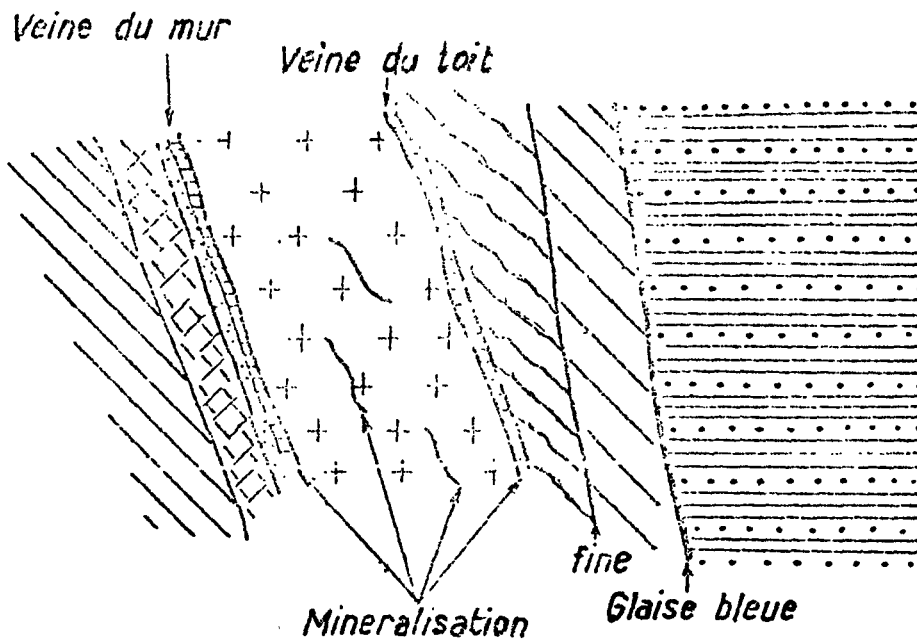
Fig. 11.25.13 - Sulfide veins following the walls of a
dolerite dyke at Pontpean (B.R.G.M., 1977)

Many veins in the Armorican Massif (including Pontpéan), in the Vosges,
in the Massif Central (including Pontgibaud, Saint-Salvy, Peyrebrune)
and in the Maures (including Les Bormettes) belong to this sub-type.

b) Veins consisting of fluorite and/or barite with minor galena and sphale-
rite. These veins are not necessarily located within or close to a
granite intrusion, and may be post-Variscan. Many small veins in the
Maures, the Alps and the Central Massif belong to this sub-type, which
has not yielded large quantities of metal. On the basis of mineralogy,
Les Farges must be classed with them although it is located within a
granite.

The question is raised whether veins may result of a remobilisation
of metal previously stored in low-grade stratiform or other deposits, at
the time when granite intrusions are emplaced. Some observations in the
Pyrenées and in the Montagne Noire support this theory. For example the
Noilhac-Saint-Salvy vein is found in an area where the sedimentary succes-
sion, probably Cambrian in age, include black shale beds rich in Zn.

11.25.G - DEPOSITS FOUND IN THE CARBONATE SUCCESSION DEPOSITED ON THE
POST-VARISCAN PLATFORM (Fig. 11.25.14 to 16)

A number of deposits have been discovered in the carbonate formations
of Triassic or Jurassic age which belong to the Cover and were deposited on
the Variscan basement of the Old Massifs. Most of them appear to be located
near topographic hills or highs of the unconformity developed over the base-
ment, or near basement faults which were active during Triassic or Jurassic
sedimentation. The limestones, dolomites and marls interbedded with them
were deposited in shallow seas and were intermittently exposed to weathering
before being buried under more recent sediments. They rest either directly
on the basement or on non-marine clastics which rest themselves on the
basement.

One of the mineralized districts is found in the Detroit Poitevin
(Poitou Narrows) between the Armorican Massif and the Central Massif (fig.
11.25.1). There Zn and Pb are found in impure dolomites of Lower Jurassic
age at a short distance above the unconformity. The grade rarely reaches
beyond 1 % except in the vicinity of Tertiary faults.

Significant tonnages have been identified at several localities in these strata-bound deposits. In the same district, basement veins are known with the same mineralogy : sphalerite, galena, chalcopyrite, iron sulfide and barite.

Deposits that are somewhat similar are known elsewhere along the margins of the Central Massif but the most important district is the Sous-Cevenole Belt with the large deposit of Les Malines, where more than 800 000 t of metal have been identified (past production + reserves). In this district orebodies are found in beds of various ages :

Upper Jurassic                      : Bois Madame

Middle Jurassic (Bathonian) : Les Avinières, Les Malines in part, St Hippo-
                                                  lyte-du-Fort (less than 100 000 t metal
                                                  identified for the whole group)

Middle Jurassic (Bajocian)  : Landas and Le Bleymard (100 000 t metal iden-
                                                  tified)

Lower Jurassic (Sinemurian) : Durfort and Trèves (100 000 to 200 000 t
                                                  metal identified)

Lower Jurassic (Hettangian) : La Croix de Pallières, Le Soulier and Cendras
                                                  (100 000 to 200 000 t metal).

A large and very complex deposit is Les Malines which is described here very briefly after B.R.G.M. (1977). See fig. 11.25.15.

At the western end of the Cevennes, the Palaeozoic basement is sur-rounded by sub-horizontal strata belonging to the Mesozoic Cover.

The lowermost of these strata are of Triassic age. They have a variable lithology as a result of their deposition on an imperfectly pene-planed erosion surface. At Les Malines, they consist of dolomitic and bitu-minous shales, dolomite and evaporites and rest on a basement where carbonate formations had previously been affected by deep and intense karstic weathe-ring. Beds of Lower Jurassic age are not found at Les Malines although they occur on both sides of the ridge which continues the Cevennes westward below the Cover.

O.N.O.

E.N.E.

Faille du minerai

333

220

190

180

160

1

2

3

4

5

0    10    20m
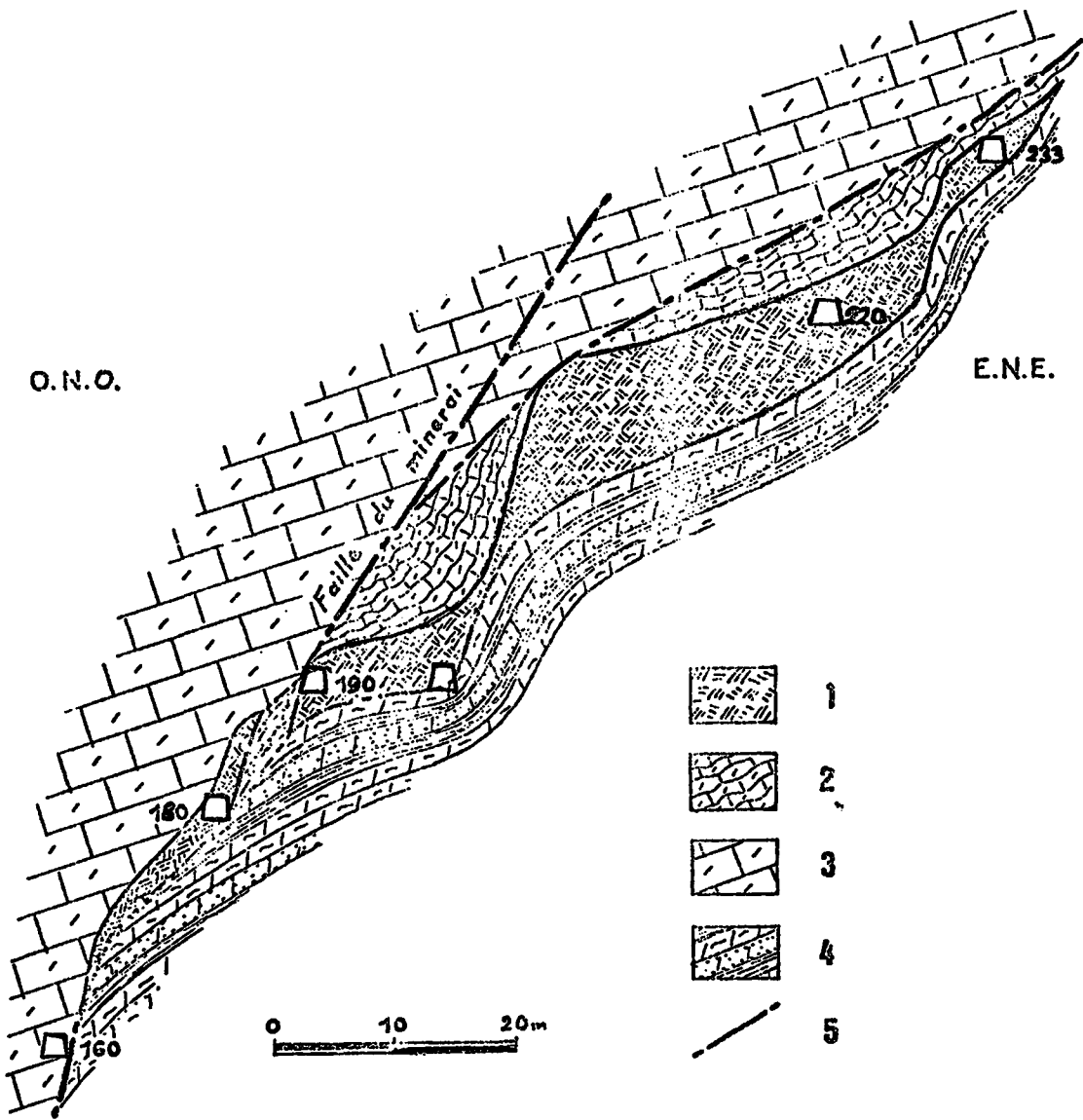
Fig. 11.25.14 - Vertical section across an orebody at La-Croix-de Pallières
(Leenhardt, 1972)

1 : ore ;

2 : wavy dolomite ;

3 : massive dolomite (Hettangian) ;

4 : Triassic.
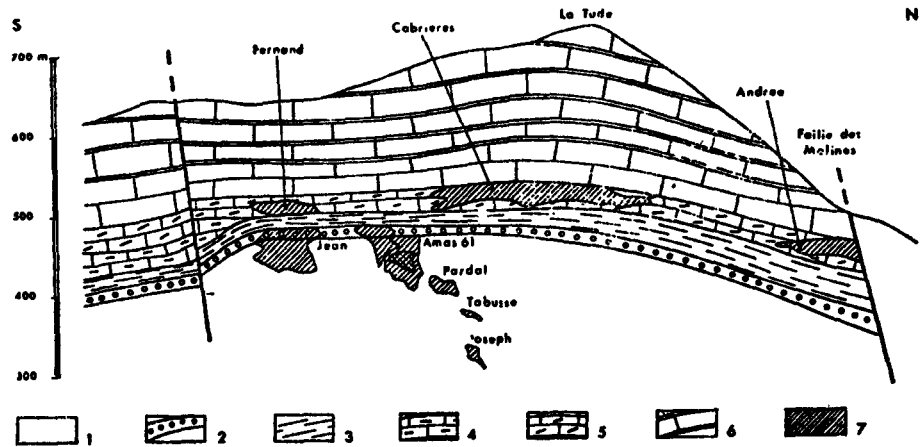
Fig. 11.25.15 - N-S section through Les Malines (Foglierini and Bernard, 1967)

1. - Cambrian dolomitic Basement.
2. - Triassic basal conglomerate.
3. - Organic rich marls (Middle and Upper Triassic).
4. - Hettangian dolomite.
5. - Upper Bathonian dolomite.
6. - Upper Jurassic strata.
7. - Orebodies.

This section shows that orebodies are found in the Basement, in the conglomerate below the marls and in the dolomites above the marls.

Middle Jurassic beds on the other hand are observed in all the area, resting
on the Triassic or even on the Palaeozoic.

Ore is found in three geological settings :

a) above the Triassic marls, as conformable lenses within Middle Jurassic
   dolomite.

b) in the Triassic marls, as beds where sphalerite and galena are dissemina-
   ted in dolomite. Black shales or marls are interbedded with this
   dolomite, where vugs and fissures are also mineralized.

c) under the Triassic marls, as lenses which straddle the basement boundary,
   as cement of conglomerates deposited on the unconformity, as cement of
   collapse breccias, as filling of karstic cavities and fissures in the
   carbonate formations of the basement.

Massive sulfide ore with 35 % combined metal is found at Les Malines
as well as lower grade ore such as found in breccias. The latter forms lar-
ger orebodies, reaching more than 1 Mt. Les Malines has yielded 810 000 t
Zn and 55 000 t Pb with 200 t Ag.

On the north-western side of the Cevennes, several Zn and Pb deposits
are also known. Among them a number of veins, emplaced only in the basement,
or only in the Lower Jurassic strata of the Cover (Villemagne) or in both
basement and cover. Partly stratiform orebodies are found in the same area.

## 11.25.H - DEPOSITS FOUND IN SANDSTONES DEPOSITED ON THE POST-VARISCAN PLATFORM

The best-known deposit of this type and the only one currently mined
is located at Largentière, on the south-eastern margin of the Central Massif,
and consists of more or less conglomeratic arkoses of Triassic age, the
ciment of which is locally rich in Pb. Several mineralized beds are known
in that area. Their thickness reaches 5 to 8 m. In addition to these stra-
tiform and disseminated mineralizations, some massive sulfide ore is also
found in faults.

Other deposits of similar type are known in the Central Massif at
Chitry-Les-Mines in beds of Lower Jurassic age, St Sébastien d'Aigrefeuille
in beds of Triassic age, and in the Alps at La Plagne, Peisey and l'Argentière-
La-Bessée.

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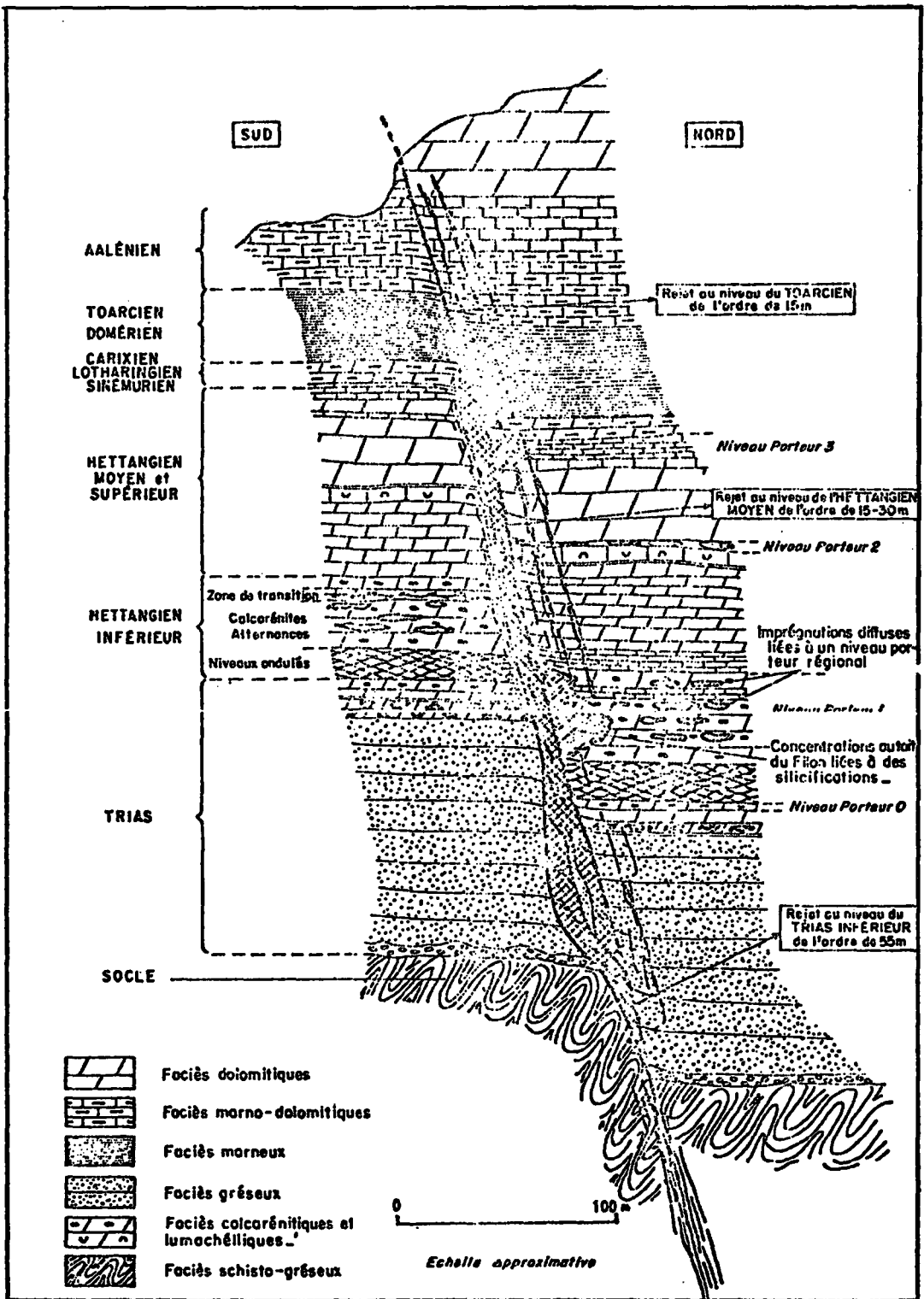
**Fig. 11.25.16** - Schematic vertical section through the
Saint Sauveur vein (Michaud, 1976).
The orebody is entirely located in the Triassic and
Jurassic Cover and does not enter the basement.

The latter group is found in much folded sandstones and quartzites of Permian or Triassic age.

Large low-grade resources have been identified in somewhat similar deposits around Saint Avold in the Vosges. They are found in Triassic sandstones but only in the vicinity of faults.

This type of deposit has yielded more than 500 000 t of metal, including 270 000 t Pb, 46 150 t Zn and 550 t Ag from the unfolded sandstones of the Central Massif and Vosges borders, 180 000 t Pb and 445 t Ag from the deposits in the Alps.

## 11.25.I - SUMMARY

In addition to veins, some of which have yielded or will yield considerable tonnages, there are several types of deposits in France. In the post-Variscan Cover, a number of deposits are found, which do not resemble either the Irish or the British deposits of the post-Caledonian Cover; some of them are emplaced in the carbonate riche part of the succession; others in the lower, sandstone part. In the Old Massifs, interesting discoveries are being made and ancient mining districts are re-examined so that the Armorican Massif, the Axial Zone of the Pyrénées and the Montagne Noire appear promising areas.

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▬ A number of papers about French Zn-Pb deposits have recently published in :

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- The sept. - oct. 1978 issue of "Chronique de la Recherche Minière" (publ. B.R.G.M., Orléans) is devoted to the volcanogenic deposits of the Armorican Massif.

## 11.26 - BELGIUM, THE NETHERLANDS AND LUXEMBURG

### 11.26.A - INTRODUCTION

Zinc and lead were mined at hundreds of localities in Belgium until the end of the 19th century, a few mines surviving during the earlier part of the 20th. Total production amounted to about 2 Mt of metal, mostly Zn.

The largest deposit, located at Moresnet (n. 1, fig. 11.26.1), is one of the very few in the world to have been actively mined for Zn in the Middle Ages. Production may have reached about 200 000 t of metal before 1837, i.e. during the period for which no complete records are available. Another 500 000 t was produced from 1837 to 1884 when the mine became exhausted. The grade was very high (30 to 40 % Zn).

Six other high-grade deposits have produced 50 000 t of metal or more : Plombières, which was the only important Pb producer, Schmalgraf, Welkenraedt, Rocheux-Oneux, Engis and Hayes-Monet (see again fig. 11.26.1). Pyrite and marcasite were the by-products of Zn and Pb in most mines while at Vedrin the situation was reversed. There are also two deposits belonging to the same group where barite was produced in large quantities.

Small amounts of Zn and Pb minerals have been observed in the Dutch coal mines E of Maastricht and also at several localities in northern Luxemburg.

### 11.26.B - REGIONAL GEOLOGY

A Younger Cover, deposited after the Variscan folding, is observed throughout the Netherlands, over the northern part of Belgium, and over the southern part of Luxemburg. It consists of mostly horizontal beds of Permian, Mesozoic and Cainozoic age. This Younger Cover, thin and patchy over central Belgium, becomes thicker towards the north. There is no indication of Zn or Pb mineralization in it.

Most of southern Belgium is occupied by the Ardennes Massif belonging to the Variscides. All Zn and Pb deposits of the country are located within the Ardennes Massif.

Fig. 11.26.1 - Schematic metallogenetic map of southern Belgium
(adapted from Bartholomé et al., in press).

The Brabant Massif, as well as the Stavelot (St), Serpont (S), Givonne (G) and Rocroi (R) Massifs, are parts of the Caledonides. They are overlain unconformably by a Devonian and Carboniferous succession which, in most of the area represented, is folded and belong to the Variscan Ardennes. Near Tournai however, this succession is unfolded and belongs to the Older Cover. The Younger Cover is shown in the area south of the Ardennes but has been omitted in the Brabant region.

Zn-Pb and related deposits mentioned in this section :

1 : Moresnet; 2 : Plombières; 3 : Schmalgraf;

4 : Welkenraedt; 5 : Rocheux-Oneux; 6 : Engis;

7 : Hayes-Monet; 8 : Vedrin (pyrite with minor Zn and Pb);

9 : Fleurus (barite); 10 : Chaudfontaine (barite); 11 : Longwilly.

Post-Variscan unconformity

Post-Caledonian unconformity

Major faults

Limits of Zn + Pb districts

Limits of the fluorite zone
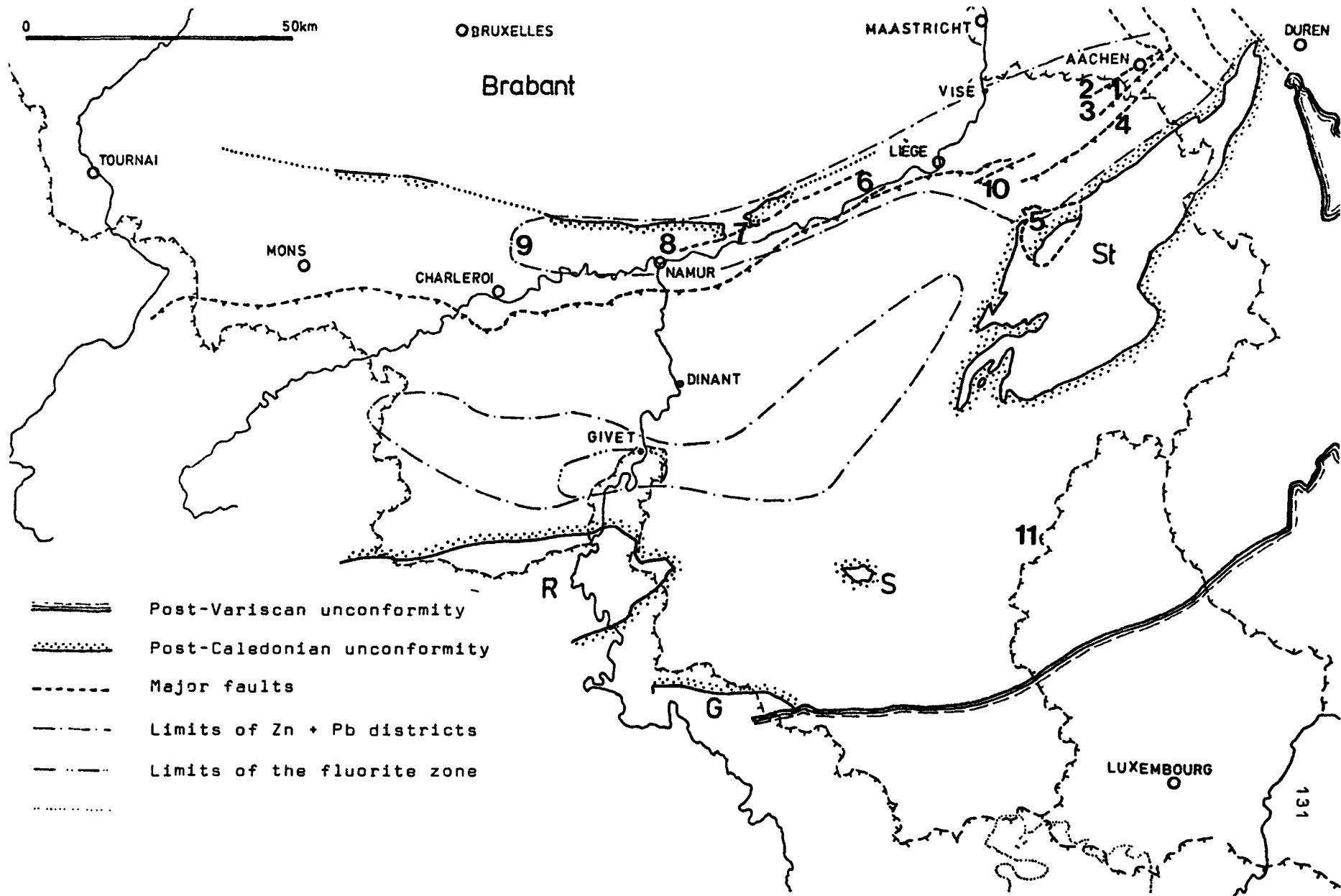
The Caledonides are represented by inliers within the <u>Ardennes,</u> and by the <u>Brabant Massif</u> north of it. The latter is overlain on both sides by an almost unfolded succession, including Carboniferous strata, which is the equivalent of the <u>Older Cover</u> of Great Britain. This succession is of greatly variable thickness, reaching several thousand meters in parts of the Netherlands; since it is itself overlain by the <u>Younger Cover,</u> it is not exposed except very locally at Tournai, and also north of Mons and Charleroi in Belgium.

## 11.26.C - <u>THE NORTHERN ZN AND PB DISTRICT</u>

All of the important Zn and Pb deposits of Belgium and most of the small ones were found in the Lower Carboniferous strata, i.e. in the <u>Carboniferous Limestone</u> which crop out almost continuously along a belt extending from Fleurus (n. 9 in fig. 11.26.1) to the German border near Aachen.

With the exception of Moresnet, all of these important deposits were found to consist of solution cavities filled with sulfide ore and connected to veins. The cavities were mostly discovered at the very top of the <u>Carboniferous Limestone,</u> just beneath the basal Namurian shale. This structure resembles the English type of deposits (see sections 11.24.C to H).See figures 11.26.2 and 3.

Moresnet was the only deposit of its kind, by being only a zinc producer while all of the others yielded some Pb and pyrite or marcasite in addition to Zn, and by consisting entirely of oxyde ore while in all the others sulfides predominated below the water level. Furthermore, Moresnet was included in the dolomitic lower part of the <u>Carboniferous Limestone</u> resting on detrital beds of Devonian age.

Recently, boreholes drilled at Chaudfontaine (n. 10 fig. 11.26.1) by the Geological Survey of Belgium met a stratiform barite orebody located on top of a reef of Upper Devonian age. Small amounts of galena and sphalerite were observed with the barite. This discovery opens new horizons with regard to exploration in the northern district where this type of deposit was previously completely unknown.
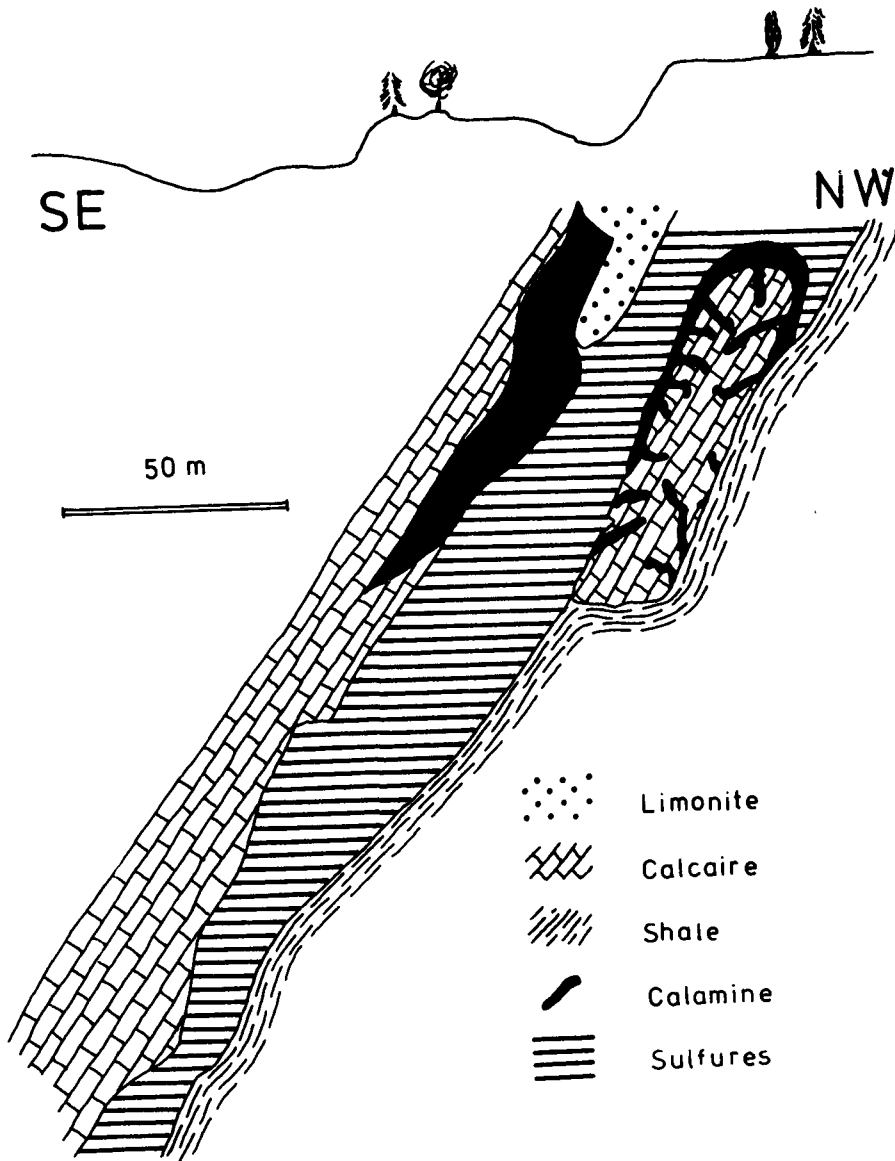
Fig. 11.26.2. Vertical section across a Zn and Pb deposit
at Engis (Bartholome and Gerard, 1976).

The sulfide orebody consists of a "column"
lying between Visean Limestone (Calcaire Carbonifère)
and Namurian Shale. At Engis the stratigraphic succession
is overturned.

Orebodies of that type are found in places
where a post-Variscan fault meets the limestone-shale contact.
They are clearly post-Variscan.

Limestone

Shale

Sulfide ore

Oxyde-ore

0  5  10m.
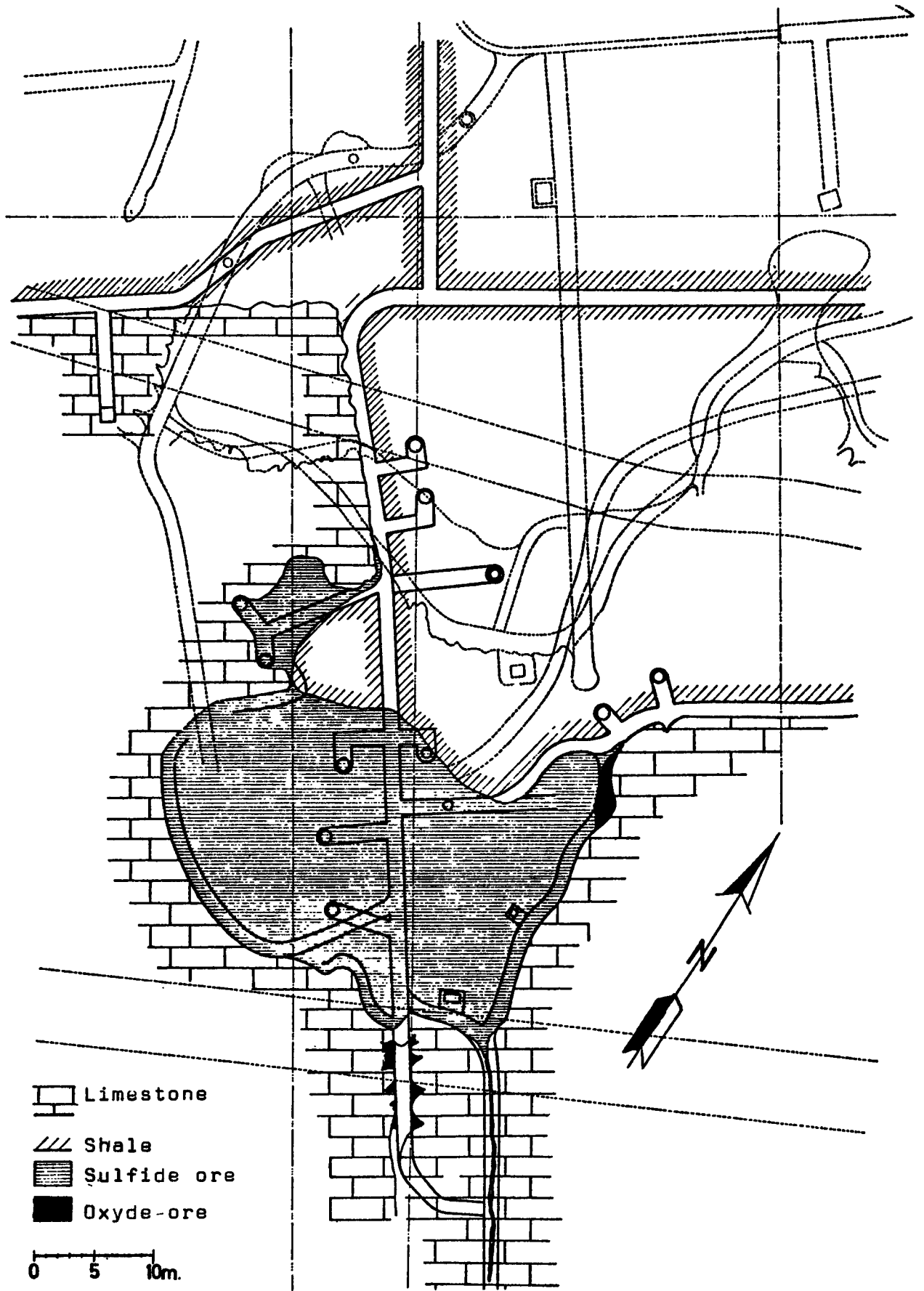
**Fig. 11.26.3.** Horizontal cross-section through the same deposit, showing the "column" and the fault. See the vein, connected with the "column", and lying in the fault plane.

## 11.26.D - THE SOUTHERN ZN AND PB DISTRICT

No large production ever came from this district, although a number of small veins were mined. They were found in a carbonate succession of Devonian age, particularly in the axial parts of anticlinal folds. There are also indications of low-grade mineralization, probably stratiform in habit, in the dolomitized reefs belonging to the same sequence. Some fluorite was mined in the central part of this district around the French town of Givet.

## 11.26.E - VEINS IN LOWER DEVONIAN STRATA

Small veins have been found in the thick detrital sequence of Lower Devonian age which was deposited in the Central Ardennes upon the eroded surface of the Caledonides. The most important of these is located at Longwilly at the border between Belgium and Luxemburg (n. 11, fig. 11.26.1).

## 11.26.F - SUMMARY

Most Zn and Pb deposits in Belgium were found in the Carboniferous Limestone. Their geological controls, which are well known, resemble those of the English deposits in the Northern Pennine region. Moresnet, however, which was the largest of them, is of a different kind.

The recent discovery, at Chaudfontaine, of a stratiform barite orebody in the Upper Devonian strata of the Ardennes Massif gives evidence that metalliferous deposits may have remained undetected even in a district which has been explored actively for 150 years.

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## 11.27 - GERMAN FEDERAL REPUBLIC

### 11.27.A - INTRODUCTION

In the area of the German Federal Republic, several thousands lead and zinc deposits have been discovered.

The great majority of them are of vein type and of small size.

Three deposits are mined today :

- Rammelsberg, in the Harz   (Nieder Saxe)
- Grund, in the Harz         (Nieder Saxe)
- Meggen, in the Rhenish Schiefergebirge (Rheinland-Westphalen)

Several significant deposits have been abandoned recently, either for economical (metal price) or technical (large quantities of water) reasons or as a consequence of exhaustion.

All the other deposits, i.e. the great majority, have been abandoned a long time ago and must be considered as devoid of economic interest. The reader is referred to Friedensburg (1971) for more information.

### 11.27.B - REGIONAL GEOLOGY

The geological consitution of the German Federal Republic includes the following units (fig. 11.27.1) :

a.  the Old Basement, mainly made of crystalline schists and granitic rocks. This basement crops out in a series of separated massifs : the Black Forest (Schwartzwald), the Odenwald, the Spessart and the western part of the Bohemian massif.

b.  the Variscides comprising a sedimantary succession (including tuffs and diabase) of Devonian and Carboniferous age which has been folded in a epizonal environment. Most of these sediments are terrigenous. They form the Rhenish Schiefergebirge, which is the eastern continuation of the Belgian Ardennes Massif. They are also observed in the Harz, a small massif emerging from the Cover.
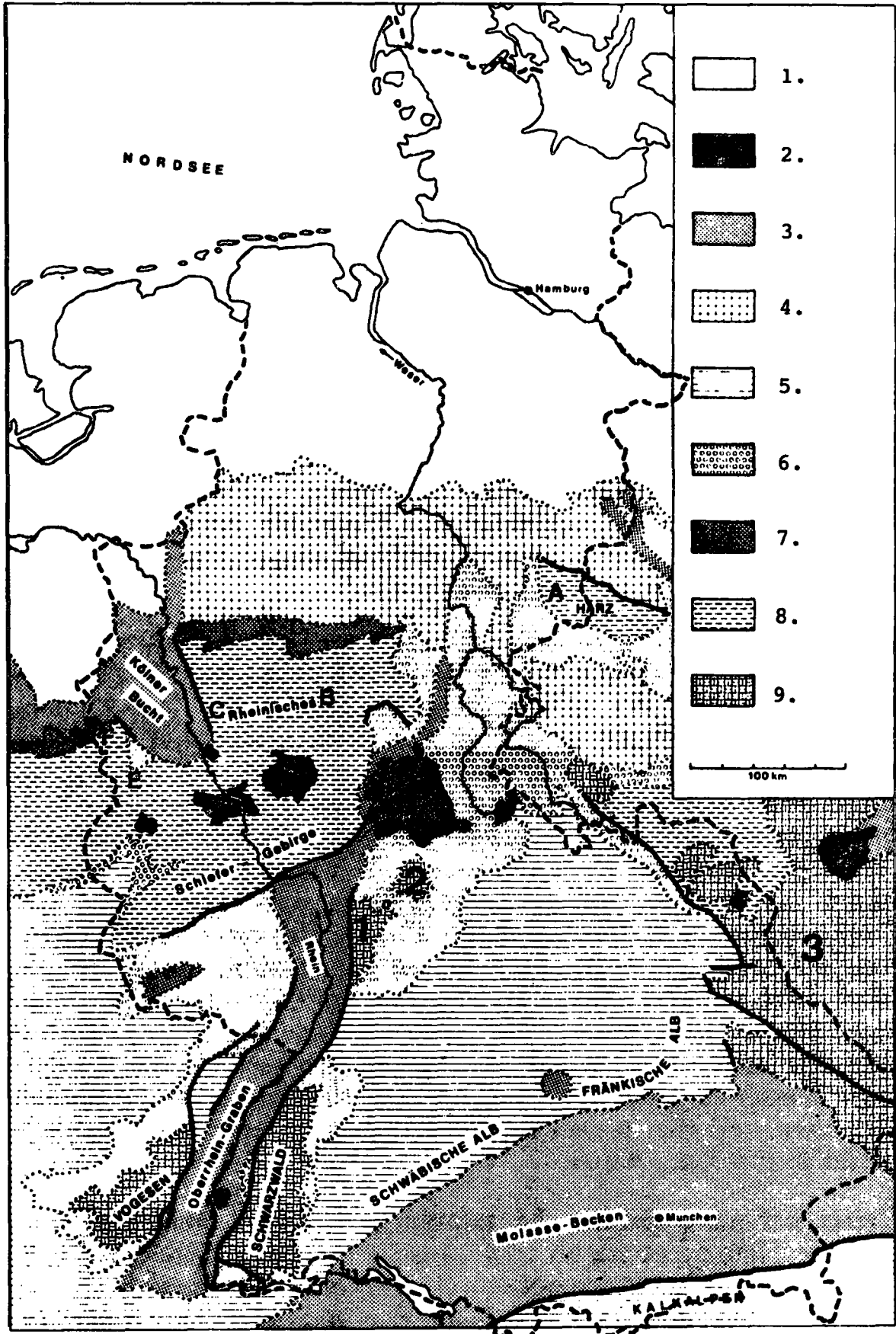
**Fig. 11.27.1.** The main geological units in the German Federal Republic (after HENNINGSEN 1976)

1 : Odenwald ; 2 : Spessart ; 3 : Bohemian Massif.

Fig. 11.27.1

Main geological units in the German Federal Republic
(after HENNINGSEN, 1976)

1. quaternary sediments

2. tertiary and quaternary volcanics

3. sediments in the tertiary graben

4. Mesozoic sedimentary rocks in N and middle Germany

5. Mesozoic sedimentary rocks in S Germany

6. sandstones and conglomerates of Permian ("Rotliegende") and
   Triassic ("Buntsandstein") age

7. coal bearing Upper Carboniferous

8. Devonian and Lower Carboniferous

9. magmatic and metamorphic rocks of the basement

Districts mentioned in this report :

A    Harz

B    Sauerland

C    Bensberg

D    Ruhr

E    Mechernich

F    Aachen

The general trend of the folding is SW-NE; the folds are assembled into synclinoria and anticlinoria, with axial planes generally dipping to the SE.

c. an unfolded Cover, lying unconformably upon the Variscides or on the Old Basement. It comprises sedimentary beds of Permian, Mesozoic and Caino-zoic age. A large part of the Republic is underlain by this Cover, and especially by Triassic strata. This unfolded cover, as well as the under-lying formations, is affected by numerous normal faults, with a general NW-SE direction, cutting transversally across the folded strctures. In several areas graben have resulted where thick successions of Cainozoic sediments have accumulated (Rhine-graben, Cologne-graben).

d. horizontal quaternary sediments, covering the whole northern part of the country.

e. a series of intruded and extruded volcanics (lavas and tuffs), mostly of basaltic character, emplaced during the Tertiary and the Quaternary.

The lead and zinc deposits of Germany are found in different geolo-gical situations. The main groups are the following :

- massive stratabound deposits in the Devonian strata of the Harz and the Rhenish Schiefergebirge;

- vein deposits cutting across Palaeozoic rocks of different ages : Lower Devonian, Middle Devonian and Carboniferous (Harz and Rhenish Schieferge-birge);

- disseminated stratabound deposits in the Triassic beds of the Cover.

It is noteworthy that :

- the latter type is the only significant one in the Cover;

- there is no indication of ore in formations younger than the Cretaceous;

- no important deposit is known in the pre-Variscan Old Basement.

## 11.27.C - THE RAMMELSBERG DEPOSIT

This deposit is located near the town of Goslar in the Harz (Nieder Saxe fig. 11.27.1 and 11.27.2).

It belongs to the stratiform type and consists of three large lenticular bodies, interbedded in the Wissenbacher Schiefer formation of Middle Devonian age. These bodies belong to the southern overturned limb of a large synclinal structure (figs. 11.27.3 and 4).

Two of them contain sulfide ore (figs. 11.27.5 and 11.27.6) :

- the "Altes Lager", exposed at the surface over a distance of 500 m and plunging to a depth of 310 m.

- the "Neues Lager", lying between the levels of 30 m and 500 m.

The average thickness of these orebodies is 10 m to 15 m and may reach locally 50 m. There is a third smaller orebody, the "Grauerz-Körper", containing essentially barite.

Ores consist of sulfides (pyrite, chalcopyrite, sphalerite and galena) and barite. There are no oxyde minerals.
On the average, they contain :

|  | | | |
|---|---|---|---|
| 12 | - 13 | % | Zn |
| 6 | - 7 | % | Pb |
| 0,5 - | 0,6 | % | Cu |
| 100 | gr/T | Ag | |

The structure is laminated. The grain size is mall. The original deposit amounted to 30 Mt, and has been mined since the Middle Age. It has been intensely prospected by several methods, mainly drilling and geochemistry. The Middle Devonian strata have been carefully explored in the neighbouring areas but no new orebody was found. The deposit itself cannot extend to great depths since it is located in a syncline. According to Dorstewitz and Friedensburg (1976), reserves would amount to 5 Mt of ore.
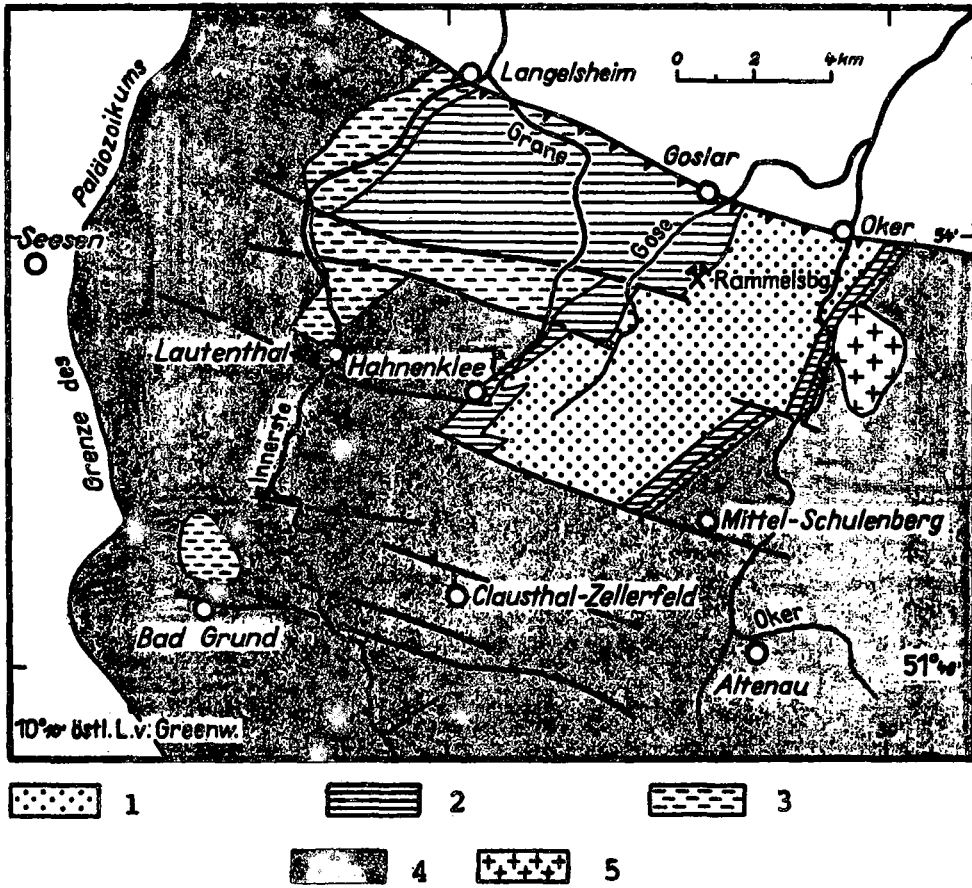
**Fig 11.27.2.**
Schematic geological map of the north-western
part of the Harz, showing the Devonian anticline
of the Oberharz (after : KRAUME, 1975).

1. Lower Devonian.
2. Middle Devonian.
3. Upper Devonian.
4. Culm.
5. Granite.
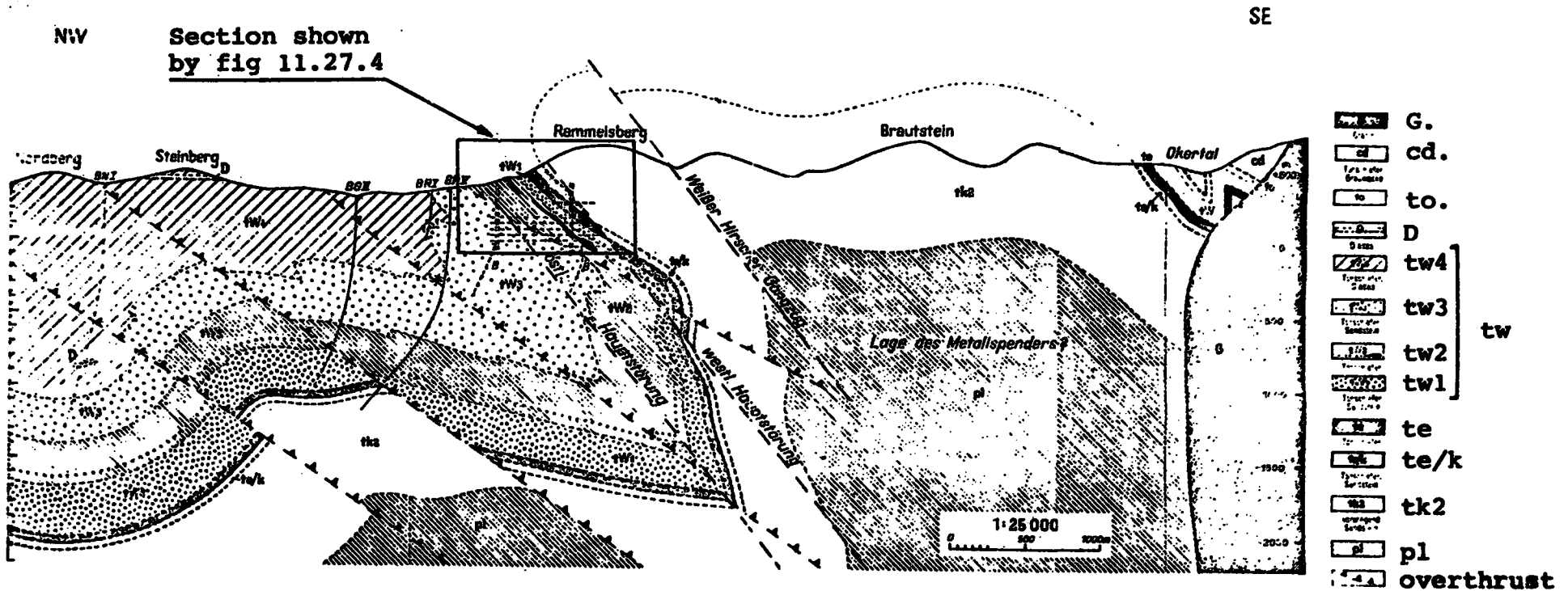
**Fig 11.27.3.** Simplified geological section across the Rammelsberg.

G.   : granite
cd.  : culm
to.  : upper Devonian
D.   : diabase
tw.  : "Wissembacher schiefer"⎫ middle Devonian
te.  : *Calceola* shales    ⎭
te/k:⎫ lower Devonian
tk2 :⎭
pl.  : pre-Devonian ?

(after: KRAUME 1955)
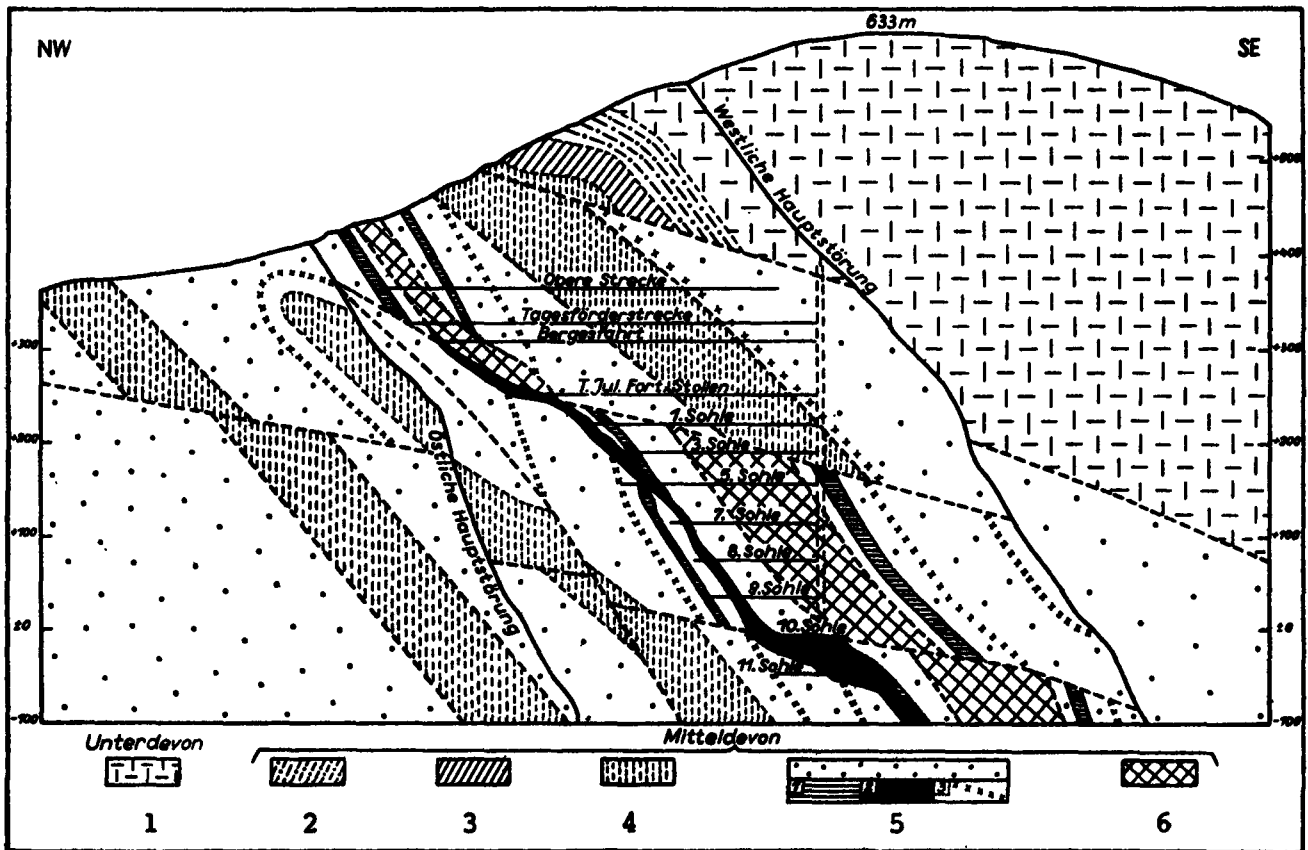
**Fig. 11.27.4.**
Geological section across the Rammelsberg (after : KRAUME, 1975).

1. *Cultrijugatus* sandstone ⎤ Upper Devonian

2. *Speciosus* beds

3. *Calceola* beds

4. Sand-banded shales

5. "Wissembacher schiefer" formation    Middle Devonian

    5.1. Ore-banded shales.

    5.2. Ore-body.

    5.3. Shales

6. "Kniest" : a local name for a kind of siliceous shale.

Fig. 11.27.5.

The ore-bodies in the Rammelsberg deposit :

    a.-   lateral view

    b.-   horinzontal sections at different levels

(after : KRAUME, 1975).
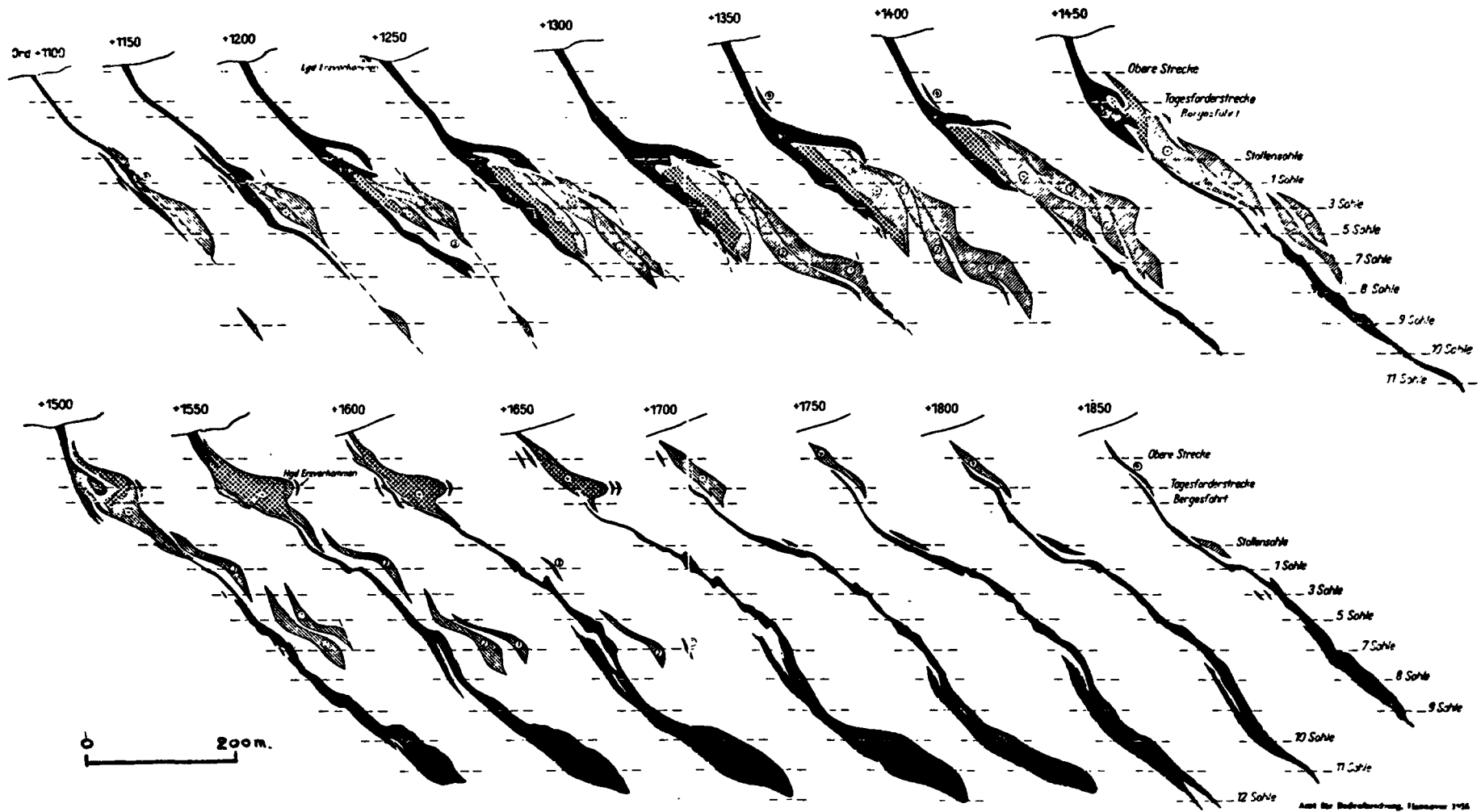
**Fig.11.27.6.** The Rammelsberg deposit. A serie of profiles across the ore bodies.

black: ore

other signatures: "kniest" (see legend of fig 11.27.4.)

(after:KRAUME 1955)

## 11.27.D - VEIN DEPOSITS IN THE HARZ. THE GRUND DEPOSIT

In the north-western part of the Harz, the Palaeozoic strata, belonging mostly to the Culm facies of the Carboniferous system, are cut by a network of veins. These veins are steeply dipping with a general WNW-ESE trend, parallel to the length of the Harz massif (fig. 11.27.7). There are of variable thickness, from a few centimeters up to 40 m. Mineralization consists mainly of sphalerite and silver-bearing galena with subordinate pyrite and chalcopyrite.

The ore is distributed within the veins as bodies of highly unequal and varied shapes and dimensions. Particularly favourable for the localization of ore are the horizons of sand-banded shales and, to a lesser extent, the thick greywacke layers. The mineralization has been emplaced in several succesive phases. The main orebodies are shown in fig. 11.27.8.

The deposits in the Harz have been mined since the 13th century. Apart from Grund, they are now abandoned and are regarded as devoid of economic interest.

The whole area has been intensely prospected, and it seems unlikely that new veins could be discovered. On the other hand mineralization may extend to great depths and also at unknown distance under the Cover.

### The Grund deposit

The Grund deposit has yielded more than 1 Mt of metal. The composition of the ore is :

|       |    |      |   |    |
|-------|----|------|---|----|
| 4     | to | 4.5  | % | Pb |
| 4     | to | 5.5  | % | Zn |
|       |    | 0.1  | % | Cu |
|       |    | 0.01 | % | Ag |

According to Dorstewitz and Friedensburg (1976), reserves amount to 8 Mt; in 1974, 400 000 t of ore were mined and yielded a Pb concentrate containing 75.4 % Pb and 0.12 % Ag and a Zn concentrate containing 60.6 % Zn and 0.03 % Cd.
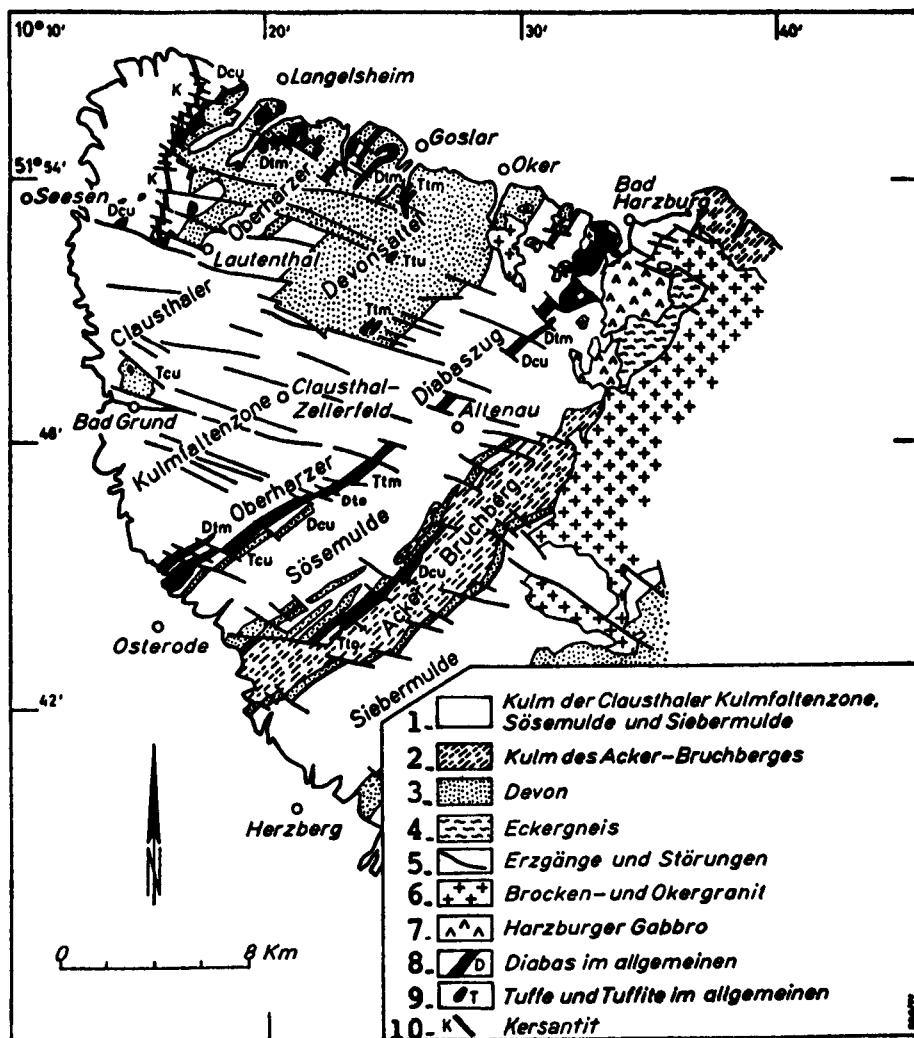
1. Culm.

2. Culm of the Acker-Bruchberg    area

3. Devonian

4. Gneiss

5. Veins and faults

6. Brocken and Oker granite

7. Harzburg gabbro

8. Diabase in géneral

9. Tuffs and tuffites in general

10. Kersantite

Fig.11.27.7.

General geological map of the Oberharz
(after BUSCHENDORF e.a.).
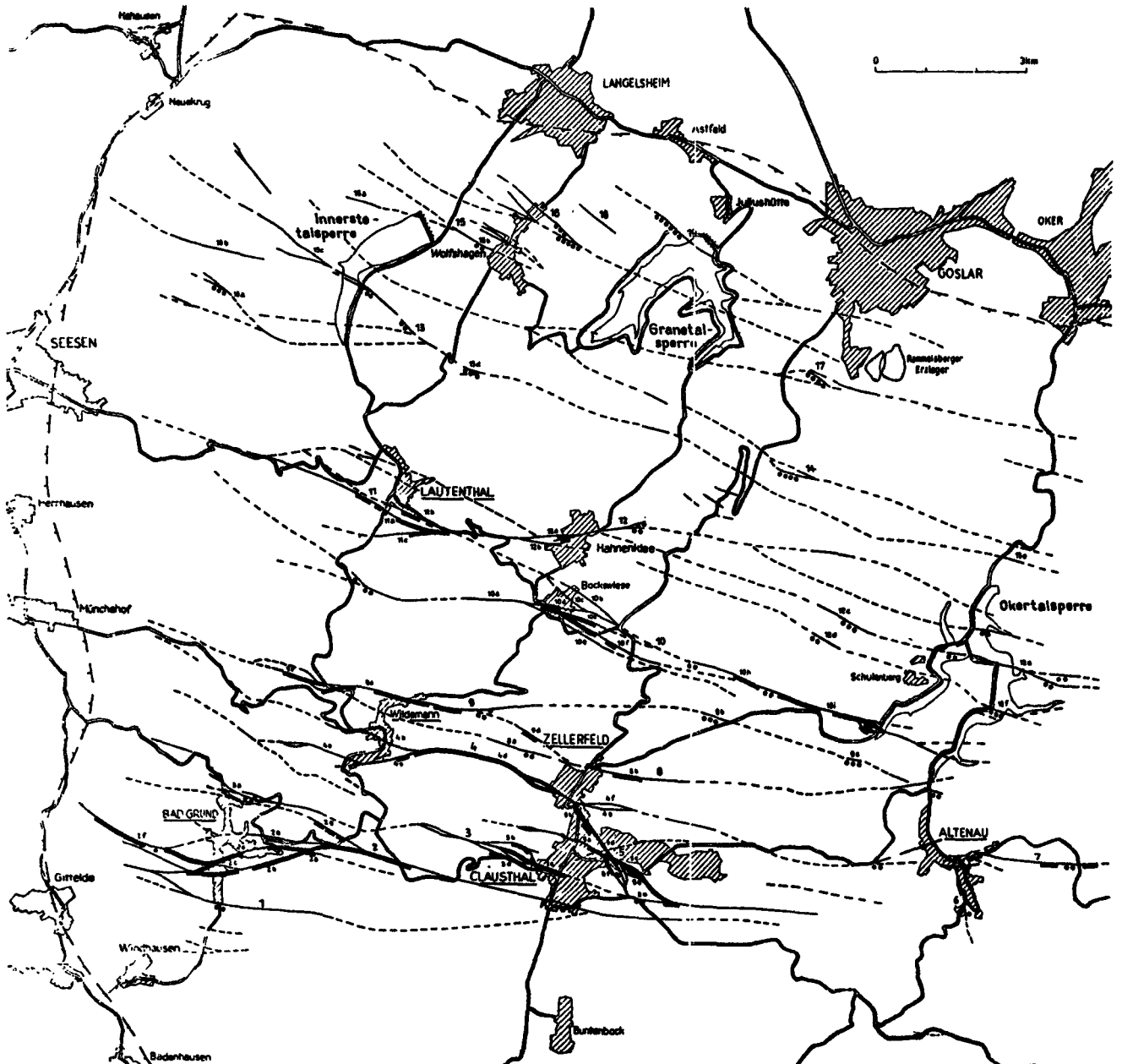
**Fig. 11.27.8.**

General map of the veins in the NW Oberharz.

——— known vein

– – – – partially known vein

▬▬▬ vein containing ore bodies

⊤⊤⊤⊤ vein with ore traces

(after:BUSCHENDORF c.a. I97I)
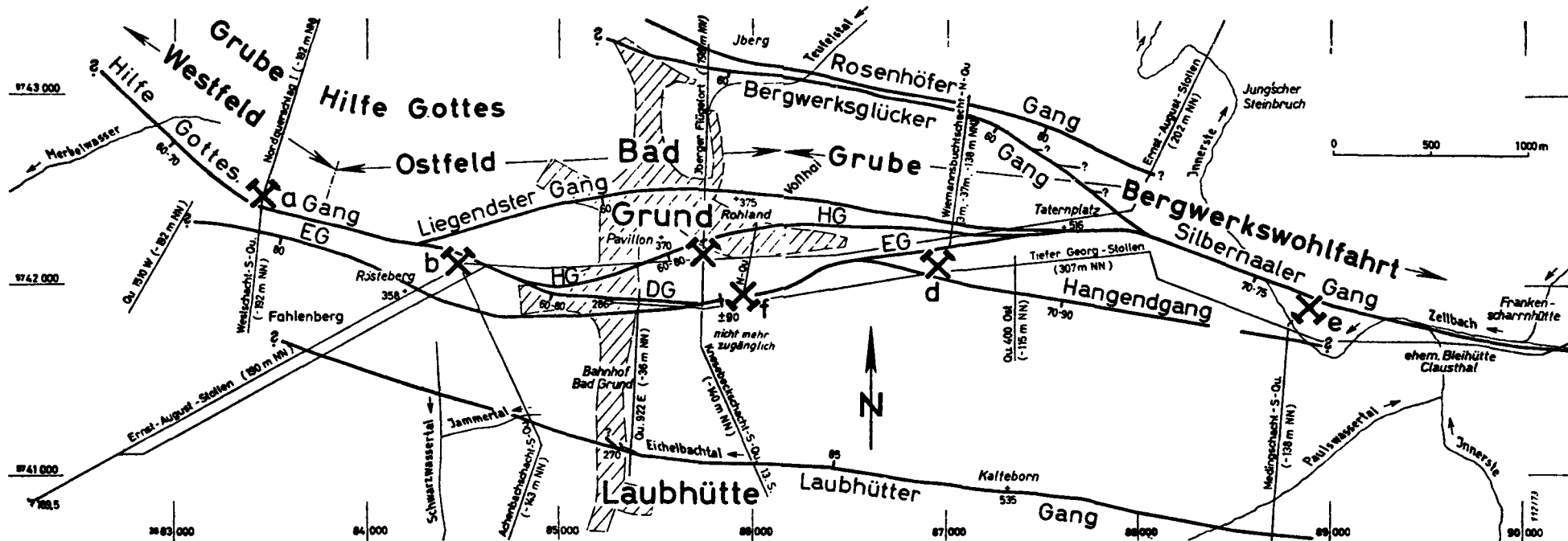
**Fig. 11.27.9.** Shafts, adits, important exploration crosscuts and surface localities in the area of the Grund veins (a = West shaft ; b = Achenbach shaft ; c = Knesebeck shaft ; d = Wiemannsbucht shaft ; e = Meding shaft ; f = Lichtloch).

(after SPERLING, 1973).

11.27.E - <u>THE MEGGEN DEPOSIT</u>

This deposit is situated in western Sauerland, about 30 km north of the town of Siegen.

It belongs to the stratiform type and forms a layer 1.5 m to 6 m thick, interbedded in the upper part of the Givetian. This layer has been folded and fractured during the Variscan orogeny. The structure of the deposit is shown in fig. 11.27.10.

The sedimentary environment and the palaeogeography of the deposit have been studied in great detail. The investigations have shown that, at the time of sedimentation and ore deposition, the Meggen area was occupied by a body of shallow water, more or less isolated from the open sea by reefs.

The ore consists of sulfides : pyrite, marcasite, sphalerite, galena and some chalcopyrite; it grades laterally into barite (see fig. 11.27.10). The ore layer, together with its barite halo, is thought to have covered an area of about 10 km2 before the folding. The structure is very fine-grained.

The ore contains 11 % Zn and 1.2 % Pb. Barite recovered before is no more mined to-day.

The deposit has been known for 2 1/2 centuries. The following figures give an idea of its size :

                total amount extracted up to 1973 : 31 Mt ore
                                                      7 Mt barite

        annual production (1973) : 0,8 Mt ore
                                   0,2 Mt barite.

"As the deposit extends to depths that have not yet been explored, the mine is certain to remain active for some time to come" (Friedensburg, 1971). Reserves amount probably to several Mt of ore (Dorstewitz and Friedensburg, 1976).
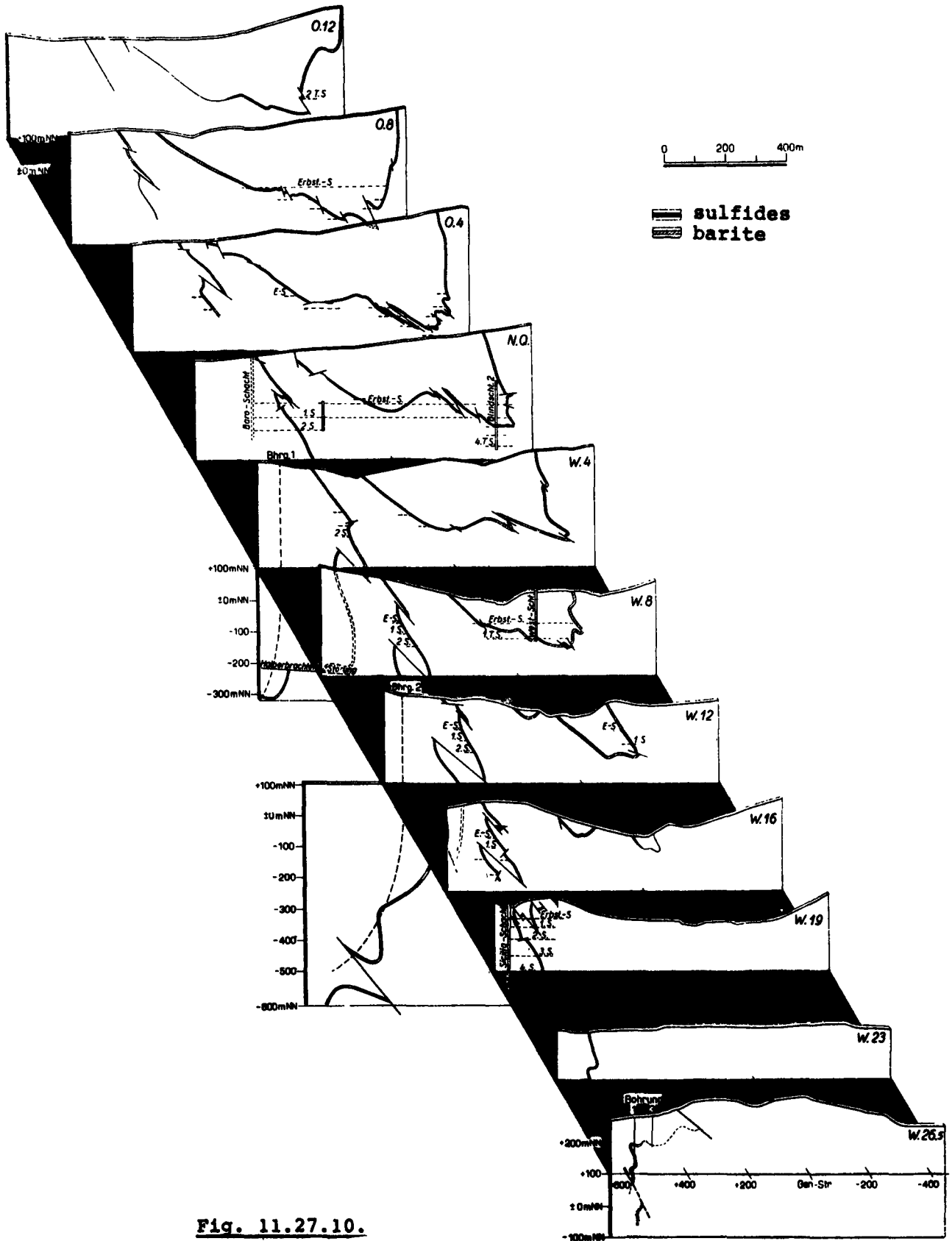
**Fig. 11.27.10.**

The pyrite - sphalerite - barite deposit of Meggen
(after EHRENBERG e.a. 1954)

11.27.F - <u>THE RAMSBEt DEPOSIT</u>

This deposit is situated in Sauerland, about 100 km east of Düsseldorf. It consists of a network of veins cutting quartzites and shales of Middle Devonian age (Couvinian). Most of the veins are dipping at low angles.

The ore is distributed rather regularly and the veins are continuous.

The deposit was discovered in the Middle Ages and has yielded 0.7 Mt of ore. The annual production in 1970 was 476 000 t at 3 % Zn and 1.5 % Pb.

The grade being too low, the mine was abandoned in 1975, although considerable resources remained available.

11.27.G - <u>THE BENSBERG DISTRICT</u>

The Bensberg district, located between 10 and 30 km east of Cologne was very significant in the past, with more than 100 active mines. Until recently remained opened the Lüderich mine (see fig.11.27.11).

In this area, all the deposits are related to a network of veins striking in various directions across the Lower Devonian strata.

The Lüderich mine consists of several N-S veins followed over a distance of 3.5 km and emplaced in normal faults dipping steeply to the E. These veins cut across the arenaceous and argillaceous sedimentary strata of Lower Devonian age transversally to the fold axes (fig. 11.27.12). The footwall consists of sandstones and the hangingwall of argillaceous rocks.

The ore consists of sphalerite, galena, siderite and various minor minerals. The grade is 7 % Zn and 1.5 % Pb. In 1970, production amounted to 0.2 Mt of ore.

The deposits of this area have been mined from the Middle Ages and have yielded more than 1 Mt of metal, out of which 0.7 Mt has come from Lüderich.
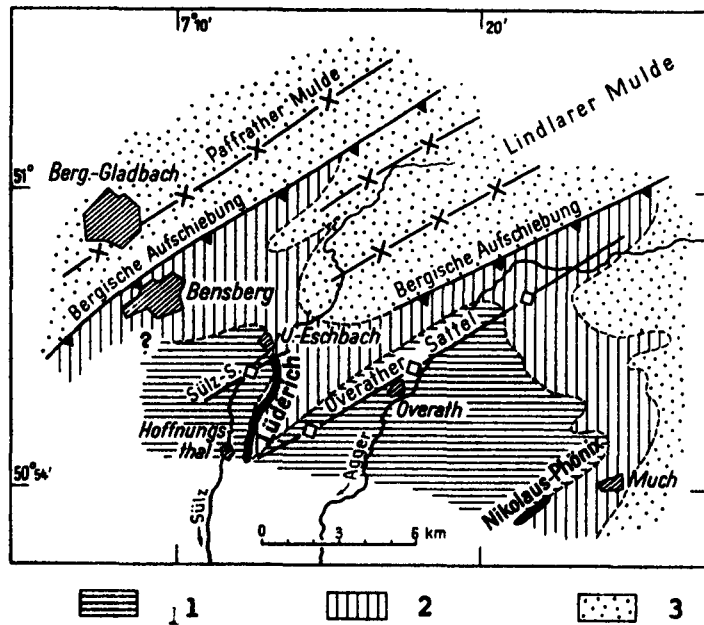
**Fig. 11.27.11.**

General geological feature of the Bensberg area
(after LEHMANN and PIETZNER, 1970).

1. "Liegend-arkose" and Wahnbach beds (Siegenian).
2. Bensberg beds (Emsian).
3. Remscheid beds (upper Emsian) and younger formations.
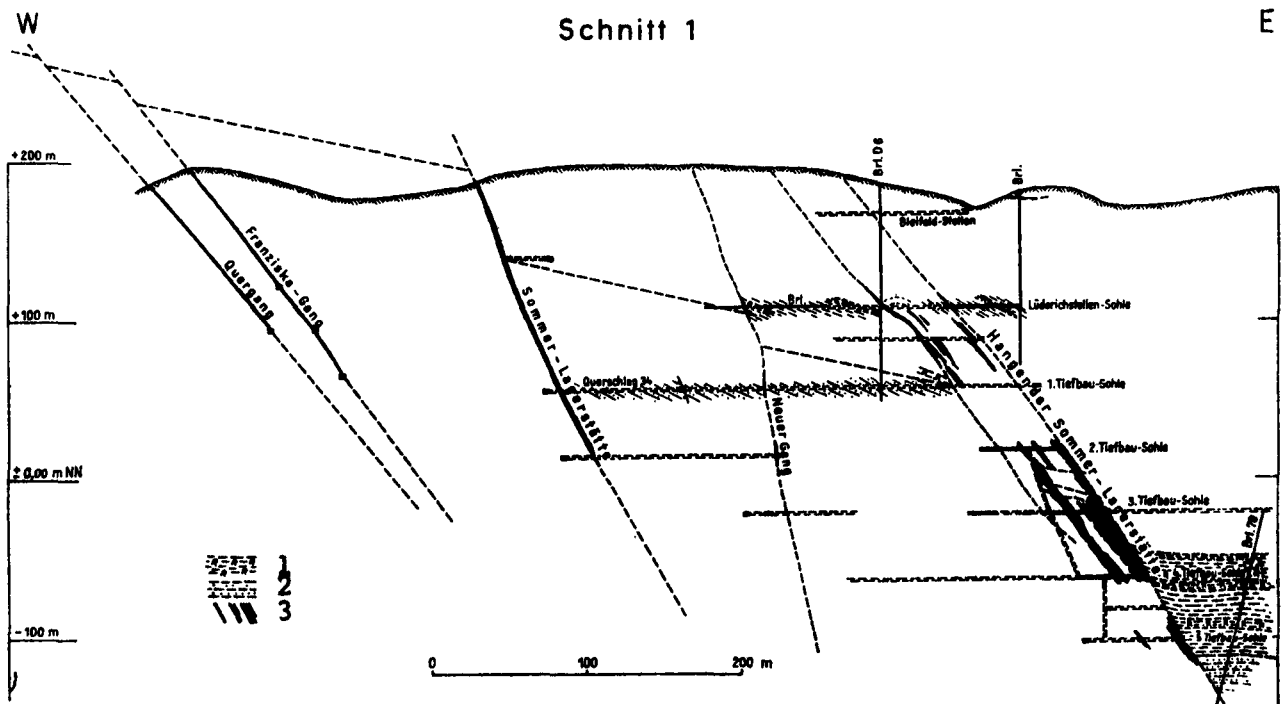


**Fig. 11.27.12.**

Profile across the Lüderich deposit.
(after LEHMANN and PITZNER, 1970).

1. Horizont of red shales.
2. "Liegend-Arkose" formation (Siegenian).    3. Ore-body.

## 11.27.H - THE RUHR DISTRICT

A number of Zn and Pb sulfide veins have been found in the Upper Carboniferous strata of the Ruhr district, which forms the northern part of the Variscides in the Federal Republic of Germany. These veins were discovered on the occasion of development work undertaken in the coal mines. They are located along major faults which may yield abundant water. Coal miners usually keep away from these faults so that there may well remain undiscovered deposits in the area.

The deposits are found at the intersection of NW-SE steep dipping faults and low angle thrusts.

The ore consists of breccias cemented with sphalerite, galena, barite and gangue minerals. In the Auguste-Victoria mine, a large orebody was found and yielded 5 Mt of ore at 7 % Zn and 4 % Pb; it was abandoned in 1962 although 2 or 3 Mt of ore remained unmined. A 2 Mt orebody with about 10 % combined metal also remains unmined in the Graf Moltke coal deposit.

Similar deposits have also been found in the Aachen-Erkelenz coal basin. According to Herbst and Stadler (1971), they are quite significant.

## 11.27.I - OTHER VEIN DEPOSITS

Zn and Pb bearing veins have been mined in many other districts of Germany. The reader is again referred to Friedensburg (1971) for more complete information.

## 11.27.J - MECHERNICH AND MAUBACH

In an area of roughly triangular outline SE of Aachen, the folded Devonian strata of the Rhenish Schiefergebirge are overlain unconformably by unfolded younger formations : the Buntsandstein of Lower Triassic age, the Muschelkalk and Keuper of Middle and Upper Triassic ages. Towards the NE, that area is bounded by the Cologne Graben, filled by Tertiary sediments.
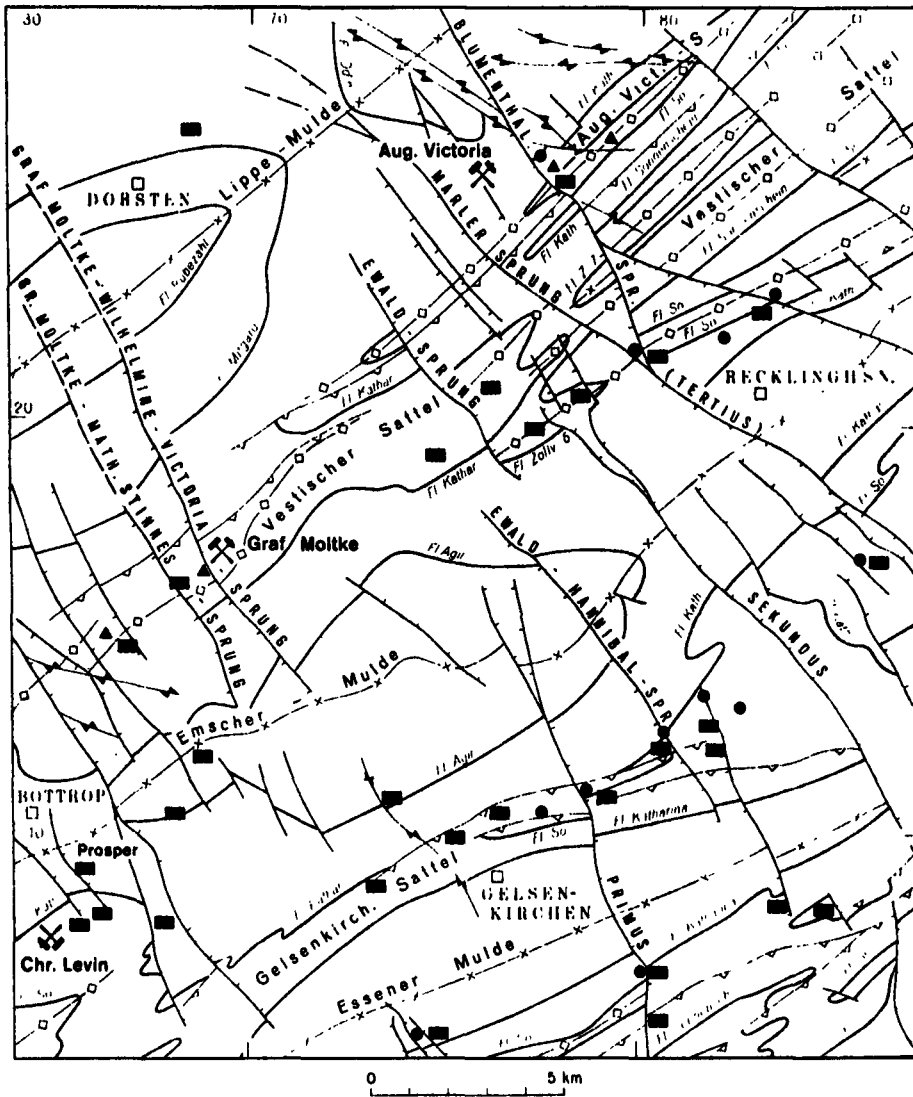
1      ▲ 2      ▬ 3

**Fig. 11.27.13.**

A part of the vein map of the Ruhr area, from :
Monographien der Deutschen Blei-Zink-Erzlagerstätten
(Beih. Geol. Jb. 40, Hannover, 1961).
(after PILGER and STADLER, 1971).

1. Mineralization of Ia - generation.
2. Mineralization of IIa - generation.
3. Mineralization of IIb - generation.
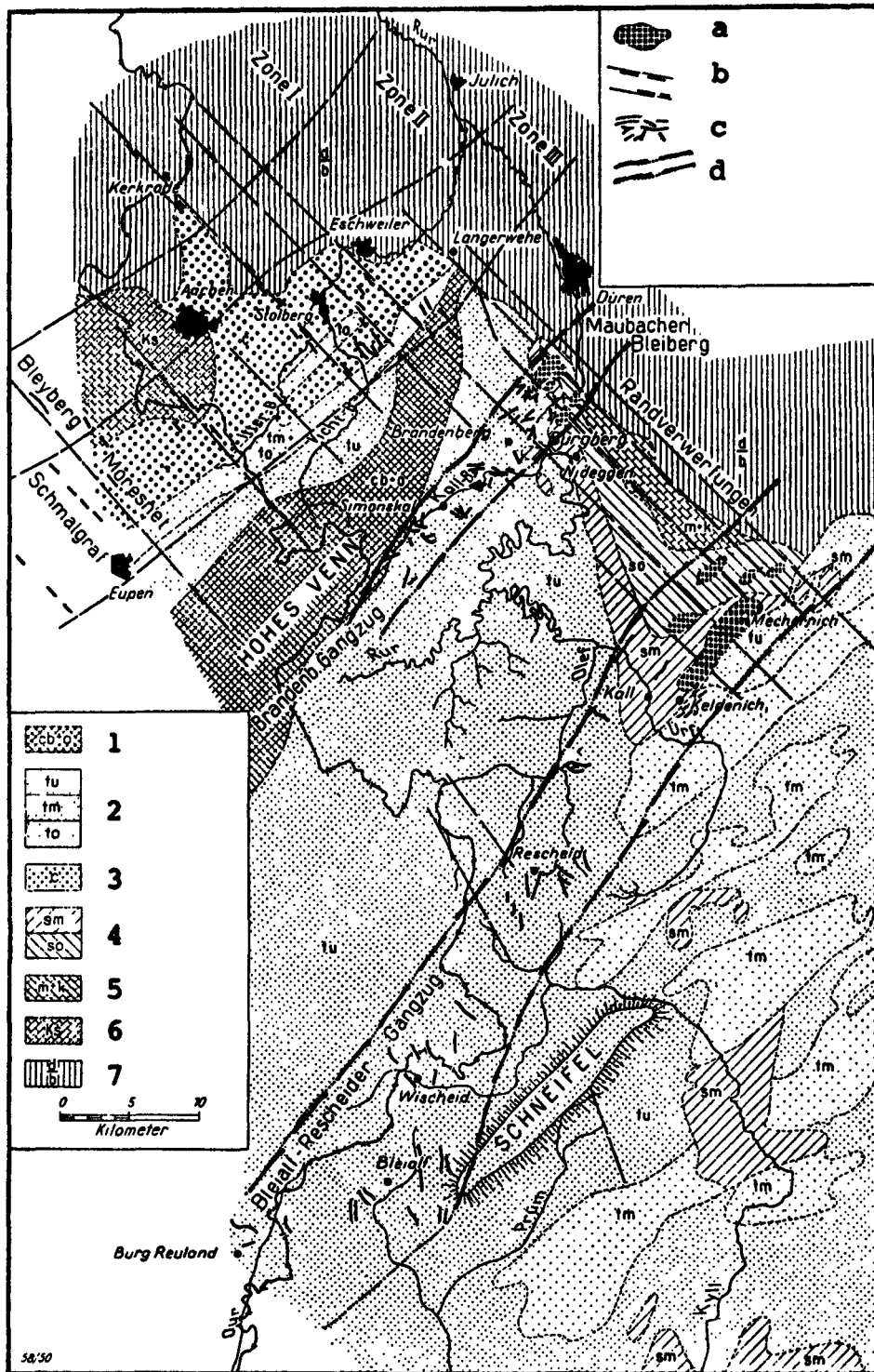
**Fig. 11.27.14.** Geological map of the N-Eifel, showing the localisation of the Maubach and Mechernich deposits.

1. Cambro-Ordovician
2. lower
   middle Devonian
   upper
3. Carboniferous
4. middle
   upper Buntsandstein
5. Muschelkalk and Keuper
6. Cretaceous
7. Tertiary under recent

a. impregnation deposit
   in the Buntsandstein
b. deposits along faults
c. Pb-Zn bearing veins in
   the Devonian
d. vein zone

(after VOIGT 1952)

**Fig. 11.27.15.** Geological profile across the Mechernich deposit.

1. mineralised sandstone
2. mineralised conglomerate
3. sterile sandstone
4. sterile Devonian

horizontal scale: 1:30.000
vertical scale : 1:6.000

(after: PUFFE 1953)

In the northern and southern parts of it, the sandstones and conglomerates of the Buntsandstein carry disseminated sulfides of Zn and Pb, giving rise to the deposits at Maubach and Mechernich respectively (fig. 11.27.14).

Voigt (1952) has pointed out that these two deposits are located at the intersection of the Triassic outlier with two narrow zones in which many vein-type deposits are found in the underlying Variscides.

Maubach has yielded 10.4 Mt of ore at 2 % Pb and 0.8 % Zn, and is now mined out.

Mechernich on the other hand (fig. 11.27.15) was abandoned in 1957 although considerable resources remained unmined. These resources are estimated at 100 Mt of low-grade ore at about 1 % Pb and 2 % Zn (Friedensburg, 1971).

## 11.27.K - THE AACHEN-STOLBERG DISTRICT

Several deposits were mined during the last century in this district which is a continuation of the Belgian Northern District (11.26.C). The largest of them was Diepenlichen, which closed down in 1919 after producing 450 000 t of Zn concentrate and 150 000 t of Pb concentrate. A map of the district is shown as fig. 11.27.16 of this report.

All these deposits are located along post-Variscan faults striking NW. Most are found in places where these faults run across carbonate formations, either of Lower Carboniferous age (Carboniferous Limestone called Dinant in Germany) or of Devonian age (Givetian and Lower Frasnian).

## 11.27.L - SUMMARY

A large number of veins have been found in Germany. In addition there are stratiform deposits belonging to two quite different types : Meggen and Rammelsberg are found in the folded Devonian succession of the Variscides; Mechernich and Maubach are the main deposits found in the overlying Triassic sandstones.
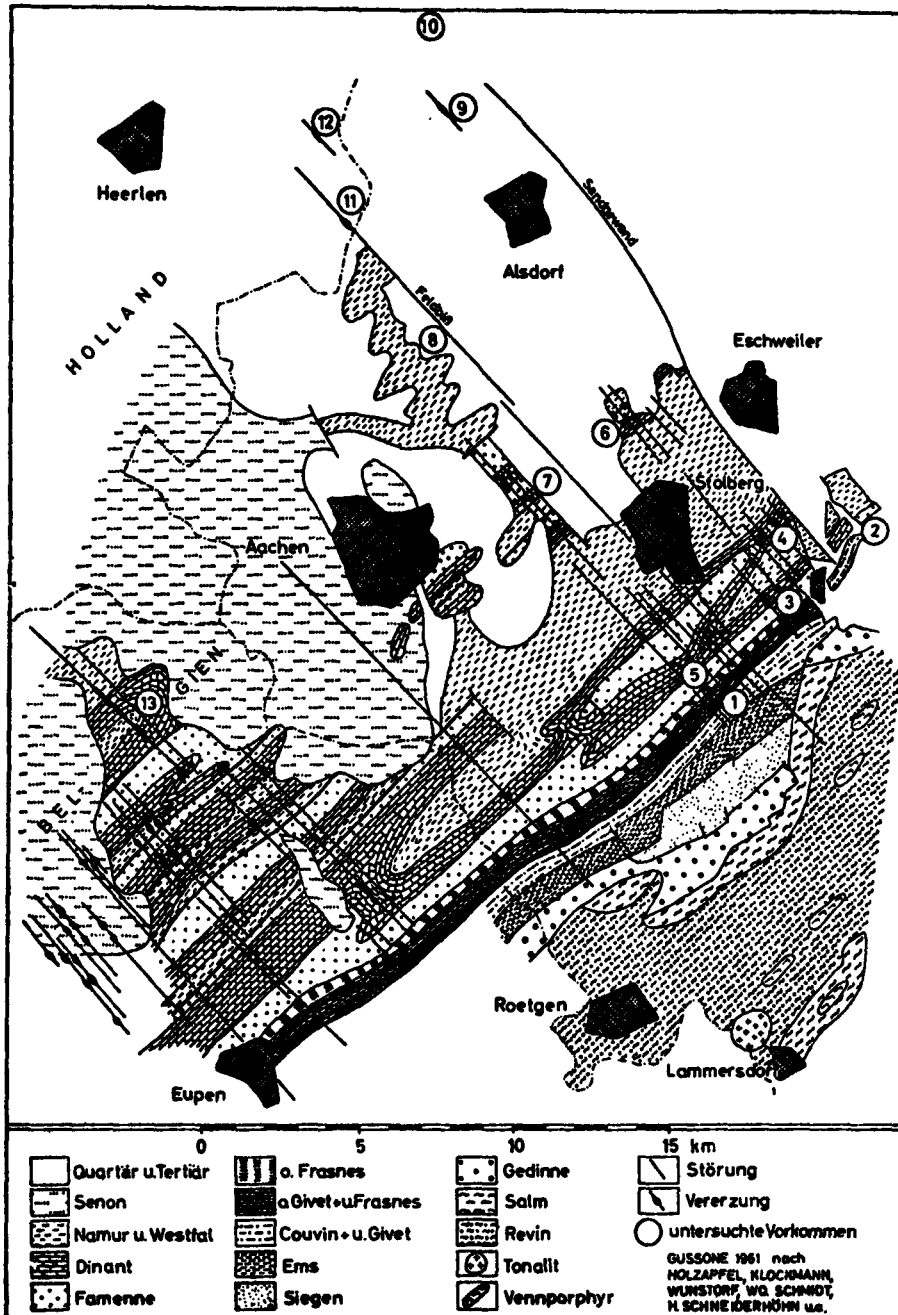
**Fig. 11.27.16** - Schematic map of the Aachen-Stolberg
district including the adjacent parts
of Belgium (after Gussone, 1967).

Numbers refer to Zn-Pb deposits, among
which Diepenlinchen (n° 3).

By contrast with many of their equivalents in Greenland, Ireland, the United Kingdom and France, German Zn and Pb deposits are not found in carbonates except at the very western border of the country near Aachen.

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## 11.28 - ITALY

## 11.28.A - INTRODUCTION

Zn and Pb are mined in two major districts in Italy : the Southern Calcareous Alps with 3 active mines and Sardinia with 15 active mines. In addition some ore comes from Monteneve in the Axial Zone of the Alps and from Fenice Capanne in Toscany.

Past production from Sardinia is considerable.
For the two major groups of mines, it is estimated at about 3.5 Mt of metal, distributed as follows (Italminière, 1977) :

|                   | Zn from       |           | Pb      |
|-------------------|---------------|-----------|---------|
|                   | sulphide ore  | oxyde ore |         |
| Monteponi group   | 400 000       | 950 000   | 550 000 |
| Montevecchio group| 730 000       |           | 940 000 |

For the whole of Sardinia, P. Zuffardi suggests the figure of 8 Mt of metal.

Two of the Italian mines of Zn and Pb have been opened in the last decade and have been built on newly discovered orebodies.

## 11.28.B - REGIONAL GEOLOGY

Several major structural units can be recognized in Italy : the Alps and the Apennines, both of which result of intense deformation during the Alpine orogeny; Calabria and Sicily, which continue the Apennines towards North Africa; and the Po basin in which several thousand meters of young sediments have accumulated and have remained unfolded. Sardinia is a quite separate unit.

The Po basin and much of the Apennines are devoid of mineralization. We are therefore concerned here mostly with two regions of Italy. The following is based on Manfredini (1964) and also on Zuffardi (1965) for Sardinia; and Rutten (1969) for the Alps.

1. **Sardinia.** The oldest sedimentary formations recognized in Sardinia are of Cambrian age. They were affected by a phase of folding along E-W axes (Sardinian phase of the Caledonian orogeny) at the end of the Cambrian period. A second phase of folding occurred after the deposition of the Silurian.   The whole Palaeozoic succession, including Devonian and Carboniferous strata, was much deformed by folding (along NNW directions) and faulting during the Variscan orogeny. In addition large granite intrusions were emplaced at that time, followed by volcanic eruptions in early Permian.

During the Mesozoic and Cenozoic, the sea invaded again the area on several occasions but the sequence deposited has remained mostly horizontal. During the Alpine orogeny, Sardinia was affected only by subvertical faults and by intense volcanic activity witnessed by abundant tuffs and lavas.

The geological structure of the island is schematised in fig. 11.28.1. The two major sets of roughly parallel faults are an important feature of the island as shown by the Campidano Valley. In this graben, striking NW from Cagliari, the Variscan basement sunk to great depths and a thick succession of sediments and volcanics accumulated.

In Sardinia, Zn and Pb mineralization is found in the Variscan basement only.

2. **The Southern Alps.** Of the Italian Alps, we are mostly concerned here with the eastern part, which is quite different from the western one. This eastern part consists of an axial zone on the south side of which the Southern Alps or Southern Calcareous Alps are developed. The Southern Alps include the Bergamo or Bergamask Alps, the Dolomites, the Carnic and Julian Alps (fig. 11.28.2 and 3).

In this area the pre-Permian basement, which is observed in most of the axial zone, consists of metamorphic rocks ranging from phyllites to gneisses and intruded by granites and other magmatic rocks. In the Carnic Alps, a Silurian, Devonian and Carboniferous succession, mostly detrital and folded along EW axes during the Variscan orogeny is observed in the basement. Elsewhere the structure and the history are more complex.

The basement is overlain by a Permian sequence including both volcanics and sediments deposited in non-marine conditions.
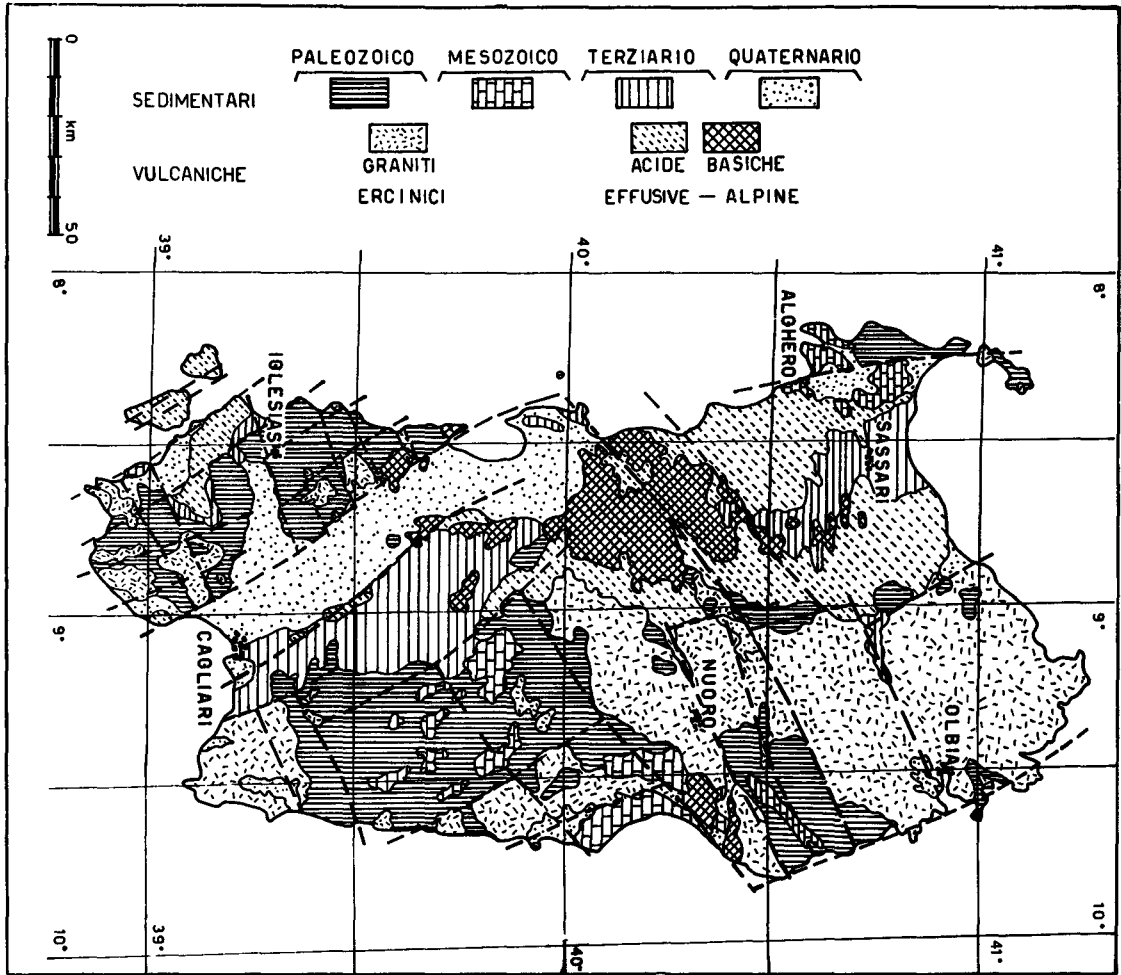
Fig. 11.28.1   Geological constitution of Sardinia
               (after Zuffardi, 1965)
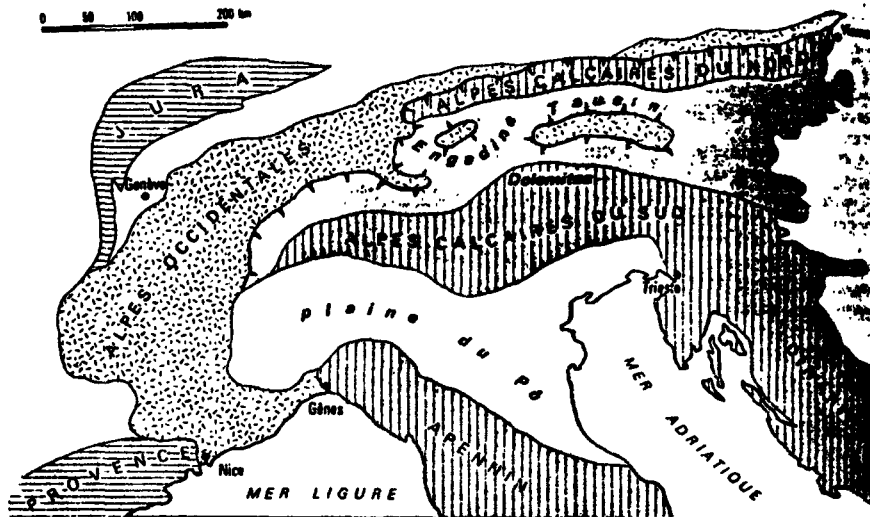


Fig. 11.28.2 - Schematic constitution of the Alps with
               the location of the Southern Calcareous
Alps (Alpes calcaires ou Sud). After Aubouin, 1972.
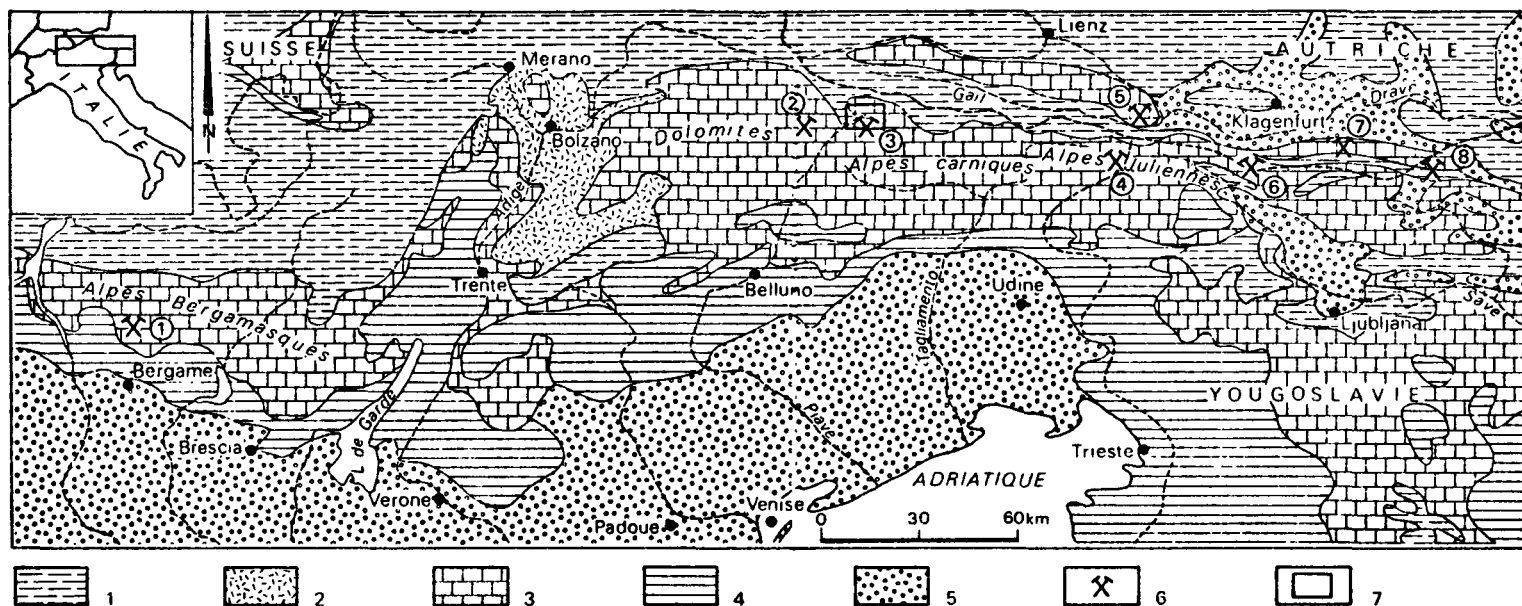
**Fig. 11.28.3.** - Major deposits found in the Triassic of the <u>Southern Calcareous Alps</u>
at the Anisian-Ladinian boundary (2 : Salafossa ; 3 : Auronzo) and at
the Ladinian - Carnian boundary (1 : Gorno ; 4 : Raibl ; 5 : Bleiberg Kreuth ;
6 : Wind - Bleiberg ; 7 : Eisenkapel ; 8 : Mezica).

<u>Legend</u> :1:Variscan basement ; 2 : Permian porphyries ; 3 : Permian and Triassic ; 4 :
Jurassic and Cretaceous ; 5 : Tertiary and Quaternary.(After Lagny, 1975)

This sequence is in turn overlain by the Triassic carbonates, which are so well exposed in the Dolomites, and are characterized by the occurrence of reefs formed either by algae or by corals.

"In lateral alternation with these carbonate reef series, submarine volcanic deposits occur, which are a special development of the Southern Alps. In the Dolomites this contemporaneous volcanism has seriously limited the extension of the reefs. As a result one finds abrupt facies changes from the massive reef and reef-rock carbonate series to the thinly bedded volcanoclastic facies. Although some interfingering occurs, the reefs probably towered high above the volcanoclastic deposits in the Triassic sea, and, schematically, the border of the reef facies is now subvertical, often over hundreds of meters ...

When seen as a whole, the thickness and the facies of the Southern Alps show rapid changes in east-west direction. Apparently there have been alternating "haut-fonds" and subsiding basins. This is thought by Bosselini (1965) to be due to blockfaulting in the basement along a set of north-south faults.

The higher Mesozoic, the Jurassic and Cretaceous, is also developed in a predominantly carbonatic facies, but well-bedded limestones are more common than in the massive limestone and dolomite facies of the underlying Triassic". (Rutten, 1969).

## 11.28.C - SOUTH-WESTERN SARDINIA. STRATA BOUND DEPOSITS.

A simplified geological map of south-western Sardinia, west of the Campidano Valley, is shown in fig. 11.28.4. This is an important mining district, covering about 2250 km2, generally known under the name of Iglesiente, but actually subdivided into three zones : Arburese, Iglesiente s.s., and Sulcis.

"Some geological differences among the three zones are evident : essentially post-Cambrian slaty and sandy formations intruded by granites occur in Arburese; a Cambrian succession occurs both in Iglesiente s.s. and in Sulcis, but limestones and dolomites are well developed in the former and scarcely in the latter; moreover granites are scarcely represented in Iglesiente s.s. and are important in Sulcis.

Differences in types of ore deposits, compositions, and economic values are more or less directly related to the geological conditions.

Peribatholitic vein type deposits are prevalent in Arburese; Pb and Zn sulfides are the most frequent ores ... Barite and fluorite are also present ...

Strata-bound syn-sedimentary, more or less metamorphosed and oxydized Pb-Zn deposits are prevalent in Iglesiente s.s. and in Sulcis; the tonnage of single deposits being conspicuous in the former district and rather limited in the latter ... Barite deposits are also important in both areas".

"Gentle folds with axes N 65° E and step gravity faults striking in the same direction are dominant in Palaeozoic formations of the Arburese; folds and faults striking N 30° W are also present but less important.

Complicated tectonics is characteristic of the Palaeozoic in Iglesiente s.s. and in Northern Sulcis, where tight folds with axes N 20° W and overthrusts striking in the same direction are superimposed to gentle E-W axis folds". (Zuffardi, 1965).

Many Zn and Pb deposits of south-western Sardinia are associated with the Calcare Metallifero (see fig. 11.28.5), a succession of limestones and dolomites of Middle Cambrian (Acadian) age, which is found in the following stratigraphic position :

| | |
|---|---|
| Shales | Ordovician |
| Conglomerate | Ordovician |
| Unconformity | |
| Shales | Acadian |
| Limestones grading laterally into shales with abrupt facies changes | Acadian |
| Shallow-water limestones | Acadian |
| Shallow-water and lagoonal dolomites partly silicified | Acadian |
| Sandstones | Georgian |
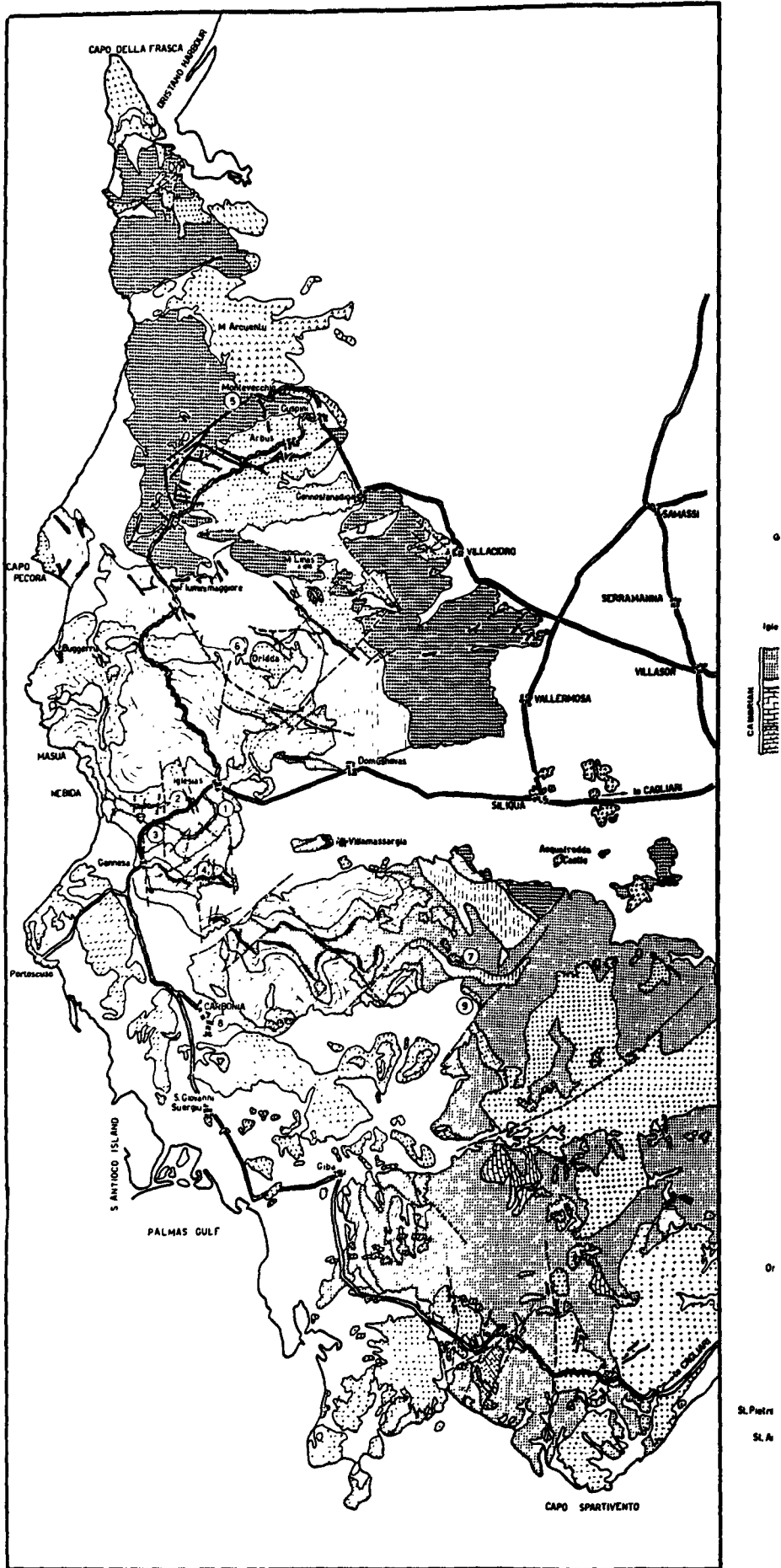
Fig. 11.28.4. - Simplified geological map of SW Sardinia

INDEX

**Sedimentary rocks**

Post - Palaeozoic

**Igneous rocks**

CENOZOIC

Volcanic basic lava and tuffs
(andesitic and basaltic lava)

Volcanic acid lava and tuffs
(trachytic and liparitic lava)

Hydrothermal veins made up
essentially by quartz, along with
Pb.Zn.Ba.F.Fe.Cu.W.Ni.Co.Sn.Mo.

Porphyries

Hercynian granites
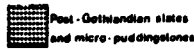
Post - Gothlandian slates
and micro - puddingstones
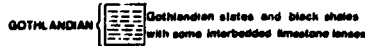
GOTHLANDIAN — Gothlandian slates and black shales
with some interbedded limestone lenses

-Porphyroides-
(laminated porphyries)
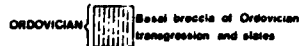
ORDOVICIAN — Basal breccia of Ordovician
transgression and slates

**Iglesiente proper**
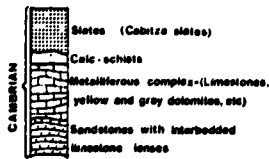
CAMBRIAN

Slates (Cabitza slates)

Calc - schists

Metalliferous complex-(Limestones,
yellow and gray dolomites, etc)

Sandstones with interbedded
limestone lenses

**Sulcis**

More or less metamorphosed
sandstones and shales
with interbedded limestone

Major faults

① Campo Pisano Mine ( Zn, Fe)
② Monteponi Mine (Pb. Zn)
③ St. Giovanni Mine (Pb Zn)
④ Barega Mine (Ba)
⑤ Montevecchio Mine (Pb.Zn.Fe.Cu)
⑥ Arenas Mine (Pb.Zn.Ba)
⑦ Se Marchesa Mine (Pb. Zn.Cu)
⑧ Carbonia (Coal district)
⑨ Mt. Tamara (Pb.Zn.Fe.Ba)

Oristano harbour

M. Arcuentu

Arbus

Iglesias
Iglesiente

CAGLIARI

St. Pietro Island

Carbonia

Sulcis

St. Antioco Island

N

Scale 1 100 000
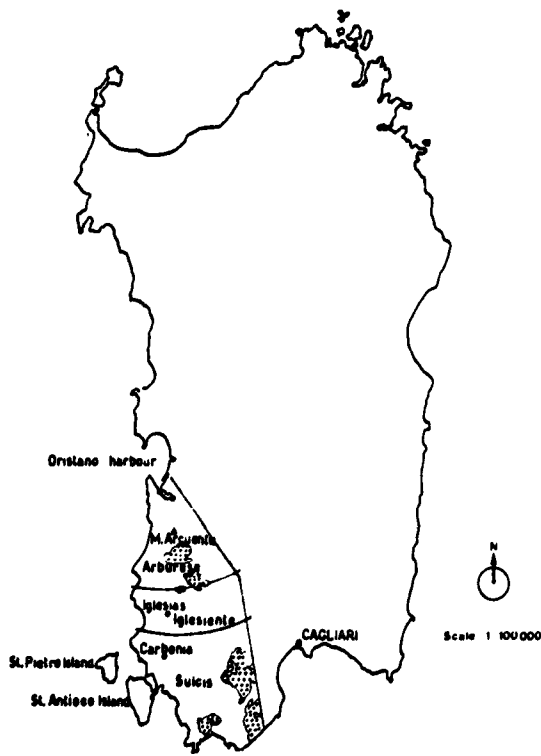
# GEOLOGICAL MAP OF IGLESIAS AREA (SOUTHERN SARDINIA - ITALY)



**: N D E X**

| | Post-paleozoic rocks |
|---|---|

**ORDOVICIAN**

| | Sandstones and slates |
|---|---|
| | Basal breccia (anagenite) of Ordovician transgression |

| (1) Campo Pisano Mine | (Zn,Fe) |
|---|---|
| (2) Monteponi Mine | (Pb,Zn) |
| (3) St. Giovanni Mine | (Pb,Zn) |
| (4) Barega Mine | (Ba) |

**CAMBRIAN**

| | Slates (Cabitza slates) |
|---|---|
| | Calc - shists |
| | Metalliferous complex-(limestone and dolomites of different genesis) |
| | Sandstones whith interbedded calcareous lenses |

| | Quartz and silica of different genesis |
|---|---|
| | Dyabase |

| | Major faults |
|---|---|
| | Strata strike and deep (about 30°-45°) |
| | Reversed strata |
| | Ore localizations |

Fig. 11.28.5

The relations between dolomites and limestones among the Calcare Metallifero are however more complex than suggested by the stratigraphic column above. For example at Monteponi, there are facies variations by which dolomite grade laterally into limestone. Furthermore a yellow ferruginous dolomite has formed locally along fractures at the expense of the limestone (Italminière, 1977).

Most Pb and Zn deposits are lenses or columns or shapeless masses within the Calcare Metallifero where their form and localization are controlled by Caledonian faults. Some of them however, e.g. Funtanaperda and Seddas Moddizzis are located in carbonate lenses within the Georgian sandstones. All were apparently emplaced before the Sardinian phase of the Caledonian orogeny so that they suffered various transformations at that time, especially where they were affected by the erosion and weathering processes associated with the overlying unconformity.

Monteponi (n° 2 in fig. 11.28.5) : "The deposit consists of numerous columns, parallel with each other, and located within the carbonate forma- tions. These columns are subvertical (with a SE pitch) and follow fractures which themselves have the regional strike of N 20 W, while the limestone beds strike about E-W. Their axes are more or less straight and plunge S-E while the limestone beds have a NNE dip. Their horizontal section is elon- gated. The horizontal section of a particular column measures between 200 and 3000 m2.

The columns are mineralized mostly with galena and sphalerite, pyrite being minor but becoming more abundant at depth. They rarely contain gangue minerals so that the mineralization is in direct contact with the host rock. The oxyde (calaminari) ore is often associated with yellow dolomite ...

The distribution of mineralization is obviously controlled by the N 20 W system of fractures (Caledonian fractures). The most important of these fractures are surrounded by an aureole of disseminated sulfides. The localization of orebodies is also influenced by the presence of schitose intercalations, of a predominantly tectonic, rarely stratigraphic, origin, which are conformable with the Caledonian tectonic direction".
(Italminière 1977).

Weathering has caused an intense oxydation down to 15 m above sea level. Below this, oxydation decreases rapidly. But at 100 m below sea level, where mining proceeds at the present time, oxydation may still be observed locally with sizeable quantities of smithsonite, hemimorphite and cerusite (ibidem).

Productions and grades found in the mines of the Monteponi group were the following in 1973 :

| | Output | $Pb_{tot}$ | $Pb_{ox}$ | $Zn_{tot}$ | $Zn_{ox}$ |
|---|---|---|---|---|---|
| | | % | % | % | % |
| Monteponi | 56 000 t | 2.20 | 1.20 | 2.95 | 1.70 |
| Campo pisano-Funtanaperda | 135 000 t | 0.20 | | 7.11 | 0,80 |
| Seddas Moddizzis | 70 000 t | 0.85 | | 5.92 | 2.58 |

On the whole, 1600 t of Pb, 10 000 t of Zn from sulphide ore and 2000 t of Zn from oxyde ore were produced in 1975 but in the past considerably higher yearly productions were achieved with a maximum in 1968 : 9 000 t Pb, 21 000 t Zn from sulfide ore and 17 000 t Zn from oxyde.

At Monteponi itself, reserves are estimated at 2.8 Mt proven (accertato) ore and 1.05 Mt probable ore. These figures include only the part of the deposit which is located above the level of 200 m below sea level. The lower parts have not been taken into account although the orebodies certainly continue downward.

At Campo Pisano-Funtanaperda, reserves amount to 2.7 Mt of proven ore and 0.95 Mt of probable ore. At Seddas Moddizzis, they amount to 0.92 Mt.

Acquaresi, Montecani Masua and Nebida."The orebodies are distributed along three linear zones trending N-S, i.e. parallel to the Caledonian tectonic direction, over a distance of about 7.5 km. These linear zone have a thickness varying from 60 to 200 m and alternate with barren calcareous or schistose zones, whose thickness varies from 30 to 500 m for tectonic reasons. Within the linear zones, successive enrichments have taken place and resulted in the formation of the orebodies, which have a S-E pitch and a cross-section between 1 000 and 5 000 m2. Mineralization consists of predominant sphalerite and galena, with minor pyrite". (Italminière, 1977).

The zone of oxydation extends to the depth of 200 m below surface. The oxydation products are hemimorphite, smithsonite, cerusite and iron hydroxydes.

At the present time, the ore grade is 1.64 % Pb and 4.95 % Zn (among which 3.74 % is oxyde zinc). There is 236 g of Ag per ton of Pb, which corresponds to 3.9 ppm Ag in the ore. Production was 262 000 t of ore in 1975 and should increase so as to reach 800 000 t/year in 1980. Reserves amount to 9.2 Mt proven ore and 3.5 Mt probable ore above the present water table.

Other mines of the same group are

|  | Production in 1975 | $Pb_{tot}$ % | $Zn_{tot}$ % | $Zn_{ox}$ % | Cu % | Ag ppm |
|---|---|---|---|---|---|---|
| San Benedetto | 35 000 t | 1.80 | 3.70 | 2.74 |  | 4.6 |
| Rosas | 20 000 t | 0.10 | 2.01 |  | 0.28 | 3.3 |

Reserves amount to 0.6 Mt proven ore in the former, and about 0.2 Mt in the latter.

San Giovanni (n° 3 in fig. 11.28.5) : "The Cambrian formations host several types of mineralization which can be distinguished as follows :

- sub-conformable mineralizations of lenticular or columnar shapes, dipping ESE and located in the middle part of the carbonate succession. The ore consists of fine-grained ZnS disseminated or in streaks, accompanied by variable amounts of PbS and very little $FeS_2$.

- conformable mineralization consisting of PbS and ZnS in veins and small masses which form a tabular orebody trending E-W and dipping markedly towards the north. The mineralizations are close to the contact between the carbonate succession and the shales.

- unconformable mineralization of variable habit, with prevailing PbS and a quartz-baryte gangue, localized close to the Variscan peneplain, which suggests a definitely supergene origin.

A remarkable feature is the high silver content of PbS with 5 or 6 kg silver per ton of concentrates". (Italminière, 1977).

At San Giovanni, the ore contains 1.5 % $Pb_{tot}$, 2.85 % $Zn_{sulf.}$, 4.00 % $Zn_{ox}$ and 7.5 ppm Ag.

For the whole group of mines, production amounted in 1974 to 255 000 t of ore, corresponding to 4 200 t of Pb, 3 800 t of Zn from sulfide ore and 1 400 t of Zn from oxyde ore; 7 000 t of baryte were produced in addition.

## 11.28.D - SARDINIA   VEIN-TYPE DEPOSITS

Montevecchio is the largest Zn + Pb deposit of the Arburese. It consists of several veins, trending N 65 ° E and dipping 70° NW. These veins are emplaced within a sedimentary succession of Carboniferous shales and sandstones in the vicinity of a granite intrusion. Presumably they follow Caledonian fractures which have been re-opened during the Variscan orogeny. The thickness of the veins may reach 6 to 8 m with an average of about 3 m. Locally a vein branches into a large number of veinlets, giving rise to a stockwork which may be 20 or 30 m wide. The ore consists of galena and sphalerite in a gangue of quartz, ankerite and siderite. Chalcopyrite is   scattered and becomes more abundant in the deeper parts. Minor silver, antimony and bismuth are associated with galena; minor cadmium, gallium, indium, germanium, thallium, nickel and cobalt with sphalerite but their concentrations are most variable. Except for a single zone where oxyde ores were found down to a depth of 100 m, weathering has not greatly affected the veins at Montevecchio.

The ore contains 1.7 % Pb and 3.5 % Zn with about 0.04 % Cu and 13 ppm Ag. In 1975, the deposit produced 180 000 t of ore, which has yielded 3 200 t Pb and 5 500 t Zn. Reserves amount to 3.2 Mt of proven (accertato) ore and 1.7 Mt of probable ore. These figures include the part of the deposit above the lower levels developed at the present time, which are situated at a depth of 300 m under sea level. Boreholes have shown however that the vein continues at greater depths (Italminière, 1977).

Past production for the Montevecchio Group amounts to about 940 000 t of Pb and 730 000 t of Zn.

Sarrabus-Silius also consists of veins emplaced in gneisses and granites of Variscan age.

Presumably these veins follow faults which were already active during the Caledonian orogeny. The ore minerals are fluorite (45 %), galena (2.5 % Pb) and baryte (12 %); gangue minerals are chalcedony, calcite and iron sulfide.

Production reaches 350 000 t per year and reserves are estimated at 10 Mt of proven and probable ore.

Sos Enattos also consists of veins trending N 60 W or NS. The thickness reaches 3 m in places and the length 1.5 to 2 km. The ore consists of sphalerite with minor galena in a gangue of quartz or iron carbonate. There is no production at the present time but reserves are estimated at 0.8 Mt of proven ore at 6 or 7 % Zn.

The veins are located in crystalline schists, presumably of Palaeozoic but post-Cambrian age, in the vicinity of a granite intrusion.

## 11.28.E - SKARN DEPOSITS OF SARDINIA

Funtana Raminosa, in Central Sardinia, consists of skarn lenses with disseminated sulfides of Pb, Zn, Cu and Fe. The lenses are found within a sedimentary sequence of Gothlandian age where beds of black pelitic schists alternate with beds of grey limestone on a scale of a few meters or a few tens of meters. "Metamorphism, and probably metasomatism have brought deep changes in the rocks of this sequence, transforming shales into hornfels of different facies and carbonate into silicate rocks (skarns). Mineralizations are related to the latter ... The areal distribution of the mineralizations is closely connected with the intrusion of igneous rocks as masses and dikes, which have been emplaced in the Palaeozoic succession along the regional tectonic directions N-S and E-W". (Italminière, 1977).

Production amounts to 47 000 t per year of ore at an average grade of 1.0 % Cu, 1.4 % Pb and 3 % Zn. Reserves are estimated at 243 000 t of proven ore and 924 000 t of probable ore.

## 11.28.F - SARDINIA. COMPLEX DEPOSITS.

Some of the Sardinian deposits cannot be classified either as veins or columns or stratiform. They consist of a complex association of orebodies of various shapes.

The Group Buggerru - Su Zurfuru, which is a good example of this type, is described as follows (Italminière, 1977).

"The geological setting can be considered in a complex identical with that already described for the San Giovanni group, with the only difference that in the Buggerru area mineralizations in "quartzites" are particularly well developed. The mineralizations are exclusively Pb-bearing and present some analogy with those of Arenas. At Su Zulfuru on the other hand, the bodies of mixed sulfides (sphalerite - galena) are located at the contact between the Calcare Metallifero, recrystallized, and the Ordovician schists changed into contact skarns, with a clear phenomeno-logy related to contact metamorphism, perhaps due to the presence of granite cupola at a moderate depth ...

In the Buggerru area, vein complexes crop out, located at the con-tact between carbonate formations of Cambrian age and schists of Silurian age. These complexes consist of breccia where fragments of pre-existing rocks are silicified and cemented by silica, with variable amounts of galena and its alteration products. They are locally called "quartzites".

These "quartzites" are constantly developed at the pre-Silurian erosion level and are overlain by the transgression conglomerate or by the Ordovician schists.

At Su Zurfuru on the other hand, the mineralization is located within the metamorphic schists, at a short distance from the contact with the saccharoid limestone.

The deposit displays, as mentioned above, diverse appearances and characters :

- in the quartzites, generally orientated in a NS direction, galena occurs as small crystals disseminated in the quartz, with a distribution which may be either homogeneous or very irregular.

The hangingwall of the deposit, always rather clearly shown, con-sists of Silurian schists while at the footwall the quartzites progres-sively grade into the dolomite through a silicified transition zone.

The latter formation may be affected by erosion features of karstic type, and hosts modest amounts of iron carbonate (Monserrau - Su Sollu).

- in the waxy limestone, striking NS, interesting calaminar bodies are found which at depth grade into low-grade sulfide zones. They consist almost exclusively of smithsonite, associated with variable amounts of sphalerite and galena strongly corroded by their oxydes (Malfidaño - Planu Sartu).

Always in the waxy limestone but at a higher stratigraphic level, there is a small mineralization of mixed sulfides, extending along a system of NE-SW fractures (Gutturu Pala)".

In 1974, the group Buggerru - Su Zurfuru produced 115 000 t of ore at 1.10 % $Pb_{tot}$, 3.00 % $Zn_S$, 5.00 % $Zn_{ox}$, and 5.5 ppm Ag. The reserves amount to 6.4 Mt proven ore and 1.3 Mt probable ore. Oxyde ores account for 60 % of these reserves, and mixed sulfides for 25 %; the remaining 15 % consists of galena ore devoid of Zn.

Arenas is also a complex deposit which consists in part of veins and in part of stratiform bodies. It is also found in the vicinity of a granite intrusion. In 1974 it produced 150 000 t of ore with a few percent Pb as sulfide or as oxyde. Reserves are estimated at 1.3 Mt of proven ore and 0.3 Mt probable ore.

## 11.28.G - TUSCANY

In this part of Italy, the oldest sedimentary formations that have been recognized consist of slates and other detrital rocks interbedded with lavas and tuffs. They belong to the Upper Carboniferous and Permian systems and were deformed at the end of the Variscan orogeny.

This Palaeozoic basement was eroded in Permian times. The subsequent geological history is described as follows :

"Some time during the Ladinian, sedimentation starts with terrigenous deposits more or less argillaceous (verrucano) being deposited on the Palaeozoic basement ... The environment of deposition varies from deltaic to littoral with evaporitic episodes in mid-Triassic times and grades upward,

through the limestone-evaporite complex of the Norian (Calcare Cavernoso),
into definitely open-marine sediments of Rhaetian age. The succession goes
on uninterrupted until the Palaeogene.

After the appeninic orogenesis, the upper part of this succession
underwent an eastward translation during the Tortonian, while the lower
part remained uncovered. Both parts were then successively covered by the
flysch of the Ligurian nappe.

More recently this complex was faulted and along the faults minera-
lization was emplaced and gave rise to the deposits.

To complete this overview of the regional geological evolution, it
should be mentioned that, from Late Miocene times the substratum of this
part of Tuscany was affected by the development of igneous activity.
Locally this has given rise to the intrusion of bodies which are now out-
croping or to the intrusion of vulcanites. Elsewhere on the other hand, it
resulted in the formation of thermal anomalies ..." (Italminière, 1977).

The Fenice Capanne deposit consists of a quartz vein, 10 m thick on
the average, which at the surface is observed in the Ligurian nappe, but at
depth runs across the Calcare Cavernoso and the underlying Triassic shales.
Lenses of evaporites are known in the last two formations. The vein occupies
a large tension fracture with a downthrow of 200 or 300 m.

In the southern part of the vein, sphalerite and smaller amounts of
galena, pyrite, chalcopyrite and arsenopyrite are found in a gangue of quartz
and carbonate. In the central and northern parts, chalcopyrite prevails and
is found in skarns with small amounts of bismuthinite, arsenopyrite, sphale-
rite and galena.

At the present time, the ore grade is 5.20 % Zn, 1.11 % Pb and 0.29 %
Cu. In 1976, the production was supposed to reach about 150 000 t of ore
yielding 9 750 t of sphalerite concentrate, 1 625 t of galena concentrate,
825 t of mixed sulfide concentrate at 10 % Cu, and 3 900 t of pyrite. In
1980, the deposit should produce 16 000 t of chalcopyrite, 12 000 t of spha-
lerite, 2 000 t of galena and 7 000 t of mixed sulfides and pyrite.

Reserves are as follows :

above drainage level :

0.900 Mt mixed sulfides ore (mostly galena and sphalerite)

below drainage level :

4.860 Mt proven chalcopyrite ore

1.485 Mt probable chalcopyrite ore

1.350 Mt proven mixed sulfide ore

0.445 Mt probable mixed sulfide ore         (*)

## 11.28.H - THE SOUTHERN CALCAREOUS ALPS DISTRICT

The three deposits currently mined in the Southern Alps of Italy
i.e. Raibl, Salafossa and Gorno belong to a province which extends into
Jugoslavia with Mezica and into Austria with Bleiberg - Kreuth (fig. 11.28.3).
In the province, the thick limestone-dolomite succession formed in Middle
Triassic times is the major ore-bearer. More precisely, within this succession
which may reach 2 000 m in thickness, four horizons may be mineralized
(fig. 11.27.6 after Schneider, 1964)

- Upper Anisian   - maximum 40 m in thickness

- Lower Ladinian - maximum 50 m in thickness

- Upper Ladinian - maximum 200 m in thickness

- Lower Carnian   - from 7 to 75 m

Well developed reef and Lagoon (fig. 11.28.7) complexes are found in
the limestone-dolomite succession, as well as volcanic rocks. Presumably
both have played a part in the genesis of the deposits although ore is not
always directly associated with the latter. Alpine tectonics has greatly
affected the geological structure of all the area but has not contributed to
the emplacement of orebodies.

Of course each deposit has its own geological environment (fig.
11.28.8). The following is taken from the files prepared by Italminière
(1977) :

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(*)   At Campiano, deep drilling has recently found mineralisation over 40 m
thickness, grading 12 % combined Cu-Pb-Zn metal  (note added in March 1978).

| AREA / STAGES | Eastern Alp. Nappes of Graubünden (Switzerland) | Northern Limestone Alps | | Southern Limestone Alps | | | |
|---|---|---|---|---|---|---|---|
| | | N-Tyrolian and Bavarian A. N. range | S. range | E. Gailtal Alps | W. Giulian Alps | Dolomites | Bergamasc Alps |
| RAETIAN | Kossen Beds | reefs / Kössen Beds | | Raetic calcareous series and shales ? | | | |
| NORIAN | Hauptdolomit | Plattenkalk \Dochstein \Limestone | | Hauptdolomit | | Dochstein Dolomite | Hauptdolomit |
| CARNIAN | Raibl Beds | | | Raibl Beds | | | |
| LADINIAN | ① Arlberg Limestone / Arlberg Dolomite | ③ Wetterstein Limestone and Dolomite / Partnach Shales ④ ⑤ | | ⑦ Wetterstein Limestone and Dolomite ⑧ | Porphyries / Schlerndolomit | | Esino Limestone ⑩ |
| ANISIAN | ② Trochiten Dolomite | Alp Muschelkalk ⑥ | | Alpine Muschelkalk | | Sarl Dol. ⑨ | Alpine Muschelkalk |
| SCYTHIAN | Alp. Buntsandst. | Werfen Beds | | Werfen Beds | | | "Servino" |

H.J. Schneider, 1963

① A ■■■ B vvv C ◁▨▷ D ◁▥▷ E

**Fig.11.28.6.** - Sulfide mineralization, volcanism and facies changes in the Triassic of the <u>Calcareous Alps</u> (after Schneider, 1964).

Typical deposits of the different areas :

1. : Bleiberg-Ramoz (Graubünden, Switzerland)
2. : Silverberg-Davos ( " " )
3. : Säuling-Füssen (Bavarian Alps)
4. : Lafatsch-karwendel (Northern Tyrolean Alps, Austria)
5. : Mursee-Mieminger Massif (id)
6. : St.Veit-Heiterwand (id)
7. : Bleiberg-Kreuth (Eastern Gailtal Alps, Austria)
8. : Raibl, Cave del Predil (Giulian Alps, Italy)
9. : Auronzo (Eastern Dolomites, Italy)
10. : Gorno-Dossena (Bergamasc Alps, Italy)

B. : Ore bearing units.

C. : weak evaporitic facies (deposition of dolomite and anhydrit gypsiferous beds) .

D. : indications of volcanism (tuffaceous shales ; agglomeratic breccias).

E. : tuff layers, porphyritic and basaltic eruptions.

FORE REEF BASIN    BARRIER REEF    BACK REEF (LAGOON)

< hypersaline and stagnant water >
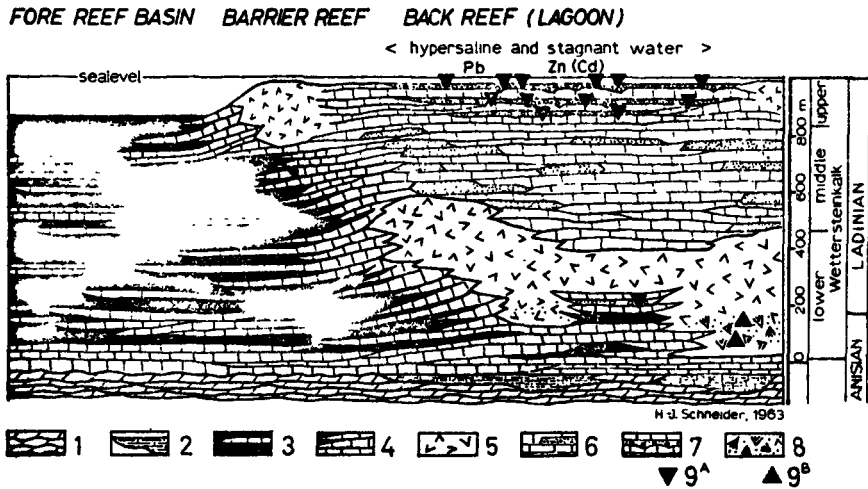


## Fig. 118.7.

The evolution of Ladinian plateau reef type, diagrammatic section.

1. = uppermost "Alpine Muschelkalk"; wavy-clumpy, thinly bedded bituminous limestone with chert nodules ;
2. = andesitic green tuffs (ash and crystal tuffs, few lapilli) with thin layers of marl and limestone ;
3. = "Partnach Mergel", clayey marls, shales with lenses of layered limestone (like 4)(Ladinian basin facies) ;
4. = "Partnachkalk", bituminous, marly, layered limestone, units (Ladinian basin facies) ;
5.-8. = different types of "Wettersteinkalk" (Ladinian reef facies) ;
5. = massive limestone and dolomite, partly cavernous or relictic patterns of bioherms (often coral colonies) ;
6. = well layered grey limestone (mainly calcarenite) with debris and colonies of algae (Dasycladacee), single algal patch reefs ;
7. = predominantly thinly layered limestone with intercalations of the "Sonderfazies" in special sequences (back reef units, tufaceous marls, slump structures, ore sediments etc) ;
8. = late diagenetic alteration of the cavernous reef body by recrystallization of dolomite, quartz and different Fe-dolomites ;
9A = Pb-Zn sulfide ores with sedimentary fabrics ;
9B = Pb-Zn sulfide ores primary enriched in metasomatic replacement bodies, locally associated by small amounts of Cu-Sb-As minerals

(after Schneider, 1964)
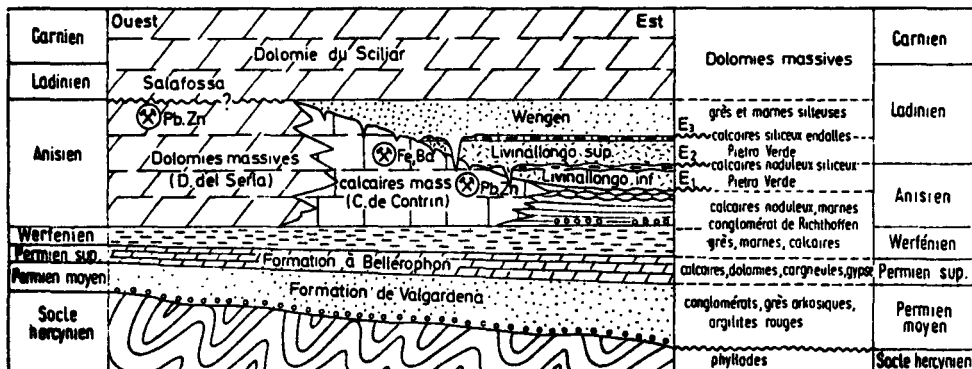


## Fig. 118.8. - Schematic stratigraphical relationships
among Permian and Triassic formations in
the Salafossa area (Lagny, 1975)

Raibl : The economic mineralization is located in the upper part of the
Dolomia Metallifera (Upper Ladinian), consisting of massive, limestone-
dolomite reefs almost devoid of fossils, where this unit is overlain by
the bituminous and dolomitic Raibl beds (fig. 11.27.9). The hangingwall
is located in the lower part of the latter formation. The footwall is in
the tuffaceous limestone (Buchenstein), which is interbedded in the lower
part of the Dolomia Metallifera. Further down, there is an interval of
tuffs and ignimbrites (vulcanites of Rio Freddo), corresponding to the
transition with Anisian beds.

The deposit consists of stratiform bodies in the Raibl beds and
in columnar or vein-type bodies in the Dolomia Metallifera (fig. 11.28.10).
The latter are developed along large faults which are a major structural
control of the deposit.

Sphalerite and galena are the ore minerals. Pyrite is present but
the gangue is mostly dolomite. In sulfide ore, the grade is 4.40 % Zn and
0.54 % Pb. In oxyde ore, it reaches 5.90 % $Zn_{ox}$, 1.70 % $Zn_S$ and 1.15 % Pb.
Yearly production amounts to 302 000 t of sulfide ore and 85 000 t of
oxyde ore, which together yield :

| | |
|---|---|
| 22 000 t of sphalerite | concentrate at 54 % Zn |
| 9 000 t of oxyde | concentrate at 38 % Zn |
| 1 000 t of galena | concentrate at 72 % Pb |
| 900 t of oxyde | concentrate at 50 % Pb |

Reserves are as follows :

| | | |
|---|---|---|
| sulfide ore | 3.5 | Mt proven |
| | 1.0 | Mt probable |
| oxyde ore | 1.25 | Mt proven |
| | 0.38 | Mt probable |

Gorno : The footwall is again in the calcareous dolomites of the Upper
Ladinian and the hangingwall in the Raibl beds. Between these two forma-
tions a well bedded grey limestone, 50 or 60 m thick, is the major ore-
bearer. Some of the ore is stratiform and associated with thin mylonitized,
laminated and altered horizons considered as tuffs, and interbedded with
the grey limestone.

In addition lenticular and columnar orebodies, roughly parallel with each other, are found in cavities and breccias developed in the dolomite along the crests of anticlines or along faults.

Yearly production amounts to 140 000 t of ore with an average grade of 2.60 % $Zn_S$, 1.80 % $Zn_{ox}$ and 0.85 Pb. This yields eventually 4 500 t Zn, 950 t Pb and 400 kg Ag. Reserves contain 1.6 Mt proven ore, 0.9 Mt probable ore and 1.0 Mt possible ore.

Salafossa : The deposit consists of a unique orebody elongated parallel to and in the vicinity of a fault. The length is 800 m, the height is 50 to 100 m in the parts that are mined and the width goes from 80-200 m. This orebody is found in the Anisian dolomite. It consists of a tectonic breccia, obviously affected by dissolution and collapse phenomena, and cimented by sphalerite, pyrite and galena. Sulfide sediments, deposited on the bottom of cavities, are also observed, as well as concretions and stalactites (fig. 11.28.11).

Production amounts to 600 000 t per year of ore at 0.7 % Pb and 4 % Zn. Reserves are estimated at 10 Mt of ore.
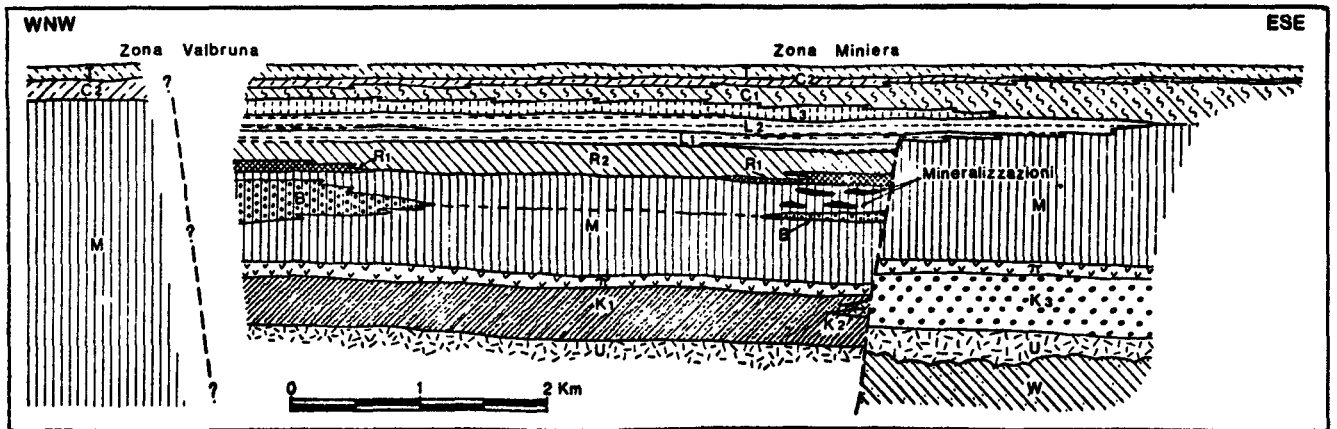
Fig. 11.28.9. – Schematic stratigraphical relationships in the area around Raibl (Aresi Rota and Vailati, 1976)

$C_1$ and $C_2$ : <u>Calcare di Rio Conzen</u> (Carnian)

$L_1$ to $L_3$ : <u>Formazione di Rio del Lago</u> (Carnian). Mostly marls.

$R_1$ and $R_2$ : <u>Calcare del Predil</u> (Lower Carnian)

         $R_1$ : Laminated bituminous dolomite

         $R_2$ : Limestone and magnesian limestone

M and B : <u>Dolomia metallifera</u> (Ladinian – Carnian).
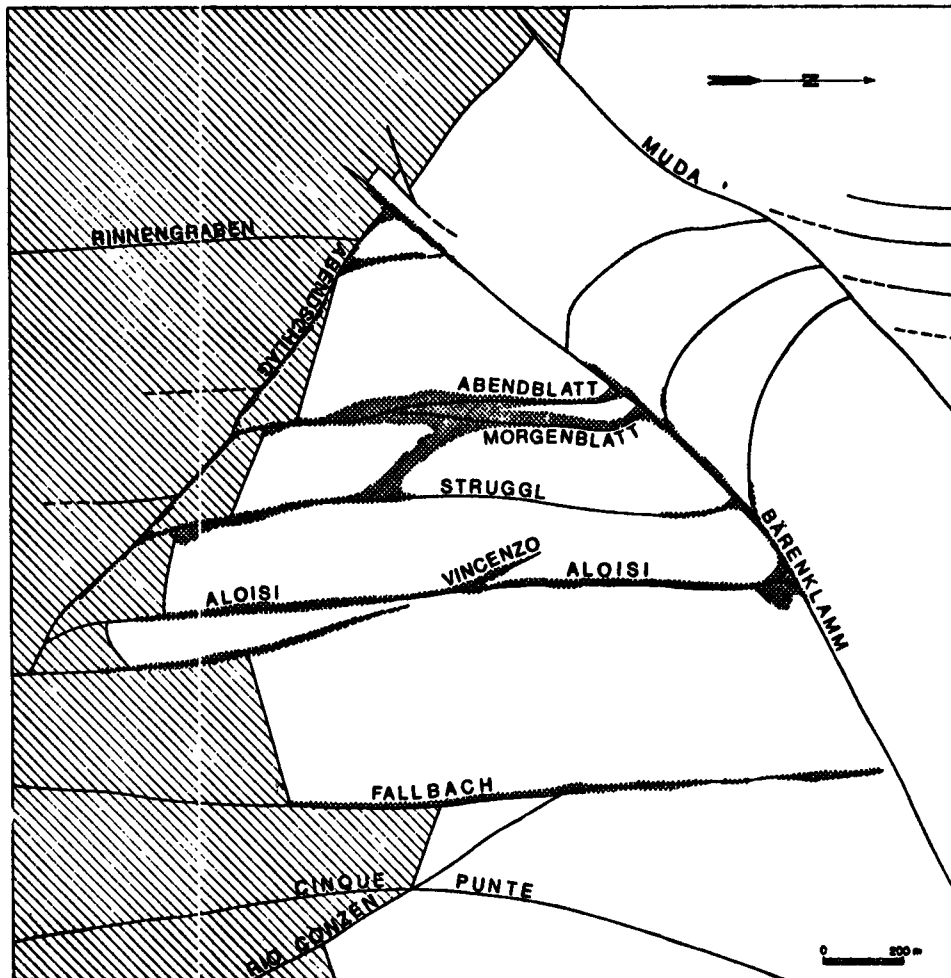
Fig. 11.28.10 - Schematic representation of the
                fracture system and associated
mineralization.

        Oblique shading : Raibl beds
        White : Dolomia Metallifera
        Cross-hatched : orebodies

After Arisi, Rota and Vailati (1976)
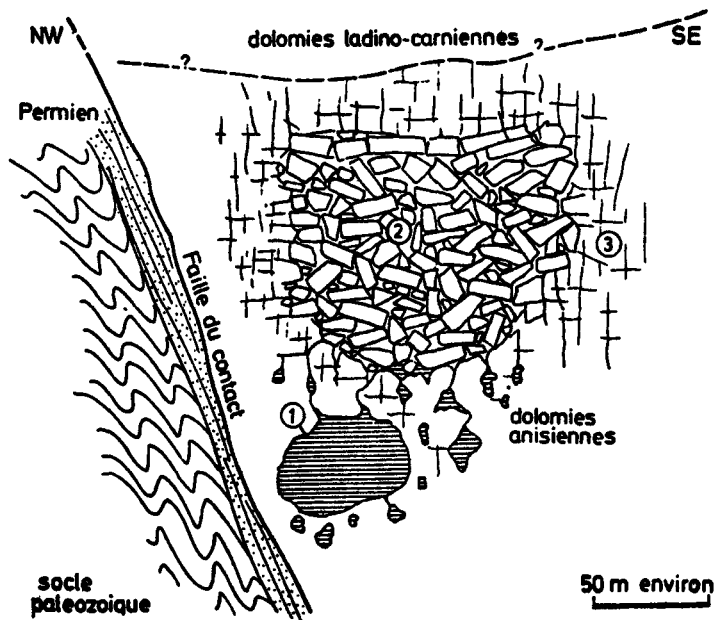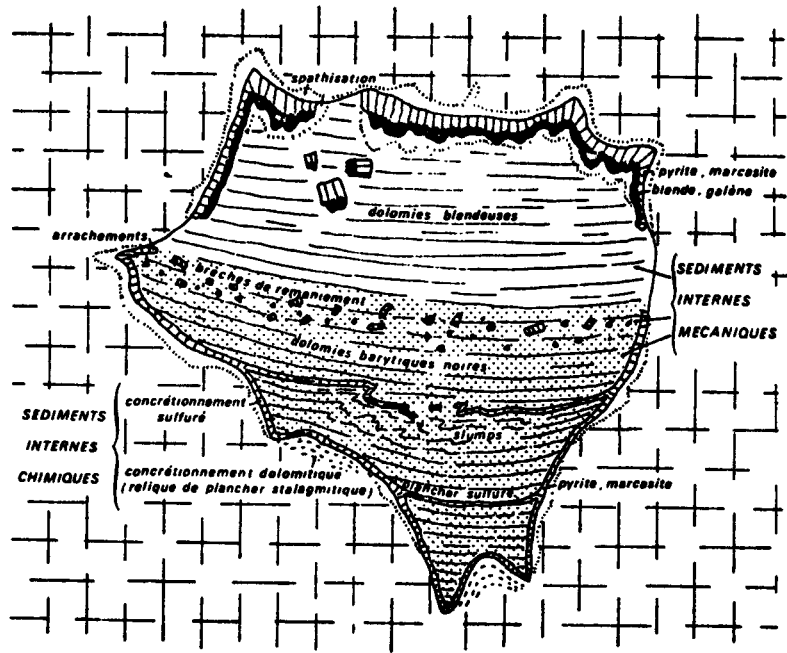
Fig. 11.28.11. - (after Lagny 1975)

Above :   Schematic representation of structure inside a cavity filled
          in part by mechanical sedimentation, in part by chemical
          precipitation on the walls.

Below :   Schematic and idealized cross-section through the Salafossa
          deposit.

          1. cavities filled by sedimentation of sulfides and dolomite
          2. collapse breccia cemented by concretionary sulfides
          3. barren dolomite of the wall rocks.

11.28.J - <u>AXIAL ZONE OF THE ALPS</u>

The geology of this area is very complex and still the subject of much controversy. The <u>Monteneve</u> deposit is found in metamorphic rocks; biotite schists with garnet, staurolite and kyanite, which form the <u>Monteneve Series</u>. It consists mainly of three veins : one of them, striking N 85° E and dipping 25° or 30° northward, is conformable with the enclosing schists; the other two are orientated NE and NW. All are much affected by later deformation.

Yearly production amounts to 40 000 t of ore at 3.80 % Zn and 1.40 % Pb which yields eventually 1 250 t Zn, 460 t Pb, 500 kg Ag and 4 470 kg Cd. The zinc concentrate contains some Cd. Reserves are estimated at 0.3 Mt proven ore and 0.25 Mt probable ore.

11.28.K - <u>SUMMARY</u>

The large deposits found in the <u>Southern Calcareous Alps</u> of Italy belong to a rather well defined type, the controls of which are broadly known.

In Sardinia, several types are present and the controls are very diverse. The province is mostly characterized by the abundance and variety of Zn and Pb deposits.

The other Italian districts, such as Tuscany and the <u>Axial Zone of the Alps</u> are less important producers but deserve more study.

11.27.L - <u>BIBLIOGRAPHY</u>


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## 11.29 - CONCLUSIONS

### 11.29.A - DIVERSITY OF ZN AND PB DEPOSITS

From the survey that has just been made, the first conclusion to emerge concerns the large diversity of sizes, shapes and geological environments of Zn and Pb deposits within the EEC countries. A number of types and sub-types are represented. Moreover considerable variability is observed within each type or sub-type; for example the three Irish deposits of Navan, Tynagh and Silvermines display significant differences although they have much in common.

From an economical point of view, this diversity is both an advantage and an inconvenient : an advantage because the possibility of discovering new deposits is not restricted to one very peculiar geological environment ; an inconvenient because, during exploration, a large number of guides have to be considered.

This large diversity is one reason why exploration for Zn and Pb is so difficult, as compared with exploration for substances such as coal and oil. It is also one reason why the deposits of these metals still give rise to so much controversy among experts. Each one of them results from a particular succession or conjonction of geological phenomena, so that statistical studies are of little help when one tries to unravel their genesis. It is not surprising therefore that considerable disagreement remains about their processes of emplacement and the geological features which control the localization of orebodies. During exploration compaigns, a geological feature which is fortuitously associated with one known deposit may be erroneously considered as a guide to ore while the true guides remain unrecognized. Unnecessary drilling may result from such mistakes.

It is suggested that a major research effort be undertaken to determine beyond reasonable doubt which processes are responsible for every major type of Zn and Pb deposits, how the different processes can be diagnosed and what geological features control each of them. At the present time research aiming at answering these questions is in progress in EEC countries. However in most cases, cross-examination of the evidence is not sufficiently severe.

Furthermore conclusions can rarely be checked by lack of means; it is for example rarely possible to drill holes specifically for research purposes. As a result there remains a considerable amount of uncertainty, due to the many hypotheses and theories which remain unverified.

## 11.29.B - THE NEED FOR MORE EXCHANGE OF INFORMATION

Some types or sub-types of deposits have so far been found in only one of the EEC countries or even in a particular district of one of them. For example no deposit similar to Navan, Tynagh and Silvermines has been found outside Ireland. Flats comparable with those of the Northern Pennines have not been recognized outside England. There are no Gorno or Raibl outside the Southern Calcareous Alps although well developed reef complexes occur in several other districts within EEC countries. Veins of the August-Victoria type have not been found outside Germany although coal bearing successions of the same age extend through the Netherlands, Belgium, Northern France and Great Britain. Until recently, marine Devonian strata seemed devoid of stratiform deposits outside Germany although they occur in rather wide areas of Belgium, France and the British Isles.

Of course each district within each country has its own distinctive geological features so that one cannot expect to find two identical deposits. The question arises however whether in each country exploration has been so much orientated by local experience that opportunities have been neglected.

With regard to the work done during the 19th and the beginning of the 20th century, the answer to this question is positive. Since then, much information and experience have been exchanged. In this regard however, there remain difficulties that are specific to the geology of ore deposits.

As a rule, a mine geologist has gathered considerable information about his deposit since he has been able to make observations over a long period of time while mining operations are in progress. However many of his observations are never published, and are eventually lost because most other geologists have access to the mine only for short visits.

It should be pointed out also that in most cases many years elapse between the time when a new orebody is discovered and the time when detailed information is published about it in scientific journals.

Such delays are partly due to confidentiality problems. They are also due to a lack of incentives : mine geologists are not always encouraged to publish their observations; visits of mines by foreign personnel are a source of inconvenience for the management; part of the information which eventually becomes available is published by university teachers and doctorate students motivated by academic rather than by economic considerations.

On the whole, the exchange of information on mined deposits and newly discovered orebodies is slow, restricted and incomplete. The slowness may prevent critical examination altogether since, in an operating mine, a given area remains accessible for a limited time only. Differences of opinion result which cannot be eliminated as they can in experimental sciences by repeating the experiment under the control of independent observers. Such differences of opinion are often in relation with "schools of thought", which are not unfrequently national in character.

Such a situation is clearly most unsatisfactory and most unfavorable to the progress of the strategies and techniques needed to discover new mineral resources. It is suggested that a major effort be made to improve and accelerate the collection, critical examination and publication of all significant information which becomes available either through drilling or through underground work in mines. This suggestion implies that visits of important deposits are arranged periodically for a small number of experts belonging to different countries. These experts should recommend in each particular case what research work should be carried out in order to check and interpret the new data and where this research work can best be carried out.

It is also suggested that mine geologists are given the possibility of taking sabbatical leaves in order to write and publish their observations.

11.29.C - MAJOR GEOLOGICAL ENVIRONMENTS OF ZN AND PB DEPOSITION

We shall refer here mostly to two major geological environments. Admittedly each of these is defined very schematically. Furthermore these environments grade into each other. As a result some arbitrariness cannot be avoided when it comes to classify a particular district. A less simplistic classification would also, however, raise problems while losing the advantage of simplicity.

In the following the term "sequence" is used to designate major informal rock-stratigraphic units traceable over large areas.

These two major geological environments correspond broadly to the subdivision made between "volcanogenic deposits" and "strata-bound deposits" in the "multiannual R and D programme in the field of primary raw materials" of the European Economic Community. They are :

a) Extensive sedimentary successions where limestones and dolomites prevail (carbonate sequences). As a rule, such successions were deposited in shallow seas extending over more or less stable platforms. Over vast areas therefore they lie almost horizontally on the basement or are underlain by mostly non-marine sandstones and shales which rest themselves on the basement. However they may also have been deposited beyond the platform over marine detrital successions. In the latter case especially, they have become part of folded miogeosynclinal successions.

b) Thick and extensive marine detrital successions with locally large volcanic contributions (volcano-detrital sequences). These successions, often much deformed, belong to the eugeosynclinal parts of orogenic belts. They may contain lenticular formations of shallow water limestones and dolomites although these rocks are not prevalent components of the sequence.

Each of these major geological environments occupies wide areas within the Community. The latter includes parts of the Caledonides in Greenland, in the British Isles and in Belgium, parts of the Variscides in several EEC countries. The former includes the Carboniferous Limestone belonging to the epi-Caledonian platform of North-Western Europe, the Triassic and Jurassic carbonate succession of France and Italy, the Marmorilik succession in West Greenland, the Upper Permian limestones of East Greenland and the Cambrian carbonate succession of Sardinia. Of these two environments the former has revealed the most fertile since almost 20 Mt of metal has been mined or identified in the Carboniferous Limestone alone.

Zn and Pb deposits are also found in a number of other environments :

a) intrusions of acid magmatic rocks and their aureoles. In the Americas,
   this environment, corresponding to Bauchau's types 6 and 7 (see section
   11.21), supplies much Zn and Pb with considerable amounts of silver in
   addition, but within EEC countries it has not proved very productive.
   In particular skarn and replacement deposits, so characteristically
   found in limestones intruded by magmatic rocks in Western North America,
   are few in EEC countries, where obviously the conditions required for
   their formation have not been fulfilled on such a large scale.

b) sandstone formations overlying unconformities. Zn and Pb deposits are
   known in Triassic sandstones and conglomerates in East Greenland, in
   Germany and France. They are mostly low grade, metal sulfides being
   found as a component of the ciment between sand grains. However since
   they may be quite extensive, they constitute resources of considerable
   interest. These deposits must be controlled in part by host-rock
   porosity, which in turn depends on palaeogeography. Some of them are
   also controlled by faults.

c) black shales deposited on anoxic sea bottoms. This type of deposit also
   constitutes an interesting low grade resource for the future.

    These three environments and especially the last two have some po-
tential. However with regard to the research suggested in sections 11.29.A
and B, emphasis should be put on carbonate and volcano-detrital sequences,
which are more widespread and where deposits with a large tonnage of high
grade ore are more likely to be found.

## 11.29.D - DEPOSITS FOUND IN CARBONATE SEQUENCES

These deposits have been the subject of much study since many of them are found in Europe and in North America. They are often referred to as belonging to the Mississipi Valley type if the beds have remained horizontal and to the Alpine type if they are folded; but other definitions of these two types are in use (see for example Sangster, 1976).

There is clearly much variation among the deposits belonging to either one of these groups. Individual orebodies may be more or less strati-form, or columns, pipes, veins, lenses, etc ... The Zn/Pb ratio varies widely. Copper and silver are occasionally present in addition to Zn and Pb although in most cases the ores are not rich in these elements. Iron sulfides, barite, fluorite may be present or even predominant. The geological setting is also quite varied : "Although many districts can be shown to be spatially related to large-scale sedimentary features such as reefs, facies changes, basin margins, and basement topography, the major factor necessary for development of deposits of this type appears to be the presence of a thick carbonate sequence" (Sangster, 1976). Occasionally mine-ralization is also found in the detrital formations underlying or overlying the carbonate sequence (the Old Red Sandstone at Silvermines, the Triassic sandstones at Largentière, and the Millstone Grit in the Northern Pennines).

Callahan summarizes the features of the Mississipi Valley type as follows (fig. 11.29.1) :

They are "spatially located in practically horizontal carbonate beds commonly below a shale or shaly lime bed in the following palaeophysio-graphic settings ... :

A) Above an unconformity in such sedimentary environments as reefs and facies changes (A-1), compaction or drape structures (A-2), and in pinch-outs, talus or landslide breccias (A-3), all of which are distri-buted relative to the topographic relief on the unconformity ... In this type of localization the rocks below the unconformity generally are not carbonates.
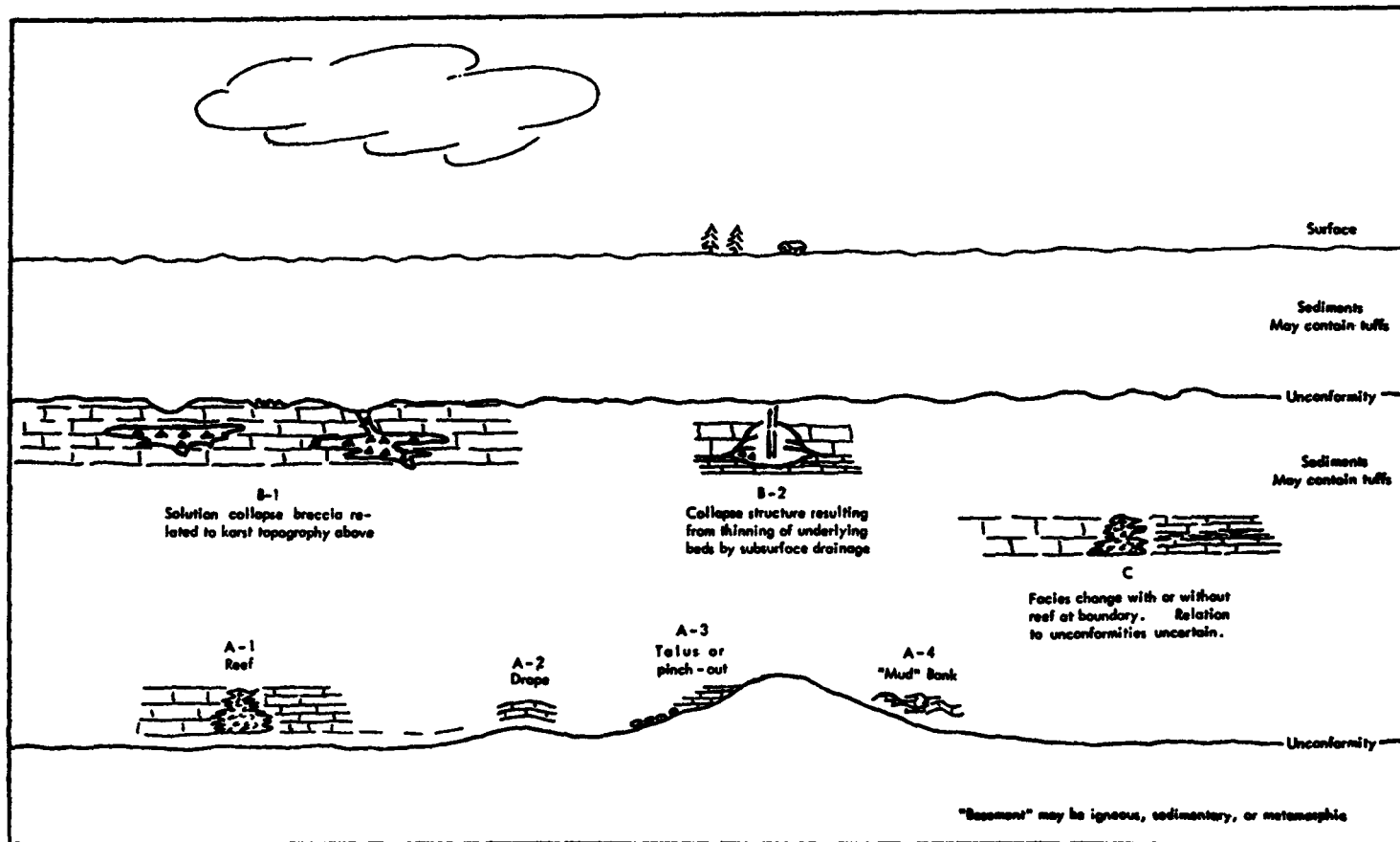
**Fig. 11.29.1.** - Idealized vertical section illustrating the range of geological situations in which limestone-lead-zinc deposits are known to occur. (From Callahan, Econ.Geol.Monograph n° 3, 1967)

B) Below an unconformity either in solution collapse breccias (B-1) related
to a karst topography on the surface of unconformity, ... or in collapse
structures (B-2) resulting from the thinning of underlying beds by sub-
surface drainage system related to the unconformity ...

C) At a facies change in the formation or between basins of deposition".

Although in his paper Callahan refers explicitly to North American
deposits, his descriptions apply to European districts as well. However in
addition to Callahan's subtypes, a number of fault controlled orebodies are
found within the EEC countries. The precise role that faults play in the
genesis of a particular deposit is often subject to controversy but, in a
general way, three types of faults have been suggested as guides to ore :

a) basement fractures, initiated before deposition of the carbonate se-
quence and having remained active during deposition.

b) fractures which do not penetrate into the basement and have been initia-
ted during deposition of the carbonate sequence.

c) fractures which are entirely younger than the carbonate sequence.

All these faults are steep dipping. Most are normal but at Navan the B
fault is a strike slip one. As a rule, deposits located in the lower part
of the carbonate sequence, at a short distance above the basement unconfor-
mity are controlled mostly by faults of the first type; those located at
the top of the carbonate sequence mostly by faults of the third type.

## 11.29.E - DEPOSITS IN VOLCANO-DETRITAL SEQUENCES

Rammelsberg and Meggen are the only large deposits which have been
mined in the EEC countries within this geological environment. However,
other occurrences being studied at the present time in the Pyrenees, seve-
ral new discoveries made in Brittany (perhaps also in Belgium), and the
presence of Zn and Pb at Avoca and Parys Mountain suggest that a conside-
rable undiscovered potential may exist in the volcano-detrital sequences
of Palaeozoic and Proterozoic age which crop out in so many areas within
the EEC countries. Is is known that a large part of the world's Zn and Pb
has been found in this type of environment (corresponding mostly to
Bauchau's type 1) on other continents.

The deposits referred to in this paragraph form a highly varied group. They usually have more Zn than Pb and contain copper as well as significant amounts of silver and gold. Several other chemical elements may be present : Sb, Cd, Se, Te, Co, Ni, Bi, Hg, Sn. Barite is abundant in some of them and pyrite in practically all. The orebodies are stratiform or veins or stockworks but they are often intensely deformed, stratiform orebodies being typically folded. They may have been affected by metamorphism. A most interesting feature of this group of deposits is the enormous size of some of them (30 Mt of metal at Broken Hill, Australia).

The reader is referred to Stanton (1972 and 1976) and to various papers in Wolf (1976) for descriptions of the different types of deposits found in volcano-detrital sequences of orogenic belts, and for a more extensive bibliography.

As a result of the variety observed within the group, the geological controls of these depostis are difficult to define in a general way. In a recent review paper (in Wolf, 1976, vol. 6), Solomon summarizes the features of the "massive" type as follows :

"(a) They occur most commonly in calc-alkaline volcanic rocks, and particularly, but not exclusively, in rhyolitic fragmental types.

(b) They also occur in oceanic and low-K tholeiites, and in addition are found in sedimentary successions containing little or no evidence of volcanic activity.

(c) There are no exclusive relationships between ore-type (defined by metal ratio) and host-rock type, except that lead-rich deposits most commonly overlie rhyolites and never overlie wholly basaltic, or ophiolitic, terrains.

(d) The orebodies in any one field tend to lie on one (in some areas more than one) stratigraphic horizon. This commonly has no unusual features apart from the mineralization and associated exhalites, and the nature of the rocks above and below may vary within one orefield.

(e) The volcanic rocks intimately associated with the ores generally have no distinctive primary features compared to those in the rest of the succession.

"(f) The deposits commonly occur in terrains intruded by acidic plutons, but appear to have no systematic relationships to the plutonic rocks. These may have intruded close to or at some distance from the deposits and be more or less the same age, or later.

(g) The limited evidence available indicates that deposits in ophiolites occur at or near the base of the pillow lava sequence and overlie dolerite dykes and gabbroic intrusives.

(h) They commonly lie on major faults or within fault zones.

(i) The lack of detritus and massive nature of the orebodies, and the lack of major changes in patterns of vulcanicity and/or sedimentation before and after mineralization, all point to rapid deposition of the sulphide masses. This contrasts with the field evidence for the Sullivan-Mt. Isa group of deposits.

(j) Many deposits have pipe-like stockwork zones beneath the massive ore that extend downwards for several hundred metres and have diameters less than that of the orebodies (e.g., Sangster, 1972). They are marked by low-grade mineralization and hydrothermal alteration. Other deposits overlie much wider zones of alteration that extend beyond the ore limits (e.g., Mt. Lyell, and the Hokuroko area; Iijima, 1974).

(k) Massive sulphide deposits seldom occur singly and have characteristic grouping patterns. For example, there are twelve major orebodies in a 50 km zone along the northern flank of the Troodos complex ...".

It is generally assumed that a submarine hydrothermal system where waters move by convection or otherwise through sediments, volcanics and intrusives, is required for this type of deposits to form. Guides to ore therefore consist mainly of faults active during deposition, hydrothermal alteration of the surroundings and sedimentation of exhalative rocks such as these iron-manganese oxyde layers which have been deposited around some orebodies and more or less simultaneously with them. Palaeogeographical features such as reefs, which may have been responsible for the formation of restricted basins within the sea, may also be helpful although they cannot be expected to be frequently associated with the deposits.

From the survey presented in sections 11.22 to 11.28, at least four provinces in the EEC countries appear to contain favorable volcano-detrital sequences :

- the <u>Southern Caledonides</u> in Ireland and perhaps Great Britain (Ordovician).

- the <u>Armorican Massif</u> (Lower Devonian and Brioverian successions).

- the <u>Variscides</u> in central Germany and in Belgium (Middle and Upper Devonian
  succession).

- the <u>Pyrenees</u> (Ordovician and Lower Devonian successions).

Presumably a particular set of guides to ore will be found in each
one of these provinces. It would therefore be particularly useful to study
some of the newly discovered deposits from that point of view, in addition
to Meggen and Rammelsberg about which much is already known.

## 11.29.F - PROCESSES OF EMPLACEMENT OF ZN AND PB DEPOSITS

The problem of palaeogeographical and tectonic guides to ore in
both carbonate and volcano-detrital sequences can also be approached from
consideration of emplacementprocesses. At least four such processes are
active :

a) chemical precipitation of sulfide and gangue minerals in open fissures,
   pores and cavities (<u>cavity filling</u>).

b) deposition of a sulfide bearing mud on the bottom of the sea.

c) fixation of metal in a sulfide bearing mud on the bottom of the sea.

d) replacement of carbonate or other minerals by sulfides.

There are simple deposits resulting from a single process and complex de-
posits resulting of several processes. The relative importance of these
four processes, especially in the formation of complex deposits, is a much
debated subject.

The host-rock features which control replacement are poorly under-
stood. Limestone beds are known where shells and other skeletons are
replaced by sphalerite without the calcite matrix being altered, which
suggests that rather subtle differences come into play.

Guides to replacement ore are therefore only empirical : it is known that in a given district a small number of beds, termed "favorable", may be replaced.

In recent years there has been a tendency to dismiss replacement as an important ore forming process. Such an attitude of mind if unfounded may cause neglect of exploration possibilities. It would therefore be useful to determine, by commissioning the appropriate research, in what conditions replacement orebodies are formed, especially in carbonate sequences, what lithological properties of the beds control their emplacement and what particular type of alteration is associated with them. The "flats" and "columns" observed in the Northern Pennines and in Sardinia would be the most adequate orebodies for such research.

Because of their high density, sulfide muds deposited on the bottom of the sea are expected to flow on slopes and to accumulate in deeps perhaps at a considerable distance from the place where metal was chemically precipitated as sulfide. The emplacement of orebodies resulting from this process must therefore be controlled by two kinds of features : the topography of sea bottom on one hand, the subsurface channels along which the metal is transported on the other. It may happen that the faults along which exhalation takes place are also responsible for the depositional deep, but it is not necessarily so. Since lithification of sulfide muds is suggested as an ore forming process responsible for the formation of large high-grade deposits it is desirable that the controls of their emplacement are known with all possible certainty. A thorough study of deposits in Ireland, the Armorican Massif, the Pyrenees and in Germany would provide the necessary information.

Fixation of metal in a sulfide bearing mud is a process which gives rise to low grade ores. It can be expected to be controlled by palaeogeography much more directly than by faults. Raibl and Gorno are deposits where the opportunity exists to check whether this process plays a significant role and in what conditions. Other possibilities can be found in the southern part of the French Central Massif and in Sardinia.

Cavity filling is undoubtedly largely responsible for many Zn and Pb deposits of the Mississipi Valley type. It results of chemical reactions by which metal dissolved in some subsurface aqueous solution is precipitated as sulfide.

Carbonates are often precipitated also in the cavities, simultaneously or not with the sulfides. The physical chemical conditions required for such reactions to take place are known in general terms. The geological conditions on the other hand are being much debated. According to some schools, the metal bearing solutions are cold, soft waters descending from the surface of a continent undergoing erosion. According to other schools, they are hot, saline waters moving within or escaping from deep aquifers (hydrothermal theory). From the point of view of exploration, it would be useful to determine beyond controversy wether both these sources of metal and the related processes do give rise to Zn and Pb deposits, what are the features of deposits resulting from each of them and what controls orebody emplacement in each case.

On the other hand pores and cavities in carbonate rocks have different origins suggesting different guides to ore. They may be primary as in reefs and sedimentary conglomerates, in which case palaeogeography is the guide. They may be due to fracturing and related to faults. Or they may be due to solution by underground waters and collapse brecciation in solution cavities. Again it is much debated whether, in addition to descending surface waters (karstic process s.s.), deep waters may also be responsible for suitable cavities (so-called hydrothermal-karstic process).

It is suggested that a thorough study of the Salafossa and Les Malines deposits would give satisfactory answers to many questions raised by the cavity filling process of ore formation in a carbonate environment. Largentière and Mechernich would give satisfactory answers with regard to pore-filling processes taking place in sandstones.

All of the deposits mentioned in this section have already been studied, some of them quite extensively. It is suggested that they are studied thoroughly, so as to reduce uncertainty to a more reasonnable level. New methods have become available to check theories of ore genesis : among them fluid inclusions geochemistry and isotope geochemistry are prominent (C.E.E. Proposal for a Multiannual R. and D. Programme, 1977), but many techniques used in mineralogy, petrology and sedimentology can contribute to the same end.

## 11.29.G - SUMMARY

There is a large variety of Zn and Pb deposits in the Community. These deposits offer the opportunity of unravelling the extremely complex set of processes which are responsible for ore deposition. If these processes and their geological controls were known with reasonable certainty, reliable models of orebodies could be devised in each area to be explored, which would allow a systematic search for traps where ore may have deposited.

It is recommended that some deposits representative of all important types be studied comprehensively and thoroughly or that studies already initiated be completed and accelerated. It is also recommended that the collection, critical examination and publication of significant information about these and other deposits within the Community be improved and accelerated.

Attention is drawn to specific difficulties encountered in the science of ore geology. These difficulties result from the restricted accessibility of ore deposits. They are responsible for much of the bias and uncertainty which afflict both the science of ore geology and its use in mineral exploration.

Two broad geological environments are especially worth being studied in the Community : the carbonate sequences and the volcano-detrital sequences. These two environments have already been referred to in the "C.E.E. Proposal for a Multiannual R. and D. Programme ..." (1977).

## 11.29.H - BIBLIOGRAPHY

Only a few of the many volumes and papers written about ore deposits and their genesis can be listed here. The reader is referred in particular to :

WOLF K.H., ed (1976) :
   Handbook of strata-bound and stratiform ore deposits (Amsterdam, Elsevier, 6 vols). The papers by Sangster and Solomon quoted in this section will be found in vol. 6 of this series.

METALLOGENIE ET GEOLOGIE MINIERE (Mem. h. série, Société géologique de France, n° 7, 1976).

Other works referred to in this section are :

CALLAHAN W.H. (1967) :
Some spatial and temporal aspects of the localization of Mississipi Valley - Appalachian type ore deposits (in : J.S. Brown, ed. : Genesis of stratiform lead-zinc-barite-fluorite deposits, Economic Geology, Mon. 3).

STANTON R.L. (1972) :
Ore petrology (New-York, Mc GrawHill, 712 p).

STANTON R.L. (1977) :
several papers on the Broken Hill deposit in Australia (Applied earth science, vol. 86).

CHAPTER 11.3 - GEOPHYSICAL AND GEOCHEMICAL METHODS USED IN PROSPECTING

11.31   GEOPHYSICAL METHODS

11.31.A - INTRODUCTION

Geophysical methods are used to detect discontinuities or differences in some physical property of the rocks in the earth's crust. The results obtained are expressed as anomalies, which depend on the contrast (or property difference actually involved), the size and shape of the rock bodies, and the distance between them and the point where the measurements are made. When an orebody is the target, the usefulness of a geophysical method decreases as the distance increases because the response of the orebody itself becomes fainter while the noise due to the environment tends to increase.

Geophysics is used mainly in petroleum exploration as shown by the following tables published by Espey (1976) :

1. Total worldwide expenditures in U.S. $ (thousands) by survey type and survey objective in 1975

| Survey type | Petroleum | Minerals | Engineering | Geothermal | Groundwater |
|---|---|---|---|---|---|
| Airborne | 18,581 | 29,249 | 182 | 12 | 125 |
| Drill hole | 292 | 898 | 131 | 82 | 378 |
| Land | 747,611 | 20,908 | 11,359 | 2,689 | 12,860 |
| Marine | 418,850 | 553 | 2,405 | | |
| Totals | 1,185,334 | 51,408 | 14,077 | 2,783 | 13,363 |

2 : Total worldwide expenditures in U.S. $ (thousands) by area and survey objective in 1975

| Area | Petroleum | Minerals | Engineering | Geothermal | Groundwater |
|------|-----------|----------|-------------|------------|-------------|
| Internat.[*] | 15,551 | | | | |
| U.S.A. | 516,536 | 7,000 | 1,738 | 2,064 | 492 |
| Canada | 117,238 | 10,774 | 905 | | 14 |
| Mexico | 37,002 | 67 | | | |
| S. America | 110,598 | 8,005 | 1,334 | | 566 |
| Europe | 127,573 | 9,083 | 4,110 | 692 | 1,267 |
| Africa | 122,862 | 10,129 | 4,027 | 27 | 7,872 |
| Middle East | 51,082 | 2,279 | 244 | | 2,550 |
| Far East | 74,254 | 847 | 1,552 | | 215 |
| Australia/ New Zealand | 10,638 | 3,224 | 167 | | 387 |
| Totals | 1,185,334 | 51,408 | 14,077 | 2,783 | 13,363 |

[*] International waters and other areas not specifically identified.

Especially in Europe gravity, magnetic and airborne surveys are however used more in the search for minerals than for petroleum :

3 : Total worldwide expenditures in U.S. $ (thousands) on gravity and magnetic surveys in 1975

| Area | Petroleum | Minerals | Engineering | Geothermal | Groundwater |
|------|-----------|----------|-------------|------------|-------------|
| Internat. | 7 | | | | |
| U.S.A. | 7,328 | 1,984 | 115 | 146 | 9 |
| Canada | 1,684 | 4,354 | | | |
| Mexico | 5,052 | 1 | | | |
| S. America | 817 | 5,928 | 111 | | |
| Europe | 1,538 | 3,088 | 288 | 48 | 10 |
| Africa | 4,983 | 6,948 | | 2 | 141 |
| Middle East | 1,313 | 1,700 | | | 37 |
| Far East | 2,321 | 309 | | | |
| Australia/ New Zealand | 22 | 1,331 | | | 7 |
| Totals | 25,045 | 25,643 | 494 | 196 | 204 |

4 : Total worldwide expenditures in U.S. $ (thousands) on airborne surveys
in 1975

| Area | Petroleum | Minerals | Engineering | Geothermal | Groundwater |
|---|---|---|---|---|---|
| Internat. | 8,378 | | | | |
| U.S.A. | 3,874 | 3,897 | 93 | 7 | |
| Canada | 88 | 7,844 | 74 | | |
| Mexico | 806 | | | | |
| S. America | 99 | 5,983 | | | |
| Europe | 887 | 1,807 | 15 | 5 | |
| Africa | 3,874 | 7,230 | | | 125 |
| Middle East | 875 | 860 | | | |
| Australia/ New Zealand | | 1,748 | | | |
| Totals | 18,581 | 29,249 | 182 | 12 | 125 |

More detailed data about geophysical methods, including unit costs,
are given by the same author :

5 : Worldwide average unit costs in mineral exploration by survey type

| Survey objective, type, method | Crew-months total | Line-miles | Acquisition costs(US $) | Average mile/ month | Average cost/ month | Average cost/ mile |
|---|---|---|---|---|---|---|
| **Minerals** | | | | | | |
| Airborne | | | | | | |
| Input | | 104,157 | 3,067,480 | | | 29 |
| Radioactivity | 42 | 211,173 | 3,721,940 | 4,992 | 87,989 | 17 |
| Remote sensing | 4 | 3,000 | 24,000 | 750 | 6,000 | 8 |
| Magnetic | 342 | 1,738,987 | 19,548,104 | 5,083 | 57,141 | 11 |
| Electromagnetic | | 1,500 | 80,000 | | | 53 |
| Combined EM/mag | 46 | 103,352 | 2,808,003 | 2,208 | 60,000 | 27 |
| VLF | 2 | 4,000 | 28,000 | 2,000 | 14,000 | 7 |
| Drill hole | | | | | | |
| Induced polarization | 19 | 966 | 168,900 | 49 | 8,472 | 172 |
| Radioactivity | 22 | 22 | 180,953 | | 8,042 | 8,225 |
| Magnetic | 42 | 18 | 105,140 | | 2,503 | 5,841 |
| Resistivity | 26 | 498 | 204,300 | 19 | 7,797 | 410 |
| Electromagnetic | 1 | | 10,600 | | 7,066 | |
| Other | 3 | 147 | 35,000 | 49 | 11,666 | 238 |

Land

| | | | | | | |
|---|---|---|---|---|---|---|
| Seismic dynamite | 147 | 10,287 | 6,045,543 | 69 | 41,070 | 587 |
| Seismic comp. air | 4 | 50 | 10,000 | 12 | 2,500 | 200 |
| Seismic weight drop | 3 | 164 | 339,255 | 52 | 109,437 | 2,068 |
| Seismic solid chem. | 4 | 18 | 40,000 | 4 | 10,000 | 2,222 |
| Seismic vibrator | 1 | 81 | 161,550 | 54 | 107,700 | 1,994 |
| Seismic other | 7 | 312 | 33,500 | 44 | 4,785 | 107 |
| Input | 30 | 1,620 | 58,770 | 54 | 1,959 | 36 |
| Induced polarization | 343 | 3,401 | 3,009,031 | 9 | 8,757 | 884 |
| Earth current | 5 | | 22,900 | | 4,403 | |
| Neutron activation | 1 | 54 | 107,700 | 54 | 107,700 | 1,994 |
| Electrical field | 58 | 13 | 97,060 | | 1,670 | 7,466 |
| Radioactivity | 840 | 47,059 | 863,396 | 55 | 1,026 | 18 |
| Gravity | 281 | 45,422 | 2,085,895 | 155 | 7,158 | 45 |
| Magnetotellurics | 6 | 129 | 101,792 | 19 | 15,660 | 789 |
| Gravity/magnetic | 94 | 46,276 | 2,266,100 | 490 | 24,005 | 48 |
| Magnetic | 353 | 16,491 | 1,525,072 | 46 | 4,312 | 92 |
| Resistivity | 231 | 4,353 | 1,513,750 | 18 | 6,544 | 347 |
| Self-potential | 2 | 81 | 3,700 | 31 | 1,423 | 45 |
| Electromagnetic | 471 | 6,336 | 1,087,461 | 13 | 2,304 | 171 |
| Combined EM/mag | 109 | 3,213 | 604,840 | 29 | 5,518 | 188 |
| VLF | 24 | 513 | 196,148 | 21 | 8,187 | 386 |
| Other | 20 | 1,089 | 874,794 | 54 | 43,522 | 803 |

Marine

| | | | | | | |
|---|---|---|---|---|---|---|
| Seismic dynamite | | 1 | 500 | 10 | 5,000 | 500 |
| Input | 2 | 195 | 488,000 | 97 | 244,000 | 2,502 |
| Magnetic | 8 | 2,475 | 85,700 | 305 | 8,111 | 26 |

## 11.31.B - PROBLEMS SPECIFIC TO ZN AND PB DEPOSITS

With regard to Zn and Pb deposits, the use of geophysics is seriously limited by the unfavorable properties of sphalerite,which is the major Zn bearing mineral. Sphalerite is not a good conductor of electricity; it is not magnetic nor radio-active. It follows that most geophysical methods cannot detect even large masses of it, unless sufficient amounts of other minerals such as galena or pyrite are also present in the orebody. It is well known that, especially in carbonate environments, the last condition is not always fulfilled.

A difference is observed between sphalerite and most wall-rock minerals with regard to density and thermal conductivity. But the latter property is awkward to use as a tool in exploration while the former can rarely be used alone in a geophysical campaign.

It is therefore very difficult to design a strategy based on geophysical methods which can detect all zinc-bearing orebodies (including those consisting of pure sphalerite) with a reasonable certainty.

On the other hand geophysics can be used indirectly to find geological structures and environments controlling, or resulting from the emplacement of Zn and Pb orebodies, once these structures and environments have been identified. Such an indirect method of approach, which is of course independent of the minerals associated with sphalerite, has one drawback : it takes much time, much study, and often much drilling to define controlling structures and environments with certainty.

It remains that detailed interpretation of geophysical data can reveal much about the surface distribution of rock bodies and their extension at depth. It is a powerful aid to three-dimensional geological mapping. In areas where outcrops are few, as it is the case in much of Western Europe, geophysics may therefore contribute greatly to mineral exploration.

## 11.31.C - PROBLEMS SPECIFIC TO OREBODIES EMPLACED IN CARBONATE SUCCESSIONS

As shown in a previous chapter, many areas which can be considered favorable with respect to exploration for Zn and Pb in EEC countries are underlain by carbonate rocks. From the geophysical point of view, they raise specific problems, which are also encountered in the Mississipi Valley Province of North America. The experience gained in the latter has been summarized by Callahan and Mc Murry (1967), to whom we shall often refer in this paragraph.

1. The overburden displays abrupt and unpredictable thickness variations due to karst development. Such variations control to some extent the distribution of electric current in the ground. Moreover the density differences associated with them contribute additional complications to the interpretation of gravimetric data.

2. Sphalerite is usually the dominant ore mineral; pyrite and galena are often present in minor amounts, and may permit detection by IP survey but rarely by EM methods.

3. The ore may be vuggy so that average orebody density may not be higher than wallrock density.

   "A resistivity contrast may exist between the ore and its environment because of the vuggy character of the ore, its galena and pyrite content or a combination of these features" But "Water bearing vuggy ground that is barren of sulfides may be responsible for distracting resistivity contrasts" (Callahan and Mc Murry, 1967).

4. Outcropping orebodies have often been oxydized to considerable depths; whether or not the oxydized part has been removed by mining, it may be difficult to detect the underlying sulfide orebody by surface measurements.

5. "While to the eye it appears that a velocity contrast should be present between the ore and its host formation, the dimensions of the ore may be too small to be detectable by conventional reflection or refraction seismic methods. Time of arrival measurements in a pattern of holes with seismometers and shot point in the host bed may be informative". (ibidem).

6. The possibility was examined that "the process responsible for ore empla-
cement might have changed the distribution of radioactivity in the ore
host or in the regional environment and that such change would survive
removal of the ore. Rather conclusive tests on the ground, underground,
and from the air over unmined and mined-out deposits failed to disclose
any consistent radioactive contrast between the ore and its environment
or any significant characteristics of environments favorable for ore
occurrence". (ibidem).

At the end of their review paper, Callahan and Mc Murry (1967)
reach the following conclusion :

"The New Jersey Zinc Company has been involved with testing of geophysical
procedures for locating strata-bound orebodies since 1928. All of the geo-
physical procedures commonly used in mining exploration, save gravity, have
been used. In addition to these, a few unconventional surveys were carried
out. Only applied potential procedures involving the use of drill holes
have been at all productive.

The applied potential method has had limited but worthwhile use in tracing
out conductive orebodies which have been penetrated by one or more drill
holes. The achievements of the method have involved reducing the number of
holes required to trace out elongated conductive ore pencils and to provide
a basis for judging whether or not conductors present in two or more drill
holes are likely to be connected.

The fact that geophysical procedures other than applied potential surveys
have been ineffective is an expected though disappointing result. Two of them,
the electromagnetic and radiowave procedures, were unpromising from a
strictly theoretical viewpoint. Several others, such as the seismic and
radiometric methods, could not be evaluated without extensive, careful field
trials and there were no a priori reasons for great expectations from them.

The induced polarization method has been used widely and successfully by
others in the search for strata-bound orebodies. The results of induced
polarization work in southwest Wisconsin which are described here should
not be considered typical.

The gravity method was not used simply because there was no sound reason
for doing so in any of the areas considered. This is not a method which
needs to be field tested".

Although undoubtedly local differences must be taken into account, much of Callahan and Mc Murry's conclusions apply to European areas under- lain by limestones and dolomites.

## 11.31.D - GEOPHYSICAL EXPLORATION IN IRELAND

The experience obtained in the Central Plain of Ireland with regard to geophysical methods is summarized by Downes and Burton (1977) :

1. Airborne electro-magnetic surveys have been flown (INPUT pulse-type system) but no significant discoveries can be credited to them. By con- trast the Avoca deposits, which are located not in the Carboniferous Limestone of the Central Plain but in a volcanic belt belonging to the Caledonian Basement (sec. 11.23), showed up clearly in a survey using Barringer Research's INPUT time-domain system.

2. Induced polarization has been the most widely used ground geophysical technique since it was first used in Ireland in 1960. Both frequency domain and time domain methods have been used with the latter becoming the more popular in recent years.

"The most successful applications of IP have been in detailed follow-up of soil geochemical anomalies, better target definition for drilling purposes and in investigation in areas of known mineralisation (old mines). In follow-up to geochemical anomalies IP surveys confirmed the significance of geochemical results and improved drilling target defi- nition at, for example, Gortdrum, Keel, Navan and Moate, and in old mining areas it    successfully indicated undiscovered sulphide depo- sits at Silvermines and Ballyvergin. Both the massive and stringer ores at Avoca give IP anomalies. On the other hand deposits such as Ballinalack have shown no distinct IP anomalies related to mineralisa- tion.

The interpretation of IP results can be complicated by the variable and often unpredictable effect of superficial deposits as in the case of the IP response of pyrite-deficient zinc mineralisation which tends to be so subdued as to be easily masked or reduced to apparent insignificance by overburden effects. When both the composition and thickness of the over- burden are known and reasonably uniform, masking effects can be minimised through the use of appropriate electrode arrays and spready, but when unknown and non-uniform results may be ambiguous.

In addition, certain rock types can give IP and resistivity anomalies similar in size and intensity to those indicative of orebodies. Formational effects can, however, allow information on buried structures to be gained. Thus, unexposed contacts between limestones of the Waulsortian reef facies and the underlying muddy lagoonal limestones can be mapped on the basis of the strong resistivity contrast between the two.

The chief criteria is assessing the significance of a geophysical (IP) anomaly are its dimensions, intensity and geological setting and whether or not it is supported by anomalous geochemistry" (Downes and Burton, 1977).

3. Ground EM surveys "are unable to detect deposits whose conductive sulphide content is less than about 10 % or where the sulphide particles are disseminated and insulated by non-conductive rock. In addition, live power and telephone lines can mask EM responses from nearby ore deposits and nearly surface ionic conductors may generate interfering or misleading anomalies. For these and other reasons EM methods have not found wide application in the Irish context. They found their greatest application in follow-up programs to the early airborne surveys, and have yielded anomalies over some Irish deposits - Slingram over Silvermines and Tynagh and Tilt Angle over Tynagh and Avoca.

VLF-EM surveys have found limited use in exploration. The method is fast and cheap and bedrock anomalies have been detected beneath 15 m of glacial overburden. Tests over known mineralisation have shown weak anomalies while natural features such as waterbearing faults, shear zones, certain rock types and lithological contacts can give strong anomalies" (ibidem).

4. Gravity surveys are generally used "in the search for large scale structures that may have associated ore mineralisation and the method has also been used in investigations of geochemical and geophysical anomalies. It has also been used in attempts to trace or find faults but there is generally insufficient density contrast between the Lower Carboniferous, Old Red Sandstones and Lower Palaeozoic rocks to allow fault contacts between them to be identified or traced.

Gravity surveys are applicable only over ores where there is sufficient density contract between the ores and the enclosing rocks. Thus a gravity survey over the Navan deposit yielded a residual gravity anomaly with peak values in the region of 0.8 milligal which reflects the massive nature of the suboutcropping ore. A similar survey over a blind deposit at Tynagh gave a well defined anomaly of 0.3 milligal" (ibidem).

More detailed information on geophysical exploration practice in Ireland will be found in a paper by Schultz (1971), whose conclusions are summarized in a table reproduced as fig. 11.31.1 of this report.

It should be mentioned also that aeromagnetic coverage of the whole country is planned under the aegis of the Geological Survey of Ireland. It is hoped that such a survey will contribute important new data to the three-dimensional geological structure of the island.

## 11.31.E - CONCLUSIONS

The use of geophysics in mineral exploration tends to increase. Presumably it will increase again in the future although, with regard to the discovery Zn and Pb deposits in Europe, geophysical methods do not contribute as much as one would expect.

Present methods are adequate to discover some concealed deposits lying at shallow depths (0 to 30 or 60 m). In most of the EEC countries however, exploration has gone on for several centuries. Apart from a few exceptions outcropping deposits were found before 1900 and their shallower parts have been removed by mining. During the 19th century, when the zinc industry developed, underground exploration by pits and tunnels proceeded on a large scale in a number of regions so that even some concealed deposits were found. New discoveries depend therefore to a large extent on the possibility of finding ore at greater and greater depths. The future of geophysical methods depend primarily, in turn, on their ability to meet this challenge.

In a recent review paper, L.S. Collett (in Govett and Govett, 1976) asserts that technical developments will take place in the near future in the following areas :

# Fig. 11.31.1. Evaluation of prospecting and exploration methods in Ireland (Schultz, 1971)

| Mineral deposit or prospect | Evidence of mineralization | Outcrop prospecting | Boulder hunting | Geochemical drainage survey | Geochemical soil survey | Airborne EM | Ground EM | IP | Resistivity | Self-potential | Gravity | Geologically directed drilling | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Abbeytown Zn–Pb deposit | m* | I+ | I+ | I+ | I+ | N–(4) | N–(4) | N–(2–3) | N–(4) | N–(4) | N–(4) | P–1 | See Appendix |
| Aclare spodumene pegmatite deposit | | P–1 | P–1 | N–(2) | N–(1) | I | I | I | I | I | N–(3) | C–1 | Spod–qtz–fsp–musc pegm dykes in granite and schist. Variable cover drift and alluvium |
| Aherlow Cu–Ag deposit | m* | 4 | C–2 | T–2 | P–1 | N–(4) | N–(4) | 3 | N–(4) | N–(4) | N–(4) | | See Appendix |
| Allihies Cu deposit | M* | I+ | I+ | I+ | I+ | I– | I– | I+ | I– | I– | I– | P–1 | See Appendix |
| Avoca Cu and pyrite deposits | M* | I+ | I+ | I+ | I+ | T–2–3 | T–2–3 | T–2–3 | T–2–3 | 2 | I+ | P–1 | See Appendix and footnote |
| Ballinalack Zn–Pb deposit | | 4 | 2–3 | N–(2) | P–1 | N–(4) | N–(4) | 3–4 | N–(4) | N–(4) | N–(4) | | See Appendix |
| Ballyvergin Cu deposit | m* | I+ | I+ | I+ | I+ | N–(4) | 3–4 | P–1 | N–(2) | T–2 | N–(4) | | See Appendix |
| Boston Hill Pb–Zn prospect | | C–2 | ? | ? | P–1 | N–(4) | N–(4) | 3–4 | N–(4) | N–(4) | N–(4) | | Gal. and sphal. in Lower Carb. limestones. Kildare. Main mineral zone covered by peat bog |
| Carrickittle Zn–Pb prospect | | 4 | C–1 | T–2 | P–1 | T–4 | T–4 | 2–3 | N–(4) | N–(4) | N–(4) | | See Appendix |
| Courtbrown Pb–Zn prospect | m‡ | 4 | ? | I | P–1 | N–(4) | N–(4) | C–2 | N–(4) | N–(4) | N–(4) | | Gal. and sphal. in Waulsortian limestone, Limerick. Partly covered by estuarine mud flat |
| Gortdrum Cu–Ag–Hg deposit | m‡ | C–1 | C–2–3 | P–1 | P–1 | T–4 | N–(4) | C–1 | N–(4?) | N–(2–3) | N–(4) | | See Appendix |
| Keel Zn–Cd–Pb deposit | | 2–3 | ? | P–1 | P–1 | T–4 | 4 | C–2 | N–(2) | N–(2–3) | N–(4) | | See Appendix |
| Maghera Cross Cu prospect | m‡ | C–2 | 4 | 4 | P–1 | N–(4) | 4 | 4 | N–(4) | N–(4) | N–(4) | C–1 | See Appendix |
| Mace MoS₂ prospect | | P–1 | N–(?) | T–2 | T–2 | N–(4) | N–(4) | 4 | N–(4) | N–(4) | N–(4) | | Widespread low-grade $MoS_2$ in granite. Detailed mapping and drilling |
| Moate Zn–Pb prospect | | 4 | C–1 | T–2 | P–1 | N–(4) | N–(2–3) | C–1 | N–(2–3) | N–(4) | N–(4) | | See Appendix |
| Navan Zn–Pb deposit | | C–2 | C–1 | 4 | P–1 | N–(2?) | N–(1?) | C–1 | N–(1) | N–(2) | C–1 | | See Appendix |
| Silvermines Zn–Pb deposit | M* | I+ | I+ | I+ | 2 | T–3 | 2 | C–1 | N–(1–2) | N–(4) | N–(2–3) | C–1 | See Appendix |
| Tynagh Pb–Zn–Cu–Ag deposits | B mt | 4 | C–1 | T–(1?) | P–1 | N–(1) | C–1 | T–1 | N–(1) | N–(1–2) | T–3 | | See Appendix |
| Tynagh eastern ore zone | Main deposit | I | I | I | I | T–4 | 4 | 4 | N–(4) | N–(4) | T–2 | P–1 | See Appendix. Blind deposit |

Evidence of mineralization (known prior to application of field methods and instrumental in initial target selection):
M, Important old mine workings.
m, Small or minor old workings.
B, Recorded mineralized boulders.
*At or very near to site of new discovery.
†Within radius of about one mile.
‡Within radius of a few miles.

P, Primary method (mainly responsible for discovery).
C, Contributory method (assisted in discovery).
T, Tested over known deposit after discovery.
N, Not tried (figures in parentheses indicate inferred success rating).
I, Inapplicable (method inherently unsuitable: or inapplicable because of geochemical contamination or geophysical interference: or application superfluous under the given circumstances). I+ and I– mean that the respective methods probably would have been successful (+) or unsuccessful (–) if used in prospecting for and exploration of the particular deposits in their virgin states).

1, Clearly successful (in most cases could by itself have led to the discovery).
2, Moderately successful.
3, Ambiguous results.
4, Unsuccessful.

The above inferred evaluations of the resistivity method refer to pure resistivity surveys as distinct from those carried out in combination with the IP method.
At Avoca most of the electrical methods were tried after the 1958–62 period of operations when the areas containing the most important sulphide deposits could not be reliably surveyed because of interference from surface-plant and underground mine installations.

a) differentiating between non-economic (geologic noise etc.) and economic geophysical anomalies;

b) deep penetrating geophysical techniques, including borehole exploration;

c) multi-frequency and broad-band EM systems, airborne and ground;

d) multi-frequency and broad-band induced polarization (IP) apparatus and removal of EM coupling;

e) increased use of multi-sensor airborne systems (EM, gamma-ray spectrometer, high-sensitivity magnetometer, and gradiometer) which will require installed mini-computers for controlling sensors and handling data for digital data recording systems;

f) electronic navigation systems for digital flight path recording and recovery;

g) marine geophysical technique development for detection of minerals on and below the sea floor;

h) mineral prospecting in difficult regions (permafrost, conductive overburden, and rugged topography);

i) improvements in interpretation and mathematical scale modelling;

j) exploration application of remote sensing technology (image-forming systems);

k) exploration strategy.

There is no doubt that many improvements will be brought to existing instruments and methods during the next decade. With regard to EEC countries however, and for the reasons mentioned above, improvements of surface methods in view of detecting orebodies at greater depths will be useful but they will bring only temporary help. Improvements of surface methods in view of detecting favorable structures and environments are more promising avenues of research, at the condition that these favorable structures and environments are known with a reasonable certainty.

On the other hand borehole techniques, if they can be developed to meet the needs of mineral exploration, could contribute very efficiently to the discovery of deeply concealed deposits. It is recommended that a major research effort be undertaken in order to improve existing techniques, to test new techniques and to make them available at a reasonable cost.

A survey of existing borehole techniques will be found in a recent book by Telford et al. (1976).

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## 11.32  GEOCHEMICAL METHODS

### 11.32.A - INTRODUCTION

Geochemical methods consist in analyzing samples of some naturally
occuring substance for one or more chemical elements which are supposed to
be especially abundant or especially rare or associated in a particular
manner with one or several minerals in the vicinity of an orebody. The
chemical elements involved are usually present at very small concentrations;
they may or may not be the elements that one hopes to find in the orebody.
The results of geochemical compaigns are usually expressed by anomalies, i.e.
areas or volumes in which, after statistical study, rock composition can be
considered abnormal.

The main types of geochemical surveys currently used are the
following (Levinson, 1974) :

- Vapor surveys. Gas samples taken either in the atmosphere or in the soil
  are analysed for mercury, or for sulfide, fluoride, bromide or iodide
  compounds which are supposed to emanate from buried orebodies.

- Vegetation surveys. Plant ash may concentrate trace elements present in
  the soil; since the roots of some species spread to considerable depths,
  suitably chosen plant material reveals information which cannot be obtained
  otherwise at the surface.

- Water surveys. Surface and underground waters contain dissolved or suspen-
  ded constituents acquired from the rocks which they meet on their way.
  In particular they may contain small amount of metals resulting from the
  weathering or alteration of orebodies.

- Stream sediment surveys. Such sediments result from the erosion of the
  drainage basin upstream, and supply information on rock bodies and ore
  bodies which may not be exposed in outcrops.

- Soil surveys. During the process of weathering, the metals contained in
  an orebody may be fixed in the soil. Again by analyzing the soil, infor-
  mation may be obtained about the composition of the underlying bedrock.

- Rock surveys. Unweathered rock samples may have chemical features charac-
  teristic of the aureoles or haloes observed around some orebodies.

Data about the cost of the various geochemical methods are summa-
rized in the table represented as fig. 11.32.1 and due to Levinson (1974).
The following figures, borrowed by Cazalet (1973, in Downes and Burton,
1977), show that, as may be expected, the cost of collecting samples for
geological exploration is strongly dependent on depth :

| Method | Sample density | Cost £/sq. mile or $/km2 |
|---|---|---|
| Stream sediment | 1 per sq. mile | 5 |
| B-C horizon | lines 1 000 ft apart stations 400 ft | 16 |
| Base of drift (for drift 3 m thick) | as above | ca 400 |

| Name | Cost of Equipment | Detection Limits (see Table 6-3) | Advantages | Disadvantages | Cost of Analysis in Commercial Laboratories |
|---|---|---|---|---|---|
| Atomic Absorption | $4,000-20,000 | Generally less than 10 ppm; some elements in ppb range | 1. Rapid, sensitive, specific, accurate and inexpensive. 2. Several elements may be determined from same solution. 3. About 40 elements applicable to exploration geochemistry. 4. Partial or total analyses possible. | 1. Accuracy suffers with high abundances. 2. Not satisfactory for some important elements such as Th, U, Nb, Ta and W. 3. Destructive. | 1. Generally $1 per sample for first element, and 50¢ for each subsequent element determined on the same sample solution. 2. Au, Ag, Hg, Te, etc., from $1.50-$3.00. 3. Biogeochemical samples about twice regular rate. 4. Sample preparation (e.g. crushing, sieving) charges usually extra. |
| Colorimetry | Usually less than $1,000 | Generally less than 10 ppm for elements commonly analyzed | 1. Inexpensive, simple, sensitive, specific, accurate and portable. 2. Partial or total analyses possible. | 1. Only one element (or a small group) determined at one time. 2. Not suitable for high abundances. 3. Some reagents unstable. 4. Tests not available for some important metals. 5. Destructive. | 1. Generally 75¢ per element for cold-extractable. 2. Fusions or hot acid leaches generally $1.00 for first element, and 50¢ for each subsequent element determined on same solution. 3. Mo and W about $2.50 each. |
| Emission Spectro-graphy | a. Visual detection $2,000-8,000  b. Photographic detection $15,000-30,000  c. Electronic (direct reader) $60,000-150,000 | a. Usually only major and minor elements detected  b. Generally from 1-100 ppm for most elements of interest.  c. Same as (b) above. | 1. Multi-element capabilities (for all instruments) 2. Only small sample required (for all instruments). | 1. Complex spectra. 2. Requires highly trained personnel. 3. Generally slow (except for direct reader). 4. Sample preparation very critical and time consuming. 5. Destructive. | 1 Qualitative or "semi-quantitative 30-element scans", $15-20. 2. Quantitative, about $5 for first element and $3 for each additional element on same film. 3. Direct-reader prices vary but probably about $30 for all elements recorded simultaneously. |
| X-ray Fluore-scence | $30,000-40,000 (laboratory models) | 50-200 ppm on routine basis; more sensitive with special procedures. | 1. Simple spectra. 2. Good for high abundances of elements. 3. Uses relatively large sample. 4. All elements from fluorine to uranium are practical on modern equipment. 5. Certain liquids (e.g., brines) can be analyzed directly. 6. Excellent for rapid qualitative checks. 7. Non-destructive. | 1 Sensitivities not as good as other methods for many elements. 2. Analyses slower than some other methods. 3. Analyses relatively expensive. | Generally $8-$12 per element per sample (quantitative); about half that price qualitative. |

Fig. 11.32.1 Comparison of analytical methods commonly
used in exploration geochemistry (Levinson,
1974).

## 11.32.B - GEOCHEMICAL EXPLORATION PRACTICE IN IRELAND

Geochemistry has been particularly successful in Ireland since it is considered "mainly responsible" for the discovery of ten ore deposits including Navan (fig. 11.31.1). The Irish exploration practice is therefore of especial interest even though it cannot be applied in other countries without changes. A large part of Ireland is covered by a layer of glacial till or by peat bogs while most of the other EEC countries have been less or not at all affected by glaciations. In each particular case, techniques and strategies used in geochemical exploration must and do take into account the climatic, physiographic, hydrographic and geological features of the area to be explored.

The geochemical exploration pratice is described as follows by Downes and Burton (1977) for Ireland :

"**Stream Sediment Geochemistry Surveys**

Stream sediment geochemistry is usually the first stage in screening large areas of ground. A sample density of one sample/two km2 is usually aimed at in reconnaissance surveys but for more effective coverage it is necessary to sample at intervals of not more than 300 m and at all confluences.

The high stream density required for reasonably effective coverage of an area is frequently not met with in many geologically favourable areas where the terrain is flat or of low relief and where distances between streams are of the order of hundreds of metres.

Sampling follows the standard practice of collecting fine sediment (usually 80 mesh) from active stream channels. Samples are usually analysed for hot-extractable copper, lead and zinc. Data interpretation can be complicated through the scavenging of metals by environmentally induced iron and manganese hydroxides and by organic matter.

The main limitation of the technique arises from the fact that within the Central Plain ground waters generally have a high pH which through inhibiting the solubility and mobility of base metals limits their hydromorphic dispersion. As a result, marked stream sediment anomalies arise through clastic dispersion of metal-rich solids either from soil or bedrock sources. This method of dispersion, however, is rectricted in parts of the low-lying Central Plain due to the low topographic relief and the consequent lack of active stream erosion. The technique, nevertheless, led to the discovery of the Keel deposit.

## Soil Geochemical Surveys

Soil sampling is the most extensively applied and, to date the most success-
full prospecting method used in Ireland. For reconnaissance surveys grids are
laid out at line and sample spacings of 150 m or more typically on rhombic
or square grids. For detailed follow up surveys sample spacings may be
reduced as low as 15 m depending on local conditions. Usually, lowever,
anomalies can be satisfactorilly outlined by samples taken at 60 m or 75 m
intervals.

Sampling depth generally varies between 0.25 - 0.5 m. Some companies consis-
tently sample at a fixed depth while others design sampling schemes to cope
with local conditions. In general, however, it appears that in zoned soils
the most satisfactory results are usually achieved by sampling the C horizon.
The general practice at present is to analyse the - 80 mesh fraction of soil
samples for hot extractable copper, lead and zinc. Cold extraction techniques
are used as a mean of discriminating between hydromorphic and clastic
anomalies. The use of potential pathfinder elements such as mercury and arse-
nic have been examined as has the partitioning of heavy metals between
different size and density fractions of soils. However, the success scored
with the simple sampling and analytical procedure outlined above have dis-
couraged their radical modification.

In areas underlain by Lower Carboniferous limestone the soils are largely
derived from and underlain by limestone till. Geochemical anomalies arise
through clastic dispersion of metalliferous material in areas where high
pH limits the chemical mobility of metals. Clastically dispersed material
is rarely transported further than about 3 km from its source and very often
it comes to surface very near to or directly above the bedrock source. In
areas where non-calcareous till and soils predominate the glacial disper-
sion will probably have been modified by subsequent hydromorphic dispersion
patterns.

Once geochemical anomalies have been identified the usual course of action
is to follow up each one by inspecting the ground for evidence of minerali‑
sation and artificial contamination and by resampling it on a tighter grid
and/or at the maximum depth attainable manually. This also applies to
single point anomalies and to anomalies close to potential sources of
artifical contamination.

## Deep Geochemical Surveys

Following up near-surface soil anomalies or the search for anomalies in areas where drift cover is thick can be very difficult, particularly where there has been strong glacial movements and dispersion, where the drift consists of till from two periods of glaciation, and where any of the above are covered by bogs. The technique of deep sampling by power tools has developed in recent years in response to these problems.

In practice a portable percussion drill is used to drive a string of steel rods, capped by a tapered probe, almost to the desired sampling depth. The rods and probe are then retrieved by means of a hand-levered jack and the probe is replaced by a hollow sampling tube. The sample is taken by driving the sampling tube from the base of the drill hole through the desired sampling depth.

This method is used to test the persistence and lateral displacement with depth of geochemical anomalies detected by shallow soil sampling : this is done by taking samples at regular depths and obtaining geochemical profiles; used as a reconnaissance tool, particularly for sampling beneath thick accumulations of drift; and used to obtain geological information from the base of the drift by driving the sampling tube into the bedrock and producing fragments for examination.

## Peat Geochemical Surveys

Peat bogs cover large areas of geologically favourable ground in Ireland but to date no mineralisation covered entirely by bog has been found so nothing is known about the geochemical expression of such mineralisation.

Peats generate anomalies through the scavenging of metals by organic matter and by iron and manganese hydroxides; this is indicated by the enrichment of metals in peat relative to the underlying lacustrine deposits and till. Morrissey and Romer (1973) report that in the Tynagh area peats in non-mineralised areas have metal (Cu, Pb, Zn) contents similar to freely draining soils from the same areas and that peats from mineralised areas are enriched in copper, lead and zinc".

## 11.32.C - PROGRESS IN GEOCHEMICAL EXPLORATION

The techniques used for sampling and analyzing soils, river sediments and other surface materials, although well established, can be improved. Presumably much progress can also be made in the interpretation of the data, which has actually remained rather empirical. If the dispersion and fixation processes responsible for anomalies were better known, the exploration value of each anomaly could be assessed with greater confidence and some unneccessary drilling could be avoided. The statistical processing of the data is also a field susceptible to improvement.

However it is unlikely that orebodies buried at more than a few tens of metres give rise to soil or vegetation or stream sediment anomalies except under special circumstances. In areas that have already been much prospected and where the search must inevitably penetrate to greater depths, the future of geochemical methods depend largely therefore on the progress that will be made in the fields of rock surveys on one hand, surveys using mobile materials such as underground water or gas on the other.

With regard to mobile materials, mercury seems to be the most promising since it is associated with many sulfide minerals and may be expected to migrate considerably further from the source orebody than any other sulfophile element. In addition to mercury, which has already been used in a number of countries for exploration purposes, various gaseous compounds could help detect geological features of interest, such as large an deep faults (Govett, 1976).

The efficiency of rock surveys depend on the recognition of haloes around the various types of orebodies. Copper deposits of the porphyry type for example are surrounded by a well-known system of concentric haloes which are used to focus the research effort on the orebody after the first indications have been obtained either from outcrops or from wildcat drilling. Uranium deposits of the sandstone type do not have haloes of the concentric type but they are found in a specific chemical environment, i.e. at the limit between oxydized and reduced facies of the same sandstone unit.

Every effort should be made to recognize and analyze haloes around the various types of orebodies known or expected in Europe. These haloes do not have to be geochemical i.e. detectable by the methods of chemical analysis; they may be petrological or mineralogical or still of another nature; in this regard the very wide range of laboratory techniques currently available should be tested on a few deposits chosen because

1°) they are considered typical of a group and

2°) they are mined and have been drilled extensively so that they may be studied in their three dimensional environment.

It would be especially useful to recognize haloes around Zn and Pb orebodies in carbonate environments, since so much of the favorable areas within the EEC countries are underlain by limestone-dolomite. From the attempts which have been made in this direction, one may conclude that many of these orebodies are not surrounded by anything as obvious as the por- phyry copper system of haloes. A thorough search should be undertaken in order to identify even subtle features which can characterize the environ- ment of each type of deposit.

Among other methods, the following should be tested in order to identify haloes :

- major element geochemistry of rocks and minerals.

- minor element geochemistry of rock and minerals.

- isotope geochemistry of lead, sulphur, carbon, oxygen and hydrogen.

- fluid inclusion techniques.

- petrography of hydrothermal alteration; dolomitization, silicification, etc ...; clay mineralogy.

- sedimentological analysis.

Sampling should be planned so as to find three-dimensional haloes such as observed around porphyry coppers as well as two-dimensional ones such as observed around uraniferous sandstones orebodies. The iron and man- ganese oxyde layers deposited on the bottom of the sea around exhalative orebodies belong to a particularly promising type of halo.

The research recommended here corresponds to that suggested by the "Proposal for a Multiannual R. and D. Programme ..." (C.E.C. 1977) under the subtitles I-A-2 (wall-rock alteration) and B-I-2 (whole-rock geochemistry).

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## 11.33 DISCOVERY OF DEEP OREBODIES. TWO CASE HISTORIES

11.33.A - THE <u>VIBURNUM TREND</u> OR <u>NEW LEAD BELT</u> OF MISSOURI (fig. 11.33.1
and 2)

"The Viburnum Trend is currently the world's most productive
lead-mining district. It is also a major producer of zinc and the ores
contain minor but significant amounts of copper, silver and cadmium. In
1974, the year of highest production, the district accounted for 85 per-
cent of total U.S. production of lead and 15 percent of the world total".
(Vineyard, 1977).

The discovery of this district, which extends 50 to 100 km SW of
the <u>Old Lead Belt,</u> is one of the major successes of modern exploration
techniques. The circumstances were however not entirely favorable : there
are few outcrops and the orebodies are located at a depth of at least
300 m. The period of active exploration by modern methods began in that
area in 1943. The first minable orebody was found in 1948, in the <u>Bonne-
terre Formation</u> of Cambrian age. The first mine was opened in 1953; the
next one around 1965; 8 mines are now active.

Several geophysical methods have been tried in the <u>Viburnum Trend</u>
but with little success (Weigel, 1965). Aeromagnetic and gravity maps
helped in indicating favorable structures. Seismic methods were of little
use because velocity values vary within individual formations. Electro-
magnetic methods were ruled out because of depth. In addition the orebodies
"are irregular, with gradational side boundaries, and vary in size from a
few hundred square feet up to as much as several hundred acres ...
Mineralization is ordinarily disseminated ... Grade average ranges from 3 %
to 10 % Pb. Total sulphides are rarely more than 20 % for any large area.
The host rock in ore areas is often shalier or more porous than normal, so
that little density contrast exists. Overlying the <u>Bonneterre</u> is the <u>Davis
formation</u> with a high shale content. This thoroughly blocked off mineral
haloes wich might be picked up by geochemical soil sampling. Mercury vapor
sampling has been negative. In short, difficulties are probably insuperable
for any direct ore finding methods" (ibidem, p. 84). The only clues that
could be used were therefore of geological nature but several years were
spent to design a workable geological model, which could confidently be
used to focus on the orebodies from the few indications obtained from sur-
face geology or by wildcat drilling.
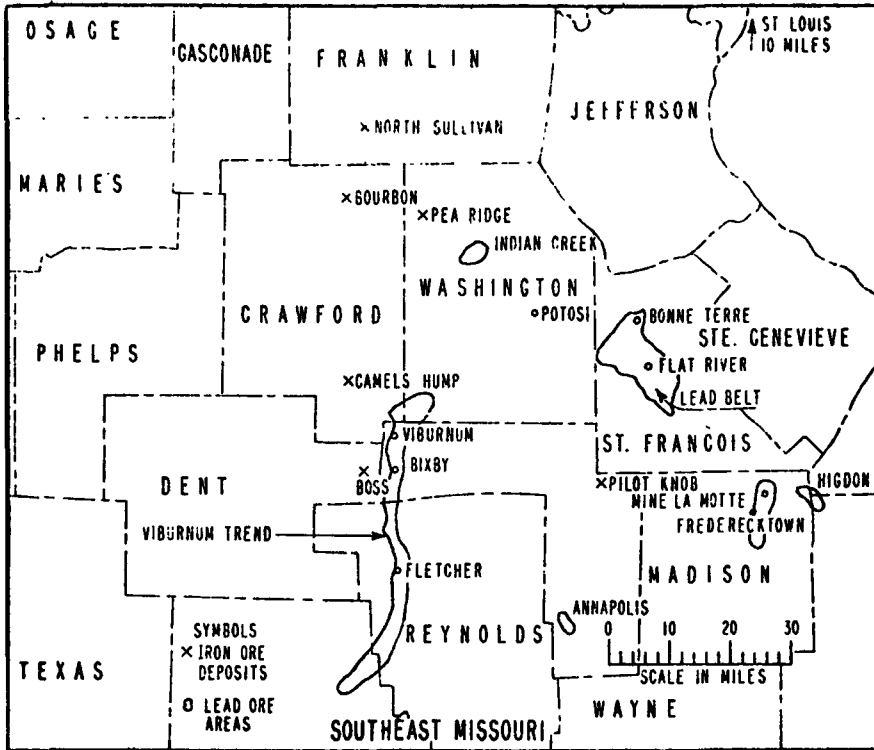
Fig. 11.33.1. Location of the Viburnum Trend and
                Indian Creek districts relative to
the old Lead Belt in Missouri (Weigel, 1965).
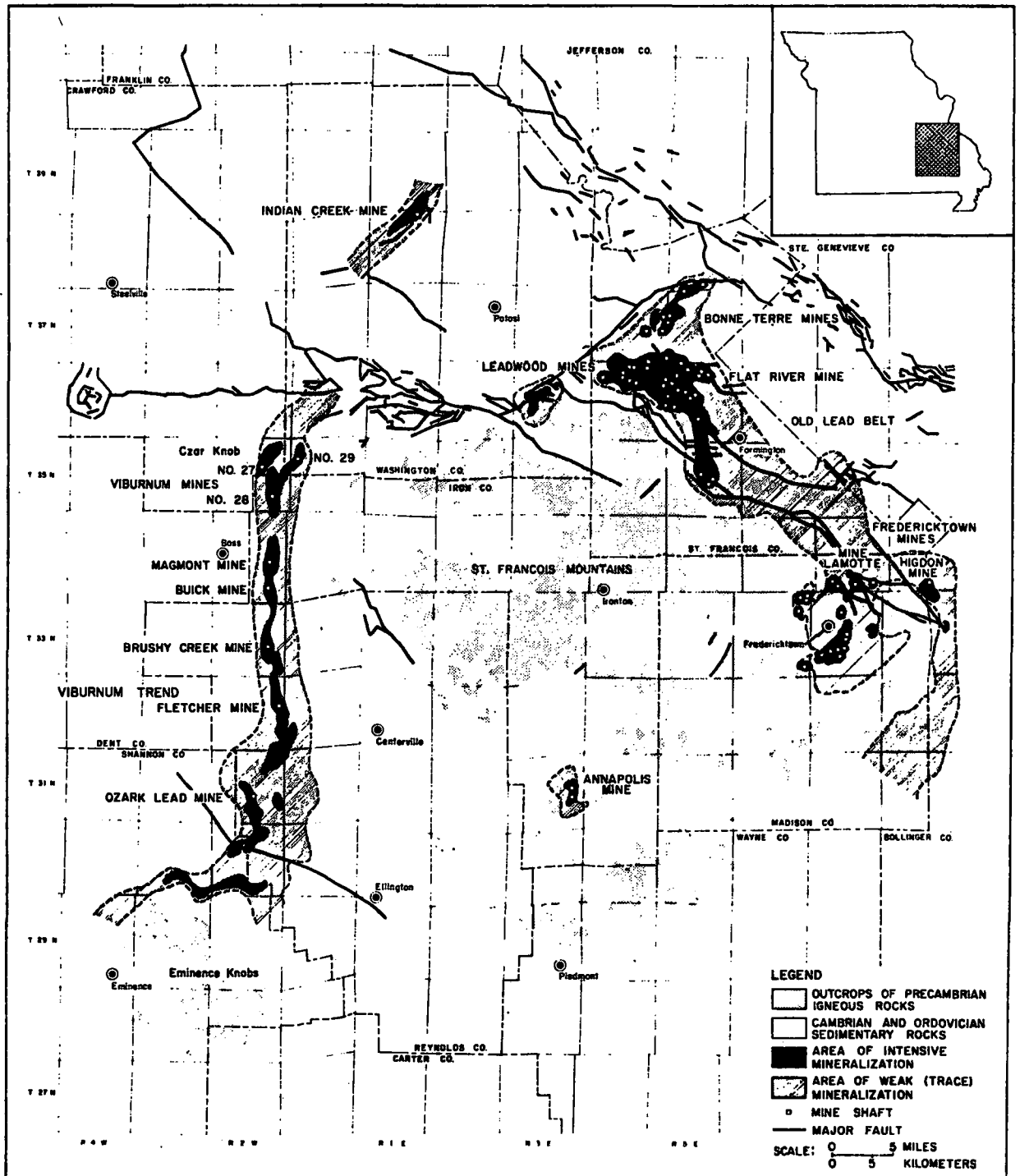
Fig. 11.33.2. The southeast Missouri lead-zinc-copper mining district (Kisvarsanyi, 1977).

At first, prospecting was undertaken in Washington County (fig. 11.33.1), more specifically in the areas which had a history of shallow lead mining because surface indications were present, and also in areas where certain trends and structures known in the Old Lead Belt were thought to extend. "Both the shallow mineral occurrences and the trends were to be largely disproved as direct guides for prospecting but it took much drilling and time to do this". (ibidem). The theory was also tested that ore was emplaced around domes overlying palaeohills of the underlying pre-Cambrian unconformity. Several such domes were known in Washington County.

"Two main plans were presented by the committee. The first was to drill several long lines of prospect holes, usually double. Holes were to be about one-half mile apart along the rows, and crossing as many of the presumably favorable areas as possible. The second was to drill from 10 to 40 holes in each of the favorable areas. It is interesting to look over these old plans now and to realize that if either one had been carried through, the north part of the Viburnum Trend would almost certainly have been found and probably Indian Creek as well. Time and the expense would have been less than that finally incurred.

Actually neither plan was followed at all. Presented  at one time to the management, each of them showed a rather formidable number of holes and too large an expense at one time to be approved. The real program, started in the spring of 1943, became a kind of opportunistic drilling on the land available, consisting mostly of the large blocks of company-owned land west of Bonne Terre, Leadwood, and Bismarck and certain additional tracts which the land department optioned not much farther away.  A little mineralization was found but nothing of economic value. Interest began to lag after a few years. The program might very well have been dropped in another year or so.  Most of the drilling up to that time had been in the east-central part of the county. As part of a package-option deal to obtain some of this land, a large tract about 14 miles northwest of Potosi had also been optioned. This was an example of the luck which often influences and determines success or failure or prospecting. An example of bad luck  was the failure to follow out the original drilling plans. In fact, the whole Missouri campaign over the years has been full of good and bad luck at different times and for the various companies". (ibidem).

After the discovery of the <u>Indian Creek</u> orebody prospecting was speeded up. "It was realized by this time that any connection of the shallow surface mineralization and the deep orebodies of the <u>Bonneterre</u> would be purely accidental. The Indian Creek ore was clearly associated with and controlled by Precambrian knob structure. This became the main structural guide for the future and certain facies relationships in the Bonneterre became the main formational guide. Direct ties with the Old Lead Belt were forgotten. The new search was independent and spread widely over many counties. Large areas of land were optioned and an extensive campaign of scout drilling was started. But several lean years lay ahead and several million dollars had to be spent before any further success in looking for lead and zinc orebodies". (ibidem).

Drilling was the main tool used for exploration in the <u>Viburnum Trend</u>. In 1965, 10 000 prospect holes had been put and the exploration expenses amounted to a total of 50 million U.S. $ (ibidem).

## 11.33.B – THE CENTRAL TENNESSEE DISTRICT (fig. 11.33.3)

An important zinc district has recently been discovered in Central Tennessee, where the first mine (Elmwood) was opened in 1974 in order to exploit a 20 Mt deposit with 4.5 or 5 % Zn.

Again the circumstances were not entirely favorable because the orebodies are extremely irregular in plan and seem, to a certain extent, randomly distributed and orientated. Geochemical soil surveys were not likely to be useful because of the depth of the favorable formation. Little contrast existed between host rocks and ores so that no meaningful response was expected from electrical, seismic, gravimetric or magnetic surveys.

The following description of the discovery is due to Hoagland (1973) :

"In 1964 the New Jersey Zinc Company began on a modest scale an exploration for ore of Mississippi Valley type in the Nashville Dome area of Middle Tennessee. As the premises for the project were verified, and favorable results were obtained, the scope and magnitude of the venture expanded to major proportions. This region was selected for exploration for the following reasons :

1. The area is underlain by Knox dolomite, the ore bearing horizon of East Tennessee some 150 miles to the south-east. The potential ore horizon is only 700 to 1500 feet deep over an area of several thousand square miles. The beds are essentially flat which would permit efficient mining in stratiform orebodies.

2. A few oil tests into the Knox had been drilled and several of these found significant amounts of zinc mineralization associated with lithologies similar to those of East Tennessee. From studies of the well cuttings, it appeared that the mineralization in Middle Tennessee was associated with dolomitized limestone in breccia zones not far below the same major unconformity which is prominent in East Tennessee.

3. Scattered veins of barite, fluorite, galena and sphalerite are present in the overlying beds throughout the area of interest. It was thought possible that these might represent "leakage" from more important deposits in "favorable" horizons below.

4. There was no activity or interest evident in the area by other explora-
tion groups and it appeared that if a discovery were made, there would
be a very good opportunity for New Jersey Zinc to secure a strong proper-
ty position and benefit significantly. The possibility of a major district
comparable to Tri State was considered, and a strategy of exploration and
property control was designed with this in mind.

The first phase of the exploration involved a small commitment for
drilling. Property control was minimal. Primarily it would be necessary to
confirm the basic premises of the project. The Knox was found to have a
favorable dolomite-limestone ratio; the post Middle Ordovician unconformity
was found to be developed with extensive karst features; dissolution and
collapse breccias were well developed; dolomitized limestone and siliceous
alteration were found in abundance; and weak zinc mineralization was found
in the expected horizons. It was concluded from these findings that the
region had been subjected to the same kind of ore associated alteration pro-
cesses that had been operative in East Tennessee. These favorable characte-
ristics of the Middle Tennessee Knox were confirmed in a very few drill holes.
The environment for large ore zones in a structural and lithologic setting
favorable for low cost mining, therefore, had been confirmed, and the conti-
nuation of exploration on a somewhat more aggressive scale appeared at this
time to be warranted.

The second phase could proceed on the assumption that since the
conditions believed to be favorable for ore were present, the chances were
good that ore could be found. A regional pattern of drilling on 5 to 6 mile
spacing was begun while property control and costs were kept to a minimum.
Careful attention was given to Knox stratigraphy and alteration. Paleotopo-
graphy on the unconformity, structure and isopachous maps on key beds, and
most important, a picture of the distribution and intensity of zinc minera-
lization were compiled from an expanding grid centered on Murfreesboro. The
focus of exploration moved northeastward, and finally, three years after the
start of the program, with hole number 79 a penetration of mineralization of
ore grade and thickness was made in the vicinity of Elmwood in Smith County.
Although this hole did not prove an orebody, the existence of ore in this
location was indicated as a very real possibility. The need for a new
approach to the program at a higher level of activity now had been clearly
established.

The third phase required a closer focus on the potential ore zone to
define its approximate location and general character.

It was now necessary to establish a secure property position before a con-
centrated drilling effort could be made, and leasing became the main order
of business until an area of several miles was brought under control. As
the leasing program was reaching a satisfactory stage, a pattern of 3 holes
spaced on a circle of 1 1/2 mile radius around hole 79 was drilled and a
4th hole was drilled at a selected point between hole 79 and two of the
circle holes. These holes were sufficiently encouraging to warrant a much
more thorough and comprehensive test. Because of the wide spread and appa-
rent strength of the mineralized structures, it appeared likely that a large
and important ore zone had been found. Depth of drill holes were averaging
about 1500 feet in this area and despite excellent ground conditions and a
favorable drill rate, the cost of drilling a closely packed screen over such
a large area would have been considerable. Furthermore, it appeared from the
drill data already available that orebodies would probably be irregular in
shape and random in distribution. The problem now was to evaluate at a mini-
mum expenditure of money and time the tonnage and grade of the deposit as well
as to determine insofar as feasible, the stratigraphic and vertical range
and the form and character of the ore. A statistical approach was selected
as the best means of reaching a practical answer to these questions.
Evaluation leaned heavily on the statistical analysis of 110 holes drilled
on a 1000 foot grid 10,000 feet square. At intervals during the drilling,
calculations of tonnage and grade were made. Holes were drilled in a random
sequence on the grid after about half of the designed holes had been drilled,
tonnage and grade values changed relatively little as confidence limits
tightened up. Initially the tonnage and grade calculations were made with a
desk calculator. Later the data were computer calculated which greatly faci-
litated the processing of information and extended the range of calculations
which were useful. Tonnage and grade estimates were made assuming minimum
mining heights of 6 feet, 7 feet, 8 feet and 9 feet using a minimum dilution
factor of 40 %. Upon completion of the 1000 foot grid it appeared reasonably
certain that sufficient tonnage of acceptable grade was indicated to warrant
a fair to large size operation. Good data were at hand to select mining level
elevations and a site for preliminary mine development.

There was, however, no evidence from drilling to indicate continuity
of ore from one hole to another and ore trends, forms and dimensions could
only be visualized on the basis of conceptual analysis for which there was
inadequate factual basis. We were dealing with a deeply buried ore occurrence
in an entirely new area.

From consideration of the general relationships it appeared that the East
Tennessee orebodies and the orebodies at Elmwood were quite similar as to
form and character. But a commitment to mine the Elmwood deposit would
require more positive evidence which could only be obtained by actually
contracting the ore with mine workings, following the ore with drifts and
raises and probing its boundaries with closely and systematically spaced
drilling from the workings. To obtain anything like the assurance that the
underground development would provide, a grossly disproportionate expendi-
ture for surface drilling would be required. It was decided, therefore, to
go underground on the basis of the drill information from the 1000 foot
grid, a decision which in retrospect appears to have been wise.

The fourth phase involved underground confirmation of the evalua-
tions which had been made on the basis of the very wide spaced pattern of
surface drill holes. A prospect shaft 12 feet in diameter, appropriately
situated within the ore zones, was sunk to a depth of 1325 feet and levels
were cut off at 1115 feet and 1275 feet. A total of 15,000 feet of level
work has been completed (95 % on the lower level) and a ramp between the
levels was driven largely in ore. Detailed geologic mapping with special
care for stratigraphic, alteration and structural features has been immen-
sely helpful in understanding the relationships between these features and
ore. Drilling from underground totalled 50,000 feet, and from this work the
following conclusions are reached :

1. The basic concepts from which the tonnage and grade estimates were made
   based on surface exploration drilling only are essentially sound and
   represent fair approximations of what may be expected in the Elmwood
   deposit.

2. The ore indicated by the drill holes extends for large distances and
   there appears to be at least a circuitous continuity between the ore in
   the drill holes. Whether all of the ore holes will be found to represent
   interconnected ore appears unlikely, however, and since the developed
   mine is only a small part of the drilled area, this question will not be
   completely answered for a long time to come.

3. The ore is of irregular and complex shape both as to its form within a
   stratigraphic unit and is shaped in the vertical dimension.

4. The dilution factor of a minimum of 40 % waste for drill hole data
   appears to be reasonably close for estimating mine grade. It will
   require, however, several years of mining experience to reach a really
   good figure to use for dilution in this orebody.

5. The distribution of metal values within the ore is highly irregular
   thus adding greatly to the difficulty of interpreting the significance
   of individual drill holes. It is evident that because of the erratic
   distribution of metal values, a fairly large number of holes is neces-
   sary to reach good approximations of average ore grade.

The significant result of the mine development program of phase four was
the critical examination and appraisal of the interpretations made from
the diamond drill information of the exploration period. Of major impor-
tance as well,was the increased knowledge of the ore occurrence provided
by the underground work which greatly enhanced the basis for feasibility
studies and the planning of mine and plant design.

Phase five, though beyond the scope of exploration is, neverthe-
less, of vital interest to all who have participated in the exploration
process. Exploration geologists discovered an ore deposit and measured
and evaluated its characteristics in economic terms. The Elmwood mill and
plant are under construction and the mine is being placed in readiness for
production which is scheduled for early 1974, just ten years after the
exploration project was initiated. The stage in which production performance
will make the ultimate judgement as to the effectiveness of the exploration
and the work of measurement and evaluation is now approaching".

11.33.C - <u>BIBLIOGRAPHY</u>

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## 11.34 - FUTURE OF EXPLORATION FOR ZN AND PB IN EEC COUNTRIES

## 11.34.A - THE THREE PHASES OF EXPLORATION

Following the "Committee of Mineral Resources and the Environment (COMRATE)" of the U.S. National Academy of Sciences, we shall consider here that in any given area containing deposits of some useful mineral or judged to be favorable to their occurrence, the search effort over time follows an evolution pattern including three phases of exploration (COMRATE, 1975).

During the first phase, exploration effort consists of surface prospecting which results in discovery of mineralized outcrops and orebodies located immediately beneath them. Most zinc and lead deposits which were mined in the past and are mined at present in the world were found in this way.

During the second phase, exploration effort consists of geological mapping and instrumental (geochemical, geophysical, airborne, etc ...) surveys around known deposits, or known metal showings, or other surface anomalies, resulting in discovery of new deposits in known mineralized districts. Substantial increases in reserves may result from this essentially pragmatic type of exploration as shown by the example of the porphyry coppers of North America : second-phase exploration efforts during the period 1950-1971 have resulted in the discovery of 40 Mt of copper contained in 39 deposits, as compared with 41 Mt contained in the previously known 17 deposits.

During the third phase, "exploration effort consists of using geological occurrence models (sometimes with genetic content) of deposits and of their settings. Such models allow the formulation of predictions about mineral provinces and mineral occurrences in the absence of mineralized outcrops and in the absence of anomalies resulting from instrumental surveys.

... This approach ... is followed, of course, by geological and instrumental field surveys". (ibidem).

Since third phase exploration compaigns do not use mineralized outcrops or other surface anomalies as starting points, they may be applied in larger areas than the previous ones, and even in areas with no mining history at all if favorable structures and environments are thought to be present at depth.

With regard to oil and gaz, a few simple geological models, devised several decades ago, proved quite reliable and were used in third phase exploration programs which resulted in the discovery of most fields currently in operation. With regard to lead and zinc on the other hand, the two North American districts mentioned in the previous paragraph, i.e. the Viburnum Trend in Missouri and the Central Tennessee district are among the few examples of third phase discoveries. The difference with oil and gaz is undoubtedly related to the following facts :

1. Zn and Pb deposits are very diverse.

2. They occur in very diverse environments.

3. Reliable geological models of their occurrence proved difficult to devise, as shown by current controversies among specialists.

4. They are smaller drilling targets than oil and gas deposits.

## 11.34.B - EVOLUTION OF EXPLORATION PROGRAMS IN EEC COUNTRIES

With regard to Zn and Pb, first phase exploration has come to an end many years ago in all the territories belonging to the EEC countries except Greenland, where a large deposit has recently been found and a number of mineralized outcrops are awaiting a thorough evaluation (sec. 11.22),

Second phase exploration programs have been going on for some time in most mining districts of Ireland, the United Kingdom, France, Belgium, Germany and Italy. A number of deposits have been found as a result. Although in most of these districts much remains to be done, there seems to be a rather general tendency to use geological models as tools to direct the research effort .

It appears therefore that the discovery of new deposits in EEC countries, Greenland excluded, will depend mainly on the success of third phase exploration, which in turn depends on

1) the availability of reliable models of Zn and Pb deposits;

2) the availability of information on the three-dimensional geological structure of areas judged to be favorable to the occurrence of Zn and Pb deposits;

3) the availability of cheap drilling.

The need for improved down-the-hole geophysical measurements methods has already been underlined. So has the need for improved rock-geochemical and gas-geochemical methods of detecting halos and other chemical environments that are specific of the various types of deposits.

## 11.34.C - DISCOVERY COSTS

The cost of discovery, which is small during the first phase of exploration, increases considerably during the second phase as shown by a table borrowed from the COMRATE report and reproduced as fig. 11.34.1 in this report. In Canada, second phase exploration started on the average in 1950. During the 20 years period that followed, discovery costs increased from 0.6 % to 2 % of the gross value of metals contained in the deposits discovered. Presumably this trend will continue but even so, discovery costs are likely to remain a small part of the total investment involved in developing a deposit for production and building corresponding smelter and refinery capacity.

Additional data are given by Derry (1975 , in Downes and Burton 1977) who calculated that "in Ireland to 1973, 14.8 million pounds spent resulted in the discovery of four previously unknown orebodies, whereas in Canada, the cost of discovering an orebody averages 6.12 million pounds and in Australia the cost is still higher".

Data about the cost of exploration are also given by B.R.G.M. (unpublished document), according to which it can be subdivided in the following way :

1. first approach : collecting technical and mineral rights information; estimating how favorable the area is; photogeology using available black and white photographs; first visits to the area : 10 to 50 F/km2.

2. search for prospects and anomalies : surface geological, geochemical and airborne geophysical reconnaissance surveys (strategic exploration); Elaborate photogeology (color, infra-red and so on); evaluation of minimum economic criteria : 150 to 300 F/km2.

3. control of prospects and anomalies : detailed geological mapping; devising a locally adequate exploration methodology; detail geochemistry and geophysics (tactical exploration); examination by pits and trenches;

| | Value of Metals Discovered | | Average per Discovery in $ Millions | |
|---|---|---|---|---|
| | Annual Average in $ Billions | In $'s per each $* of Expl. Expend. - Total Industry | Exploration Expenditures | Value of Metals Discovered |

**A. Canada**

Nonferrous metals (and asbestos)
1971 $ - 1971 metal prices.

Period

| | | | | |
|---|---|---|---|---|
| 1951 - 55 | 4.4 | 160 | 2 | 320 |
| 1956 - 60 | 5.4 | 110 | 6 | 670 |
| 1961 - 65 | 5.2 | 95 | 6 | 570 |
| 1966 - 70 | 5.4 | 55 | 14 | 770 |

**B. Western U.S.A.**

Metals excluding Uranium
1970 $ - 1970 metal prices.

Period

| | | | | |
|---|---|---|---|---|
| 1955 - 59 | 2.8 | 80 | NA | NA |
| 1960 - 64 | 3.2 | 59 | | |
| 1965 - 69 | 4.1 | 45 | | |

* Equivalent to efficiency of Exploration Dollar. The expenditures include expenditures for all exploration programs whether successful or not.

Fig. 11.34.1   Mineral exploration costs and results in North America
(after Statistics Canada 1973 and Amax 1971, in Comrate, 1975)

percussion drilling; preliminary geostatiscal study, preliminary study of the economics : 20 000 to 50 000 F/km2.

4. delineation of orebodies : diamond drilling, controlled sampling, tests of beneficiation; preliminary feasibility study : 1 to 2 million francs per target.

5. evaluation of the deposit : diamond drilling, development underground work, pilot plant tests, feasibility study : several million francs per deposit.

Drilling contributes more and more to the cost of exploration as targets become deeper or less directly associated with mineralized outcrops and surface anomalies. It has already been mentioned that between 1943 and 1965, 100 000 holes have been drilled in Missouri. In Ireland, according to Dr. C. Williams, Director of the Geological Survey, 75 to 150 kilometers of holes are drilled per year for exploration purposes only. In addition, from 5 to 10 km per year are drilled at Tynagh and at Silvermines for development purposes. At Tara alone, 75 km were drilled before production started.

It is therefore obvious that cheap drilling is essential if mineral exploration is to proceed successfully. Improved technologies may help in this regard. However technology is not the only parameter that determines the cost of drilling. At Silvermines, Ireland, development drilling in the summer of 1977 cost  5 pounds per feet (personal communication of E. Swail, Chief Geologist). This is considerably less than in at least some other areas of western Europe : for example the few holes drilled in Belgium for mineral exploration in 1977 cost 4 to 5 times as much.

It is recommended that

1) drilling technologies be improved and new technologies be developed in order to drill 500 m holes at lower cost while providing suitable rock samples and allowing a large spectrum of borehole geophysical techniques to be used (Proposal for a Multiannual R. and D. programme, CEC, 1977).

2) a special study group be appointed to examine how, with existing techno- logies, drilling could be made cheaper in EEC countries.

## 11.34.D - GEOLOGICAL MODELS

Reliable geological models are useful at all stages of exploration. They are essential in third phase programs. They play an increasingly important role in exploration programs within the EEC countries; and this trend is likely to continue.

However Zn and Pb deposits are so diverse, as shown in sections 11.21 to 11.29, that they have given rise to many models. Of these few are sufficiently elaborate and precise to be good exploration guides. Most are of uncertain value because they have not been submitted to severe verification.

The recommendations made in section 11.29 aim at devising geological models which are more efficient and more reliable.

## 11.34.E - BACKGROUND INFORMATION USEFUL IN MINERAL EXPLORATION

More or less detailed geological maps are available at different scales for most of the areas belonging to the EEC countries. Every one of them displays an enormous amount of information, summarized, analyzed and co-ordinated so that interesting relationships are clearly shown. These maps are indispensable tools in mineral exploration, even though they have not been made specifically for that purpose and although they often have to be complemented and redrawn at a larger scale for the areas of interest. It is highly desirable that geological maps are periodically revised and improved.

Regional geophysical, geochemical and remote sensing surveys, which serve a number of purposes, also provide maps and photographs useful to the exploration geologist. In particular regional magnetic and gravimetry surveys help greatly in unravelling the three-dimensional geological structure of a country. Reconnaissance geochemical surveys, during which many chemical elements are analyzed, provide blackground information about the large scale distribution of chemical elements.

In addition to maps and photographs, an abundant literature has been published about the geology of all regions of Western Europe.

Information of interest to the exploration geologist is scattred through this literature, i.e. through a multitude of books and papers dealing mainly with historical and structural geology, palaeontology, stratigraphy, sedimentology, petrology, mineralogy, etc ... Thus although a wealth of data has already been published, the problem of retrieving and assimilating them is a real one.

It is recommended that, for each area considered favorable to the occurrence of Zn and Pb deposits, all the relevant information be collected, inventorized, screened, critically examined and eventually published under a convenient form so as to be readily available to the exploration geologist.

## 11.34.F - SUMMARY

In the EEC countries (except in Greenland) deposits with surface out-crops have been discovered long ago. A number of deposits concealed at depths of a few tenths of meters have also been found, usually by a combination of geological, geochemical and geophysical techniques.

However, as it has been shown in the Viburnum Trend of Missouri and in the Central Tennessee district, it has now become possible to locate Zn and Pb orebodies at depths of several hundred meters. Entirely new vistas are thus opened to exploration.

Two conditions must be fulfilled to make deep discoveries possible :

1) reliable models of orebody emplacement must be devised;

2) the geological structure and constitution of the area must be known in three dimensions.

Of all geochemical methods, it is thought that rock geochemistry will contribute most to deep discoveries; primary haloes and other specific geochemical environments should be looked for around each type of orebody in order to make rock geochemistry a more powerful tool.

Geophysics will contribute greatly to deep discoveries if more effi-cient and more varied borehole techniques become available at a reasonable cost.

It is recommended that all existing techniques are tested around known orebo-
dies of different types and that research be undertaken or pursued to
improve them. Some geophysical methods, in particular magnetometry and gravi-
metry will also help in unravelling the three dimensional geological
structure of the areas to be explored.

Deep discoveries will require much drilling. It is therefore essential
that drilling becomes as cheap as possible. It is also essential that the
best use is made of every hole drilled, which implies improvement of rock
geochemical and borehole geophysical techniques along the lines just sugges-
ted. It should be pointed out however that geophysical and geochemical
methods cannot be very powerful if reliable geological models of the deposits
and their haloes are not available.

## 11.34.G - BIBLIOGRAPHY

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## CHAPTER 11.4 - RESERVES IN EACH COUNTRY

## 11.41 - INTRODUCTION AND RECOMMENDATION

A few words of caution are necessary at the beginning of this paragraph :

a) Fig. 11.42.1 illustrates a classification of reserves and resources which has been proposed a few years ago by the U.S. Geological Survey and the U.S. Bureau of Mines. Other systems of classification are in use. Furthermore it proves extremely difficult to define terms such as "measured", "indicated", "inferred", or "proven", "probable", "possible" without a certain amount of vagueness. Data obtained from different sources are therefore not strictly comparable. It has often been pointed out also that, in addition to "increasing degree of geological assurance" and "increasing degree of economic feasibility" (see fig. 11.42.1), a third parameter related to the possible rate of mineral production should be taken into account in a classification of reserves and resources.

b) Numerical values of reserves and resources belonging to different categories are as a rule given without standard error or confidence level appreciations. It is therefore not possible to assess their accuracy.

c) When the data are given is tons, it is not always clear whether these are metric, short or long tons. In this report we have applied the corrections which, to the best of our knowledge, are necessary to convert all data into metric tons.

d) It is not always clear whether the figures available refer to in situ ore or to recoverable ore.

e) The date to which the estimate refers is not always mentioned. Additional uncertainty results for deposits which are currently mined.

f) The maximum depth to which the estimate refers is not always mentioned. For vein type deposits especially, this is another source of uncertainty.

g) Reliable data on reserves and resources may be difficult to obtain because of their confidential nature.

In this paragraph, we have used the data supplied by government agencies when available. The reader may find somewhat different figures in the literature. As a result of the difficulties encountered in estimating and defining reserves and resources, published figures are far from being entirely consistent.

An effort should be made to refine and systematize the gathering of such data so that a running inventory of reserves and resources within the EEC countries can be kept. Simultaneously, future production rates should be calculated according to the various scenarios that appear likely. The results of such studies should of course be published only to the extent that they respect the confidentiality of data.

## TOTAL RESOURCES

| identified | | | undiscovered | |
|---|---|---|---|---|
| demonstrated | | | hypothetical | speculative |
| measured | indicated | inferred | (in known districts) | (in undiscovered districts) |

reserves

resources

increasing degree of economic feasibility →

subeconomic — paramarginal / submarginal

← increasing degree of geological assurance →
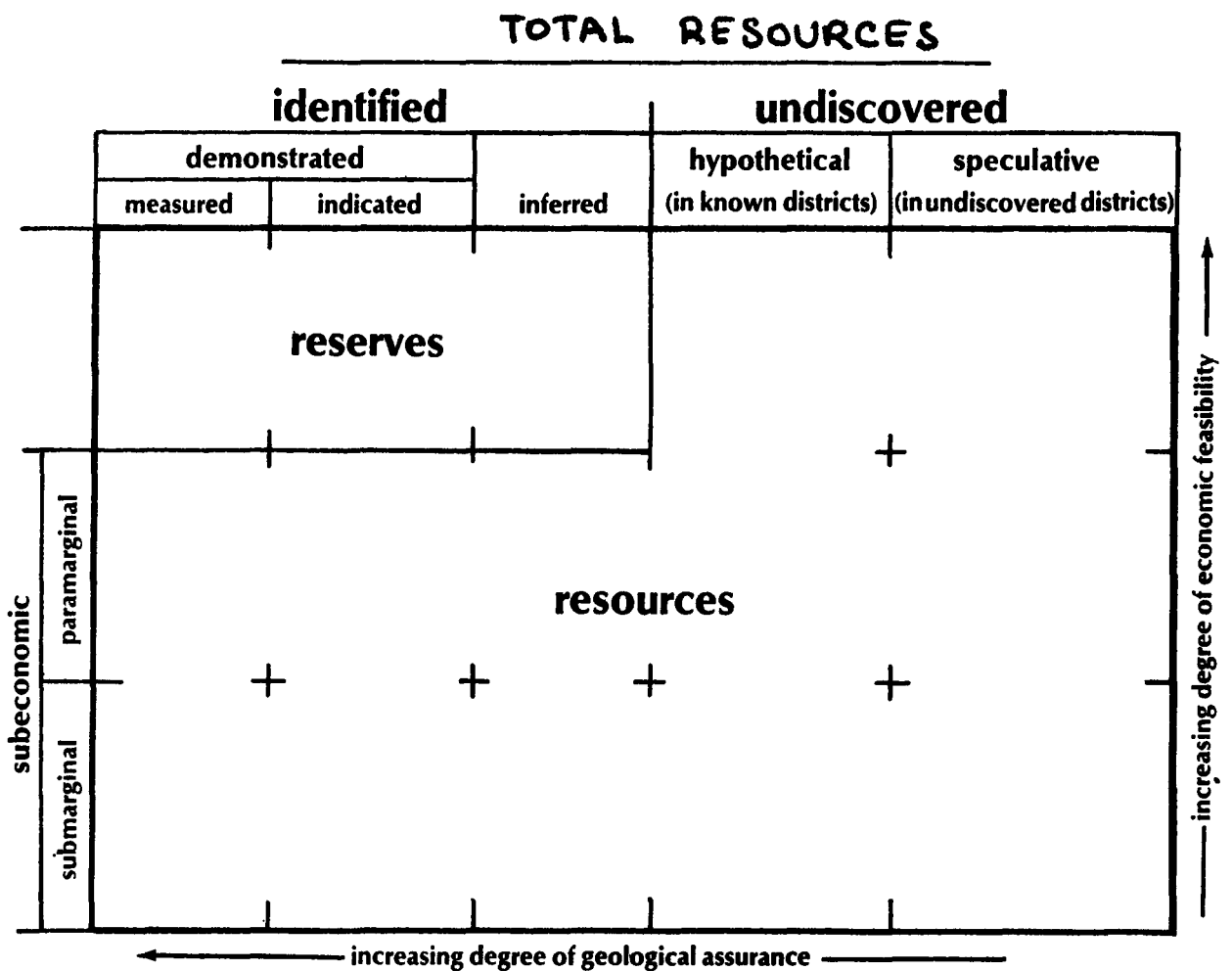
Fig. 11.42.1. Classification of reserves and resources used by the
U.S. Geological Survey and U.S. Bureau of Mines

## 11.42 - WORLD RESERVES

The information presented in this section has been gathered by our Italian partners.

## 11.42.A - LEAD

The world reserves of lead (metal content) are shown in table 11.42.2. The following explanatory notes refer to this table.

1) Estimates of the U.S. Geological Survey (U.S. Mineral Resources, Professional Paper 820, Washington D.C., 1973, p. 325). Reserves, according to the notation used therein, refer to : "identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions".

2) Estimates updated by U.S. Bureau of Mines (U.S.B.M. Bulletin 667, Mineral Facts and Problems, Washington D.C., 1975, p. 596).

3) Estimates of the U.S.B.M. (id.). They include "hypothetical undiscovered and some identified economically paramarginal resources". They exclude "speculative and some identified and undiscovered subeconomic resources".

4) Other resources are given in round numbers, the unit being a million metric tonnes (Mt).

## 11.42.B - ZINC

The world reserves of zinc (metal content) are shown in table 11.42.3, according to the Bundesanstalt für Bodenforschung (Untersuchungen über Angebot und Nachfrage mineralischer Rohstoffe, vol. 5, Zinc, Hannover. December 1974, p. 17).

Table 11.42.2 - WORLD RESOURCES OF LEAD (Mt)

| | RESERVES (1) | | OTHER RESOURCES (3) | |
| | Mt | % | Mt | % |
|---|---|---|---|---|
| U.S.A. (2) | 53.5 | 35.3 | 54 | 36.3 |
| Canada (2) | 17.2 | 11.4 | 18 | 12.5 |
| Greenland | 0.1 | 0.0 | n.r | n.r |
| Total N.America | 71.0 | 47.3 | 72 | 48.5 |
| Mexico | 4.1 | 2.7 | 4 | 3.0 |
| Honduras | 0.2 | 0.1 | n.r | n.r |
| Other | 0.1 | 0.1 | 1 | 0.6 |
| Total C.America | 4.4 | 2.9 | 5 | 3.6 |
| Peru | 3.2 | 2.1 | 4 | 2.4 |
| Argentina | 0.9 | 0.6 | n.r | n.r |
| Bolivia | 0.7 | 0.5 | n.r | n.r |
| Brazil | 0.7 | 0.4 | n.r | n.r |
| Chile | 0.1 | 0.1 | n.r | n.r |
| Colombia | 0.02 | 0.0 | n.r | n.r |
| Total S.America | 5.6 | 3.7 | 5 | 3.6 |
| Bulgaria | 3.2 | 2.1 | 3 | 1.8 |
| Yugoslavia | 2.7 | 1.8 | 3 | 1.8 |
| Spain | 2.5 | 1.6 | 3 | 1.9 |
| Poland | 2.3 | 1.5 | 3 | 2.1 |
| Sweden | 2.3 | 1.5 | 1 | 0.9 |
| East Germany | 0.4 | 0.3 | n.r | n.r |
| Rumania | 0.4 | 0.3 | n.r | n.r |
| Greece | 0.3 | 0.2 | n.r | n.r |
| Austria | 0.2 | 0.2 | n.r | n.r |
| Finland | 0.1 | 0.1 | n.r | n.r |
| Norway | 0.1 | 0.1 | n.r | n.r |
| Other | 0.4 | 0.3 | n.r | n.r |
| Total non EEC Europe | 14.9 | 10.0 | 23 | 15.2 |
| Total EEC Europe | 7.4 | 5.0 | | |
| Morocco | 1.4 | 0.9 | 1 | 0.9 |
| S.W.Africa | 1.4 | 0.9 | 2 | 1.5 |
| Algeria | 0.7 | 0.4 | 2 | 1.4 |
| Zambia | 0.7 | 0.4 | n.r | n.r |
| Tunisia | 0.4 | 0.3 | n.r | n.r |
| Tanzania | 0.1 | 0.1 | n.r | n.r |
| Other | 0.2 | 0.1 | n.r | n.r |
| Total Africa | 4.7 | 3.2 | 8 | 5.5 |
| U.S.S.R. | 16.3 | 10.8 | 16 | 10.9 |
| China | 2.7 | 1.8 | 3 | 1.8 |
| Iran | 1.8 | 1.2 | 2 | 1.2 |
| N.Korea | 1.6 | 1.1 | n.r | n.r |
| Japan | 1.1 | 0.7 | n.r | n.r |
| Burna | 0.7 | 0.4 | n.r | n.r |
| S.Korea | 0.4 | 0.3 | n.r | n.r |
| India | 0.1 | 0.1 | n.r | n.r |
| Turkey | 0.1 | 0.1 | n.r | n.r |
| Thailand | 0.02 | 0.0 | n.r | n.r |
| Total .Asia | 24.9 | 16.7 | 24 | 16.3 |
| Australia | 16.8 | 11.2 | 11 | 7.3 |
| World Total | 149.6 | 100.0 | 150.0 | 100.0 |

Table 11.42.3 - WORLD RESOURCES OF ZINC (Mt)

| | RESERVES (1) | | OTHER RESOURCES | |
|---|---|---|---|---|
| | Mt | % | Mt | % |
| Canada | 37.6 | 20.3 | 7 | 5.6 |
| U.S.A. | 31.8 | 17.1 | 32 | 27.3 |
| Total N.America | | 69.4 | | 37.4 | 39 | | 32.9 |
| Peru | 7.1 | 3.8 | 1 | 1.3 |
| Mexico | 3.6 | 1.9 | 1 | 0.8 |
| Brazil | 1.8 | 1.0 | 0.5 | 0.4 |
| Bolivia | 0.9 | 0.5 | 0.8 | 0.7 |
| Argentina | 0.5 | 0.3 | 1 | 1.3 |
| Other | 1.0 | 0.5 | 0.5 | 0.4 |
| Total Latin America | | 14.9 | 8.0 | 6 | 4.9 |
| Rep. S. Africa | 1.4 | 0.7 | 2 | 1.5 |
| S.W.Africa | 1.0 | 0.6 | 6 | 5.3 |
| Zaïre | 0.9 | 0.5 | 0.9 | 0.8 |
| Zambia | 0.7 | 0.4 | - | - |
| Algeria | 0.6 | 0.3 | 0.3 | 0.3 |
| Morocco | 0.6 | 0.3 | 0.1 | 0.1 |
| Rhodesia | 0.6 | 0.3 | - | - |
| Other | 0.1 | 0.1 | 0.1 | 0.1 |
| Total Africa | | 5.9 | 3.2 | 10 | 8.1 |
| Spain | 5.1 | 2.7 | 1 | 1.0 |
| Sweden | 4.0 | 2.2 | 2 | 1.7 |
| Yugoslavia | 3.5 | 1.9 | 2 | 1.7 |
| Finland | 2.0 | 1.1 | 1 | 0.6 |
| Norway | 1.5 | 0.8 | 1 | 0.8 |
| Other | 0.7 | 0.4 | 0.3 | 0.3 |
| Total non EEC Europe | | 16.8 | 9.0 | 8 | 6.1 |
| Total EEC Europe | | 14.1 | 7.7 | 4 | 3.5 |
| Japan | 9.1 | 5.0 | 6 | 5.2 |
| Iran | 3.7 | 2.0 | 2 | 1.5 |
| India | 2.6 | 1.4 | 3 | 3.0 |
| Burma | 0.5 | 0.3 | 0.1 | 0.1 |
| Other | 0.6 | 0.3 | 3 | 2.5 |
| Total Asia | | 16.7 | 9.0 | 14 | 12.3 |
| Australia | | 17.6 | 9.5 | 28 | 23.7 |
| URSS | 24.5 | 13.2 | 7 | 6.4 |
| Poland | 4.5 | 2.4 | 2 | 1.7 |
| Other | 1.0 | 0.6 | 0.5 | 0.4 |
| Total Communist Country | | 30.0 | 16.2 | 10 | 8.5 |
| WORLD TOTAL | | 185.3 | 100.0 | 118 | 100.0 |

(1) measured and indicated reserves

(2) inferred reserves and hypothetical economic resources

## 11.43 - RESERVES IN THE COMMUNITY

### 11.43.A - INTRODUCTION

We have obtained data of uneven quality and completeness concerning reserves and resources of Zn and Pb in EEC countries. Estimates of hypothetical and speculative resources are scarce. When the reserves and resources are given in tonnes of ores or concentrates, we have converted them into tonnes of contained metal. This "contained metal" is clearly not entirely recoverable since various losses should be taken into account :

a) losses due to incomplete mining if the figures refer to in situ reserves; 20 % or more of the deposit may be left in abandoned pillars;

b) losses due to ore processing since the degree of recovery reaches at best about 90 % and may be considerably lower for oxide ores or complex ores;

c) losses due to smelting (5 % is the order of magnitude).

Many deposits were abandoned in the last quarter of the ninetienth century because of drops in metal prices. Among them some were veins where unmined ore may remain in depth. Such resources may be significant but as a rule no estimates of them are available.

### 11.43.B - DENMARK

At Black Angel, Greenland, "extractable reserves" at the end of 1976 amounted to 3.6 Mt of ore, containing some 175 000 t of Pb and 496 000 t of Zn. At the current rate, these reserves correspond to only 6 years of production. However it should be pointed out that reserves have been maintained at the same level since the beginning of the operation in 1973 (section 11.22.C).

### 11.43.C - IRELAND

Reserves and resources in Irish deposits are listed in table 11.42.4.

The mining rates obtained or planned in the Irish deposits are as follows :

| | | |
|---|---|---|
| Bula | : | 0.9 Mt of ore per year |
| Tara | : | 2.25 |
| Silvermines | : | 0.9 |
| Tynagh | : | 0.6 |

As shown by these figures, reserves at Silvermines and Tynagh correspond respectively to only 5 and 6 years of production at the current rates.

Among the unmined deposits of Ireland, Keel may be considered as a high-grade low-tonnage deposit.

## 11.43.D - UNITED KINGDOM

According to the information received from I.G.S. (1977), identified resources are very small in the United Kingdom :

- 0.3 Mt of ore at Greenside, Lake District

- 1   Mt of ore containing 70 000 t Zn and 26 000 t Pb in the Minera district, North Wales.

On the other hand, hypothetical resources are considerable. A statistical appraisal suggests that some 4 Mt of Pb may still be discovered in the Northern Pennines alone.

## 11.43.E - FRANCE

Reserves and resources in French deposits are listed in table 11.42.5.

The 1976 production of French mines is given below in tonnes of contained metal :

| | | |
|---|---|---|
| Largentière | 23 000 t Pb | 4 100 t Zn |
| Les Malines | 2 000 | 9 300 |
| Les Farges | 2 300 | - |
| Saint-Salvy | - | 21 100 |

As shown by these figures, reserves at Largentière correspond to only a few years of production at the current rate.

Identified resources mentioned in table 11.42.5 are mostly low-grade deposits.

## 11.43.F - BELGIUM, THE NETHERLANDS AND LUXEMBURG

There are no reserves known in Belgium and adjacent countries at the present time. Hypothetical and speculative resources may be considerable but they have never been estimated.

## 11.43.G - GERMANY

The data we have obtained about reserves and resources in Germany come from indirect sources : a paper by Friedensburg published in Erzmetall in 1971 (Bd. 24., 369-378 and 441-445) and a book by Dorstewitz and Friedensburg in 1976 (Die Bergwirtschaft der Erde, Stuttgard, F. Enke). At least some of these estimates are very rough. See table 11.42.6.

The rate of production is 0.3 Mt per year at Rammelsberg and 0.4 Mt at Grund. In these deposits, reserves are therefore satisfactory. In the Lüderich deposit, on the other hand, they amount to only a few years of production.

Among German deposits which are not mined at the present time, Auguste-Victoria and Graf Moltke are typical high grade-low tonnage deposits. At Mechernich, low grade resources are considerable.

## 11.43.H - ITALY

Reserves and resources in Italian deposits, as given by our Italian partners, are listed in table 11.42.7. As compared with mine production (table 11.42.8) they appear satisfactory. In addition to the reserves mentioned in the table, considerable low grade resources are known in Sardinia.

## 11.43.J - CONCLUSIONS

The total identified resources of normal grade in the Community amount to about 17.5 Mt of metal (about 13 Mt of Zn and 4.5 Mt of Pb). These figures are somewhat lower than those given in tables 11.42.2 and 3, but they do not include the large Meggen deposit for which we have obtained no data. Identified unmined high grade-low tonnage deposits account for a small part of the total (1 Mt of metal).

The largest unmined low grade resources are at Mechernich, Germany, and consist of 2 or 3 Mt of metal. Other identified low grade resources are found in Triassic sandstones of the Vosges district, in Jurassic lime-stones of the Detroit Poitevin and in black shales of the Montagne Noire (sec. 11.25.H, G and E respectively). Other low grade resources are known in Sardinia.

It is likely that both low grade and high grade-low tonnage deposits are incompletely surveyed. The figures referring to them underestimate the frequency of these types of deposits.

In 1976, the total mine production in the Community reached 332 000 t of Zn and 135 000 t of Pb. The reserves appear large in comparison. However the Navan deposits, which account for half of the reserves within the Community, were not in production in 1976.

In fact reserves amount to only a few years of production in several deposits currently mined. Presumably in some of these new reserves will be discovered in due time. But others will reach depletion. It is therefore highly desirable that new deposits should be found in the near future.

## LEAD AND ZINC RESERVES AND RESOURCES OF KNOWN IRISH DEPOSITS (DOWNES AND BURTON, 1977)

| DEPOSIT | | Amount Mt | ORE Pb % | ORE Zn % | ORE Pb + Zn % | METAL CONTENT Pb (x1000t) | METAL CONTENT Zn (x1000t) | METAL CONTENT Pb + Zn (x1000t) | Cu (x1000) | Ag t |
|---|---|---|---|---|---|---|---|---|---|---|
| Abbeytown | ? | ? | ? | ? | ? | | | | | |
| Avoca | | 0.18 | | | 8 to 9 | | | 15 | | |
| Ballinalack | | 1.8 | 0.66 | 4.35 | | 13 | 87 | | | |
| Keel | | 1.6 | 4.0 | 3.0 | | 65 | 49 | | | |
| Moate | | 0.11 | 1.0 | 6.4 | | 1 | 7 | | | |
| Navan a) Bula | proven | 13.6 | | | 9.2 | | | 1 260 | | |
| | probable | 6.0 | | | 5.2 | | | 310 | | |
| b) Tara | proven + probable | 31 | 2.35 | 11.43 | | 725 | 3 525 | | | |
| | possible | 30 | 2.35 | 11.43 | | 710 | 3 450 | | | |
| c) Sabina | | 1.2 | | | 7.6 | | | 90 | | |
| d) Tatestown | | 1.15 | | | 6.72 | | | } 100 | | |
| | | 0.3 | | | 13.36 | | | | | |
| Silvermines Upper G | | 2.5 | 1.77 | 7.67 | | 44 | 190 | | | |
| Lower G | | 0.32 | 3.34 | 4.52 | | 11 | 14 | | | |
| B | | 2.5 | 3.18 | 5.29 | | 79 | 132 | | | |
| Tynagh Zone ii | | 1.5 | 4.06 | 3.23 | | 61 | 49 | | 4 | 70 |
| Zone iii | | 0.7 | 2.44 | 4.45 | | 17 | 31 | | 3 | 10 |
| | potential | 1.0 | 4.41 | 4.50 | | 44 | 45 | | 3 | 23 |
| TOTAL : APPROX. | | | | | | 1 800 | 7 600 | 1 770 | 10 | 100 |

Table 11.42.5 - RESERVES AND RESOURCES IN FRENCH DEPOSITS (B.R.G.M., 1977)

(thousand tons of contained metal)

| | RESERVES | RESOURCES identified | RESOURCES hypothetical |
|---|---|---|---|
| **DEPOSITS LOCATED IN THE <u>COVER</u>** | | | |
| A) in the carbonate succession | | | |
| <u>Detroit Poitevin</u> | | 10 | |
| South of the <u>Central Massif</u> including <u>Les Malines</u> | 200 | | |
| B) in the sandstone succession | | | |
| Vosges including <u>St. Avold</u> | | 20 | |
| Corsica (<u>La Finosa</u>) | | 27 | |
| <u>Central Massif</u> (including <u>Largentière</u>) | 100 Pb 20 Zn | 45 Pb | |
| **DEPOSITS LOCATED IN THE <u>OLD MASSIFS</u>** | | | |
| A) <u>Pyrénées</u> (in part stratabound) | 30 | 200 | 200 |
| B) <u>Montagne Noire</u> (stratabound) | 50 | 100 | |
| C) <u>Massif Armoricain</u>. Veins | 50 | 30 | 200 |
| Other | ? | ? | ? |
| D) <u>Les Maures</u>. Veins | 80 | | |
| E) Central Massif. Veins Including <u>Les Farges</u> and <u>St. Salvy</u> | 450 | 50 | 100 |
| APPROX. TOTAL : | 1 000 | 500 | 500 |

Table 11.42.6 - Zn and Pb RESERVES AND RESOURCES IN A FEW MAJOR GERMAN DEPOSITS

|  | ORE | METAL CONTENT | | | BY-PRODUCTS |
|---|---|---|---|---|---|
|  | Mt | Zn 1 000t | Pb 1 000t | Ag t |  |
| **HARZ** |  |  |  |  |  |
| Rammelsberg | 5 | 600 | 300 | 500 | copper |
| Grund | 8 | 400 | 300 | 800 | copper |
| **RUHR** |  |  |  |  |  |
| Auguste-Victoria | 2 - 3 | 60 | 240 |  |  |
| Graf Moltke | 3,5 | 70 | 280 |  |  |
| **MECHERNICH** | 100 | 1000-2000 | 600-1000 |  |  |
| Westfeld | 25 | 250 | 600 |  |  |
| Meggen | ? |  |  |  |  |
| Ramsbeck | 0.5 | 15 | 5 |  |  |
| Luderich | 1 | 70 | 15 |  |  |

Table 11.42.7

LEAD AND ZINC RESERVES AND RESOURCES OF ITALIAN DEPOSITS

| | | ORE | METAL CONTENT | | | BY-PRODUCTS |
|---|---|---|---|---|---|---|
| | | Mt | Zn 1000t | Pb 1000t | Ag t | |
| Gorno | proven | 1.6 | 71 | 13 | 6 | |
| | probable | 0.9 | 39 | 8 | | |
| | possible | 1.0 | 34 | 8 | | |
| Raibl | proven | 4.7 | 249 | 33 | | |
| | probable | 1.4 | 72 | 6 | | |
| Salafossa | proven | 10 | 450 | 100 | | |
| Monteneve | prov.+prob. | 0.5 | 20 | 7 | 7 | cadmium |
| Fenice Cap | proven | 2.2 | 117 | 25 | | |
| | probable | 0.4 | 23 | 5 | | copper |
| Buggeru-Su Z. | proven | 6.4 | 240 | 28 | 14 | |
| | probable | 1.3 | 49 | 5 | 2 | |
| Funtana R. | proven | 0.2 | 7 | 3 | 13 | copper |
| | probable | 0.9 | 28 | 13 | 50 | |
| Montevecchio | proven | 3.2 | 112 | 54 | 40 | Bi, Sb, Ga, |
| | probable | 1.7 | 59 | 29 | 22 | In, Ge |
| Silius | pro.+prob. | 10 | | 250 | | fluorite,barite |
| Arenas | proven | 1.3 | | 65 | | |
| | probable | 0.3 | | 15 | | |
| Sos Enattos | proven | 0.8 | 50 | | | |
| San Giovanni | proven | 3.3 | 226 | 50 | 25 | |
| | probable | 1 | 68 | 15 | 7 | |
| Acquaresi, Montecani, Masua, Nebida. | proven | 9.2 | 455 | 151 | 36 | |
| | probable | 3.5 | 173 | 57 | 13 | |
| San Benedetto | proven | 0.6 | 22 | 11 | 3 | |
| Rosas | proven | 0.2 | 4 | | | copper |
| Monteponi | proven | 2.8 | 83 | 61 | 30 | |
| | probable | 1 | 31 | 23 | 11 | |
| Campo P.- Funtan. | proven | 2.7 | 192 | 5 | | |
| | probable | 1 | 67 | 2 | | |
| Seddas Modd | proven | 0.9 | 54 | 8 | | |

APPROX. TOTAL  :  3 000    1 100    280

Table 11.42.8    PRODUCTION OF ITALIAN MINES

| Locality | Year of production | ORE | GRADE | | METAL CONTENT | | |
|---|---|---|---|---|---|---|---|
| | | | Zn | Pb | Zn | Pb | Ag |
| | | t | % | % | t | t | t |
| Gorno | ? | 140 000 | - | - | 4 500 | 950 | 0.4 |
| Raibl | ? | 387 000 | - | - | 15 300 | 1 170 | - |
| Salafossa | ? | 600 000 | 4.0 | 0.7 | 24 000 | 4 200 | - |
| Monteneve | ? | 40 000 | 3.8 | 1.4 | 1 250 | 460 | 0.5 |
| Fenice-Cap. | supposed 1976 | 150 000 | 5.2 | 1.11 | | | - |
| Buggeru-Su Z. | 1974 | 115 000 | | 1.1 | 9 200 | 1 260 | 0.6 |
| Funtana R. | ? | 47 000 | 3.0 | 1.4 | 1 400 | 660 | - |
| Montevecchio | 1975 | 180 000 | 3.5 | 1.7 | 5 500 | 3 200 | 2.3 |
| Silius | ? | 350 000 | - | 2.5 | - | 8 750 | - |
| Arenas | 1974 | 150 000 | | | | | |
| San Giovanni | 1974 | 255 000 | - | 1.5 | 5 200 | 4 200 | 1.1 |
| Acquaresi Montecani Masua Nabida | 1975 | 262 000 | 4.95 | 1.64 | 13 000 | 4 300 | 1.0 |
| San Benedetto | 1975 | 35 000 | 3.7 | 1.8 | 1 300 | 630 | 0.2 |
| Rosas | 1975 | 20 000 | 2.01 | 0.1 | 400 | 20 | 0.1 |
| Monteponi | 1973 | 56 000 | 2.95 | 2.2 | 1 650 | 1 230 | - |
| Campo P. Funtan. | 1973 | 135 000 | 7.11 | 0.2 | 9 600 | 270 | - |
| Seddas Modd. | 1973 | 70 000 | 5.98 | 0.85 | 4 150 | 600 | - |
| Monteponi Group | 1975 | - | - | - | 12 000 | 1 600 | - |

TABLE 11.42.9    Identified Zn and Pb resources (excluding low grade resources) in the Community

| | million tons (Mt) of metal | | |
|---|---|---|---|
| | Zn | Pb | Zn + Pb |
| Denmark | 0.5 | 0.175 | |
| Ireland | 7.6 | 1.8 | |
| France | | | 1.0 |
| Germany (incomplete data) | 1.2 | 1.0 | |
| Italy | 3.0 | 1.1 | |
| Total : | 12.3 | 4.1 | 1.0 |

PART 1.2

TECHNOLOGY OF CONCENTRATES PRODUCTION

## 12.1  - INTRODUCTION

Most ores currently mined cannot be directly treated in chemical or metallurgical plants in order to yield the valuable components. The content of gangue minerals is generally so high that, at the end of the treatment, the major part of the metal would remain imbedded, occluded, dissolved or slagged in the tailings.

It is thus necessary to somehow upgrade the ore, concentrating its mineral content in a marketable product and rejecting the gangue minerals in a tailing to be disposed of.

In ore dressing techniques, the beneficiation is based on a difference in one specific physical characteristic among the constituent minerals of the ore. This difference can be used in mechanized operations to yield two products : a concentrate containing most of the valuable mineral, and a tailing containing most of the useless minerals (or gangue). In some cases, more than one mineral can be fruitfully recovered from the ore : this is called a bulk concentration if they are recovered together, and a selective concentration, when each valuable mineral is concentrated separately.

In order to successfully apply the ore dressing techniques, each solid particle must contain no more than one mineral species, the degree of achievement of this objective is termed "degree of mineral liberation". It can be shown that the average particle size of a fully liberated ore is much smaller than the average size of a single mineral grain in the feed ore. The liberation degree depends mainly on the grade, the nature and size of the crystals and the dissemination of the minerals in the run-of-mine ore.

Mineral liberation is actually controlled by the crushing and grinding of the ore, i.e. by a comminution process. When the liberation is considered adequate, one can apply separation processes based upon the following physical properties :

- electrical conductivity;
- magnetic susceptibility;

- specific weight;
- floatability.

The first two properties are never used to separate lead and/or zinc concentrates. Differences in specific weight are basic in a number of processes called "gravimetric concentration processes" and briefly outlined below :

- jigging : gravimetric separation in a particulate bed made to pulsate by water injection or by a moving screen;

- tabling : spatial separation on a shaking deck across which a water layer is made to flow;

- heavy media separation (HMS) or sink-float process :
  separation of minerals according to their real specific weight in a pulp of intermediate density; this pulp consists of a fine dispersion of chosen fine particles (galena, ferro-silicium, magnetite) in water.

Floatability of a mineral is its ability to adhere to an air bubble when that mineral surface is rendered hydrophobic by specific chemical reagents. Typically, these reagents include :

- pH regulators, since the floatability of the minerals is adequate only within certain pH limits (milk of lime, soda ash, sulfuric acid);

- collectors or promoters, heteropolar molecules which can adhere to the mineral by their polar group ($-OCS_2^-$, $=O_2-PS_2^-$, $-COO^-$, $-NH_3^+$, etc ...) and form a hydrophobic layer with their hydrocarbon chain or ring ($-CH_2^-$, $C_6H_5^-$, etc ...). For sulfide minerals, collectors are anionic and of the xanthate or dithiophosphate (aerofloat) type. For oxide minerals, collectors can be fatty acids or amines;

- frothers, heteropolar molecules of the alcohol or other type, able to stabilize the air-water interface of the bubbles;

- activators, which facilitate the action of the collectors ($CuSO_4$ for the sulfides, $Na_2S$ for oxide minerals) and render the mineral more floatable;

- depressors, that inhibit the action of the collectors and tend to prevent flotation.

Flotation is a very complex operation, depending on an incredible number of factors, but it can be made selective by modulating the use of the various reagents. It can yield up to four or five different concentrates.

An important characteristic of the concentration processes is the size of the particles that can be fed in industrial plants; as only average figures can be given, the following table is purely indicative :

jigging    : from 25 mm to 0,2 mm (according to machine type)

tabling    : from  2 mm to 75 microns

HMS        : from 50 mm to 5 mm (static separators)
                      down to 0,5-1 mm (dynamic separators)

flotation : from 0,2 mm to 1 micron (best range : 10 - 100 microns).

In the past decades, the tendency has been to mine ores of decreasing metal content and decreasing grain size. These ores often contain several valuable components which must, as much as possible, be sold as single-metal concentrates. It is therefore not surprising if the flotation process is, by far, the most widely used of all the beneficiation processes. However, since the comminution necessary to reduce the ore to the liberation size is a very costly operation, it is advisable, when part of the minerals are liberated at a coarse size, to apply first a gravimetric concentration step, which will either eliminate part of the gangue (preconcentration) or recover part of the metal values (scalping).

Lead and zinc are mainly produced from mixed ores, containing these metals as sulfides, or, less frequently, as oxide minerals (carbonates, silicates, or sulfates). In some areas, the ores are sulfidic, with a certain amount of oxide minerals which have an important influence on the mineralurgical and/or the metallurgical treatment.

Lead and/or zinc concentrates can also be obtained as by-products during the beneficiation of other ores (fluorite, tin). Sometimes lead and

zinc ores contain other valuable minerals (copper sulfides, pyrite, barite) that can be selectively separated in a few cases.

Because of the characteristics of Pb-Zn ores currently available, beneficiation is now carried out by flotation, giving a selective separation into single-metal concentrates (which obviously contain a number of other minerals). It is not usual to treat coarsely disseminated ores for which a preconcentration stage can be applied; however, where it is convenient to do so, it is a common practice to use gravimetric concentration by heavy media separation, a part of the gangue with low metallic content being rejected in the process.

Generally (fig. 12.1.1), run-of-mine ores are crushed in stages in jaw crushers and cone crushers so that a feed suitable for fine grinding is obtained. Where preconcentration is included, it is common practice to treat crushed ore at that stage after removal of the fine particles by screening.

After one or two fine grinding stages in rod and/or ball mills in circuits closed by mechanical classifiers or hydrocyclones, lead-zinc ores are selectively floated.

Current practice involves first the flotation of the more floatable galena; the selectivity of the operation is then enhanced by depressing sphalerite and pyrite through the addition of sodium cyanide and/or zinc sulfate. A short-chain xanthate is the generally used promoter, at a slightly basic pH controlled with soda ash or milk of lime. Sphalerite is floated next after reactivation with copper sulfate, and a stronger promoter is used (long-chain xanthate, sodium aerofloat or Z-200, a proprietary collector); when pyrite is present, it is depressed at a high pH controlled by the addition of milk of lime; when there is no pyrite present, pH can be maintained at moderate or slightly acidic values.

Concentrates obtained after repeated flotation to improve metal grade are dewatered by thickening and filtration (drying eventually) before shipping.

The above-mentioned procedure is known as the "Sheridan-Griswold process", but there can be modifications applied according to the ore type; thus it is impossible to find two identical flowsheets.

Lead oxide minerals (almost exclusively cerusite) can be floated by sulfidization with sodium sulfide or sulfhydrate, and by using a powerful xanthate (amyl or hexyl).

Zinc oxide minerals are much more difficult to float; it is sometimes possible to use the "Rey-Raffinot process", consisting of a vigorous sulfidization followed by collection with an amine-type promoter; it is mandatory to eliminate the very fine particles (the slimes) prior to flotation, in a single-or two-stage hydrocycloning (Ek and Masson, 1973).

Run-of-mine ore

Fixed grizzly

Jaw crusher

Vibrating screen

Cone crusher
(one or two stages)

Rod mill

Hydrocyclones

Ball mill        Conditioner

Lead roughers

Lead cleaners

Lead recleaners

Lead concentrate

Conditioner

Zinc roughers

Zinc cleaners        Final tailing

Zinc recleaners

Zinc concentrate
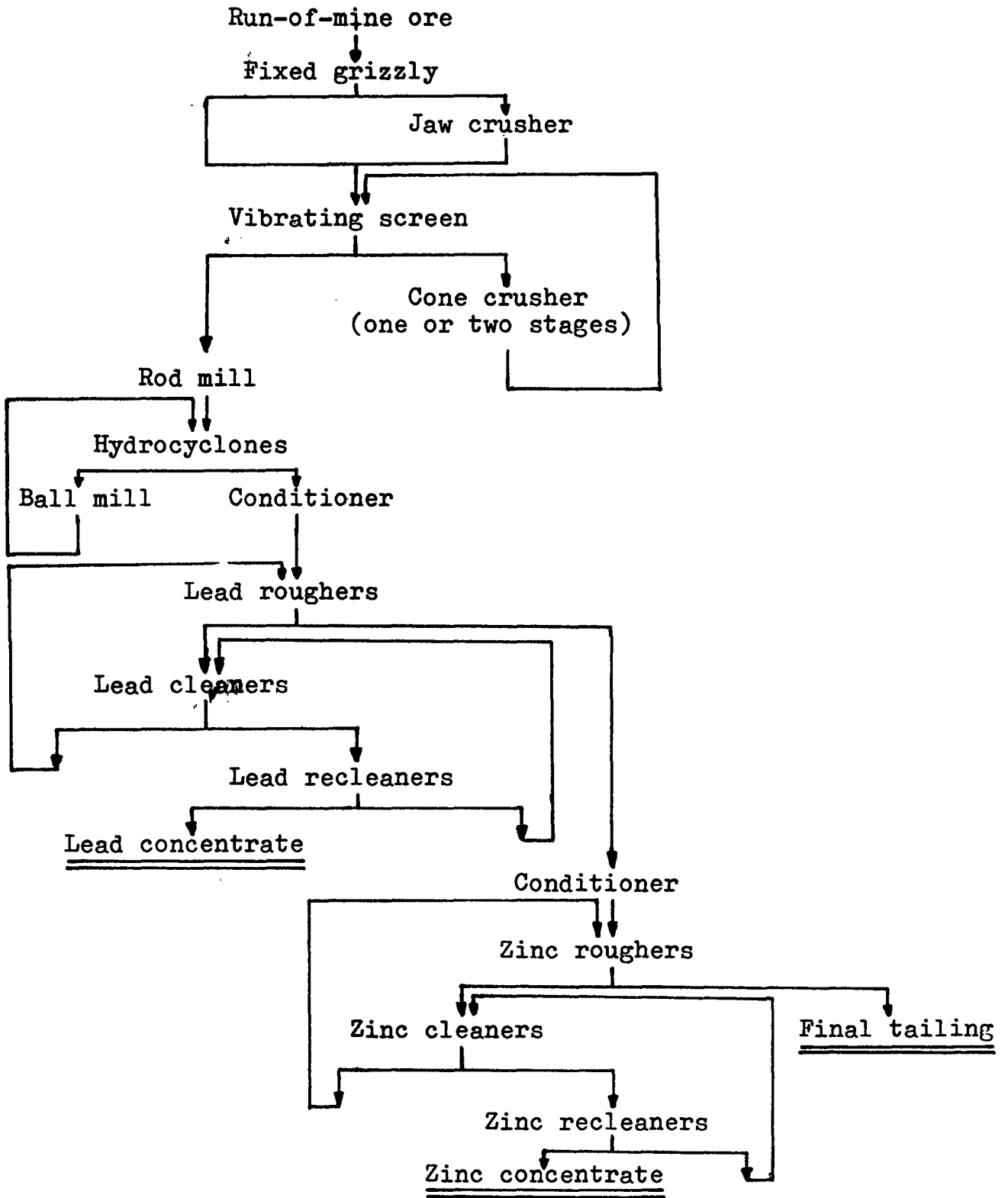
Fig. 12.1.1.    Typical flowsheet for Pb-Zn selective flotation

12.2 - DENMARK

12.2. A - GREENEX

Greenex is a wholly owned subsidiary of Vestgron Ltd in Canada, which in turn is a subsidiary of Cominco Ltd, also based in Canada.

Greenex operates the Black Angel mine at Marmorilik, on the west coast of Greenland (section 11.2.C.). A concentrating plant located on the mine site handles the ore from the mine only. All the ore is concentrated on site, at the rate of approximately 600 000 t/year.
The concentrates are shipped during the open-water season, and in wintertime when shipments cannot be made, the concentrates are stored at the site. The lead concentrates and most of the zinc concentrates are sold to various European smelters. The balance of the zinc concentrate is tolled on contract through custom smelters and then sold as metal, mainly on the British market.

The mine is inside Black Angel mountain, at 600 m above sea level. Access to the mine is possible only by cableway. Daily mining capacity is about 2 000 t. Inside the mine, the ore goes through a primary jaw crusher and a secondary cone crusher. The crushed ore (75% - 3/4") is stored in bins, and then loaded in two skips with a capacity of 10 t, which carry the ore across the fjord to the concentrating mill. From the receiving bin, ore is fed into a two-stage grinding circuit (1 rod mill and 1 ball mill), closed by hydrocyclones to obtain a particle size of 0,1 mm (60 % - 200 mesh).

After conditioning, a lead rougher concentrate is produced in two banks of Denver rougher cells in series. Rougher concentrate is mixed, then cleaned in three straightforward stages to obtain the final lead concentrate. The various cleaner tails are recycled to the preceding stage, the first cleaner tails being sent back to the primary ball mill together with lead scavenger concentrate for additional grinding.
As to the zinc flotation lead rougher tails are - after two stages of conditioning - fed into a Maxwell unit flotation cell ($33,6m^3$), then in two parallel banks of Denver roughers from where final tailings are disposed of. All the zinc rougher concentrate is mixed and cleaned in three straightforward stages, and the various tails are recycled to the preceding stage.

The first cleaner tails and zinc scavenger concentrate are being sent back to the head end of the Denver roughers without additional grinding.

Lead and zinc concentrates are dewatered in thickeners, vacuum filters and rotary dryers.

Lead flotation is carried out at a constant natural pH (7.8 - 8.4). Reagent additions are as follows :

| Type | Dilution | Point of addition | Amount (g/t) |
|------|----------|-------------------|--------------|
| Sodium cyanide | 10% solution | Ball mill discharge | 40 |
| | | Regrinding mill | 30 |
| Zinc sulfate | 10% solution | Ball mill discharge | 200 |
| | | Regrinding mill | 150 |
| K Amylxanthate | 10% solution | Cyclone overflow | 30 |
| Dowfroth 1012 | pure | Cyclone overflow | 5 |

Zinc flotation is carried out at a pH of 9.2 to 9.8 controlled by the addition of milk of lime.

Reagents for zinc flotation are added as follows :

| Type | Dilution | Point of addition | Amount (g/t) |
|------|----------|-------------------|--------------|
| Lime | 20% suspension | Zn conditioner (pH 9.2-9.8) | |
| | | 2nd Zn cleaner (pH 10.8-11.2) | 1 800 |
| | | 3rd Zn cleaner (pH 11.2-11.8) | |
| Copper sulfate | 20% solution | Zn conditioner | 600 |
| | | Denver rougher middlings | 100 |
| K Amylxanthate | 10% solution | Maxwell rougher feed | 50 |
| | | Denver rougher feed | 10 |
| Dow Z-200 | pure | Denver rougher middlings | 6 |
| Bate Frother 41 G | pure | Maxwell rougher feed | 7 |

Mineral processing of the Black Angel ore presents some difficulties due to the high pyrite content in the ore (15-18%).

The lead recovery is only moderate in part due to overgrinding of galena. It is proposed to modify the grinding circuit to double stage classification including coarse lead flotation on rod mill discharge during 1978.

The major part of losses in the zinc flotation circuit is mainly due to coarse middlings. Additional grinding of the zinc scavenger concentrate and first cleaner tails will therefore be introduced into the circuit during 1978 in order to achieve optimum metallurgical results.

It is noteworthy that a double stage of zinc conditioning has been introduced into the flowsheet, and the original installed regrinding unit in the lead circuit has been redundant by using the primary ball mill for regrinding of the scavenger concentrate and lead returns.

This regrinding unit is now available for the zinc circuit.

The above information was kindly supplied by F. Worm Andersen, Assistant to the Managing Director, and G. Mortensen, Senior Concentration Engineer, or borrowed from the Company's 1975 Annual Report, technical booklet and flowsheet.

## 12.3 - IRELAND

The content of this chapter is borrowed from a report by C. Burton (1977).

## 12.3 .A - TYNAGH

### Treatment of Secondary Open Pit Ore

"The concentrator was built to handle 2,000 tpd of the muddy secondary ore, which contained about 30 % slimes. Blended openpit ore was fed to primary and secondary Hazemag rotary crushers. The crusher screen undersize passed through a bank of cyclones, with overflow going to two large 120-ft-dia thickeners. Cyclone underflow was dewatered and joined the plus 10 mesh oversize (from crushing) to feed the two 9 x 11-ft ball mills. Two parallel flotation circuits were run on open-pit ore - one for slimes and one for sands. A 50 % lead-plus-zinc bulk concentrate was produced from the slimes and a 65 %-lead and a 55 %-zinc concentrate produced from the 'sand'. This arrangement was later modified to handle mixed-oxide ores.

"It was necessary to classify the ore into a number of treatment types" (Table 12.3.1).

"The criteria used are such that the sulphide ore contains only small amounts of oxide minerals. On the other hand, the oxide ores can contain substantial amounts of sulphide minerals. For example, 20 % to 30 % of the lead mineral in the lead oxide ore is usually galena.

"Within each treatment type the ore can still vary considerably in metal content and in physical characteristics. In order to minimise these variations in the feed to the mill, an ore blending stockpile, known locally as the "ore-pad" is used".

### Flotation of Different Ore Types

"The methods used in treating lead oxide ores, mixed oxide ores and zinc oxide ores differ appreciably, so each type is discussed separately".

TABLE 12.3.1          <u>TYPICAL ASSAYS OF ORE TREATMENT TYPES</u>

|  | Pb % | Pb Ox % | Zn % | Zn Ox % | Cu % | Ag oz/t | Fe % | BaSO$_4$ % |
|---|---|---|---|---|---|---|---|---|
| Sulphide | 10.8 | 1.5 | 10.6 | 0.8 | 0.16 | 3.56 | 4.0 | 26.0 |
| Sulphide/Cu | 12.6 | 1.5 | 8.8 | 0.8 | 0.42 | 3.53 | 5.0 | 25.0 |
| Lead Oxide | 13.3 | 10.6 | 2.0 | 1.8 | 0.30 | 2.45 | 4.60 | 22.0 |
| Lead Oxide/Cu | 13.9 | 10.6 | 2.0 | 1.8 | 1.46 | 4.23 | 5.6 | 28.0 |
| Copper Oxide | 12.7 | 11.9 | - | - | 2.20 | 4.30 | 2.5 | 25.0 |
| Zinc Oxide | 2.0 | 1.0 | 20.0 | 18.0 | 0.10 | 0.97 | 6.0 | 13.0 |
| Mixed Oxide | 3.5 | 6.2 | 6.8 | 5.1 | - | 2.47 | 8.5 | 14.0 |

TABLE 12.3.2

<u>LEAD OXIDE ORE.   REAGENT USAGE - OXIDE FLOTATION</u>

| <u>Reagent</u> | <u>lb per ton</u> | <u>Point of Addition</u> |
|---|---|---|
| <u>First Stage Oxide</u> | | |
| Sodium Hydrogen Sulphide | 3.08 | Stage Addition |
| Sodium Hydrogen Sulphide | 0.17 | Cleaners |
| Sodium Silicate | 1.01 | First Conditioner |
| Sodium Silicate | 0.29 | Cleaner |
| Potassium Amyl Xanthate | 0.27 | Stage Addition |
| Potassium Amyl Xanthate | 0.01 | Cleaner |
| Methyl Isobutyl | 0.01 | Second Conditioner |
| Sodium Cyanide | 0.06 | Cleaners and Conditioner |
| <u>Second Stage Oxide</u> | | |
| Sodium Hydrogen Sulphide | 1.24 | Stage Addition |
| Sodium Hydrogen Sulphide | 0.10 | Cleaners |
| Potassium Amyl Xanthate | 0.20 | Stage Addition |
| Potassium Amyl Xanthate | 0.01 | Cleaners |
| Sodium Cyanide | 0.09 | Cleaners |
| Sodium Silicate | 1.18 | First Conditioner |
| Sodium Silicate | 0.76 | Cleaner |

## 1. Lead Oxide Ores (See Figure 12. 3.1)

"The lead oxide ores are subdivided into two types; those containing copper minerals and those without copper minerals. Both types contain 20 % to 30 % of the lead in the form of galena, the balance of the lead being mostly cerusite, with minor amounts of anglesite and mimetite. The copper minerals, when present, occur mainly as members of the tennantite-tetrahedrite series and also as malachite and azurite.

"The reasons for sub-dividing lead oxide ores into two types are to produce, on the one hand, concentrates containing as much copper as possible, and, on the other hand, concentrates containing as little copper as possible. This paradox arises because the method of payment for copper in lead concentrates required a deduction of 1.3 % from the assay of copper in the concentrate, payment being made on any amount in excess of 1.3 %. It happens therefore that the higher the assay of copper, the greater the proportion of the copper one is paid for. It follows that copper bearing concentrates should not be diluted with non-copper bearing concentrates. The treatment of the two ore types (with the exception of "copper oxide ore") is essentially the same, being flotation of the sulphide minerals followed by sulphidisation and flotation of the oxide.

"The primary aim is to float all the copper into the sulphide lead concentrate and keep the copper in the lead oxide concentrate to a minimum, preferably less than 1.3 % Cu.

"The amounts and points of addition of the reagents in the flotation of lead oxides are given in Table 12.3.2. The sulphidising agent is sodium hydrogen sulphide, chosen mainly because it does not give as high a pH as sodium sulphide when used in large quantities.

"The relationship between sulphidising agent and collector is a very critical one and a change in the level of one usually means a change in the other. The collector used is potassium amyl xanthate and it is added in stages as is the sulphidising agent and at the same points.

A typical metallurgical balance is shown in Table 12.3.3.

FIGURE 12.3.1. – FLOWSHEET FOR LEAD OXIDE FLOTATION AT TYNAGH

(From "Technology of mining, concentrate production and metallurgy in Ireland", a report prepared by C. Burton (1977) for this dossier )



Sulphide Lead Flotation          Oxide Lead Flotation

From Crushing Plant

Sands          Slimes          Conditioner          Conditioner

Fine Orebin    Thickener        Lead Sulphide Flot.   First Stage Lead Oxide Flot.

Ball Mill                        Rougher      Tailing    Rougher Conc.        Tailing
                                 Conc.
Cyclone                                       Scavgr.              Cleaner          Second Stage
                                              Conc.                                 Oxide Flot.
U/F    O/F                                                         Tailing   Conc   Conc.      Tailing
                                              Cleaner
                                                                  Recleaner         Cleaner
                                         Conc.    Tailing
                                                                Tailing   Conc.   Tailing   Conc.

                                 Cleaner

                                 Tailing   Sulphide                                       Final
                                           Lead Conc.                                     Tailing

                                                        Oxide Lead
                                                        Concentrate

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## TABLE   12.3.3

## LEAD OXIDE ORE - METALLURGICAL BALANCE

| | Assay | | | Distribution | | |
|---|---|---|---|---|---|---|
| | Pb % | Cu % | Ag oz/t | Pb % | Cu % | Ag % |
| Feed | 14.0 | 0.96 | 4.30 | 100.0 | 100.0 | 100.0 |
| Sulphide Lead Conc. | 45.4 | 5.24 | 18.02 | 24.0 | 40.4 | 31.1 |
| Oxide Lead Conc. | 47.0 | 1.86 | 7.62 | 59.8 | 34.5 | 31.5 |
| Tailing | 3.23 | 0.35 | 1.86 | 16.2 | 25.1 | 37.4 |

## 2. Zinc_Oxide_Ores (See_Figure_12._3.2)

"The ore is brownish yellow in colour and contains 20 % to 25 % of material finer than 43 micron. The ore minerals are smithsonite, sphalerite, galena and cerusite. The gangue is largely composed of clay minerals, barite, pyrite and limestone.

The process proceeds in the following steps :

1.  Desliming
2.  Flotation of sulphide lead
3.  Flotation of sulphide zinc
4.  Desliming
5.  Flotation of lead oxide
6.  Flotation of barite
7.  Desliming
8.  Flotation of zinc oxides.

"The testwork showed that the presence of slimes made flotation of barite and zinc oxide very difficult. The cause of the trouble is found to be the minus 10 micron fraction. The final flowsheet therefore incorporated a cycloning stage for the removal of the minus 10 micron fraction in the crusher slimes products.

FIGURE 12.3.2     - <u>FLOWSHEET FOR ZINC OXIDE FLOTATION</u>

(From same source as fig. 12.3.1.)

**Sulphide Flotation**     **Lead Oxide & Barite**     **Zinc Oxide Flotation**

From Crushing Plant

Sands    Slimes

Fine Orebin   Thickener

Ball Mill

Cyclone

U/F    O/F

Cyclone

O/F     U/F

Final Tailing

Conditioner

Lead Sulphide Flot.

Rougher Conc.    Tailing

Cleaner

Tailing    PbS Conc.

Conditioner

Zinc Sulphide Flot.

Rougher Conc.   Tailing

Regrind

Cyclone

U/F    O/F

Cleaner

ZnS Conc.    Tailing

Cyclone

U/F     O/F

Lead Oxide Flot.

Rougher Conc.    Tailing

Cleaner

Tailing    Pb Ox Conc.

Conditioner

Barite Flot.

Rougher Conc.    Tailing

Cleaner

Tailing    Barite Conc.

Cyclone

U/F     O/F

Conditioner

Zinc Oxide Flot.

Rougher   Tailing
Conc.

Scavgr.
Conc.

Cleaner

Tailing     Zinc
Oxide
Conc.

Final Tailing

"The best collector for smithsonite was dodecylamine derived from vegetable oil and of those tested, Armeen C proved to be most suitable. The amine was added as an emulsion containing 40 % Armeen C, 50 % fuel oil, 5.5 % Pine Oil and 4.5 % Ethomeen C25.

"Sodium sulphide proved to be the most satisfactory sulphidizing agent and the final grade of the concentrate was improved by the addition of dispersants to the conditioner. Ekapsesil S was used.

Table 12.3.4 shows the amounts and points of addition of the reagents.

The final zinc oxide concentrate assayed about 40 % zinc and this was upgraded further by calcination to 50 percent zinc".

## 3. Mixed Ores

"The mixed oxide ores contain varying amounts of lead and zinc sulphides and oxides. Some 20 % to 30 % of the lead and zinc ore is present as galena and sphalarite, the balance being mostly cerusite and smithsonite. In the grade control programme, any ore which did not fit neatly into one of the main ore categories, has tended to be put on the mixed oxide stockpile, especially if the ore was low grade or particularly refractory, such as ore containing a high proportion of slimes, or low grade zinc oxides. As a result, this is the most difficult ore type to treat.

"The flowsheet used is similar to that used for lead oxides, bulk sulphide flotation being followed by two stages of oxide lead rougher flotation. The sands are ground to 65 % minus 43 micron, soda ash being added to the mills. Aero depressant 633, copper sulphate and potassium amyl xanthate are added to the cyclone feed pumps and to the conditioner and bulk concentrate of lead and zinc produced. The bulk rougher concentrate is cleaned once with soda ash and sodium cyanide added to the cleaners to depress pyrite. The rougher tailings are sulphidised with sodium hydrogen sulphide, and a lead oxide concentrate made in two stages as with normal lead oxide ore.

TABLE 12.3.4

## ZINC OXIDE ORE. REAGENT USAGE

| Reagent | lb per ton | Point of Addition |
|---|---|---|
| Soda Ash | 2.07 | Ball mill feed |
| Zinc Sulphate | 1.55 | Ball mill feed |
| Sodium Cyanide | 0.16 | Sulphide lead cleaner |
| Copper Sulphate | 0.78 | Sulphide zinc conditioner |
| Methyl Isobutyl Carbinol | 0.13 | Stage Addition |
| Potassium Amyl Xanthate | 0.55 | Sulphide lead + zinc and lead oxide |
| Lissapol D/R107 | 1.50 | Barite conditioner |
| Sodium Sulphide | 14.50 | Zinc oxide (Stage) |
| Amine Emulsion | 2.58 | Zinc oxide (Stage) |
| Ekapersil S | 0.71 | Zinc oxide conditioner |
| Sodium Silicate | 1.03 | Sulphide lead conditioner |
| Pine Oil | 0.16 | Froth breaker zinc oxide circuit |

TABLE 12.3.5

## MIXED OXIDE ORE. REAGENT USAGE

| Reagent | Usage lb/ton | Point of Addition |
|---|---|---|
| Cyanamid Reagent AC 633 | 0.33 | Ball mill feed |
| Lime | 1.23 | Ball mill discharge |
| Sodium Cyanide | 0.66 | Ball mill discharge |
| Copper Sulphate | 0.31 | Conditioner |
| Sodium Isoproptl Xanthate | 0.18 | Conditioner |
| Sodium Silicate | 0.72 | Oxide Conditioner |
| Sodium Hydrogen Sulphide | 2.81 | Stage addition to oxide circuit |
| Potassium Amyl Xanthate | 0.37 | Stage addition to oxide circuit |
| Sodium Cyanide | 0.22 | Oxide cleaners |

TABLE 12.3.6

## MIXED OXIDE ORE - TYPICAL RESULTS

| | ASSAYS | | | | | DISTRIBUTION | | |
|---|---|---|---|---|---|---|---|---|
| | Pb % | Pb Ox % | Zn % | Zn Ox % | Ag Oz/t | Pb % | Zn % | Ag % |
| Feed | 8.46 | 6.20 | 6.83 | 5.10 | 2.47 | 100.0 | 100.0 | 100.0 |
| Bulk Conc. | 25.70 | - | 19.0 | - | 9.10 | 47.5 | 43.5 | 41.4 |
| Oxide Lead Conc. | 45.10 | - | - | - | 5.86 | 20.1 | - | 10.5 |
| Tailing | 3.39 | 2.70 | 4.51 | 3.80 | 1.42 | 32.4 | 56.5 | 48.1 |

## Treatment of Primary Sulphide Ore

"The character of the harder primary sulphide underground ore will change the initial crushing step that was used for open-pit ore. Full production from underground will be about 850,000 tpy of ore containing 4.28 % lead, 3.12 % zinc, 0.35 % copper and 1.4 oz per ton silver. Two Nordberg Cone crushers now provide a minus 1 1/2-in. primary ore feed to the ferrosilicon-based Wemco heavy media plant. Some 31 % of the 2,400 tpd of run-of-mine feed is scalped off in the Wemco plant, with only 5 % of the metal values being lost (see Figure 12.3 .3).

"The mill grinding circuit will now have to treat 590,000 tpy of preconcen-trated ore. The reagents used and the points of addition are given in Table 12.3.7.

### TABLE 12.3.7

### LEAD SULPHIDE ORE. REAGENT USAGE

| Reagent | Usage lb per ton | Point of Addition |
|---|---|---|
| Soda Ash | 1.10 | To ball mill feed |
| Sodium Cyanide | 0.09 | To ball mill discharge |
| Potassium Amyl Xanthate | 0.07 | To ball mill discharge |
| Potassium Amyl Xanthate | 0.02 | To junction box |
| Sodium Silicate | 0.34 | To slimes before joining cyclone overflow |
| Methyl Isobutyl Carbinol | 0.05 | To conditioner |

"Metal recoveries for the primary ore will be high as the ore is very clean. The overall recovery (including heavy media losses) is expected to be 88 % for lead, 77 % for zinc, 72 % for copper and 74 % for silver, for an annual concentrate production of 53,000 tons of lead concentrates assaying about 60 % lead, 4.5 % copper and 15.6 oz per ton of silver. Zinc concentrate production will be around 41,300 tpy assaying 50 % zinc.

FIGURE 12.3.3.

(From same source as fig. 12.3.1.)



FLOW DIAGRAM OF TYNAGH HEAVY MEDIA PLANT

LEGEND
— — — Heavy media
— · — · — Dilute media
— — — Water

① Double - deck vibrating screen
② 5 1/2' standard Cone crusher
③ Vibrating screen
④ 10' x 10' heavy media drum
⑤ Sink screen
⑥ Float screen
⑦ Vibrating screen
⑧ 5 1/2' Short Head Cone crusher
⑨ Magnetic separator
⑩ 48" classifier
⑪ Heavy media tank
⑫ Demagnetizer
⑬ Dilute media tank
⑭ Recirculating water tank
⑮ 48" classifier
⑯ 750 - ton bunker
⑰ Thickener

## TABLE 12.3.8

### (CONCENTRATE PRODUCTION - TYNAGH)

PRODUCTION (Tons* x 1000)                                    OPERATIONAL START NOV. 1965

| | 1965 | 1966 | 1967 | 1968 | 1969 ** | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | Total to date |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tonnage Mined | | 546 | 704 | 710 | 501 | | 676 | 661 | 683 | 667 | 684 | 6576 |
| Tonnage Milled | 46 | | | | | 698 | 676 | 422 | 529 | 490 | 488 | 5810 |
| Zinc conc. | 1.0 | 26.4 | 42.2 | 30.4 | 24.8 | 22.1 | 43.8 | 35.9 | 22.8 | 42.5 | 42.0 | 333.9 |
| Zinc Grade (%) | 49.0 | | | | | | | | | 46.4 | 41.3 | |
| Lead conc. | 1.3 | 64.5 | 105.9 | 93.6 | 77.3 | 92.8 | 53.9 | 57.8 | 74.4 | 38.1 | 29.7 | 689.3 |
| Lead Grade (%) | 63.4 | | | | | | | | | 69.7 | 74.0 | |
| Mixed conc. | 3.0 | 30.6 | 42.9 | 57.9 | 29.6 | 29.7 | 52.9 | 39.1 | 14.4 | 4.8 | 4.3 | 309.2 |
| Mixed Grade (%) | 25.7Pb 27.7Zn | | | | | | | | | | | |
| Copper conc. | | | | | | | | | | 7.0 | 2.0 | 9.0 |
| Copper Grade (%) | | | | | | | | | | 7.8 | 12.2 | |
| Silver (ounces X 1000) | 100 | 1218 | 2067 | 1516 | 1445 | 1748 | 1057 | 1242 | 1458 | 870 | 584 | 13303 |

\* All tonnages are short tons, except tonnage mined which is expressed as long tons
\*\* Production effected by prolonged strike (July 7-Oct.1)

"Concentrates are sent 20 mi to the port of Galway in 17-ton trucks. Ships of up to 5,000-ton capacity can be loaded at the rate of 200 tph from the 200,000-ton storage building at Galway. The initial concentrates were shipped to Metallgesellschaft of Germany, Soc. des Minerais of Belgium, and Penarroya of France".

## Concentrate Production at Tynagh
See Table 12.3.8.

## 12.3.B - MOGUL

"The Upper zone is predominately a massive sulphide. The matrix mineral, pyrite, occurs in two forms : an oolitic structure with inclusions of sphalerite and an idiomorphous form with inclusion of sphalerite and galena. In lower zone ore pyrite, sphalerite, and galena are disseminated in a dolomite matrix. Some 22 % of the total lead in both zones occurs in a non-sulphide form, predominantly as anglesite and to a lesser degree plumbojarosite and cerussite.

"The ore from underground is generally a mixture of both ore zones, inconsistent in blend and varying on a daily basis.

"Grinding : The ore is dry crushed in two stages to $-\frac{5}{8}$" and stored in ore bins to provide surge capacity prior to milling. The milling rate varies from 125-140 S.W.T./hour depending on ore availability and head grades etc ... Two stages of milling are used; the first being a rod mill, grinding down to 60 % +55 mesh, 24 % -270 mesh. The second stage is by two closed circuit ball mills, in parallel, with Krebs 15 inch cyclones. These cyclones give an overflow sizing of 100 % -65 mesh, 14 % +200 mesh, 30 % -8 microns. This would be feed.

"The lead 1st cleaner tails and scavenger concentrate are used to dilute the ball mill discharge and hence recycloned but, theoretically, unsubjected to further grinding. The % solids of the overflow is maintained at 42-45 %.

"Lead Flotation : (Fig. 12.3 .4) The pulp is conditioned with cyanide, potassium amyl xanthate (made in Hoechst), and lime to maintain a pH of 9.7. It is found that a higher pH promoted zinc flotation. Cyanide consumption is 0.290 lb/S.D.T. and excess has been shown in the past to again encourage the flotation of zinc.

Sipx 0.133
NaCN 0.361
MIBc 0.022

Sipx 0.006
(7TH CELL)

Sipx 0.041

NEW FEED

Conditioner
RT≃15 MINS

Pb Roughers
2×12 × DR 30 (RT≃12MINS)

Pb Scavengers
2 × 6 × DR 30 (RT≃5MINS)

TO ZINC FLOTATION

Ca(OH)₂
pH=9.7

RT = CELL RETENTION TIME

REAGENTS - LB/S.D.T. OF NEW MILL FEED

Sipx 0.015

Sipx 0.074

Sipx 0.036

1ST CLEAN 2×12×DR24
(RT ≃ 10 MINS)

2ND CLEAN
2×5×24 SUBA
(RT≃16 MINS)

3RD CLEAN
2×3×24 SUBA
(RT≃10 MINS)

4TH CLEAN
2×2×24 SUBA
(RT≃12 MINS)

Ca(OH)₂
pH 11.0

Ca(OH)₂
pH=11.0

FINAL CONC.

Fig. 12. 3.4 - Lead flotation
Mogul Mine (Jan.Feb. 1975)

( From same source as fig. 12.3.1.)

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"The rougher concentrate is cleaned four times to give a final product, while the cleaner tailings and scavenger concentrate are recycled to the head of the flotation.

"It is proposed to modify the lead circuit to open the roughing stage. Cleaner tails and scavenger concentrates will be refloated in new cells to give a concentrate, which will go the cleaners, and a tail which will be returned to the head of the scavenger, or (possibly) discarded to the zinc side.

"Mine water is used for milling with the respective concentrate thickener overflow being used for the launder sprays. There would appear to be very little advantage in using the mine water which has a natural pH of about 7.3.

"Zinc Flotation : (Fig. 12. 3 .5) The lead rougher tails are conditioned with copper sulphate solution (30 % W/V) and zinc activated with sodium isopropyl xanthate. Rougher flotation pulp density is 39 % solids and pH is controlled at 10.0. Potassium amyl xanthate is used in scavenging.

"The rougher concentrates are refloated three times to produce a finished product. Scavenger concentrates and cleaner tailings are reground to 98 % -50 microns, prior to a separate refloat which permits open circuit roughing while being able to rescavenge the refloat tailings in closed circuit.

"Results : Normal plant performance is 65 % lead recovery at a concentrate grade of 55.5 % Pb and 3.5 % Zn. Zinc recovery is normal at 86 % with a concentrate grade of 52.5 % Zn and 2.5 % Pb.

"High pyrite type ores produced the following efficiencies using S.I.P.X. in late 1974. With current reagent levels and operating practices it is unlikely that zinc recovery would drop to the low eighties again.

| | | |
|---|---|---|
| % Pb Recovery | 56-59 % | |
| Pb Concentrate | 53.5 % Pb | 4.17 % Zn |
| % Zn Recovery | 80-81 % | |
| Zn Concentrate | 51.84 % Zn | 3.19 % Pb |
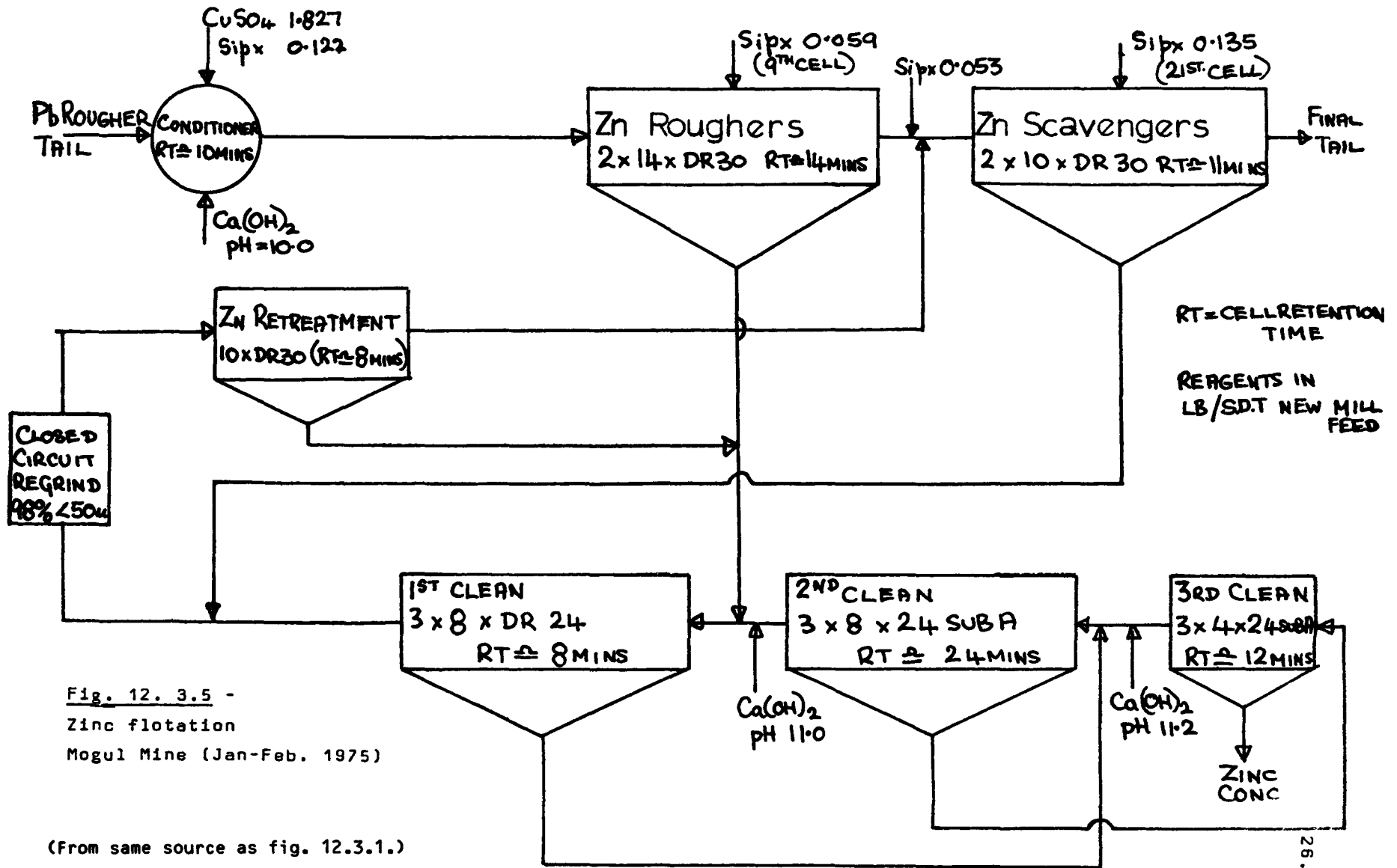
Fig. 12. 3.5 -
Zinc flotation
Mogul Mine (Jan-Feb. 1975)

(From same source as fig. 12.3.1.)

"The prime detriment for poor lead recovery is, in part, due to the presence of oxidized lead minerals which accounts for some 22 % of the total lead in the feed. Anglesite would be the major mineral followed by plumbojarosite with only traces of the less refractory cerussite.

"The principle losses in the zinc circuit are relatively coarse middlings. All previous work indicates that to achieve optimum metallurgical results, the product grinds should b₃ such that the -7 micron and +40 micron fractions are kept at a minimum.

Data - Mogul Concentrator (see lead and zinc circuit flowsheets)

Crushing

| | |
|---|---|
| T.P.H. | 228 |
| % Op. Time | 59 % - Based on Sch. shifts |
| Op. Hours Mth. | 370-400 per month |
| Av. T. per month | 86,000 |

Conveyors

| | |
|---|---|
| 36" | 1, 2, 3, 4 and 5 |
| 30" | Remainder |
| Type | Red T. Trelleborg Belting |

Screening

| | |
|---|---|
| Grizzly | Rubber Deck - 1 1/2" opening |
| Screens | Rubber Deck - $\frac{5}{8}$" |

Crushing General

| | |
|---|---|
| Coarse Ore Bin | 1,700 Tons max. |
| 5 1/2' Std. Crusher | Closed side - 1 1/2" |
| 5 1/2' S.H. Crusher | Closed side $\frac{5}{8}$" |
| Crushers H.P. | 220 each |
| Fine Ore bins | 3   3,200 Tons each - 42' Dia. x 50' High |
| Conveyors | 36" belting, in line slot feeders, vari speed drive - 20-80 T.P.H. each |

## Grinding

| | |
|---|---|
| Rod Mill Feed | $100 \% - \frac{5''}{j}$ |
| Feed Rate | 120-145 `.P.H. |
| % Op. Time | 88-97 %, M.A. 97.5 % |
| Rod Mill | 9' 6" x 16' - 600 H.P. |

82 % Solids

Trommel - $\frac{1''}{2}$

Critical Speed - 65 %

Rods - 3 $\frac{1''}{2}$ dia.

Consumption - .45-.6 lbs/t.

Grind - 60 % +55M, 24 % -270M

Liners - lifters - mang.

           liners - cr -mo.

**Ball Mills**

11' 6" x 17' - 1,300 H.P. Synchronous

87-80 - % solids

Scroll - ball rejects

Critical Speed - 69 %

Balls - 2"

Consumption - 1.4-1.7 lbs/t.

Grind - cyc. o/f - 100 %

- 65M, 14 % +200M, 30 % -8M

Control - 88 % - 200 %

Cyclones - 42 % o/f solids, D15B, 4 per norm up hou

        - 8 x 6 - S.R.L. pumps

Liners - Rubber - Skega

Life Lifters - 2 years

Plates - 4 years

**Regrinding**

Feed - Scav. Conc. + 1st cleaner tailings

Mill - 9' x 12' - 500 H.P.

Balls - 1"

Consumption - .27 lbs/t

Control - 98 % - 325 M

Cyclones - DIOB -5

## Flotation

Rgt. Cons.

Pb - M.I.B.C. - .03 lbs/t

    Lime - 1.5 lbs/t

    Xan. - .24 lbs/t

    NaCn - .28 lbs/t

Zn - Lime - 1.0 lbs/t

    Xan - .27 lbs/t

    $CuSO_4$ - 2.0 lbs/t

### Pb Flotation

Heads - 1.8 - 2.5 % Pb, 14 1 19 % Fe
(Anglesite + plumbojarosite) .6 - .8 % $PbO_2$

Conc. -55-57 % Pb, 22 - 24 % S, 2.2-2.7 % Zn

Grind - 30 % -8M

Rec. - 65-68 % Total Pb, 80-81.8 % Sul. Pb, 18-22 % Ox. Pb

Flotation Machines - Rghr/Scav

Ph 9.8 DR30

Cleaning - 1st - DR24-

        2nd - 4 - sub A - 24

pH - 11.2 - 11.5

### Zn Flotation

Heads - S.S. 7.0 %

Conc. - 52 % Zn, 2.2 % Pb

Grind - 33 %, 2.2 % Pb

Rec. - 85-87 %

Flotation Machines - Rghr/Scav

pH 9.0 DR30

Cleaning - 1st - DR24

        2nd + 3rd - sub A-24

pH 11.2-11.5

### Pb Thickening, Filtering and Drying

26' Dia x 10' - Thickener D.O.L.

70 % Solid - u/f

Floc. - 0.01 lbs/t

Filter - 11' 6"x10'

Vacuum - 22" Hg Nash Vacuum

Moist - 13-16 % Filter Dis

Dryer - 54" x 55' Rotary - Bunker C

Moisture Dis - 7.5 %

## Zn Thickening, Filtering and Drying

65' Dia x 12' - Thickener

65-70 % Sol - u/f

Flocc - .01 lbs/t

Filters 11' 6" x 14'

Vacuum - 22" Hg - Nash

Moisture - 13-16 %

Dryer - 90" x 60' long

Moisture - 8.0-9.0 %

## Backfilling

Zn Tails - 1st stage - D10B - 8

2nd stage - D10B - 4

2nd stage u/f - 3.7 %  +210M

6.7 %  -11M

T.P.H. Backfill Prod - 40

% Rec. - 40 -24

## Personnel

| | | |
|---|---|---|
| Mill superintendent | - 1 | |
| Chief Metallurgist | - 1 | |
| General Foreman | - 1 | |
| Maintenance Foreman | - 1 | |
| Met. Research | - 1 | |
| Op. Foremen | - 4 | |
| Day Foreman | - 1 | |
| Crushing | - 9 | |
| Plant | - 24 | |
| Fitters and Helpers | - 16 | (greaser and tool crib) |
| Day shift personnel | - 10 | |

## Concentrate Production

See Table 12.3.9.

TABLE  12.3.9

(CONCENTRATE PRODUCTION  -  SILVERMINES)

PRODUCTION  (Tons* x 1000)                                    OPERATIONAL START - MAY 1968

|  | 1968 | 1969 | 1970 | 1971** | 1972 | 1973 | 1974 | 1975 | TOTAL TO DATE |
|---|---|---|---|---|---|---|---|---|---|
| Tonnage Mined | 448 | 1019 | 1009 | 789 | 813 | 917 | 914 | 1013 | 6922 |
| Zinc Conc. | 61.6 | 172.7 | 178.4 | 115.20 | 121.3 | 115.9 | 96.3 | 97.7 | 959.1 |
| Lead Conc. | 12.4 | 36.4 | 38.1 | 27.4 | 36.3 | 34.7 | 23.6 | 31.0 | 239.9 |

*   See Note on Figure 4
**  Production interupted by strike (May 31-Aug.12)

12. 3 .C - <u>TARA</u>

<u>Treatment of Primary Ore</u>

"The concentrator (Fig. 12.3 .6) has been designed to process 7 500 ston/day.
It is predicted that the zinc recovery will be 90 % in a 55 % concentrate
and that the lead recovery will be 82 % in a 62 % grade concentrate. When
in full production it is expected that 400,000 dry stons of zinc concen-
trate and 70,000 dry stons of lead concentrate will be produced each year.

"Secondary crushing takes place in two 7-ft Cone crushers. Crushed ore will
be fed to a 13 $\frac{1}{2}$ x 20-ft rod mill in open circuit with a primary cyclone.
A 16 x 20-ft and an 11 x 14ft ball mill will each be closed on separate
secondary cyclones. The cyclone overflow from the smaller ball mill will
constitute the feed for the lead flotation circuit. A flotation rougher
concentrate is made from a combination of the cyclone overflow from the
larger ball mill and the lead cleaner tails. This concentrate, when reground
in a 13 $\frac{1}{2}$ x 20-ft ball mill, becomes the feed to the zinc flotation circuit.
An unusual feature in the zinc circuit is the leaching of the concentrates
with sulphuric acid to extract magnesium oxide. The drying process for the
concentrates employs disc filters and rotary-kiln driers".

Major items of equipment are listed in Table 12.3.10.

<u>Predicted Concentrate Production</u>

See Table 12.3.11.

12.3 .D - <u>BULA</u>

<u>Treatment of Primary Ore</u>

"The ore will be trucked to a crushing operation comprising jaw crusher,
ore surge bin, vibrating screen, two cone crushers, vibrating screen and
fine ore storage. Concentration will involve a flow-sheet comprising ini-
tial ball milling and cycloning; lead separation by rougher and scavenger
flotation plus zinc separation by similar means; cleaning, thickening,
filtration, drying and storage of the lead concentrate; and a parallel
processing of the zinc concentrate which additionally employs concentrate
cycloning.

Tailings will be pumped to the two storage ponds. Output will be in the region of 150,000 tonne/year of concentrate which will be trucked to the port of Drogheda, at least until a smelter is built at Navan to process the concentrates from Bula and Tara".

Predicted Concentrate Production

See Table 12.3.12 and the flowsheet on fig. 12.3.7.

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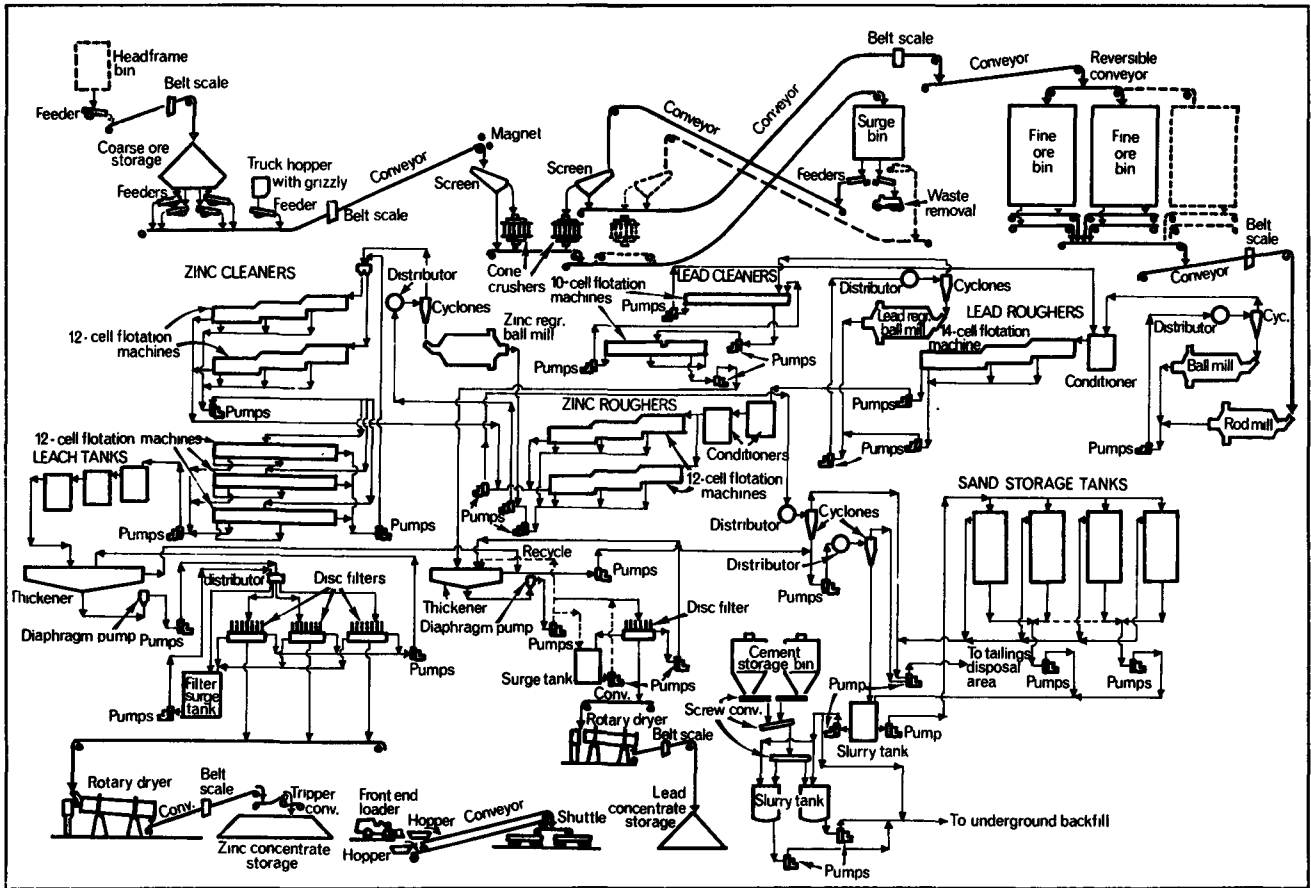
Fig. 12-3-6  Flowsheet of Tara mill
(from Mining Magazine, october 1977, p. 309)

FIG. 12.3.7.

(From same source as fig. 12.3.1.)

## MILL FLOWSHEET  -  BULA MINE

**Grinding**                    **Lead Circuit**                    **Zinc Circuit**
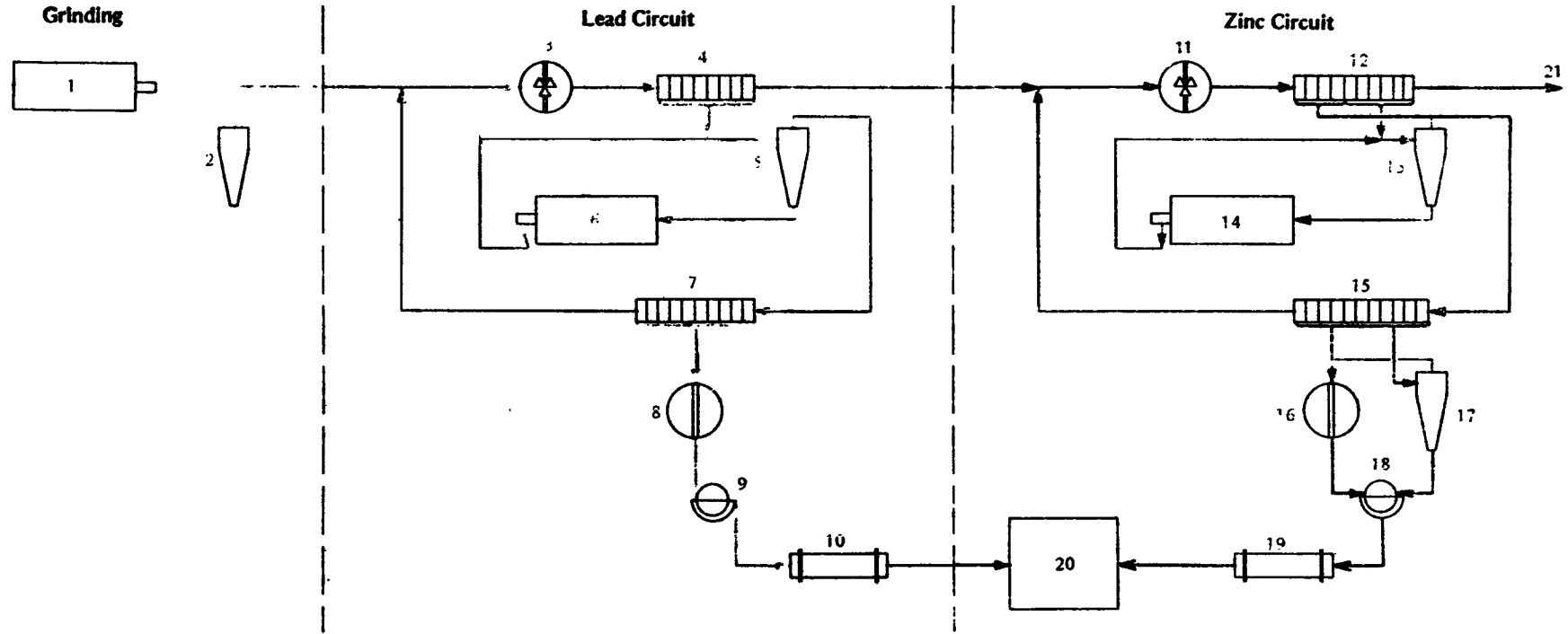


**CONCENTRATING SECTION**

(1)  Ball Mill
(2)  Cyclones
(3)  Lead Conditioner
(4)  Roughers + Scavengers
(5)  Cyclones
(6)  Lead Regrind Ball Mill
(7)  Cleaners
(8)  Lead Thickener
(9)  Filter
(10)  Drier

(11)  Zinc Conditioner
(12)  Roughers + Scavengers
(13)  Cyclones
(14)  Zinc Regrind Ball Mill
(15)  Cleaners
(16)  Zinc Thickener
(17)  Zinc Concentrate Cyclone
(18)  Filter
(19)  Drier
(20)  Concentrate Storage
(21)  Tailings

TABLE  12.3.10

## MAJOR ITEMS  OF SURFACE PLANT EQUIPMENT

| Supplier | Item | Supplier | Item |
|---|---|---|---|
| Allis Chalmers | (1) 1784 Cone Crusher<br>(1) 584  "  " | Tierney | (2) Main Power<br>Transformer<br>110KV/6.6KV/12MVA:- |
| Allis Chalmers | (1) 13½ft x 20ft Rod<br>        Mill | ASEA | 350V Motors |
| | (1) 16ft x 20ft Ball<br>        Mill | ESB Ireland | 6.6KV Switchboard |
| | (1) 11ft x 14ft Ball<br>        Mill | Eimco, Canada | (1) 6 x 6 Agidisc<br>        Filter |
| | (1) 13½ft x 20ft Ball<br>        Mill | | (3) 8ft x 10in x 7ft<br>        Agidisc Filter |
| Allis Chalmers | (2) 8 x 20 Screens | Ducon - Mik. | Wet Collectors |
| Allis Chalmers | (16) 3 x 3 Slurry Pumps | | (4) 10,000  ft$^3$/min |
| | (7) 5 x 4     "     " | | (1) 23,000     " |
| | (13) 8 x 6    "     " | | (1) 6,000     " |
| | (12) 10 x 8   "     " | | (1) 4,480     " |
| | (3) 12 x 10   "     " | | (1) 40,000     " |
| | (10) 14 x 12  "     " | | (1) 26,400     " |
| | (4) 16 x 14   "     " | Eimco, G.B. | (1) 45ft Thickener Mesh |
| Allis Chalmers | (2) 60 x 48 Jaw Crusher | | (1) 95ft    "      " |
| Denver | Flotation Machines | | (2) 6in Dia. Pumps |
| Equipment | (2) 12 cell 400ft$^3$ D-R | | (1) 3in   "     " |
| | (2) 12  "  200ft$^3$ D-R | Herbert Morris | (1) 20-T EDT Crane |
| | (3) 12  "  100ft$^3$ 30 | | (1) 5-T   "     " |
| | (1) 14  "  400ft$^3$ D-R | | (4) 3-T   "     " |
| | (2) 10  "  100ft$^3$ 30 | Sala, U.K. | 10-20in Cyclones |
| Head | (1) 10ft x 60ft Rotary | | 18-10in    " |
| Wrightson | Dryer | Sala, U.K. | 6-10in Cyclones |
| | (1) 5ft x 30ft Rotary | | 8-15in    " |
| | Dryer | | 6-15in    " |
| CGE | 6.6KV Motors | | 2-10in    " |
| | (1) 3,200hp | Siemens, Can. | (3) 4,500 ft$^3$/min Vac.<br>        Pumps |
| | (2) 2,200hp | Dresser | (1) 40/10T EDT Crane |
| | (1) 900hp | English Electric | 6.6KV MCC's |
| Stephens-<br>Adamson | Conveyor Components | | |
| Sala | On-Stream Analyser | | |
| Canron | D.I. Pipe and Fittings | | |

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TABLE 12.3.12.

(PREDICTED CONCENTRATE PRODUCTION - BULA)

ESTIMATED CONCENTRATE PRODUCTION (SHORT TONS x 1000) - OPERATIONAL START - 1979/80 ?

|  | 1980 | Total production based on present reserves |
|---|---|---|
| TONNAGE MILLED | 1,000 | 18,367 |
| Zinc Conc.<br>Zinc Grade | 134.3<br>54.0 | 2,446 |
| Lead Conc.<br>Lead Grade | 18.9<br>62.0 | 347 |

TABLE 12.3.11

(Predicted concentrate production)

ESTIMATED CONCENTRATE PRODUCTION (SHORT TONS x 1000)

|  | 1977 | 1978 | Total production based on Present Reserves |
|---|---|---|---|
| Tonnage Milled | 1,000 | 2,500 | 65,000 |
| Zinc Conc.<br>Zinc Grade (%) | 150.0<br>56.0 | 420.0<br>56.0 | 11,000 |
| Lead Conc.<br>Lead Grade (%) | 30.0<br>62.0 | 80.0<br>62.0 | 2,000 |

## 12.4 - UNITED KINGDOM

## 12.4 .A - GENERAL SURVEY

Dr. R.N. Crockett, of the Institute of Geological Science, supplied the following information :

"At the present time lead and zinc concentrates are only produced in the United Kingdom as flotation by-products from the mining of fluorspar and of tin. Fluorspar mining is concentrated in the Peak district of Derbyshire and in the Northern Pennine orefield situated in the counties of Durham and Northemberland and some lead concentrate production is recorded from both areas. In Derbyshire some raw material is provided to the concentrators by the activities of tributers working old mine dumps or backfilled workings. The accompanying flowsheet (figure 12.4 .1 in this report) shows the beneficiation of fluorspar at the Cavendish mill operated by Laporte Industries Ltd. near Eyam in Derbyshire which is one of the largest and most efficient in Europe. It also appears that British Steel is not now producing lead concentrate. Laporte Industries records as such the lead concentrate recovery from their Cavendish mill :

| 1971 | 5 796 tonnes | 82.8 % |
| 1972 | 5 320 tonnes | 80.6 % |
| 1973 | 4 691 tonnes | 65.2 % |
| 1974 | 5 433 tonnes | 100 % |
| 1975 | 4 832 tonnes | 100 % |
| 1976 | 4 090 tonnes | 100 % |

The percentages represent the proportion of total British production. It appears that Laporte has been the only producer since the end of 1973.

In Cornwall some zinc concentrates are produced at the South Crofty tin mine and are sold to Sweden. The Wheal Jane and Mount Wellington tin mines produced mixed sulfide concentrates; for Wheal Jane, it is mainly Cu-Zn concentrates also sent to Sweden".

ORE FEED

↓

Washing

Crushing

Sizing

35-40 per cent. CaF₂ (fluorspar)
20-25 per cent. BaSO₄ (barytes)
15-20 per cent. CaCO₃ (limestone)
15-20 per cent. SiO₂ (silica)
1-2 per cent. Pb(lead)

2 in.-¼ in. (51mm.-6mm.)          -¼ in. (6mm.)

Limestone-silica tailings ← Dense media separation plant — "sinks" → Grinding Classification → Slimes

↓                                          ↓

METALLURGICAL-GRADE FLUORSPAR (75-80 per cent. CaF₂)          JIGGED LEAD

↓

Flotation Filtration → Tailings

↓

LEAD CONCENTRATES (70-75 per cent. Pb)     BARYTES CONCENTRATE (98 per cent. BaSO₄)     ACID-GRADE FLUORSPAR (minimum 98 per cent. CaF₂)

Source: Based on Quarry Managers'Journal, 1965, Vol. 49, No.10, pp. 416-418

Fig. 12.4.1   Cavendish mill

## 12.4.B - SOME MORE DETAILS

Wheal Jane's operations have been thoroughly described and discussed in a paper presented at the Tenth International Mineral Processing Congress, held in London (Boulter et al., 1973). Tin ore contains a marked amount of sulfides, including pyrite and arsenopyrite. A bulk sulfide flotation is made after the primary ball mill grinding, at a pH of 6 controlled by the addition of $H_2SO_4$ with $CuSO_4$ as activator and Z-200 as collector. Clean bulk concentrate is floated with $CuSO_4$ and $Ca(OH)_2$ (up to pH 12.3) in order to discard pyrite and arsenopyrite and recover a mixed sulphide concentrate (assays given for 2 months in 1972 : 30.2 % Zn and 5.74 % Cu, with 69 % recovery for both metals).

A recent review (Shrimpton, 1977) reports that "the mine has been producing a mixed zinc and copper product but now will be able to produce separately 4 000 tonnes of zinc and 250 tonnes of copper".

The above paper gives the following mineral production figures for lead + zinc + copper in the United Kingdom :

| | | |
|---|---|---|
| 1974 | 14 000 | |
| 1975 | 11 000 | |
| 1976 | 11 000 | (estimated). |

The paper also states : "The Force Crag mine, partly owned by the Toronto based New Force Crag Mines Ltd, is undergoing an underground exploration programme; the mine, which has produced barytes, lead and zinc, last worked in 1966 and has reserves currently estimated at 16 250 t of ore containing 1.75 % Pb, 8.6 % Zn and 6.68 % barytes; it is hoped to outline some 100 000 tonnes of 10 % combined lead/zinc ore initially, and subject to viability and planning permission it is anticipated that production will be at the rate of 50 tonnes/day".

11.4.C - <u>BIBLIOGRAPHY</u>

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Mineral engineering and analytical development at Wheal Jane Ltd.
(10th International Mineral Processing Congress, London, I.M.M.,
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Mining Annual Review-United Kingdom, Mining Journal, London, p. 502-
509.

## 12.5 - FRANCE

This section is an abridged version of a report prepared by the B.R.G.M. for the present dossier.

## 12.5.A - INTRODUCTION

In France, the production of lead-zinc concentrates is almost exclusively obtained in four flotation mills :

| | Production in contained metal, t | | | |
| --- | --- | --- | --- | --- |
| | Pb | | Zn | |
| | 1975 | 1976 | 1975 | 1976 |
| Largentière (Ardèche) | 18 342 | 23 704 | 3 352 | 4 087 |
| Les Malines (Gard) | 1 858 | 1 964 | 6 978 | 9 348 |
| Saint Salvy (Tarn) | - | - | 2 340 | 21 265 |
| Les Farges (Corrèze) | 974 | 2 328 | - | - |

The complexity of the mineralurgical treatment is, in increasing order : St Salvy, where the ore contains only sphalerite as the valuable component; Largentière and Les Malines, where the selective flotation produces both lead and zinc concentrates; and Les Farges, where lead is present in sulfide and oxide forms and is separated from a barite concentrate which represents the major tonnage produced from the ore.

The lead mine and mill in La Plagne (Savoie) were closed in 1973 .

The lead and zinc mines and mills in La Croix de Pallières (Gard) and Peyrebrune (Tarn) were closed in 1971 and 1972, respectively.

In 1974 and 1975, Villemagne (Gard) produced a small amount of lead and zinc concentrates.

## 12.5.B - SAINT SALVY

The Noailhac-Saint Salvy group's mine is located east of Toulouse. The orebody was discovered in 1965 by B.R.G.M.

Since 1975, Penarroya has been operating a flotation mill which was enlarged
to 900 tpd in 1977.

The principal minerals of the ore are siderite, and argentiferous galena
and sphalerite. The average content of the orebody is 9 % Zn, 0.5 % Pb,
and 80 g/t Ag. Cadmium and germanium are associated with the metallic
values. In 1976,189 500 t of run-of-mine ore were treated, producting
43 700 t of Zn concentrates assaying 49.40 % Zn, 6.28 % Pb and 5 159 g/t
Ag.

The extracted ore is coarsely crushed at the mine to -300 mm, and then
conveyed to the mill, where it is dumped in separate bins for the different
sections of the mine.

Semi-autogenous grinding (figure 12.5.1) is carried out in a 4.6 m Cascade
mill, fitted with a 10 mm trommel screen. Minus 10 mm is classified at
200 microns in a D30L Krebs hydrocyclone; the cyclone overflow becomes
flotation feed; cyclone underflow joins the +10 mm trommel fraction to
feed a ball mill in closed circuit with the hydrocyclone.

A second Cascade mill, 10' x 3', is used in parallel as a sampling unit
for some ore lots.

All the grinding units operate at 70 % solids, and hydrocyclone overflow
contains 45 to 46 % solids.

Hydrocyclone overflow is conditioned for 6 to 8 minutes with 475 g/t
$CuSO_4$, then floated (figure 12.5.2) in a roughing bank composed of eight
4.4 m3 cells, and in a scavenging bank of the same type. Scavenger con-
centrate is recycled to the roughers, and scavenger tailing is disposed of.

Rougher concentrate is cleaned and recleaned in an 8-cell and a 6-cell
bank, respectively, with cleaner tailing joining the scavenger concentrate.
Flotation time is about 35 minutes.

Bulk zinc-lead concentrate is thickened, then filtered to 7-10 % $H_2O$.

It is noteworthy that a high degree of automation and regulation exists in
that mill, leading to a total manpower requirement of 11 workers and 2
staff per operating day.

To flotation
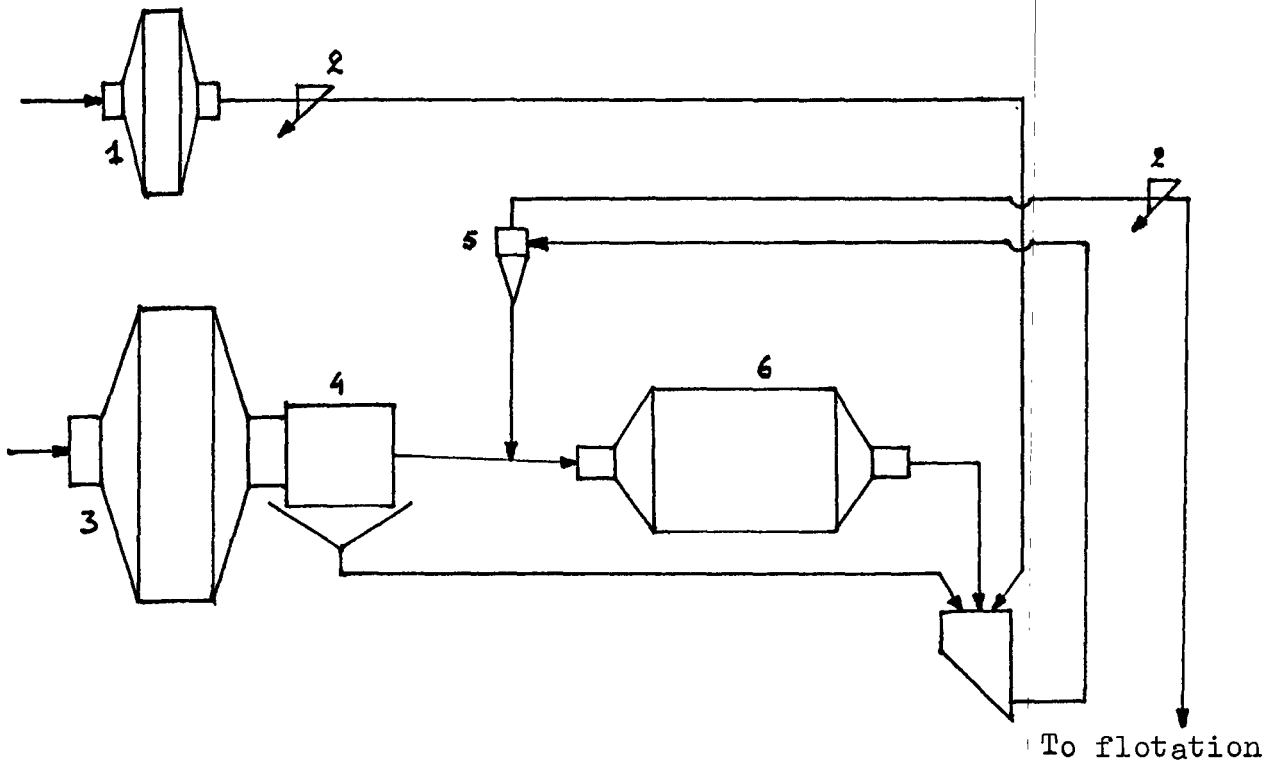
Legend

1. 10' x 3' Stein and Roubaix Cascade mill for sampling.

2. Minemet electrical samplers

3. Fives-Cail-Babcock 4,6 x 1,6 m Hydrofall mill; grate apertures : 10 mm; 16,9 rpm.

4. 1,6m x 1,2 m trommel; screen made in Forsiplast synthetic polymer; 10 mm square apertures.

5 Krebs D30L hydrocyclones; intake section : 320 $cm^2$; vortex finder : 200 mm $\emptyset$; apex : 20 mm $\emptyset$.

6. Unidan Smith ball mill, with grate discharge; grate aperture 12 mm; 24 rpm; rubber lining.

Figure 12. 5.1  SAINT SALVY grinding flowsheet
(from a B.R.G.M. report for this  dossier)
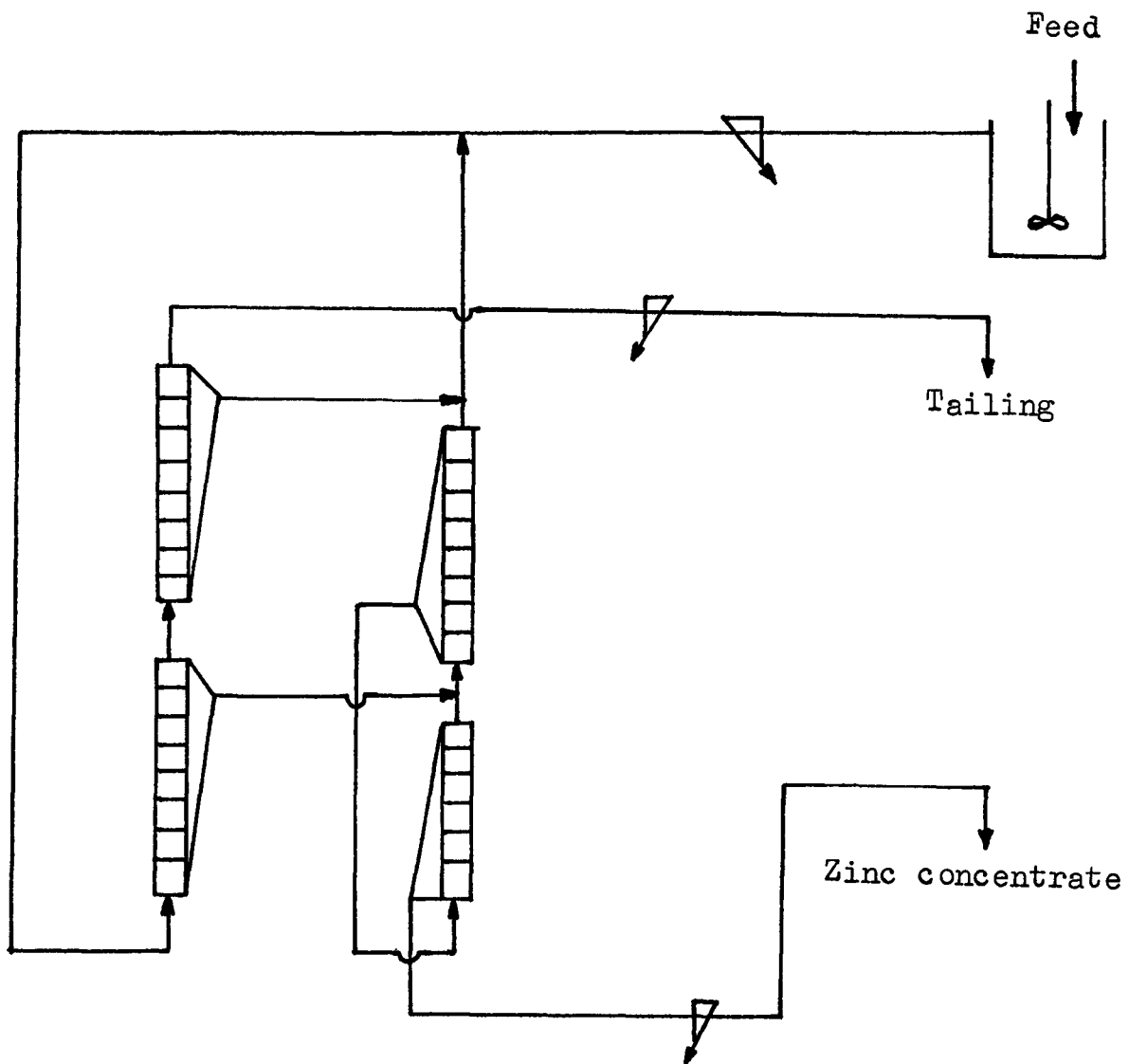
Figure 12. 5.2 SAINT SALVY flotation flowsheet
(from a B.R.G.M. report for this dossier)

Energy consumption is about 27.5 kWh/t.

Environmental aspects received due consideration in choosing the mill site, aesthetics of the buildings, sound isolation, etc ...

Metallurgical treatment is rather simple, as only a bulk lead-zinc concentrate is produced. Grinding size is controlled by the trommel screen and by the secondary ball mill in closed circuit; the hydrocyclone overflow is 20 % + 200 microns. This coarse size is adequate to attain a good recovery of the sulfide minerals without requiring any further regrinding to upgrade the concentrate.

Flotation reagents are :

| | Place of addition | Amount, g/t |
|---|---|---|
| CuSO$_4$ | Conditioner inlet | 475 |
| K Amylxanthate | Grinding mill outlet, conditioner outlet, roughers outlet | 240 |
| K Ethylxanthate | Conditioner and roughers outlet | 85 |
| Hexyl alcohol | Conditioner and roughers outlet | 30 |

Ores from the different sections of the mine are treated separately. The eastern ores are soft, rather rich, and give generally good recoveries in high grade concentrates. Sodium fluosilicate is added to them at the outlet of the conditioner. The western ores are hard (sometimes even very hard), less rich (mainly in galena), and difficult to float. A third cleaning has been installed to upgrace their concentrate. These ores contain 0.6 to 1.2 % oxidized zinc. The natural pH of the pulp is 6 - 7 for the eastern ores, and 7 - 9 for the western ores. Silica often tends to float with the concentrate, and a penalty is applied when its content is higher than 6 %.

Results obtained in 1976 are reproduced in Table 12.5.1. A zinc recovery of 95 % is aimed for with a content of 52 to 54 % Zn depending on the lead content of the feed.

Reserves in 1977 are calculated at 4 500 000 t of ore with an average assay of 9 % Zn.

## TABLE  12.5.1

## METALLURGICAL RESULTS AT SAINT SALVY  (1976)

| | t | % | % Pb | % Zn | g/t Ag | Pb | Zn | Ag |
|---|---|---|---|---|---|---|---|---|
| | | | | Assays | | | Recoveries | |
| Feed | 189 500 | 100 | 1.79 | 12.53 | 1430 | 100 | 100 | 100 |
| Concentrate | 43 700 | 23.06 | 6.28 | 49.40 | 5150 | 80.8 | 90.9 | 83.5 |
| Tailing | 145 800 | 76.94 | 0.45 | 1.48 | 310 | 19.2 | 9.1 | 16.5 |

## 12.5.C - LARGENTIERE

The Largentière mine and mill complex, located in the Ardèche department, has been operated by Penarroya since 1964; mining dates back to the Middle Ages, in which silver was already produced (as indicated by the town's name).

The mill was gradually enlarged from 1 200 tpd in 1964 to 2 200 tpd in 1971. Today, 2 500 tpd are treated with average contents of 3.6 % Pb, 0.6 % Zn, and 84 g/t Ag.

The principal sulfide minerals are galena and sphalerite, with minor amounts of pyrite, chalcopyrite, freibergite, and bournonite. Gangue is mainly quartz (in arkose rocks), with some ankerite and fluorite.

Run-of-mine ore is crushed in two stages : first, by a 32" x 42" jaw crusher (to -125 mm), then by a 4 1/4' Symons cone in closed circuit with a 30 mm screen. Screen undersize, at 80 % -15 mm, is conveyed to 2 bins.

Crushed ore is ground in two stages : by a 9' 1/2 x 10' cylindrical ball mill, in open circuit, with overflow discharge, to 80 % - 1 500 microns at 75 % solids; the pulp density is maintained constant automatically. The second stage is carried out in a 9' 1/2 x 16' cylindrical ball mill with a rubber grate discharge, in closed circuit with a 750 mm hydrocyclone; the overflow is controlled at 50 % solids and feeds two identical flotation circuits.

In the galena circuit, after depression, the first two cells give a primary concentrate. In the roughing stage, 24 cells give a preconcentrate that is cleaned twice in two 2-cell banks to obtain a secondary lead concentrate. Froth from the 12 scavenging cells is recycled to the roughers. Sphalerite is then activated in a conditioner. Twelve roughing cells give a concentrate that is cleaned twice in a bank of 4 cells and one of 2 cells to obtain the zinc concentrate. Froth from the 18 scavenging cells is recycled before the zinc roughers.

Lead concentrate is thickened and filtered to 6 % moisture; zinc concentrate, to 10 % moisture.

| | Weight | Assay | | | Recovery, % | | |
|---|---|---|---|---|---|---|---|
| | % | % Pb | % Zn | g/t Ag | Pb | Zn | Ag |
| **ROUBREAU COUCHE S** | | | | | | | |
| Flot. feed | 100,00 | 2,28 | 0,29 | 39 | 100,0 | 100,0 | 100,0 |
| Pb conc. | 2,83 | 77,00 | 1.10 | 1238 | 95.7 | 10.8 | 90.2 |
| Zn conc. | 0,34 | 2,44 | 50.85 | 334 | 0.4 | 60.5 | 3.0 |
| Pb tail. | | 0,10 | 0.26 | 4 | 4.3 | 89.2 | 9,8 |
| Zn tail. | | 0,09 | 0.09 | 3 | 3.9 | 28.7 | 6.8 |
| **VOLPILLIAIRE** | | | | | | | |
| Flot. feed | 100,00 | 8.45 | 0.89 | 138 | 100.0 | 100.0 | 100.0 |
| Pb conc. | 8,55 | 73.11 | 0,94 | 1500 | 98.9 | 9.0 | 93.2 |
| Zn conc. | 1,34 | 2.25 | 49.03 | 344 | 0.5 | 74.0 | 3,4 |
| Pb tail. | | 0.22 | 0.89 | 11 | 3.1 | 91.0 | 6,8 |
| Zn tail. | | 0.18 | 0.17 | 5 | 2.6 | 17.0 | 3.4 |
| **MONTREDON** | | | | | | | |
| Flot. feed | 100,00 | 7.13 | 1.73 | 159 | 100,0 | 100,0 | 100,0 |
| Pb conc. | 9,27 | 74.77 | 1,87 | 1589 | 97,2 | 10,0 | 92,7 |
| Zn conc. | 2,55 | 1.34 | 52,94 | 304 | 0,5 | 77,9 | 4,9 |
| Pb tail. | | 0.22 | 1,72 | 13 | 2,8 | 90,0 | 7,3 |
| Zn tail. | | 0.18 | 0,24 | 4 | 2,3 | 12,1 | 2,4 |
| **FAILLES MADELEINE** | | | | | | | |
| Flot. feed | 100,00 | 3,83 | 3,16 | 90 | 100,0 | 100,0 | 100,0 |
| Pb conc. | 4,87 | 75,55 | 2,06 | 1451 | 96,1 | 3,2 | 78,5 |
| Zn conc. | 4,94 | 0,69 | 54,34 | 302 | 0,9 | 85,1 | 16,6 |
| Pb tail. | | 0,16 | 3,21 | 20 | 3,9 | 96,8 | 21,5 |
| Zn tail. | | 0,13 | 0,41 | 5 | 3,0 | 11,7 | 4,9 |
| **FAILLES COLOMBIER** | | | | | | | |
| Flot. feed | 100,00 | 4,05 | 1,92 | 95 | 100,0 | 100,0 | 100,0 |
| Pb conc. | 5,27 | 73,65 | 2,19 | 1523 | 95,8 | 6,0 | 84,7 |
| Zn conc. | 2,92 | 0,94 | 53,01 | 275 | 0,7 | 80,7 | 8,5 |
| Pb tail. | | 0,18 | 1,90 | 15 | 4,2 | 94,0 | 15,3 |
| Zn tail. | | 0,16 | 0,28 | 7 | 3,5 | 13,3 | 6,8 |
| **ALL TOGETHER** | | | | | | | |
| Flot. feed | 100,00 | 4,29 | 0,98 | 89 | 100,0 | 100,0 | 100,0 |
| Pb conc. | 5,54 | 74,77 | 1,44 | 1466 | 96,6 | 8,1 | 91,0 |
| Zn conc. | 1,44 | 1,44 | 52,30 | 311 | 0,5 | 76,6 | 5,0 |
| Pb tail. | | 0,15 | 0,96 | 9 | 3,4 | 91,9 | 9,0 |
| Zn tail. | | 0,13 | 0,18 | 4 | 2,9 | 15,3 | 4,0 |

TABLE   12.5.2

METALLURGICAL RESULTS AT LARGENTIERE (1976)

The Largentière ore is a lead-zinc ore with a very fine sandstone gangue :
gravimetric separation would be difficult, so selective flotation is pre-
ferred. Separate treatment of 5 different ore types, at the rate of 2 or 3
in 24 hours, results in the need for instantaneous adaptation of grinding
and flotation plants. Since the machines' capacity, grinding charge, and
flotation time are fixed, it is necessary to balance the feed rate with
the grinding fineness, and the flotation flowsheet with the assay of the
ore :

a) Grinding : galena and sphalerite liberation demands a grind of 330 to
   160 microns depending on the ore type (Table 12.5.2).

   - "Roubreau couche S" ore represents 47 % of the feed; it is a coarse
     sandstone, liberated at about 330 microns, that can be ground at the
     rate of 125 tph, or 3 000 tpd, i.e. the maximum capacity of the flo-
     tation plant;

   - "Failles Roubreau" ore is 12 % of the run-of-mine ore; it is libera-
     ted at 210 microns, for a feed rate of 100 tph, or 2 400 tpd;

   - "Failles Montredon" ore amounts to 21 % of the total feed; it is libe-
     rated at 190 microns and can be treated at the rate of 95 tph, or
     2 280 tpd;

   - "Failles Volpilliaire" ore, 20 % of the feed, is the finest and
     hardest sandstone; it is liberated at about 160 microns and the feed
     rate is limited to 78 tph, or 1 870 tpd.

   As the grinding feed is automatically adjusted, grinding conditions can
   be instantaneously modified without significant variation of the flota-
   tion pulp density, even in the transit state.

b) Flotation : this a common Pb-Zn selective flotation.
   Sphalerite is depressed by a 3/1 mixture of zinc sulfate and sodium
   cyanide, added in the grinding mills. The promoter is a 1/1 mixture of
   K Amylxanthate and K Ethylxanthate, and frother is MIBC. These reagents
   are used in both the galena and the sphalerite circuits. Some sodium
   sulfhydrate is added during galena roughing to float the cerusite. The
   sphalerite is activated with copper sulfate.

Table 12.5.2 shows the average results obtained in 1976 when treating the different ore types. In general, the treatment for galena is based upon the highest metal recovery that results in the better silver recovery, with the metal assays kept at satisfactory levels. This balance can be maintained by an economic evaluation of plant performance with a formula of daily calculation. On the other hand, the sphalerite treatment is aimed at the best metal content in concentrates with a low amount of silica.

The treatment flowsheet is adapted to the assays of the ore. For instance, "Couche S" and "Montredon" (Table 12.5.2) show the extremes of galena assays; the average content of Montredon is composed of lots assaying up to 10 % Pb. In the roughing flotation stage (depending on the assay of the froth), 2 or 4 more cells will produce primary lead concentrate. For the sphalerite, one can observe that the content in "Failles Madeleine" is 10 times that of "Couche S". In the former double cleaning will be suppressed, and 6 cells will produce a final concen.rate; in extreme cases, the first 4 rougher cells will produce the zinc concentrate directly.

## 12.5.D - LES MALINES

Les Malines ore is a typical BPG ore, with sphalerite predominance over pyrite and galena. The main gangue is dolomite, with barite, some quartz, calcite, clays and partially decomposed organic matters.

Mineralization is rather fine, and the Pb-Zn sulfides are liberated well only after grinding to 50 microns.

The quality of the treated ores is rather variable. There frequently is some syn-crystallization between the various components of the BPG minerals.

Built in 1947 to treat 120 tpd of ore, the mill now has a capacity of 1 200 tpd.

Run-of-mine ore is stockpiled in 4 bins and then crushed to 100 mm in a 1 000 mm x 500 mm jaw crusher; a vibrating double-deck screen separates a 0-8 mm fraction; the final crushed product is sent to 2 bins; a 8-22 mm fraction is crushed in a 3' Symons cone set a 6 mm; and a 22-100 mm fraction is crushed in a 4-36 Hydrocone set at 10 mm.

Both crushed products are recycled on the screen.

Crushed ore is fed in a cylindrical ball mill in open circuit, giving a product (at 80 % - 800 microns) which is pumped to a hydrocyclone. Cyclone overflow (at 80 % - 210 microns) becomes the flotation feed; cyclone under-flow is ground in a secondary ball mill that is in closed circuit with the hydrocyclone.

The lead circuit (figure 12.5.3) is composed of a group of 18 rougher cells, a group of 6 cells for the retreatment of the middlings, and a group of 2 cleaners. The rougher concentrate is reground in a 900 mm x 900 mm ball mill in closed circuit, with a hydrocyclone cutting at 40 microns. Hydro-cyclone overflow is floated in retreatment cells whose concentrate is cleaned, thickened, and filtered to 12 % moisture.

The lead tailings are sent to 4 conditioners and then to the zinc circuit (similar to the lead circuit); it is composed of a group of 38 rougher cells, a group of 10 retreatment cells for the middlings, and a group of 4 cleaner cells. Here again, the hydrocyclone for middlings regrinding cuts at 40 microns. Zinc concentrate is thickened and filtered to 11 % moisture.

Since the beginning of the operations, the ore has been treated by selective flotation. Galena and sphalerite liberation requires a very fine grind, less than 80 microns. Grinding was at first very fine, until it was observed that the primary grind could be rather coarse (210 microns) if middlings were floated and reground. Presently circulating load on the secondary ball mill is 255 %.

For selective flotation, the ore is receiving additions of zinc sulfate and sodium cyanide in the secondary ball mill and at the regrinding of the middlings. It seems that cyanide has little depressing effect on the spha-lerite and that it is mainly the zinc sulfate which is effective. The presence of cyanide is, however, necessary : either it reacts in combination with zinc sulfate to form a cyanate that could be the effective depressant, or it activates the slightly oxidized galena by superficial pickling. Galena is floated with a mixture of ethylxanthate and amylxanthate; hexyl-alcohol is the frother.
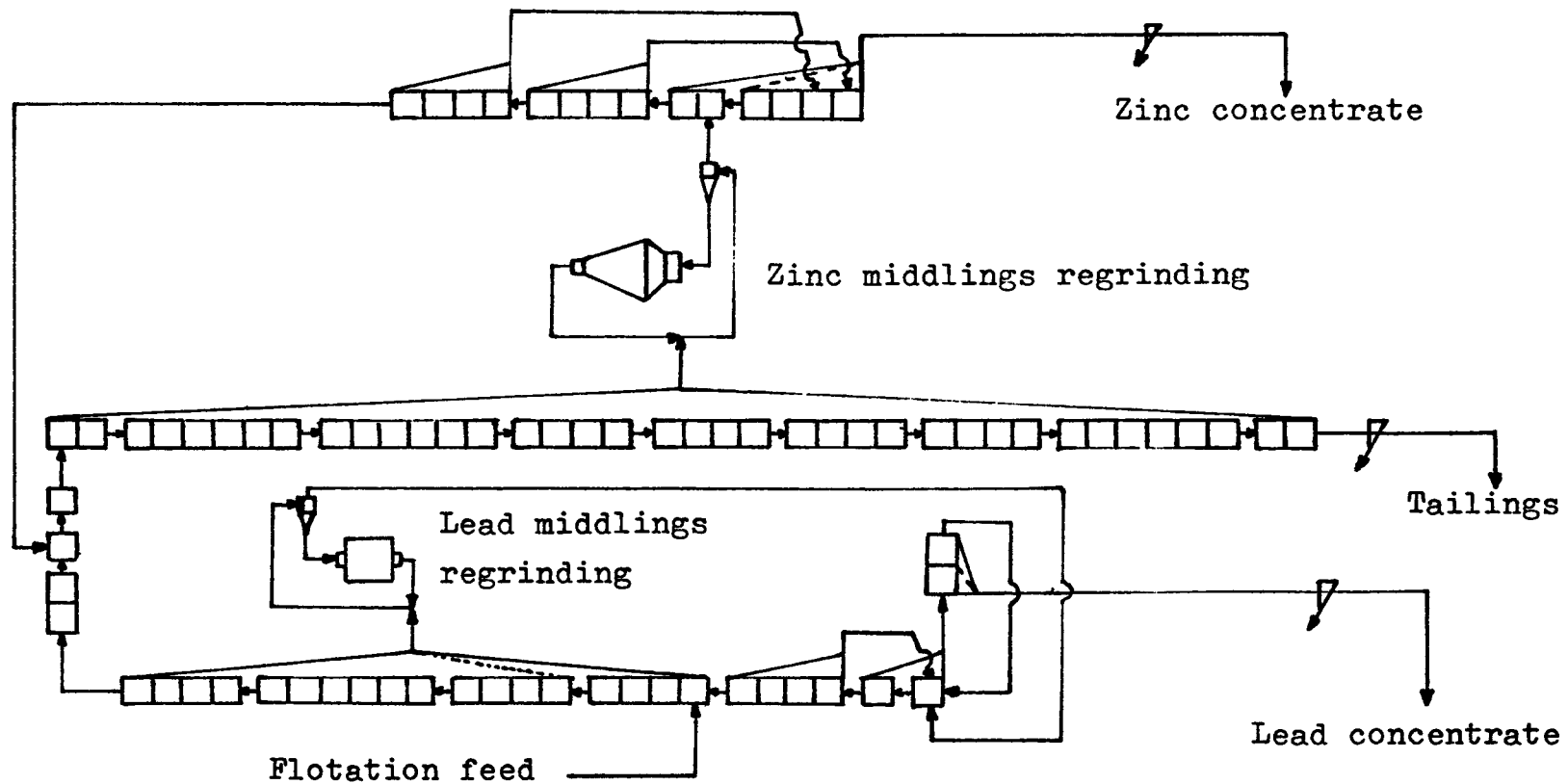
Figure 12.5.3  LES MALINES flotation flowsheet

(from a B.R.G.M. report for this dossier)

# TABLE 12.5.3

## METALLURGICAL RESULTS AT LES MALINES (1976)

| | Weight | | Assay | | | Recovery, % | | |
|---|---|---|---|---|---|---|---|---|
| | t | % | Pb, % | Zn, % | Ag, g/t | Pb | Zn | Ag |
| Run-of-mine ore | 331 800 | 100,00 | 0.74 | 3.37 | 24 | 100.00 | 100.00 | 100.00 |
| Lead concentrate | 2 700 | 0.81 | 53.65 | 4.69 | 1022 | 59.03 | 1.13 | 34.75 |
| Lead tailings | 329 100 | 99.19 | 0.31 | 3.36 | 16 | 40.97 | 98.87 | 65.25 |
| Zinc concentrate | 19 210 | 5.79 | 2.33 | 53.36 | 137 | 18.24 | 91.65 | 33.22 |
| Zinc tailings | 309 890 | 93.40 | 0.18 | 0.26 | 8 | 22.73 | 7.22 | 32.03 |

Sphalerite is very sensitive to the depressing effect of zinc sulfate; it is reactivated by copper sulfate in the presence of lime (pH 10.3), used to depress the pyrite. The sphalerite promoter is amylxanthate, and the* frother is once more hexylalcohol.

Energy consumption is about 20 kWh/t.

Metallurgical results for 1976 are given in Table 12.5.3.

Lead recovery is only moderate, due to numerous inclusions of galena in the sphalerite and to galena partial oxidation.

12.5.E - LES FARGES

The vein-type orebody of Les Farges is situated near the town of Ussel, in the Correze department. Known since the days of the Romans, it was recently drilled by B.R.G.M. and traced underground in 1971. At the same time, Rhone Poulenc initiated test work to concentrate the values (lead and barite); a concentrating mill was installed in 1974 to treat stockpiled and run-of-mine ore at the rate of 720 tpd and 250 d/year.

The mining and crushing operations are carried out in two shifts, and the selective flotation in three 30 tph shifts.

Although mining is conducted to blend the ores, .some variations appear in the contents of the values, as shown below :

lead    :  4 -   6 %
silver  :  90 - 130 g/t
barite  :  12 -  35 %

Planned production is 13 200 tpy of lead concentrate with 65 % Pb and 1 200 g/t Ag, and 30 000 tpy of 97 % barite concentrate.

In fact, from an ore assaying 5 % Pb (( .3 % as oxidized lead and 0.75 % Pb as pyromorphite) and 20-25 % $BaSO_4$, the concentrates assay 71 % Pb (with a recovery of 90 %) and 97-98 % $BaSO_4$ (with a recovery of 82-95 %). Tailings contain 0.8-0.9 % Pb and 10-12 % $BaSO_4$.

Sulfides in the ore are mainly galena and sphalerite, the latter in small amount (maybe less than 0.5 %). Part of the lead is oxidized in cerusite and pyromorphite, $Pb_5$ ($PO_4$, $AsO_4)_3Cl$. The main elements of the gangue are quartz and barite.

Present ore reserves are computed at about $1.3 \times 10^6$ tonnes with 5.87 % Pb, 134 g/t Ag and 27.5 % $BaSO_4$.

The ore feeding the mill comes either directly from the mine or from an open stockpile of open-pit ore and some underground-mined ore.

After primary crushing, the feed is deslimed in a trommel with 6 mm aper-tures. The undersize from the trommel is again deslimed in 3 stages of hydrocyclones. The +6 mm oversize is screened on a 50 mm grizzly; oversize is crushed in a jaw crusher. The product of this crusher and the -50 mm size fraction are fed to a vibratory screen with 25 mm apertures. The oversize is crushed in a 4' Symons cone SH, and recycled on the screen to close the circuit.

The 0-25 mm crushed ore is fed to a cylindrical ball mill which discharges the pulp in a hydrocyclone; cyclone underflow is ground in a conical ball mill in closed circuit with the former hydrocyclone.

Cyclone overflow goes to lead flotation, where the galena, cerusite, and pyromorphite are successively floated in Minemet cells equipped with crossed bar impellers.

Flotation pulp is first conditioned, and then fed into a 6-cell rougher bank and a 4-cell scavenger bank. Cleaning and recleaning are carried out in a 4-double-cell bank. Cerusite is next floated in a 4-cell bank after sulfidization in a 5 m3 conditioner. Finally, the pulp is both acidified and sulfidized in a 3.5 m3 conditioner, then floated for pyromorphite in a 4-cell rougher and a 4-cell scavenger. Both cerusite and pyromorphite rougher concentrates are cleaned and recleaned, like galena, in a 4-double-cell bank.

Lead tailings are floated to obtain a barite concentrate.

Metallurgical results obtained in 1976 are reproduced in Table 12.5.4.

## TABLE 12.5.4

## METALLURGICAL RESULTS AT LES FARGES

| | Weight | Pb | | | BaSO$_4$ | | |
| | % | % | Weight | Recov., % | % | Weight | Recov., % |
|---|---|---|---|---|---|---|---|
| Run-of-mine ore | 100,0 | 5.00 | 5.000 | 100.00 | 19.50 | 19.500 | 100.00 |
| Desliming losses | 5 | 4.50 | 0.225 | 4.50 | 22.00 | 1.100 | 5.64 |
| Grinding feed | 95 | 5.03 | 4.775 | 95.50 | 19.37 | 18.400 | 94.36 |
| Unground material | 0.5 | 1.50 | 0.008 | 0.16 | 5.00 | 0.025 | 0.13 |
| Flotation feed | 94.5 | 5.04 | 4.767 | 95.34 | 19.44 | 18.375 | 94.23 |
| Lead concentrate | 6 | 70.00 | 4.200 | 84.00 | 3.00 | 0.180 | 0.92 |
| Barite concentrate | 15 | 0.30 | 0.045 | 0.90 | 97.50 | 14.825 | 75.00 |
| Tailings | 73.5 | 0.71 | 0.522 | 10.44 | 4.86 | 3.570 | 18.31 |

There is 2.0 % Zn and 1 500 g/t Ag in the lead concentrate, and 0.90 % $SiO_2$ in the barite concentrate.

There are regulating devices in the mill which ensure the smoothest possible operation :

- control of the ore level in the intermediate bin of crushed ore, just ahead of the primary grinding mill, and operation of the feeders;

- control of the ore feed to the primary grinding mill by a constant-weight feeder;

- control for a constant level in the sump of the hydrocyclone;

- control of the pulp density of the hydrocyclone overflow by the addition of water to the secondary ball mill;

- recording of the parameters of the grinding mills and of the hydrocyclone.

The reagents used in both flotation circuits are :

| Reagent | Consumption, g/t | Point of addition |
|---|---|---|
| Sulfuric acid | 1 000 | Lead circuit |
| Amylxanthate | 150 | Lead circuit |
| Soda ash | 700 | Barite circuit |
| Alkylsulfate[°] | 1 000 | Barite circuit |
| Pine oil | 50 | Lead circuit |
| Sodium silicate | 1 000 | Barite circuit |
| Sodium sulfide | 400 | Lead circuit |

[°] Galoryl MT 508 : made with synthetic saturated fatty alcohols in the $C_{16}$ - $C_{18}$ group.

Energy consumption is about 51 kWh/t.

Problems arose before 1975, when the desliming trommel was not yet installed, because the run-of-mine ore was very wet and contained some clays. It still seems worthwhile to improve the pyromorphite flotation.

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12.6 - BELGIUM, THE NETHERLANDS, LUXEMBURG

There is no concentrating mill for Pb and Zn ores in Belgium, the
Netherlands and Luxemburg.

## 12.7 - GERMANY

## 12.7.A - INTRODUCTION

In this country, four Pb-Zn mines and five concentrating mills are still operating in 1977 (Fachvereiningung Metallerzbergbau, 1976).

Extraction and beneficiation of mixed ores has given the following concentrate productions, in terms of contained metal (mt) :

|                   | 1973    | 1974    | 1975    | 1976    |
|-------------------|---------|---------|---------|---------|
| Lead              | 33 533  | 29 385  | 31 372  | 32 000  |
| Zinc              | 118 026 | 112 361 | 111 551 | 112 000 |
| % Pb + Zn in ores | 6.8     | 7.4     | 7.3     | 7.5     |

The contribution to mine production by the 3 operating companies was, in 1975 :

|            | Lead    | Zinc    | Lead + Zinc |
|------------|---------|---------|-------------|
| Preussag   | 74.4 %  | 42.0 %  | 49.1 %      |
| Sachtleben | 13.0 %  | 46.6 %  | 39.2 %      |
| Altenberg  | 12.6 %  | 11.4 %  | 11.7 %      |

A.G. des Altenbergs, a wholly-owned subsidiary of the Belgian company Vieille Montagne, operates the Lüderich mine and mill complex at Untereschbach, near Cologne.

Preussag A.G. Metall has two active mines, in Bad Grund and in Rammelsberg, near Goslar, in the Harz region. Ore from Bad Grund is treated in the company's own mill, and complex ores from Rammelsberg are beneficiated in the Rammelsberg and Bollrich mills.

Sachtleben Bergbau, in Lennestadt, is a wholly-owned subsidiary of Metallgesellschaft A.G.; it is running the Meggen orebody, where lead-zinc pyrite and barite ores are produced.

All these mines are underground.

## 12.7.8 - <u>LUEDERICH</u> (*)

Run-of-mine ore is first crushed to -120 mm in a jaw crusher located near the hoisting shaft, and then transported to the mill in railroad cars, at a rate of about 830 tpd. Average metal content is 1.8 % Pb and 6.5 % Zn; gangue is mainly siliceous (40 % $SiO_2$); ore is rather wet, with 6.4 % $H_2O$. The mill also treats dump tailings (80 tpd) from gravimetric concentration tailings produced earlier in that region.

Feed (either ore or tailings) is washed with water on a 25 mm screen, and oversize is crushed in a Symons cone crusher. All the ore is then washed with water on a double-deck screen, the -25 + 12 mm fraction (about 52 weight-%) going to sink-float separation, the -12 + 1.5 mm fraction (about 16 weight-%) going to the fine ore bins, and the -1.5 mm fraction being classified at about 0.1 mm in a hydrocyclone. Cyclone overflow (about 8 weight-%) is sent to a 25 m thickener; cyclone underflow (about 24 wt-%) is dewatered to 7-8 % $H_2O$ in an electromagnetic vibrating screen, and sent to the fine ore bins which receive either ore or dump tailings.

The -25 + 12 mm fraction is treated by sink-float separation in a static box at a density of 2.77-2.78, obtained by a suspension of floateu galena. Sink-float tailings represent around 70 % of the feed and contain 0.5 % (Pb + Zn). The sink fraction is sent to the fine ore bins.

Run-of-mine flotation feed (consisting of the -25 + 12 mm sink fraction, the primary -12 + 1.5 mm fraction and the dewatered + 0.1 mm hydrocyclone underflow) is ground to -0.3 mm in an open circuit rod mill, and in two ball mills in closed circuit with spiral classifiers. Classifier overflow is selectively floated in a 20 tph plant. The lead circuit includes roughing, scavenging, and 3 cleaning stages. The zinc circuit includes roughing, scavenging, and 2 cleaning stages.

Fine dump tailings are also received by truck; after dilution with water, they are ground in an open circuit ball mill; the resulting pulp is partly reground in ball mills in closed circuit with rake classifiers; classifiers overflow is dewatered in a 10 m thickener; then sent to a 6 tph selective flotation plant.

(*) This section on Lüderich was written before the recent closure of the mine.

Another part of the pulp is mixed with finely-crushed dump tailings and, after grinding in ball mills in closed circuit with rake classifiers, is sent to the 25 m thickener; thickener underflow is selectively floated in two plants of 2.5 tph and 8 tph capacity. All these flotations are similar to the run-of-mine ore flotation, except for minor changes in the distribution of the flotation stages, the capacity and number of flotation cells, and the amounts of added reagents.

All the flotation concentrates are directly dewatered on rotary drum filters; lead concentrates are smelted in Germany and zinc concentrates are sent to Belgian metallurgical plants.

For the Lüderich run-of-mine ore, lead flotation is carried out at pH 8.5-9.1, controlled by the addition of NaOH + $Na_2CO_3$; gangue is dispersed with $Na_2SiO_3$, and zinc sulfate is the only depressant for sphalerite; a small amount of $Na_2S$ is added in the rod mill to activate the tarnished surfaces; the promoter is sodium isopropylxanthate. Lead concentrate assays 71 % Pb and 4.5 % Zn. Lead flotation of the dump tailings is similar, but the amount of $Na_2S$ used is increased to float the oxidized minerals.

Zinc flotation is carried out after activation with copper sulfate, at a pH of 6.5-7 controlled by the addition of $H_2SO_4$. Here again, sodium isopropylxanthate is the promoter. Zinc concentrate assays 61 % Zn and 0.2 % Pb.

The thickeners are supplemented by a small amount of Sedipur flocculent, which does not interfere at all with subsequent flotations.

Flotation tailings contain about 0.6 % (Pb + Zn), compared to 0.5 % for the float fraction in sink-float separation. These results lead to a recovery of about 91 % of the lead and 93 % of the zinc.

The Lüderich operating features are as follows :

- simultaneous treatment of run-of-mine ore and dump tailings;

- high moisture leading to the washing of the ores before secondary crushing;

- a significant degree of gangue liberation at a coarse size suitable for sink-float preconcentration;

- low content of pyrite, giving a rather easy selective flotation (with the production of pure concentrates), and zinc flotation at low pH;

- a high degree of liberation of medium-sized lead and zinc minerals, so that grinding is very moderate, flotation concentrates are coarse and need no thickening before filtration;

- excellent metallurgical results.


## 12.7.C - BAD GRUND

The Bad Grund mine and mill were modernized and enlarged in the late sixties; the present capacity of the mill is 2 000 tpd.

The principal metallic values are lead in galena and zinc in sphalerite; silver and cadmium are present as by-products. Gangue minerals are mainly quartz, limestone, barite, and iron carbonate; some kaolinite results from weathering of the ore and influences the treatment somewhat.

Mineral dissemination is rather coarse, and a sufficient degree of liberation is obtained at 80 % -0.2 mm for the selective flotation of lead and zinc sulfides.

In the first six months of 1976, feed ore contained 3.75 % Pb, 5.53 % Zn, 50 g/t Ag, and more than 50 % $SiO_2$; it averaged 3.6 % $H_2O$.

Ore minus 400 mm is passed over a grizzly at 100 mm. Oversize is fed in two 800 x 400 mm jaw crushers; crushed ore is washed with the grizzly undersize in a 2 500 x 6 300 mm trommel, with a capacity of 100 tph, and screened at 3 and 40 mm, respectively.

The minus 3 mm fraction goes directly to a spiral classifier; the + 40 mm fraction is crushed in a hammer mill and joins the -40 + 3 mm; both fractions are screened and the + 15 mm fraction is crushed in two n° 3 cone crushers set at 10 mm.

A final screen separates the -3 mm, which is sent to the classifier, from the -30 + 3 mm, which is cleaned in a sink-float cone separator (3 m diameter, 62 tph capacity), using a Fe-Si suspension of 2.68-2.70 density. Floats represent 60 to 70 % of the feed or 40 % of the total ore, and are discarded.

Sinks are fed to 3 ball mills, with the +0.2 mm fraction coming from the spiral classifier. These mills are in closed circuit with 3 duplex rake classifiers. The overflow from these classifiers and the thickened over-flow from the spiral classifier, at 75 % -0.2 mm, form the flotation feed.

Lead flotation is carried out at 43 % solids in a bank of 16 2.3 m3 cells, with 4 cells as primary roughers, 6 ce.ls as secondary roughers, and 6 cells as scavengers. Scavenger concentrate is recycled to the fifth rougher cell.

Lead rougher concentrates are cleaned twice in a bank of 8 1.5 m3 cells. Lead primary rougher concentrate flows to the third cell, lead secondary rougher concentrate to the fourth cell. Lead cleaner scavenging concentrate (cells 6 to 8) is sent to the fifth cell, and tailing is recycled in the first rougher cell. Cleaner concentrate from cells 3 to 5 is recleaned in cells 1 and 2, giving the final lead concentrate.

Zinc flotation follows exactly the same pattern.

Both flotations are realized in neutral pulps.

Lead and zinc concentrates are dewatered to 7-10% $H_2O$ by thickening and filtration.

In the first half of 1976, there was a production of 10 110 t of lead con-centrates with 75 % Pb (recovery : 91 %) and 903 g/t silver, and 20 020 t of zinc concentrates assaying 59 % Zn (recovery : 95 %).

A number of detailed data are available for 1972 (Lange, 1973) :

- Results of sink-float separation in static cone :

        feed                    : 63 tph

        feed size             : -30 + 3 mm

        density of the medium : 2.7

        operating density    : 2.89 (at 50-50 distribution of feed)

        operating characteristics : $E_p$ = 0.027; I = 0.014

- Results of the sink-float separation :

|  | Weight, % | Assay, % | | Recovery, % | |
|---|---|---|---|---|---|
|  |  | Pb | Zn | Pb | Zn |
| Ore feed | 100.00 | 4.75 | 4.23 | 100.00 | 100.00 |
| Discarded float | 38.62 | 0.15 | 0.07 | 1.26 | 0.60 |
| Thickener overflow | 4.44 | 1.88 | 1.07 | 1.76 | 1.13 |
| Flotation feed | 56.9ʲ | 8.05 | 7.26 | 96.98 | 98.27 |

- Results of flotation :

|  | Weight, % | Assay, % | | Recovery, % | |
|---|---|---|---|---|---|
|  |  | Pb | Zn | Pb | Zn |
| Feed | 100.00 | 8.05 | 7.26 | 100.00 | 100.00 |
| Lead concentrate | 10.03 | 76.49 | 1.72 | 95.25 | 2.38 |
| Zinc concentrate | 11.66 | 1.04 | 59.14 | 1.50 | 95.06 |
| Tailing | 78.31 | 0.33 | 0.24 | 3.25 | 2.56 |

- Reagent consumption (October-December 1972) :

|  | g/t, total feed | g/t, flotation feed |
|---|---|---|
| Zinc sulfate | 318 | 558 |
| Copper sulfate | 168 | 296 |
| K-Ethylxanthate | 54 | 95 |
| K-Amylxanthate | 27 | 47 |
| Tragol 4 | 42 | 74 |
| Pine oil | 4 | 7 |

- Electrical energy consumption :

installed power       : 2 700 kW
consumption (1972)   : 17.8 kWh/t.

Company-supplied metallurgical results for 1975 :

|  | Weight, % | Assay, % | | Recovery, % | |
| --- | --- | --- | --- | --- | --- |
|  |  | Pb | Zn | Pb | Zn |
| Ore feed | 100.00 | 3.79 | 5.21 | 100.00 | 100.00 |
| Sink-float tails | 42.08 | 0.13 | 0.08 | 1.48 | 0.63 |
| Thickener overflow | 3.37 | 1.91 | 1.77 | 1.77 | 1.15 |
| Flotation feed | 54.55 | 6.66 | 9.30 | 96.75 | 98.22 |
| Lead concentrate | 4.52 | 75.57 | 1.45 | 90.96 | 1.27 |
| Zinc concentrate | 8.22 | 1.13 | 59.72 | 2.47 | 95.13 |
| Tailings | 41.81 | 0.30 | 0.23 | 3.32 | 1.82 |

## 12.7.D - RAMMELSBERG

The different ore types (Reicherz    rich ore; Banderz = banded ore)
are crushed at Rammelsberg to -20 mm in jaw and Symons cone crushers. The
rich ore is treated on site, while the banded ore is sent to Bollrich mill.

Due to the very fine dissemination of the ore components, it is necessary
to grind very finely to liberate the minerals. In the Rammelsberg mill,
this is carried out in 4 ball mills in closed circuit with mechanical
classifiers. The modern Bollrich mill uses 3 steps, i.e. rod mill and rake
classifier in open circuit as well as ball mills and spiral classifiers in
closed circuit. The third step uses a hydrocyclone that classifies the two
classifiers' overflow. An additional ball mill grinds the underflow of the
hydrocyclone. The ground pulp is recycled to the spiral classifier, and
the cyclone overflow is sent to flotation.

Electric power for the total comminution process is 730 kW. Steel consump-
tion in grinding is 610 g/t. The ore is ground to 60 % - 40 microns, which
results in a 50 % degree of liberation. Due to different specific weights,
the flotation pulp contains 900 g/l for rich ore and 600 g/l for banded
ore.

The flotation process gives a copper concentrate, a mixed lead concentrate,
and a mixed zinc concentrate; with rich ore, there is also a recovery of a
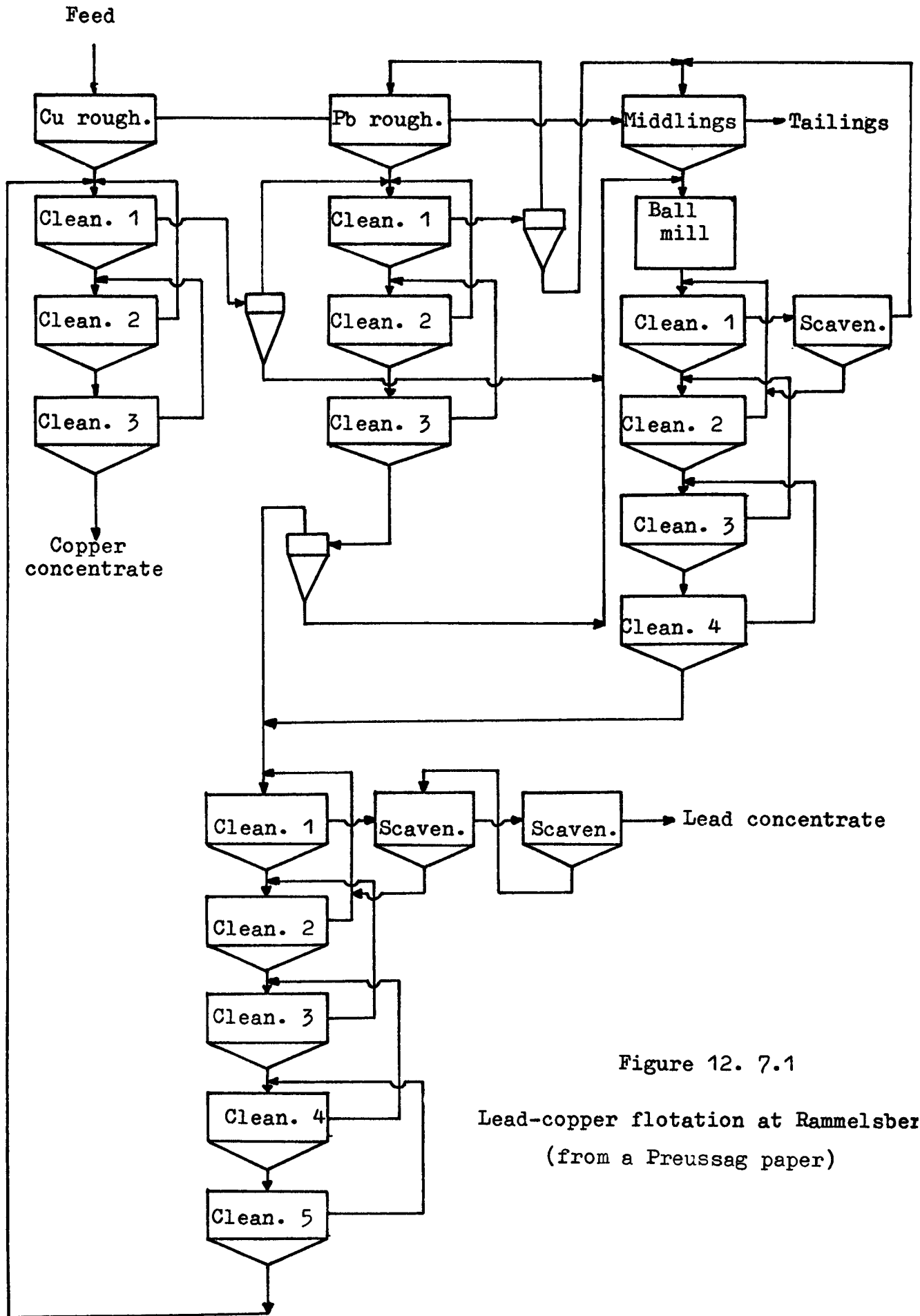pyrite concentrate and a barite concentrate.

Figure 12. 7.1

Lead-copper flotation at Rammelsber

(from a Preussag paper)

The pyrite concentrate is presently not saleable and is discarded in tailings ponds, but it must be floated to enable the flotation of a pure barite concentrate. The flotation process follows these principles : in the individual circuits, the liberated minerals are first floated in a roughing stage with starvation amounts of promoter, then cleaned to give concentrate I. The middlings particles are next floated in the middlings circuit, ground to - 40 microns, and floated again to give a somewhat poorer concentrate II.

The flotation cells are of the Fahrenwald-Denver type, with 3 m3 and 1.5 m3 capacities. The barite cleaning is made in 1 m3 cells. In the Rammelsberg mill, the flotation pulp is thickened between each flotation circuit.

In the Rammelsberg mill, the raw ore' s copper content is usually over 0.6 %. In that case, the copper minerals are selectively floated (with $SO_2$ addition) in the first cells; the lead minerals are floated in the following cells of the roughing machine (figure 12.7.1). The copper rougher concentrate is cleaned three times with further additions of $SO_2$, to give a final copper concentrate with over 20 % Cu; the lead rougher concentrate is also cleaned three times to give a concentrate with over 38 % Pb and under 2 % Cu.

In the middlings circuit, the middlings particles are floated with greater amounts of xanthate, classified in a hydrocyclone, reground, and refloated. The concentrate II thus obtained is treated like the Pb-Cu bulk concentrate which is floated from rich and banded ores when the Cu ore content is lower. It is conditioned with potassium dichromate, and chalcopyrite is selectively floated from the depressed galena.

As the floatability of the mineral of the ores depends largely on the dissemination and the particle size, the copper cleaners' tailings and the Pb concentrate I in the Rammelsberg mill are classified, and the underflow is further comminuted in the lead middlings regrind mill. The degree of liberation is so high that copper recovery in the copper concentrate could be significantly increased for a same concentration ratio.

In the zinc flotation circuit (figure 12.7.2) the rougher concentrate is cleaned twice, then classified in a hydrocyclone; cyclone overflow is again cleaned twice to give a final concentrate with 48 % Zn.
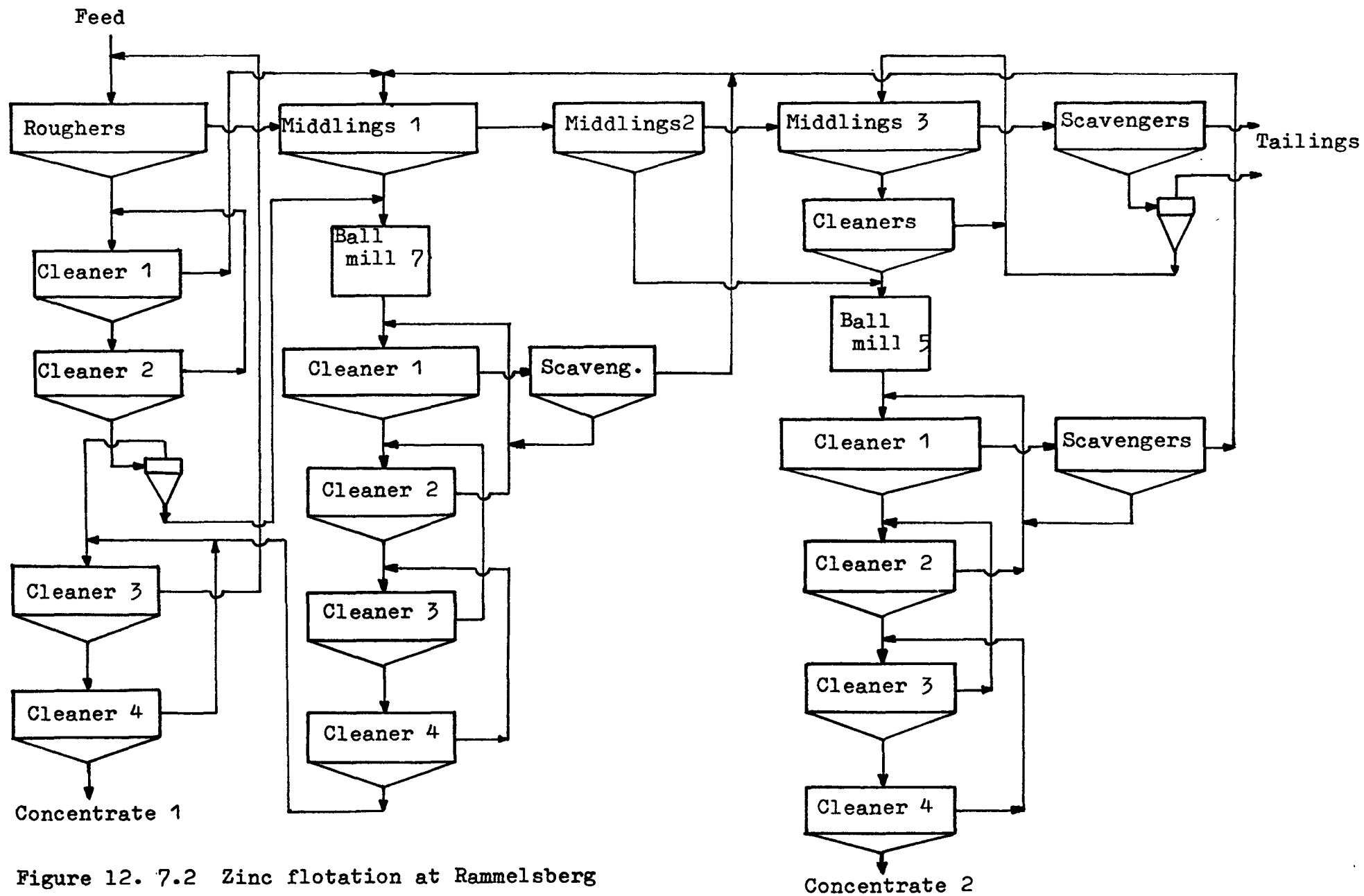
Figure 12. 7.2  Zinc flotation at Rammelsberg
(from a Preussag paper)

The cyclone underflow is reground and cleaned several times.

The middlings, finely disseminated with pyrite, are reground to -40 microns in a ball mill. The hydrocyclone overflow is floated to give a poorer concentrate assaying about 40 % Zn. A mixture of the concentrates contains about 44 % Zn.

The tailings of the sulfide flotation in Rammelsberg still contain 40-60 % $BaSO_4$. A 95 % $BaSO_4$ concentrate is floated by addition of oleic acid, Resanol, and sodium silicate.

The concentrates are thickened and filtered before railroad transport.

## Metallurgical results

| | Weight dry t | Pb | Zn | Cu | Fe | Ag $^{(\circ)}$ |
|---|---|---|---|---|---|---|
| Copper concentrate | 8 605 | 6.79 | 11.90 | 22.23 | 22.98 | 673 |
| Lead mixed conc. | 23 788 | 38.86 | 21.79 | 2.05 | 8.45 | 401 |
| Zinc mixed conc. | 65 855 | 5.40 | 44.60 | 1.26 | 10.40 | 123 |
| Barite concentrate | 15 368 | $BaSO_4$ content : 94,5 % | | | | |
| Total metal recovery, % | | 92.36 | 96.57 | 93.20 | | |

## Data for 1976

Rammelsberg mill capacity : 720 tpd

Bollrich mill capacity : 600 tpd

Average ore contents : 7-8 % Pb, 16-19 % Zn, 1.3 % Cu, 11-14 % Fe, 20 % $BaSO_4$, 130 g/t Ag, 1 g/t Au.

## 12.7.E - MEGGEN

The Meggen mine and mill complex of the Sachtleben Bergbau is located in Lennestadt, in the southern part of the Ruhr district. The mine has been in operation for more than 100 years, producing to date more than 32 million tons of ore.

(°) g/t

Feed from primary crusher (underground)

↓

- 170 mm

↓

Bin

↓

Screen

| - 1,5 mm | - 15 + 1,5 mm | - 170 + 15 mm |
|---|---|---|
| ↓ | ↓ | ↓ |
| Spiral classifier and hydrocyclone | Sink-float hydrocyclone | Sink-float separation |

- 0,1 mm    + 0,1 mm      Sinks      Barren rocks      Sinks

Thickener    Dewatering classifier        Tailings disposal      Crushing plant

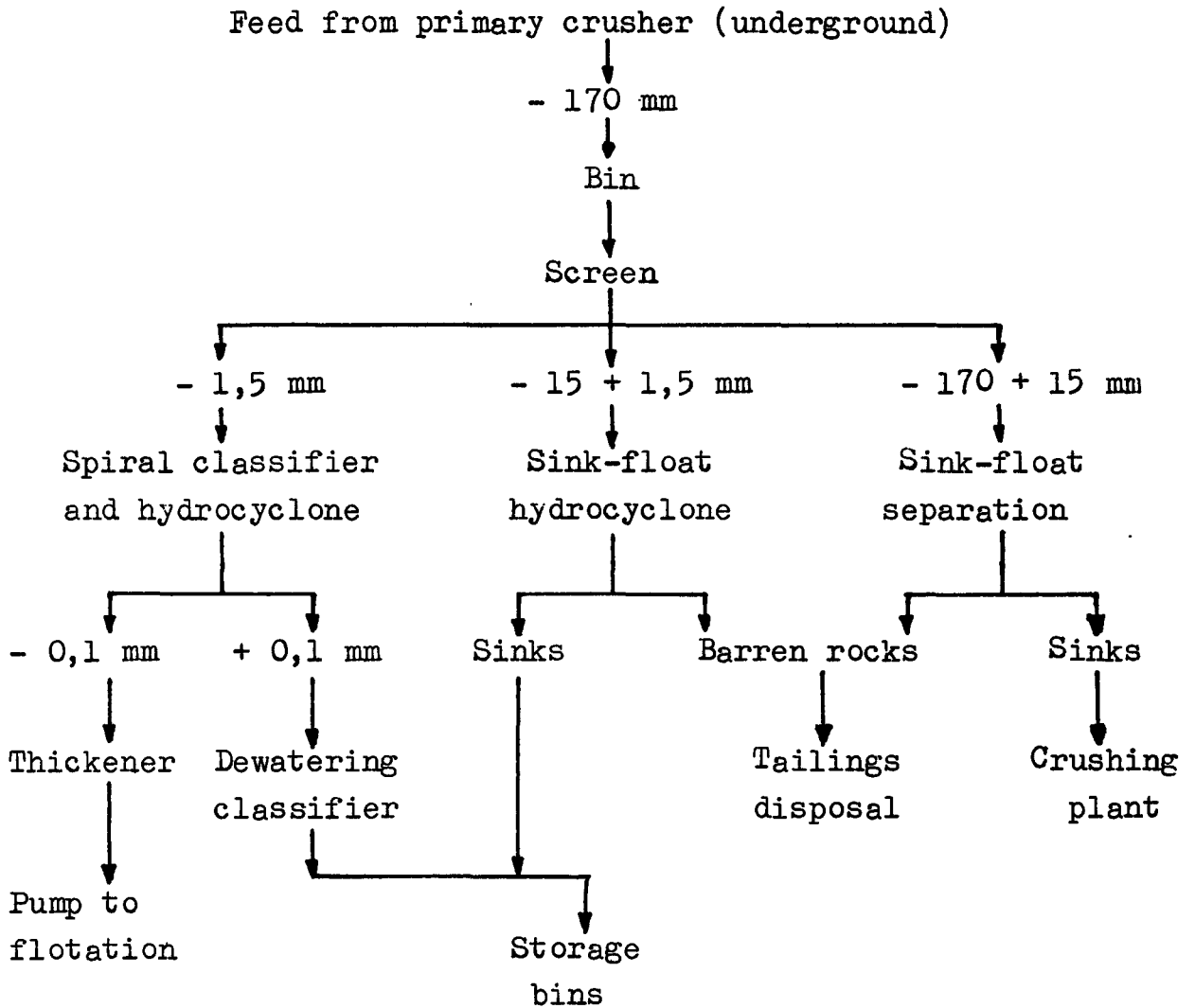Pump to flotation        Storage bins

Figure 12. 7.3 MEGGEN sink-float separation plant

(from Mining Engineering, june 1973, p. 44)

The ore consists of about 80 % sulfides and 20 % gangue (mainly silicates from the host rocks). The principal ore minerals are 67 % pyrite, 14 % sphalerite, and 1.5 % galena. The latter two are finely disseminated in the massive pyrite; a very fine grind combined with special flotation techniques is required to liberate the minerals and produce three concentrates : Pb, Zn, and pyrite.

Due to the mining method, the ore is diluted with coarse barren host rock from the hanging wall and the footwall. In order to reduce operating costs, the ore (950 000 t in 1977, soon to be increased to 1 million tons) is treated in a sink-float separation, so that the flotation plant handles only 780 000 t.

Underground ore is crushed to 170 mm, then transported by skip to the surface plant. It is wet-screened into three fractions : -170 + 15 mm, -15 + 1.5 mm and -1.5 mm (figure 12.7.3).

There are two types of sink-float separators : a static one treating the coarse fraction and two hydrocyclones treating the intermediate fraction. The medium is ferrosilicium for the former unit, and a 2/1 ferrosilicium-magnetite mixture for the latter. In that preconcentration stage, about 18 % of the ore is discarded with less than 0.2 % Pb and Zn, and 3 % pyrite. The crushing and sink-float plants operate 5 days a week.

The -1.5 mm material is classified by a spiral classifier and hydrocyclones to separate the -100 microns slimes, which are thickened and pumped to the flotation plant.

Secondary crushing of the -170 + 15 mm sinks is performed in two n° 4 Symons cones ST and one n° 3 Symons cone SH, operating in closed circuits with screens.

From the 8 000 t bins, ore primary grinding is carried out to 80 % - 80 microns in a rod mill - ball mill circuit. The rod mill discharge at 80 % solids is classified in two steps by means of a spiral classifier and a hydrocyclone; energy consumption is around 3.7 kWh/t. The underflow of both units, which represents about 80 % of the original feed, is conveyed to the ball mill by means of conveyor belts; this rubber-lined mill uses about 9.5 kWh/t and is filled with hard cast cylpebs.

The grinding plant's maximum capacity is 96 tph.

The ball mill discharge at 72 % solids is pumped to two spiral classifiers; overflow is 80 % - 80 microns; underflow is sent back to the ball mill by conveyor belt; these belts permit very precise control of the circulating load.

As the raw ore contains little lead (1.1 %), only zinc and pyrite were recovered by flotation when the mill was started. The assay of the zinc concentrate reached only 48 % Zn at that time, since a gel-like part of the finest pyrite (called melnicovit-pyrite) could not be depressed in zinc flotation circuit, and floated together with the sphalerite even at pH 12.4.

After a lead circuit was added, the melnicovit-pyrite was floated with the galena. The zinc concentrate grade increased accordingly from 48 to 51 % without decrease of the assay. Even after three cleanings, however, lead concentrate assayed only 25 % Pb at a 40 % recovery. It has been observed that - 8 microns galena does not float at all.

The pulp is now pumped to two conditioners; in the first one, milk of lime is used to raise the pH to 12.2; sodium isopropylxanthate promoter is added in the second one. The lead rougher concentrate is cleaned three times, and the cleaner tailings are returned to the grinding circuit.

The 10 % Pb lead rougher concentrate gives finally a 52 % Pb concentrate with a recovery of 50 %.

The tailings from lead flotation, after grinding to 80 % - 45 microns, are pumped to three conditioners in series. As grinding has decreased the pH through sulfate ion formation, lime is added to raise it to 12.1; copper sulfate is the activating reagent for sphalerite, and potassium amylxanthate is the promoter. In the first conditioner, retention time is 15 min., allowing an oxide film to form on the surface of the pyrite particles, acting as a depressant.

As shown on figure 12.7.4, a characteristic feature of the zinc flotation at Meggen is the separate treatment of the middlings.

Crushed ore - 15 mm

Rod and ball milling

$$k_{80} = 85 \ \mu m$$

Lead flotation ⟶ Lead rougher con.⟶Lead final conc.

Ball mill regrinding

$$k_{80} = 45 \ \mu m$$

Zinc flotation ⟶ Zinc rougher conc.⟶Zinc final conc.

⟶ Zinc middlings

Thickener

Regrinding

$$k_{80} = 20 \ \mu m$$

Zinc mid. flot. ⟶ Zn preconc.

$SO_2$ flotation

Thickener
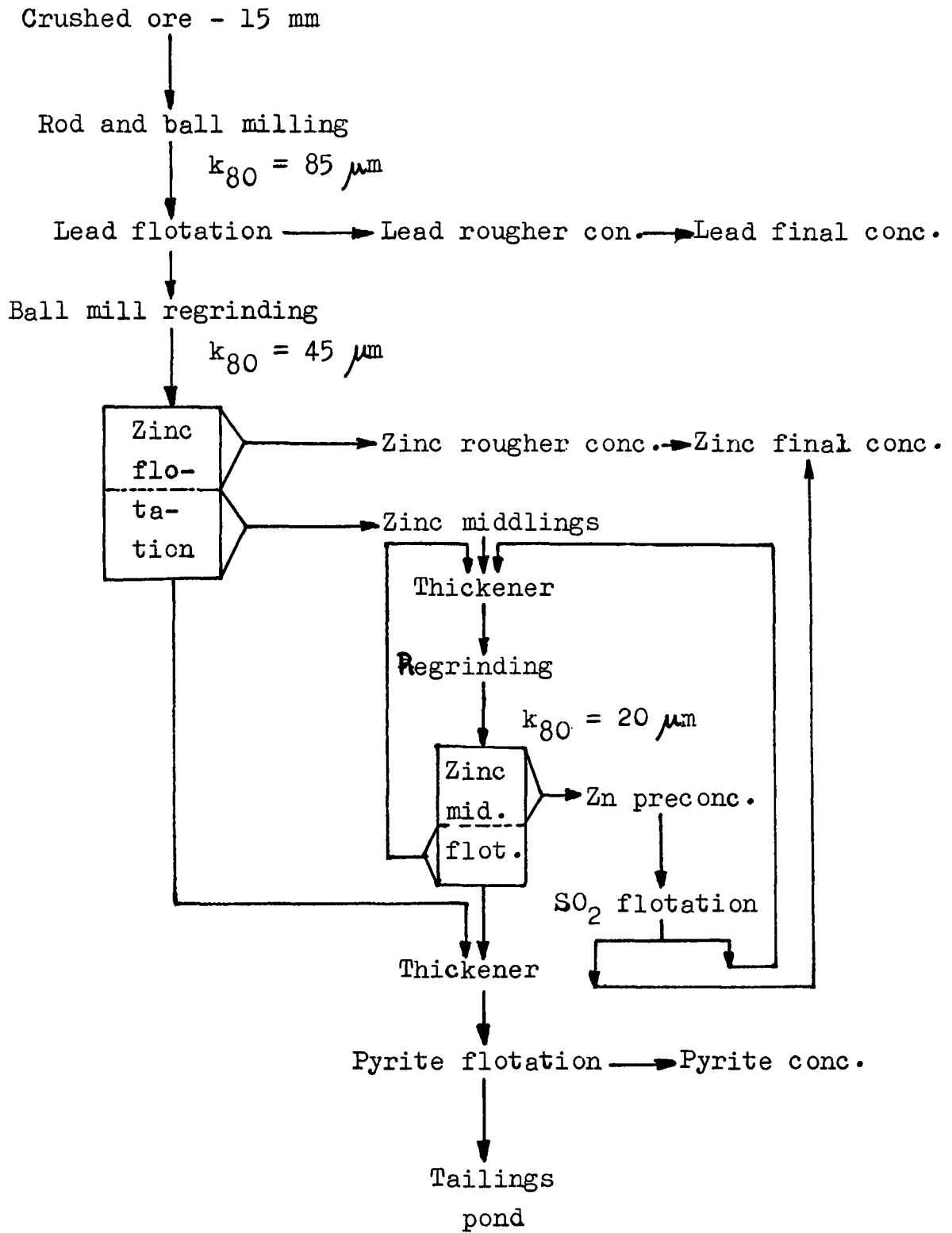
Pyrite flotation ⟶ Pyrite conc.

Tailings pond

Figure 12. 7.4 MEGGEN flotation schematic flowsheet

(from a Sachtleben paper)

The zinc rougher concentrate is cleaned three times, and gives a final con-
centrate; cleaners tailings are sent to a thickener with the zinc scavenger
concentrate. After dewatering to 65 % solids, the pulp is reground to 80 %
-20 microns and floated again to give a zinc middlings concentrate and a
zinc middlings scavenger concentrate that is sent back to the thickener.

The zinc middlings concentrate is steam-heated and treated with $SO_2$ gas
for 4 min. Pyrite is then floated without additions to bring the zinc
content from 38 % in the feed to 52 % in the tailings. Froth is recycled
to the thickener.

Both zinc concentrates are blended to give a 56 % Zn concentrate with a
91 % recovery. The zinc flotation tailings, assaying 0.8 % Zn and 0.5 % Pb,
are thickened, and then conditioned for 25 min. prior to pyrite flotation.
Pyrite is floated at pH 5 (adjusted with sulfuric acid), using sodium
isobutylxanthate as a collector to give a 48 % S rougher concentrate.

After thickening, the concentrates are filtered on vacuum rotary drum
filters, and the zinc concentrate is further dewatered in a rotary dryer
to 6-8 % $H_2O$.

At present, the pyrite concentrate is sent to the tailings pond.


Reagent consumption

|  |  |  | g/t |
|---|---|---|---|
| Lead flotation | : | CaO | 1 500 |
|  |  | Na Isopropylx. | 300 |
|  |  | Flotol B frother | 40 |
| Zinc flotation | : | CaO | 500 |
|  |  | $CuSO_4$ | 1 000 |
|  |  | K Amylx. | 270 |
|  |  | Flotol B | 8 |
| Pyrite flotation | : | $H_2SO_4$ | 8 900 |
|  |  | Na isobutylx. | 450 |
| Tailings neutralization | : | CaO | 900 |

## Typical metallurgical results

|  | Weight, % | % Pb | % Zn | % S |
|---|---|---|---|---|
| **Sink-float plant** | | | | |
| Tailings -170+15 mm | 13.5 | 0.1 | 0.1 | 1.0 |
| Tailings - 15+1.5 mm | 4.5 | 0.1 | 0.2 | 1.5 |
| Total sinks | 71.7 | 1.1 | 8.1 | 40 |
| Slimes | 10.3 | 0.9 | 6.0 | 22 |
| **Flotation plant** | | | | |
| Flotation feed | 82.0 | 1.1 | 8.1 | 38.94 |
| Lead concentrate | 1.0 | 52 | 4.0 | 36 |
| Zinc concentrate | 11.0 | 1.8 | 55.0 | 34 |
| Pyrite concentrate | 50.0 | 0.5 | 0.8 | 48 |
| Recoveries | 62 | 50 | 91 | 78.5 |

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## 12.8 - ITALY

The content of this section is borrowed from unpublished reports by Italminiere (1977).

## 12.8.A - THE ORES

In Italy, the lead-zinc ores which are beneficiated in industrial plants represent a broad spectrum of types, due to the different types of orebodies (see section 11.28) :

1. hydrothermal, vein-type orebodies, with well differentiated sulfide ores and a silicious gangue (Montevecchio, Sarrabus, Silius);

2. column-type orebodies in limestones, following a mobilization of synge-netic deposits, with finely disseminated sulfide ores, partially oxidized (San Giovanni, Raibl, Masua "sulfide ore", Monteponi, Campo Pisano); some orebodies contain supergene enrichment zones with oxidized minerals (Masua "oxide ore", Nebida, Campo Pisano "Calamines");

3. epigenetic orebodies whose cavities in dolomitic rocks are filled; minerals are sulfides, more or less finely interstratified (Salafossa).

The Italian lead-zinc ores sometimes contain rather large amounts of pyrite, and economically significant quantities of fluorite (Silius), baryte (San Giovanni) and, rarely, chalcopyrite (Funtanaraminosa, Rosas).

## 12.8.B - TREATMENT PROCESSES

Beneficiation by heavy-media separation

This separation process is applied in three distinct cases :

1. partially oxidized ores, further treated in 4 or 5 flotation stages; they show a relatively high content of Pb + Zn (6 - 7 %), but they are generally complex, including 2 sulfide minerals and 2 oxide minerals. There is a strong incentive to preconcentrate in order to decrease the flotation costs (Monteponi, Raibl).

2. sulfide ores with a rather hard gangue that can be largely eliminated in the floats (Montevecchio).

3. calamine ores, that cannot give flotation concentrates with a sufficiently high metal content to feed the usual metallurgical plants; this is the reason why a fuming process in Waelz Kilns was introduced. As its treatment costs are relatively moderate compared to other metallurgical processes, it is possible to proceed in two different ways :

   a) production, at high recovery and low costs, of a low-grade concentrate by heavy-media separation (Masua, Monteponi "vecchi discariche");

   b) production, at low recovery and higher cost, of a higher-grade concentrate by flotation.

In cases 1 and 2, it is sufficient to carry out the preconcentration in static separators on the size fraction higher than 5 mm. When preconcentrating the - 5 mm size fraction, there is a risk of losing minerals which are easily recovered by flotation, and the cost of beneficiating the fines in HMS is higher; so it appears to be wise to limit the sulfide feed in the HMS to the 5 mm size.

In the third case, it is more convenient to treat most of the ores in the HMS, in order to decrease the amount of fines going either to the Waelz kiln without enrichment or to the cationic flotation, which is always a costly and not very efficient process. The introduction of a dynamic HMS in conical or cylindrical cyclones to treat the - 5 + 0,5 mm size fraction is questionable; when the liberation size is under 20 mm, the ore can be processed completely in a dynamic separator (Masua "oxide ore"). Recovery varies from 70 to 85 %, and the concentrate grade from 15 to 25 % Zn.

Flotation

In Italy, the choice of the flotation process is greatly influenced by the type of available metallurgical processes. In Sardinia, where an Imperial Smelting furnace exists, the trend is to produce Pb-Zn mixed concentrates; on the Continent, where zinc is produced electrolytically, they mainly produce selective concentrates.

There can be special cases due to ore characteristics (as in Montevecchio) in which a high grade zinc concentrate (-60 % Zn) can be produced : it is selectively floated and sent to Porto Maghera by sea.

In some cases, selective concentrates are floated in Sardinia to facilitate blending of the charge to the ISP, where imported mixed concentrates show highly variable assays.

There are also special cases in which the control of the mining companies by different groups does not favor the best metallurgical yield.

Italian flotation circuits can be classified as follows :

1. Bulk flotation : the most representative case in Masua sulfide ore (Marx orebody, S. Benedetto), where production of ore (2 % Pb, 4 % Zn) has increased from 1 200 t/d to 2 000 t/d.

   After grinding to 80 % - 150 microns, conditionning, roughing and 3 cleanings, concentrates are floated to 55 % (Pb + Zn) with 95 % recovery. The promoter is amylxanthate in a neutral or slightly alkaline pH.

2. Flotation of only one sulfide (Pb or Zn) and possible recovery of the second one. The most complex case is Monteponi's Campo Pisano- Funtana-perda orebody (6,5 % Zn) where there is a very fine sphalerite-pyrite dissemination. Grinding must be very fine (80 % - 40 microns), with two stages of hydrocyclone classification, in order to obtain satisfactory tailings; regrinding is in two stages to produce a concentrate with acceptable content. The first regrinding works in a closed circuit with a bank of auxiliary cells which recycle a low-grade froth and give definitive tailings; it can thus be considered as a classification based more upon the degree of liberation than upon the particle size. The second regrinding is conventional, and is followed by two conventional cleanings. The concentrates assay 53 - 54 % Zn, with a 94 - 95 % recovery; a pyrite concentrate is produced after the zinc flotation.

   As far as galena flotation is concerned, one can mention the Assemini plant (where fluorite and baryte are by-products).

3. Selective flotation : most of the Italian production of Pb - Zn concentrates is obtained by this process. In only one case (Monteponi), galena and sphalerite are so finely disseminated that a regrinding step of the galena concentrate is required.

Sphalerite and pyrite are very often intermingled, and regrinding is
nearly always introduced in the zinc circuit. In order to liberate
the mineral values or the flotation middlings from the gangue, grin-
ding is moderate (from 80 % - 200 microns to 80 % - 90 microns), and
due to the rather low capacity of each individual mill, there is a
tendency to close the grinding circuit with mechanical classifiers.
On the other hand, regrinding circuits are nearly always closed with
hydrocyclones. There generally are 2 or 3 flotation stages, for lead
as well as for zinc. In one case (Salafossa), there is an auxiliary
circuit to refloat the zinc rougher concentrate after regrinding, as
well as one cleaning stage; the tailings of that circuit join the
tailings of the rougher cells. The selectivity of the Pb - Zn separa-
tion and the recoveries vary with the ore feed within the following
limits :

|                   | Assay, % | | Recovery, % |
|-------------------|----------|-------|-------------|
|                   | Pb       | Zn    |             |
| Lead concentrates | 65 -75   | 2- 6  | 85-95       |
| Zinc concentrates | 0.6- 1   | 53-61 | 85-92       |

The lowest zinc assay in galena is probably obtained at Salafossa, the
lowest lead assay in sphalerite being at Montevecchio. At the latter
one can also observe the highest zinc assay in galena. As far as
reagents are concerned, the following can be pointed out : only some
Italian sphalerites can be floated solely with compounds of thio-
phosphoric acids (solid or liquid aerofloats); when these reagents are
used, they must be mixed with xanthates, mainly in the final part of
the roughing. When a lot of pyrite is present with a high content of
sulfate ions in solution, optimum technical and economical results are
obtained by adding sodium cyanide with copper sulfate and floating at
a pH of 7.5 - 8.0 instead of using lime or soda ash at a high pH.
To increase the Pb - Zn selectivity, sodium cyanide and zinc sulfate
are generally used, but they require the installation of special ponds
to recover the water.

4. Flotation of oxide minerals : these are mainly present in Sardinian
   orebodies. When they are mixed with sulfides, extremely complex cir-
   cuits can be developed, with 5 successive flotations (galena, sphale-
   rite, pyrite, cerusite, calamine, as for Monteponi semi-oxidized ores).

Since cerusite is very sensitive to sulfidization (minimal addition of sodium sulfide), it may be convenient with a low pyrite content to float the cerusite before the sphalerite (with the galena, as Raibl) and to decrease to 3 the number of flotation circuits.

The case of oxidized minerals is more typical. The rule is to float the cerusite with the low amount of galena which is always present; this is often followed by a calamine flotation. There are however, exceptions in which the galena is floated first, and the cerusite next, in order to avoid any loss of the silver minerals; recycling is kept at a minimum; concentrates contain 60 % Pb and 2 000 g/t Ag, with a 85 % recovery for lead and, in most cases, for silver as well.

Among the mills treating only lead ores, one can mention those from Arenas (2.5 % Pb), in which there are a series of lead minerals, the most floatable being anglesite, and a noticeable amount of shale and iron oxides requiring a complex classification procedure (gross recovery of 60 - 65 %).

In most cases, cerusite accompanies calamine; as already mentioned, their beneficiation has been initiated in Sardinia, where there were successive developments; in the sixties, it was treated on the island at about 2 000 t/d of calamine ores; it is now treated at about 1 600 t/d, of which 700 t/d are floated.

After the first years of intensive research, to which internationally-known studies and enthusisastic experts such as Angotzl, Quay and Steri contributed, the standard flotation process was set up as follows : classification at $d_{50}$ between 5 and 10 microns, addition of $Na_2S$ and silicate in a short conditioning step (5 min maximum), stage additions of amines (generally stearyl and coco) and some $Na_2S$; pH generally over 10.

In the orebodies of the S. Giovanni and Masua mines, and in the Seddas Modizis orebody, the mineral is smithsonite, and the gangue contains only moderate amounts of iron oxides. The latter are abundant in the Monteponi ores, as are noticeable quantities of hemimorphite; furthermore, zinc minerals are disseminated at submicron sizes in the iron oxides (3 - 4 % Zn) and the host rocks (0.70 % Zn). The results obtained vary according to the ore type and to the metal content, which is always less than 7.5 % Zn :

| | Assay, % | | Recovery, % | |
| --- | --- | --- | --- | --- |
| | Pb | Zn | Flotation | Classification + Flotation |
| Lead concentrates | 50-65 | 3-5 | 35-70[x] | - |
| Calamine concentrates | 0.5-1.5 | 30-39 | 65-85 | 45-65 |

[x]The lower figure concerns calamine ores with rather low Pb content.

## Plants and automatization

Due to the low capacity of the Italian mills, primary crushing is mainly carried out in jaw crushers; cone crushers are generally used for secondary and tertiary crushing. Level sensors in silos and bins are frequently coupled with the feeding devices; treatment is more often based on a constant volume or weight than on the maximum capacity.

To remove tramp iron, magnets are placed after a detector that, using transistors, increases the magnetic field to 10 V.

For static sink-float separation, the drum separator is preferred; for dynamic separators, there is one case in which, instead of hydrocyclones, a static Dynawhirlpool separator is used. In order to control the density of the medium, $\gamma$-ray sensors are being used more and more; for the static separators, only the addition of water is automatically controlled, but for the dynamic ones, the trend is to obtain automatic variations of the recycling of the concentrated medium.

A constant-weight feed is sought.

When the capacity of a grinding section is higher than 1 000 t/d, two stage circuits are installed; however, one-stage grinding is preferred when the grinding size is moderate. First-stage grinding is carried out not only in rod mills, but also in ball mills. The largest mills are in Salafossa (12' x 16') and Raibl; ore is fed at constant volume or constant weight.

In one-stage grinding, the circuits are preferably closed with special classifiers; and, in two-stage grinding, with hydrocyclones; in regrinding circuits, there are always hydrocyclones. In all cases, pulp density is automatically controlled.

In flotation plants where the mills have been modernized, cell-to-cell banks with compressed air blowing have been installed.

The largest cells have a 8 m3 capacity (Assemini), but in the most recent
mills, preferred cells have a 3 m3 or 4 m3 capacity. For obvious use of
pre-existing machinery, there still exist rougher parallel circuits where
a single bank could now be installed.

Reagent additions are controlled with rotameters or temporized valves.
The low capacity of the Italian mills, and their division into multiple
sections for the treatment of various ores, do not call for the introduc-
tion of on-line analyzers with their complex system of sampling. Further-
more, many ores contain oxidized minerals, whose metal should be assayed
in order to check the efficiency of the sulfide circuits; these data
cannot be obtained from presently available X-ray or isotope spectrometers.

In the filtration plants, rotary drum filters prevail, generally with sub-
merged electrodes to actuate the diaphragm pumps.

For large-capacity thickeners not followed by a filtration unit, diaphragm
pumps are preferably replaced by centrifugal pumps.

One can say that all the main sampling is carried out automatically, in
some cases down to the preparation of the final sample drying included
(Masua).

## Problems and future prospects

The building of an ISP furnace in Sardinia has contributed to the
simplification of the treatment of sulfide ores and to the relative de-
crease of the costs.

However, the case of partially or totally oxidized ores, where that sim-
plification could be the most desirable, has still not been solved; in the
present state of the art, there can be no flotation of mixed oxide and
sulfide ores, nor of lead carbonates with carbonates or silicates of zinc.
Another problem in the development of oxidized lead-zinc orebodies, parti-
culary in Sardinia, is the practical impossibility of upgrading the
extremely fine particles. In fact, the present recoveries that can be
achieved by coarse-size flotation, although lower than for sulfide ores,
should be acceptable if it is not necessary to

a) recover particles under 5 microns ($d_{50}$ = 5 microns);

b) introduce a costly cycloning in order to remove the size fraction that
cannot efficiently be floated or that is detrimental to the treatment of
other sizes.

Many people do not encourage the adoption of gravimetric concentration processes that produce less fines,but give much lower concentration ratios. This fact is preventing the possibility of an alternative to the fuming process (Waelz), and is requiring that these pyrometallurgical processes be fed with lower-grade concentrates which render them more expensive. Bulk flotation of the oxide or mixed sulfide-oxide ores, not affected by the extremely fine sizes, would permit the exploitation, with a good profit margin, of millions of tons of ore which now remains untreated, or is treated at a small profit.

Another process that could open new prospects for the oxide ores is the hydrometallurgical treatment of calamine concentrates. This treatment could be thought of as an alternative to the Waelz Kiln for low-grade concentrates, or as an intermediate (replacing calcination) to render flotation concentrates, that are always lower than sulfides in metal content and purity, acceptable for electrolytic plants.

Developments such as those indicated above could take place in Italy, where not only ores to be processed, but also the beneficiation plants that can best develop the various possibilities may be found.


## 12.8.C  - MILL DESCRIPTIONS


### SORGESA (Monteponi and Montevecchio group)


#### a) Montevecchio

The concentrating mill now in operation (Levante) was partially modernized in the beginning of the sixties, but most of the equipment is more than 40 years old.

The mill should be almost completely remodeled, with bigger flotation cells and a crushing-grinding circuit which would eliminate the complexity due to numerous equipment in parallel and the necessity of wet crushing.

Crushing is carried out in two steps, with closed circuit in the second step; screening between 5 and 35 mm for preconcentration by sink-float; crushing of the sink; grinding and flotation.

The mill's capacity is 1 700 t/d, with the following figures :

<div align="center">

crushing   :   100 t/h

sink-float  :    85 t/h

grinding   :    60 t/h.

</div>

Energy consumption : 25 kWh/t of ore.

Present results are :

|  | % Pb | % Zn |
|---|---|---|
| Feed | 1.7 | 3.5 |
| Pb concentrate | 72 | |
| Zn concentrate | | 61 |
| Recovery | 88 | 95 |

Some problems are due to the presence, in some ores, of argileous fines that cause a less selective flotation, and to the presence of small quantities of oxidized lead and zinc, that cannot be economically recovered. It is necessary to neutralize most of the water used.
Operating costs are high because the equipment is obsolete and used at reduced capacity, due to the low level of production in the current restructuring phase.

b) Monteponi

The central plant was originally designed for the simultaneous yet separate treatment of a wide variety of ores. However, what was valid for many years may change in the future as the amounts of the various ores change.

When the pumping station will go down, the orebody will in fact produce a higher extraction of one, or at most two types of ores, for which fewer flotation cells of a bigger size should be used.

The present plant comprises : crushing in two stages, with the second one in closed circuit; preconcentration by sink-float of the -35 + 5 mm fraction; crushing of the sinks; grinding of the sinks and the primary -5 mm fraction; flotation to produce a galena concentrate (48 % S), a cerusite concentrate (50 % Pb) and a calamine concentrate (35 % Zn).

The two lead concentrates are mixed.

The central beneficiation plant of the Monteponi group has a total capacity of about 6 000 t/d and presently operates as follows :

| All the ores | Crushing 300 t/d |
| | ( Sink-float 45 t/h |
| | ( Grinding 15 t/h |
| "Semi-oxidized" ores, | ( PbS flotation |
| from Monteponi and | ( ZnS flotation |
| Seddas M. | ( Pyrite flotation |
| | ( PbCO$_3$ flotation |
| | (Calamine flotation |
| "Zn sulfide" ores, of | ( Grinding 45 t/h |
| the Campo Pisano and | ( ZnS flotation |
| Funtanaperda types | ( Pyrite flotation |
| "Mixed sulfide" ores, of the | ( Grinding 40 t/h |
| primary mineralization type | ( Bulk PbS-ZnS |
| from AMMI SARDA | ( flotation |

Due to the exhaustion of the calamine ores, the sink-float plant, with a capacity of 130 t/h in static and dynamic units, is now closed. In the present design of the plant, the energy consumption is 30 kWh/t.

Present results :

| ORE | Semi-oxidized | | | | Zn sulfide | | Mixed sulfides [2] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Assays,% | | Recoveries,% | | Assay,% | Recovery,% | Assays,% | | Recoveries,% | |
| | Pb | Zn | Pb | Zn | Zn | Zn | Pb | Zn | Pb | Zn |
| Feed | 1.5-2/3-4.5 (1) | | | | 7.11 | | 2.2 | 2.7 | | |
| Pb +Pb$_{ox}$ conc. | 65 | | 65 | | | | | | | |
| ZnS conc. | | 53 | | 90 | | 95 | | | | |
| Bulk conc. | | | | | | | 26.6 | 28.9 | 96.5 | 92 |
| Calamine conc. | | 35 | | 50 | | | | | | |

(1) Depending on the mined orebody fractions, which in turn contribute to the feed mixing.
(2) From the AMMI SARDA orebodies.

The calamine mineralization is clayey, ferruginous and often finely disseminated; zinc appears also in solid solution in the calcarous gangue.

The treatment is broken down into independent sections, each receiving different ore types.

It is necessary to maintain highly complex treatments in operation (up to five flotation sections, and filtration of four different concentrates). All these facts impede automatization and increase the operating and handling costs.

## SILIUS (Gennas Tres Montis and Muscadroscin orebodies)

The concentrating mill is of standard design. The flotation cells and reagent feeding system were recently rebuild.
A further expansion is being planned.
The following results are presently obtained :

| | Assay, % | | | Recovery, % | | |
|---|---|---|---|---|---|---|
| | Pb | $CaF_2$ | $BaSO_4$ | Pb | $CaF_2$ | $BaSO_4$ |
| Feed | 2.5 | 45 | 12 | 100 | 100 | 100 |
| Pb conc. | 65 | | | 92 | | |
| $CaF_2$ conc. | | 97.3-97.4 | | | 97.3 | |
| $BaSO_4$ conc. | | | 95 | | | 65 |

The mineralization is rather coarse; hence, notwithstanding the grinding to only 60 mesh, there are neither locked grains nor selectivity problems. There are some problems during the barite flotation due to the presence of fines, but these are solved by cycloning on microcyclones before the flotation.

## AMMI SARDA

a) The San benedetto orebody produced 35 000 t of ore in 1975, containing 1.8 % $Pb_{tot}$, 3.7 % $Zn_{tot}$, 2.74 % $Zn_{ox}$ and 275 g Ag/t $Pb_{tot}$.

The gangue is dolomitic limestone. This ore is treated in the sulfide section of the plant described below (Masua).

b) "Miniera de Masua" (or Ponente section) comprises the orebodies of Acquaresi, Montecani, Masua (Marx) and Nebida. In 1975 212 000 t of ore were produced containing 1.64 % $Pb_{tot}$, 4.95 % $Zn_{tot}$, 3.74 % $Zn_{ox}$ and 236 g Ag/t $Pb_{tot}$.

The gangue is limestone for the sulfides and yellow dolomite for the oxides. It is hoped that 800 000 t of ore will be extracted in 1980. The Masua concentrating mill has a crushing section operating in 3 stages, the third of which is in closed circuit. After crushing, treatment is different, depending on the ore type :

- oxidized ore is enriched in a Dynawhirlpool heavy media process for the - 12 + 0.5 mm size fraction, with production of a sink assaying 18 % Zn that is fumed in a Waelz furnace to give oxides assaying 63 % Zn; the -0.5mm size fraction is ground and floated to produce a calamine concentrate with 35 % Zn (not operating at the present time);

- sulfide ore is ground and floated to give a bulk Pb-Zn concentrate (55 % Pb + Zn).

The plants, some parts of which are still in the building stage, form a complex unit of 4 500 t/d capacity, distributed as follows :

- all the ores : crushing : 250 t/h

    Dynawhirlpool HMS : 100 t/h

        (presently, the - 0.5 mm size fraction is filtered and some is sent directly to the Waelz furnace)

    Waelz furnaces : 2 x 400 t/d (in Porto Vesme)

- oxide ores : grinding : 25 t/h

    flotation: lead, then calamine

- sulfide ores : grinding : 85 t/h

    flotation: bulk Pb-Zn concentrate

- energy consumption : 26 kWh/t

The sulfide concentrating plant did not undergo the same rapid techno-
logical development as the mine, mostly because of the opportunity of
using part of the Monteponi (Sorgersa Company) facilities. The large
rise in freight costs as well as the plans of Sogersa itself led to
the use of the flotation facilities sited in Masua, and already enlarged
to 1 500 t/d, and of one section of the HMS Dynawhirlpool preconcentra-
ting plant due for 2 000 t/d of sulfide ores.

On the other hand, it was necessary to change the treatment of the oxide
ores that had to be directly fumed in the Waelz furnaces at Porto Vesme.
The high increase of the freight and carbon costs has made it uneconomi-
cal to feed the ores directly into the Waelz furnaces, and a DWL
preconcentrating plant was built in Masua in order to increase the
products' metal content and decrease the amount transported. This treat-
ment results in a relatively low metal recovery (65 %), but it markedly
decreases the cost of the metal unit produced in the metallurgical plant.
The products of the concentrating mill are :

|  |  | Pb, % | Zn, % |
|---|---|---|---|
| Sulfides : | ore feed | 2 | 3 |
|  | bulk conc. | 26 | 32 |
|  | recovery | 93-94 % | |
| Oxides : | ore feed | 1.0 | 6.3 |
|  | DWL preconc. | 2.0 | 16.0 |
|  | fines | 2.0 | 8.0 |
|  | recovery | 65 % | |

These results are such that it appears necessary to undertake a research
program in order to improve the economic management. This program will
be initiated along the following lines :

a) evaluation of the orebodies by the most modern geostatistical means;

b) optimization of the mine-mill-smelter cycle, to minimize the total
   production costs;

c) technological up-dating of the mine.

CUPRIFERA SARDA

The Funtana Raminosa orebody produces 47 000 t/y of ore containing 1.0 % Cu, 1.4 % Pb and 3.0 % Zn. It is planned to develop the mine to 120 000 t/y of ore containing 1 % Cu, 1 % Pb and 2.5 Zn.

Presently, the ore is fed at 200-250 mm and crushed in two stages to 14 mm. The ore is hard and the capacity is only 40 t/d.

The plans for the new crushing plant include a new jaw crusher (90 t/h) for the comminution of a coarser feed coming from new levels in the mine. The present primary unit will be the future secondary unit, working under much better conditions.

The following comminution stage is operated in two old ball mills grinding to 150-200 mesh; in fact, they are now the plant's bottle-neck.

The plans call for the installation of a new 500 t/d ball mill, followed by bigger flotation cells, and a new filtration plant.

The metallurgical results are :

|  | Zn, % | Pb, % | Cu, % |
|---|---|---|---|
| **Present practice** | | | |
| Ore feed | 2.0 | 0.7 | 0.8 |
| Zn concentrate | 46.5 | | |
| Pb concentrate | | 46.8 | |
| Cu concentrate | | | 29.0 |
| Recovery | 78 | 82 | 80 |
| **Future practice** | | | |
| Ore feed | 2.5 | 1.0 | 1.0 |
| Zn concentrate | 47.0 | | |
| Pb concentrate | | 50.0 | |
| Cu concentrate | | | 29.0 |
| Recovery | 78 | 82 | 80 |

Mathematical models will be produced for the entire metallurgical treatment, and the production cycle will be optimized by an integrated program of operational research.

## PIOMBO ZINCIFERA SARDA

a) "Miniere de Arenas" : this orebody produced 150 000t of ore in 1974, with 5 % $Pb_{tot}$ in ore from the underground works, 2 % $Pb_{ox}$ in the form of cerusite in the open pit ore and 300 g Ag/t $Pb_{tot}$. The gangue is always very complex, containing quartz, limestone, clays and a number of minerals such as iron oxides, lead jarosite, pyrite, grey copper, arsenopyrite, linarite and dufrenite. It also contains other minerals and soluble salts which result in difficult lead recovery. Crushing is in 3 stages, in open circuit, with a capacity of 100 t/h. There is a desliming at -10 microns and a wet screening to give a product with 80 % -12 mm.

Grinding is made in ball mills with a capacity of 28 t/h. Flotation in 3 parallel banks gives a PbS + $PbCO_3$ concentrate assaying 55-60 % $Pb_{tot}$, and an average recovery of 60-65 %. However, before the introduction of Agitair cells in the tail sections of the flotation circuits, recovery attained only 50 %, due to the increase in the non floatable part of the lead (pyromorphite).

The following points of the flowsheet can be stressed :

1) the recovery cycle of the deslimed fines (-10 microns) is complex; the overall loss amounts to 4.5 %. Generally the fines have a lead content 1-2 % higher than the flotation feed, but the recovery of the contained metal has not as yet been possible;

2) steel consumption in the mills is high; the linings must be replaced every 6-10 months;

3) conditioning must be realized in a set of 3 conditioners in series, providing a 15-minute contact time;

4) there are 3 flotation circuits in parallel, especially designed to avoid the dilution of the pulp in the final cells and the excessive recycling of the cerusite, which are harmful for recovery.

The reagent consumption in 1974 was in g/t :

| Sodium sulfide | 1562 | Aerofloat | 14 |
|---|---|---|---|
| Sodium silicate | 1678 | Amylxanthate | 37 |
| Dowfroth 250 | 23 | Ethylxanthate | 7 |
| Aerofloat 25 | 41 | | |

b)"Gruppo San Giovanni" : it produced, in 1974, 225 000 t of ore, with the following assays, in % : 1.50 $Pb_{tot}$, 2.85 $Zn_s$, 4.00 $Zn_{ox}$ and 500 g Ag/t $Pb_{tot}$. The gangue is generally composed of limestone, dolomite, quartz, and shale.

Mining is carried out in four different operations :

- "contact" orebody, where mineralization consists of irregular masses or small veins of galena, with a little sphalerite in dolomite; these are often accompanied by pyrite, grey copper, chalcopyrite and renierite;

- "blendous" orebody, where mineralization is almost exclusively of light-coloured sphalerite, found in limestone in grains of 5 to 50 microns;

- "silver-rich" orebody, where galena with a high silver content (from 2 kg/t to 5-6 kg/t of 70 % Pb concentrate) is found; silver is mainly present in tetrahaedrite;

- "oxidized" orebody, in the higher part of the sulfide masses; mineralization is mainly of smithsonite and galena in cavernous nodules.

There are three crushing stages in open circuit, with a reduction ratio of 50; the capacity varies from 8C to 100 t/h, and the crushed product is 80 % - 12 mm; it is sent for treatment in four different sections :

- The first section treats the oxidized ores at the rate of 14 t/h, and the ball mill-classifier circuit gives a product sized at 80 % - 100 microns; after 2 min. conditioning with sodium sulfide and silicate, lead is floated very quickly with the addition of sodium sulfide and silicate (pH 8-8.5); the lead tailings are deslimed by hydrocycloning in two steps, 20 and 7 microns respectively; 12-15 % of the feed is discarded as slimes; after conditioning with sodium carbonate and silicate (pH 11-11.5), calamine is floated with stearylamine and sodium sulfide fed in starvation quantities.

- The second section treats the silver-rich galena at the rate of 10 t/h; after grinding to 80 % - 65 mesh, galena is recovered in Denver cells and cerusite in Agitair cells, with only one cleaning stage; after desliming of the lead tailings in hydrocyclones, barite is floated with cetylsulfate at a pH of 10-10.5 controlled by the addition of caustic soda.

- The third section treats "contact" ore, which contains both galena
  and sphalerite (the ore is also named "mixed sulfides"), at the rate
  of 13 t/h; after grinding to 90 % - 48 mesh (to avoid the production
  of galena slimes), the galena is floated with zinc sulfate acting
  only as zinc depressant, in a neutral pulp; the sphalerite is then
  floated : it is of characteristic reddish color and contains germa-
  nium.

- The fourth section treats the blendous ore at 28 t/h; grinding to 80 % -
  65 mesh is carried out in two parallel circuits; galena is first
  floated with zinc depression by sodium cyanide and zinc sulfate; spha-
  lerite is activated with copper sulfate, and scavenger concentrates
  (low grade middlings) are reground before recycling.

Three types of concentrates are produced : galena with 70 % Pb, sphale-
rite with 55 % Zn and calamine with 39 % Zn.

There is a preconcentrating plant of 20 t/h in a heavy-media process;
it is presently idle because of a lack of compact ore that can be
treated without too much loss of metal (the ore is now mainly cavernous
dolomite).

Energy consumption is 23 kWh/t.

c) "Gruppo Buggerru-Su Zurfuru" : these orebodies produced, in 1974,
   115 000 t of ores averaging 1.10 % $Pb_{tot}$, 3.00 % $Zn_s$, 5.00 $Zn_{ox}$ and
   500 g Ag/t $Pb_{tot}$. The gangue is generally composed of limestone,
   dolomite, quartz, and shale.

   The Buggerru mill comprises two independent sections treating, respecti-
   vely, the oxidized ores (PbS - $PbCO_3$ - calamine) and the sulfide ores
   (PbS - $PbCO_3$ - ZnS) :

- The first section has two crushing stages treating 70 t/h in open cir-
  cuit; the crushed product is 80 % - 18 mm; grinding is carried out in
  two stages, with a rod-mill in open circuit feeding a rake classifier,
  the underflow being ground in 2 biconical ball mills; the overflow of
  the classifier (12 t/h) is 80 % -65 mesh and goes to the PbS + $PbCO_3$
  flotation machine (roughing + 2 cleanings); lead tailings are deslimed
  and floated for calamine in a 22 - cell bank.

- The second section has two crushing stages treating 70 t/h in open
  circuit; the crushed product is 80 % - 18 mm  between the two crushing
  stages, the ore is deslimed to - 2 mm in a log-washer and a washing
  screen, slimes go directly to the ball mill; grinding is made in a
  single ball-mill of 10 t/h, in closed circuit with a rake classifier;
  the classifier overflow is first floated for PbS (two cleaning stages)
  then, after conditioning, for $PbCO_3$ when present; lead tailings are
  conditioned and floated for ZnS in two parallel banks, with two clea-
  ning stages and a scavenging stage, the concentrate being reground
  before recycling.

The concentrates have the following average assays :

Pb concentrates  :  55-60 % Pb

ZnS concentrates :  50-52 % Zn

Calamine

concentrates :  38-40 % Zn.

The Buggerru plant is badly situated and, after the discovery of abun-
dant mixed sulfide mineralization in the nearby Fluminese area, the
Company is planning to build a new 2 000 t/d flotation plant. It will be
called Fluminese and situated inland, equidistant from the two mining
areas.

d) "Sos Enattos" : this orebody is still in the research and development
   phase; it is similar to Montevecchio and present content is around
   6 - 7 % Zn, with a gangue of ankerite and quartz. The mill has capacity
   of 400 t/d, but it operates only per campaign to treat the development
   ore. Crushing is carried out in two stages, the second one closed with
   a screen; grinding is made in a single stage of ball milling in a cir-
   cuit closed by a spiral classifier; selective flotation gives galena
   and sphalerite concentrates, respectively.
   Energy consumption amounts to 25 kWh/t.

SOLMINE

The Fenice Capanne orebody, in Toscany, produced, in 1976, about
160 000 t of run-of-mine ore, composed of sulfides of Zn, Pb, Cu and Fe in
a siliceous gangue. The present contents average 5.20 % Zn, 1.11 % Pb,
0.29 % Cu and 7.30 % Fe.

In 1976, 9 750 t of sphalerite concentrate, 1 625 t of galena concentrate, 825 t of mixed sulfides with 10 % Cu, and 3 900 t of pyrite were produced by selective flotation in the 500 t/d mill.

AMMI S.p.a.

a) The Raibl orebody gives wo types of ores, a sulfide ore containing galena, sphalerite, and pyrite in a dolomitic gangue, or an oxidized ore containing smithsonite and hydrozincite.

The sulfide mill has a capacity of 2 000 t/d of ore assaying 4.40 % $Zn_s$ and 0.55 % Pb. Crushing is in two stages, and the size fraction - 30 + 3 mm is preconcentrated in a HSM separator; the sink fraction is crushed ($3^{rd}$ stage) and ground in one stage after mixing with the - 3 mm primary fraction. Selective flotation gives a 71 % Pb concentrate with a recovery of 46 % and a 54 % Zn concentrate with a recovery of 85.5 %.

The oxide mill has a capacity of 400 t/d of ore assaying 6 % $Zn_{ox}$, 2 % $Zn_s$ and 1.20 % Pb. After a two-stage crushing, one-stage grinding, flotation of galena-cerusite, flotation of sphalerite, desliming in hydrocyclones, and flotation of calamine, the following results are obtained :

calamine concentrate     :  37 % Zn, recovery 66 %
sphalerite concentrate :  54 % Zn, recovery 65 %
cerusite concentrate    :  49 % Pb, recovery 51 %

The sulfide mill now in operation was recently revamped as far as grinding and second stage crushing are concerned; however, the HMS separator is 30 years old, and part of the machinery should be replaced.

In order to hold down the costs and to increase the recoveries, it would be advisable to change the flotation cells, as they are small and subdivided into 6 zinc circuits and 3 lead circuits. It would be better to install larger ones, so as to have only one zinc circuit and one lead circuit.

The oxide mill was built recently (1971). The crushing section has a capacity on the order of 500 t/8 h, but the grinding and flotation sections' capacity is limited to 370 t/d. It is likely that hydrocyclone installations will be bettered and flotation circuits will be reinforced.

b) The Gorno orebody comprises mainly Pb-Zn sulfides with very little
pyrite. In the upper part of the orebody there is a zone containing a
complete range of zinc carbonates and silicates. The gangue is
limestone.

The annual ore production is about 140 000 t, with 2.5 % $Zn_s$, 2.10 %
$Zn_{ox}$, and 0.90 % Pb. The mill has a capacity of 700 t/d, but most of
the machinery dates back to 1936. Crushing is carried out in 3 stages
and there is only one grinding stage. Three flotation sections produce
a 44 % Pb concentrate with an 80 % recovery, a sphalerite concentrate
with 54 % Zn and an 85 % recovery and a calamine concentrate with
34 % Zn and a 70 % recovery. One can frequently observe the presence
of carboniferous shales from some sulfide zones; they reduce the acti-
vity of the reagents and result in a decrease of the assay of the lead
concentrate.

c) The Monteneve orebody contains mixed Pb-Zn sulfides, with pyrite and
cadmium in a gangue composed of metamorphic siliceous shales.
Cadmium has a content of about 3.5 kg/t of Zn concentrate.
Production of run-of-mine ore is 40 000 t/y, and the mill can treat
290 t/d of ore assaying 4.1 % Zn and 1.6 % Pb. Two-stage crushing is
followed by grinding in two ball-mills in parallel. Lead concentrate
is floated in a bank of 9 cells, and zinc concentrate in a bank of
14 cells. Metallurgical results are :

Lead concentrate : 62 % Pb, recovery 82 %
Zinc concentrate : 49 % Zn, recovery 82 %.

SOCIETA DI PERTUSOLA

The Salafossa orebody contains about 10 million tons of ore with 4.5 % Zn
and 1 % Pb. Ore extraction amounts to 2 500 t/d during 230 d/y, i.e.
about 600 000 t/y. The principal mineral in the gangue is dolomite, and a
secondary white dolomite is present.
Run-of-mine ore is first crushed underground to - 150 mm, then brought on
a belt-conveyor belt to the 3 000 t/d mill. It is then crushed in two
stages to - 12 mm, and ground in a primary 12' x 16' and two secondary
9' x 11' ball mills, in closed circuit with spiral classifiers; classifier
overflow contains 40 % solids with 80 % - 170 mesh. Lead is floated in 8
cells of 7 cubic meters, and cleaned twice.

Zinc is floated in 2 rougher circuits with 1.7 m3 cells, and in 4 circuits for cleaning and recleaning; there is a regrinding mill in the scavenging section. The concentrating mill is equipped with a high level of control and automatization that permit very high recoveries and manpower productivity.

The following results are obtained :

|  | Weight | | Pb | | | Zn | |
|---|---|---|---|---|---|---|---|
|  | % | % | weight | Rec, % | % | weight | Rec, % |
| Feed | 100 | 0.7 | 0.700 | 100 | 4.0 | 4.000 | 100 |
| Pb conc. | 0.821 | 75.0 | 0.616 | 88 | 2.0 | 0.016 | 0.40 |
| Zn conc. | 6.655 | 0.70 | 0.047 | 6.71 | 55.0 | 3.660 | 91.5 |
| Tails | 92.524 | 0.04 | 0.037 | 5.29 | 0.35 | 0.324 | 8.10 |

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## 12.9 - GENERAL CONCLUSIONS FOR MINERAL PROCESSING

## 12.9.A - COMMON SULFIDE ORES

Common lead-zinc ores are floated by the direct method of successive differential flotation, as typified by the general flowsheet in fig. 12.21.1.

Some differences appear according to whether or not the ore contains a noticeable amount of pyrite. For example, the Luederich mill obtains excellent results at neutral or slightly acid pH despite its age, because pyrite is practically nil in the run-of-mine ore.

According to the particular environmental conditions in each country, the use of the sodium cyanide as a sphalerite depressant is either favored or not.
Although there are various galena collectors, it may be noted that sphalerite is floated mainly with amylxanthate after current reactivation with copper sulfate. It seems that French mills favor flotation in rather long circuits with a great number of cells; it may be interesting to check how this system compares with the new circuits at Salafossa or Bad Grund which use a few very large cells.

Two innovations merit a detailed examination :

- use of semi-autogeneous mill at St Salvy, followed by a classical ball mill-hydrocyclone circuit;

- use of a Maxwell giant flotation cell in first-stage roughing at Greenex.

When the minerals are not too finely disseminated in the gangue or in another sulfide such as pyrite, well-crystallized clean galena and sphalerite ores can generally be treated in a preconcentrating stage in order to eliminate part of the calcareous or siliceous gangue. It appears that heavy-media separation is only used for that stage and there is no example in the E.E.C. countries of gravimetric concentration by another process.

The so-called "static sink-float separation" operates only on particle sizes not under about 5 mm, and ores sufficiently liberated at coarser sizes are not common.

It is possible to go finer with the dynamic system as applied in the Dynawhirlpool cyclone; it may be worthwhile to intensify the studies on such processes in order to determine conditions for working at ever decreasing sizes.

It can be noted here that slightly tarnished or oxidized ores, mainly galena, are simply floated like sulfide ores by surface sulfidization with small amounts of $Na_2S$ or NaHS.

## 12.9.B - PYRITIC SULFIDE ORES

Some large orebodies in Europe contain pyritic ores with finely disseminated sulfides (Meggen, Rammelsberg); the selective flotation of galena and sphalerite offers a challenge to the metallurgical engineer : beneficiation requires a very fine grind to particle sizes for which flotation is difficult. A balance has to be found between selectivity and recovery of the minerals.

There now seem to be various fields of research needing exploration in order to make the best use of this type of ore, which could represent a significant part of the lead and zinc reserves in Europe.

## 12.9.C - OXIDIZED ORES

Oxidized ores are mainly treated in Tynagh (Ireland) and Sardinia (Italy). Although cerusite, and in one plant pyromorphite, are floated without much problem, this is not true for the zinc oxidized minerals. Generally called "calamines", these ores have a variable composition, of mainly smithsonite, willemite, and hemimorphite. It is not fully known yet why some calamines can float with a relatively good recovery and why others cannot. Current practice requires the use of intense sulfidization and collection by an amine after the thorough desliming of the pulp. Five to 20 % of the oxidized zinc in the hydrocyclone product (cut between 7 and 20 microns) is discarded. In any case, colloïdal solid particles, clays, etc ... are very noxious, yet it remains to be demonstrated that a finer cut is not practicable.

When flotation of the entire ore is not possible, and the metal contents are too low for direct feeding into a metallurgical beneficiation

process, some Sardinian mills now carry out a preconcentration by dynamic sink-float separation (Masua).

However, it can be said that the present method of treating these ores is still questionable and that many more improvements are needed before balanced use can be made of the oxidized zinc ores.

PART 1.3.

METALLURGY

CHAPTER 13.1    METALLURGICAL PROCESSES

13.11  -  LEAD PYROMETALLURGY

13.11.A.  INTRODUCTION

1) Lead is mainly produced from gravimetric or flotation concentrates, where the principal mineral is galena, PbS (86,6 % Pb). Beside gangue minerals, the concentrates also contain sulfides of zinc, iron and some-times copper; common impurities are arsenic, tin, antimony, bismuth, silver, etc. Oxidized minerals can also be present ($PbCO_3$, $PbSO_4$), but they rarely constitute the bulk of the concentrates.

Lead can also be produced from by-products coming from other metallurgical plants, but at the present time, the only source of this type is residues of zinc metallurgy.

2) Lead is a noble metal, with a low affinity for oxygen and a small negative electrode potential (-0.13 V). Its specific weight is high (11.34 $g/cm^3$); its melting point is very low (327.4°C) but boiling point is rather high (1750°C).

3) Lead is insoluble in sulfuric acid, which is the principal solvent used in hydrometallurgical plants (particularly for electrowin-ning). There can be no lead production through this process.

4) PbS can be reduced directly by iron, according to the equation

$$PbS + Fe = Pb + FeS$$

but FeS forms a matte that can dissolve a significant amount of PbS; this procedure is sometimes used in conjunction with other processes.

5) PbS is able to react with its oxidation products PbO and $PbSO_4$ (the basic sulfates $xPbO.PbSO_4$ are neglected for simplification) to give directly the metal and $SO_2$ gas; for example :

$$PbS + PbSO_4 = 2Pb + 2SO_2$$

On a continuous basis, the process is autogenous and very simple mecha-
nically; In fact, the reaction is very difficult to balance stoichiometri-
cally and thermally : gangue minerals and excess lead components form
a by-product called "grey slag", which must treated by other means.
The charge must contain a small amount of carbon to make up for thermal
losses. The gases are too low in $SO_2$ for economic recovery and carry a
significant amount of dusts that must be recovered and recycled. The
porosity of the charge is imperative and low melting point compounds
must be avoided (maximum Cu content : I %).

This "roast-reaction" process is operated in some countries where
pure lead concentrates (more than 70 % Pb) are available, and various
methods are used to avoid some of the drawbacks cited above (Bleiberg
process in Austria, Boliden process in Sweden, Lurgi process in
Yugoslavia).

6) PbS can be easily transformed into oxide PbO by roasting, and
PbO can be easily reduced by carbon to Pb metal. This "roast-reduction"
process is the primary process used in Europe to extract lead from its
concentrates.

13.11.B. ROAST-REDUCTION PROCESS

Lead oxide is easily reduced to metal by carbon with liberation
of $CO_2$. On the other hand, PbS and $PbSO_4$, the latter being immediately
reduced to PbS, cannot be reduced to the metal in this way. They can be
partially cemented by iron or oxidized by oxygen in furnace gases when
conditions permit. Lead oxide is a basic compound that has a good affinity
for $SiO_2$; when lead silicate is formed, it dissolves in the slag and
can be reduced only at high temperature when a strong base such as CaO,
is present. Therefore, roasting :

- must be complete and oxidizing ("dead-roasting");
- must avoid lead silicate formation;
- must be agglomerating, as the reduction is done in a blast furnace, as
  is described below.

Since reduction Is very easy, It Is the slagging of the gangue materials which governs the temperature. The other sulfides can form mattes that dissolve lead metal; they are oxidized by dead roasting. Copper oxide Is reduced before lead oxide and copper Is soluble In lead metal. It Is eliminated during the refining process. However, when the copper content of the charge Is high (more than 4-6 %), It Is more suitable to form a copper matte with the charge's sulfur often added as a low-copper matte. Arsenic likewise dissolves In the lead and Is eliminated In the refining operation; It Is best to have It volatilized during roasting. When the furnace atmosphere Is highly reducing, as when a matte Is formed, arsenic can combine with Cu, Fe, NI and Co to form a "speiss", that Is soluble In lead at high temperatures. This speiss Is drossed during the cooling of the tapped lead bullion. Gangue materials are slagged In the furnace. The slag must be melted at moderate temperature; It must also be rather basic In order to avoid lead silicate dissolution, and sufficiently light when the matte Is formed.

## 13.11.C. ROASTING PRACTICE

To be most effectively treated In a blast furnace, the oxidized product should be In the form of a hard but porous sinter, hence the almost exclusive use of the Dwight-Lloyd sintering machine.

As shown In figure 13.11.1, It Is essentially an endless system of pallets with grate bottoms driven by a rear sprocket. The pallets hold the charge, Initially fired by an Ignition box. Air Is sucked through the charge Into a suction box, by downdraft or updraft, to maintain the generation of heat. The high temperature Is locally sufficient to cause Incipient fusion of the charge and to agglomerate the particles. To reach Incipient fusion, It Is necessary to control the charge's sulfide sulfur content, by recycling bad sinter (up to 50 %) and by-products,as well as by the addition of fluxes and, sometimes, part of the furnace slag. As the decomposition of lead sulfate Is always Incomplete, the sinter's sulfur content Is about 1-1,5 %. Sometimes there Is a pre-roasting stage In a multiple-hearth furnace as when the S content of the charge Is higher than 20 %; another procedure consists of a double sintering being used to obtain better mechanical characteristics, the second pass done with the addition of 1-2 % of coal or coke fines.
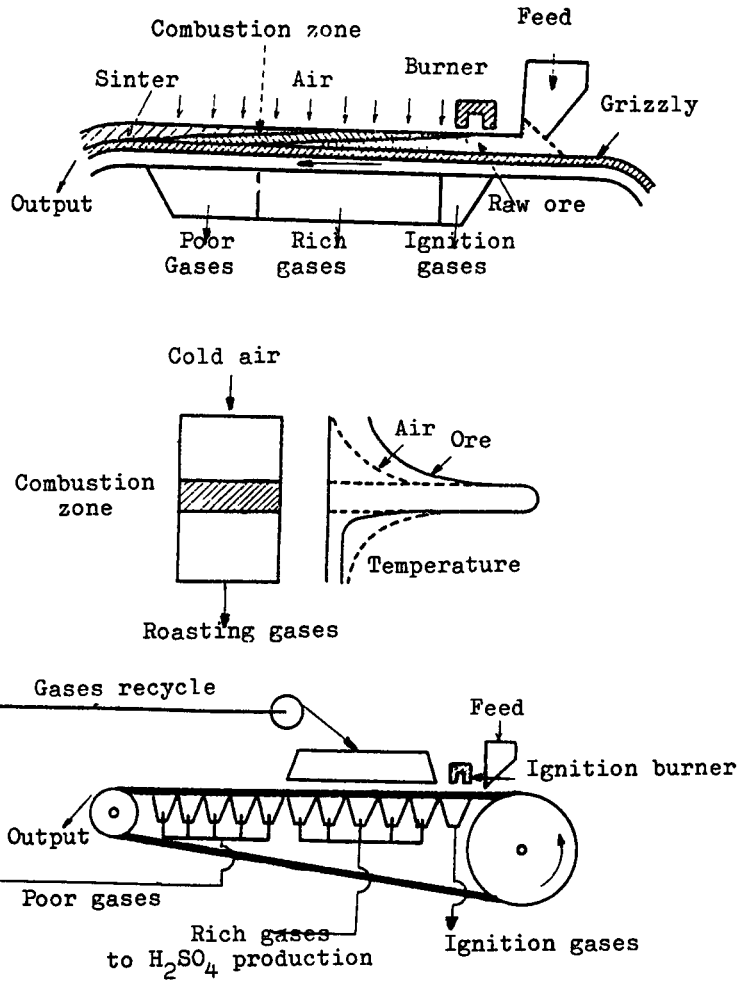
Figure 13.11.1 Roasting on a DWIGHT-LLOYD sintering machine
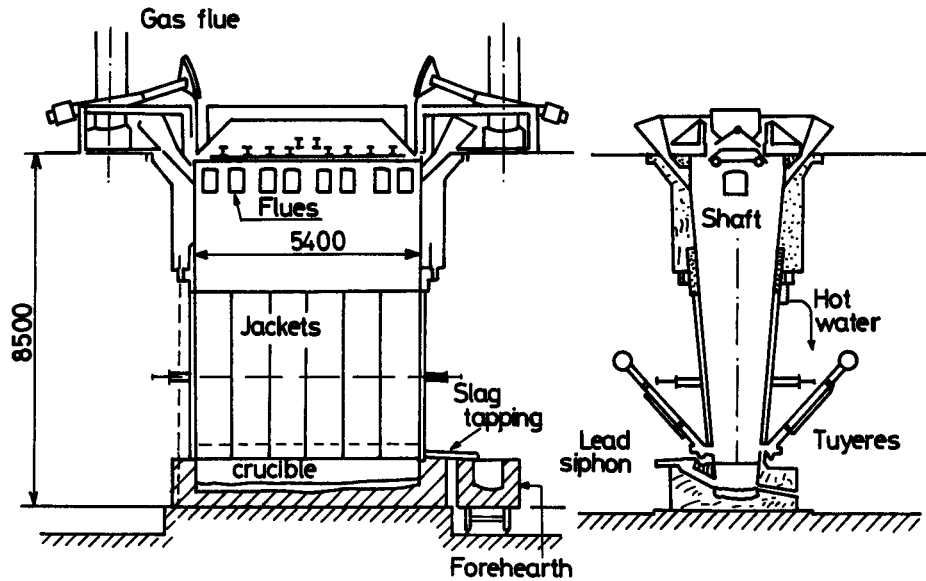(from C. EK, Cours de Métallurgie des Métaux non ferreux)



Fig 13.11.2. Water jacket-blast furnace
(from a B.R.G.M. report for this dossier)

The oxide (or sulfate) - sulfide reaction always tends to form a certain amount of metallic lead that partially clogs the slots of the grates; plants treating rich lead concentrates now prefer to use updraft D.L. machines. The capacity of a D.L. machine for Pb roasting can reach 200000 t/y of sinter.

## 13.11.D. REDUCTION PRACTICE

In many countries, energy costs preclude the use of electric furnaces.

The reverberatory furnace Is only used for smelting very special charges (lead-vanadium or- molybdenum compounds), for the following reasons :

- lead, very fluid at slagging temperature, seeps easily into the hearth;
- basic slags are highly corrosive for furnace refractories;
- outcoming gases carry away too much lead dust.

The blast furnace Is normally used with waterjackets, as shown In figure 13.11.2. Lead charge and coke, with possible fluxes and additions, are put at the top of the vertical shaft, and tuyeres deliver an air blast to burn the coke. The descending charge Is progressively reduced and transformed Into two main liquid phases (lead bullion and slag) that are collected In a crucible at the furnace base, from which they are removed periodically. Refractories are replaced by water-jackets on which a layer of cold slag solidifies. Dust, which has to filter through the charge, exists In small amounts in the gases. When the charge Is rich In lead, the metal (which Is easily reduced and melted) occupies most of the cross-section of the furnace shaft; gas flow Is thus hindered. Lead content of the charge Is, therefore, generally limited to 50 % by recycling part of the easily-melting slag. The slag still contains 1,5-4 % Pb, 22-26 % $SiO_2$, 14-17 % CaO, and 10-22 % Zn; It Is often treated for zinc oxide production In a "slag-fuming" operation.

Flue dust is recycled to the roaster charge, sometimes after cadmium removal by leaching. The lead bullion obtained is rather impure and must be refined.Iron scraps are often added to the charge for lead sulfide reduction. In general, the furnace atmosphere is slightly reducing; it is sometimes slightly oxydizing at the top, except when a matte must be produced. The matte may contain up to 40 % Cu and 8-20 % Pb. When speiss is formed, it is skimmed from the bullion surface while cooling in ladles.

In order to save coke, many plants now use a process of oxygen enrichment of the blast. Furnace capacity varies from 90 to 500 t/d of lead bullion.

## 13.11.E. REFINING OF LEAD BULLION

The refining of lead bullion requires a number of steps (6 at maximum) that can be arranged as shown in figure 13.11.3. Some steps are occasionnally simultaneous : for example, electrolytic refining eliminates Bi, As, Sn, Zn and precious metals in one step. In pyrometallurgy, the first two steps can be carried out continuously in small reverberatory furnaces, or, in batch, in semi-spherical kettels of ± 250 t capacity. The reverberatory furnace is best suited for large capacity plants (100-200.$10^3$ t Pb/year). The last steps are very often operated in kettles.

1) First step : copper drossing. When the lead bullion is melted just above the metal's melting point, impurities such as Cu, Fe, Ni and Co are slightly soluble and form a dross, that can be skimmed off. To obtain a small enough copper content, it is necessary to repeat the drossing with addition of sulfur to render the copper less soluble. The dross is rich in lead and is often treated in a small reverberatory furnace to obtain recyclable lead, copper-enriched matte and soda slag.

2) Second step : softening. It is an oxidizing step that removes As, Sb, Sn and Te. By slowly oxidizing the bullion with air in a reverberatory furnace held at about 650° C, one can remove Sn, then Sb,

Lead bullion

↓

Liquation

Pb + Ag + Bi + Sn, As, Sb     Dross : Cu, Co, Ni, Fe + As, Sb (few), Pb (Ag)

↓       ↓

Oxydation       Treatment for Cu

Slags with As, Sb, Sn     Pb + Ag + Bi

↓       ↓

Hydrometallurgy Recovery of Sn and Sb     Zinc addition

Pb (Bi) + 0,06 % Zn       Zinciferous dross + entrained lead

↓       ↓

Dezincing       Liquation

Zinciferous product recycled     Pb + Bi     Triple alloy (Pb - Zn -Ag)     Pb

↓       ↓

Debismuthizing with Ca + Mg     Distillation

Bismuthiferous dross     Refined Pb     Pb + Ag     Zn

↓       ↓

Treatment for Bi       Cupellation
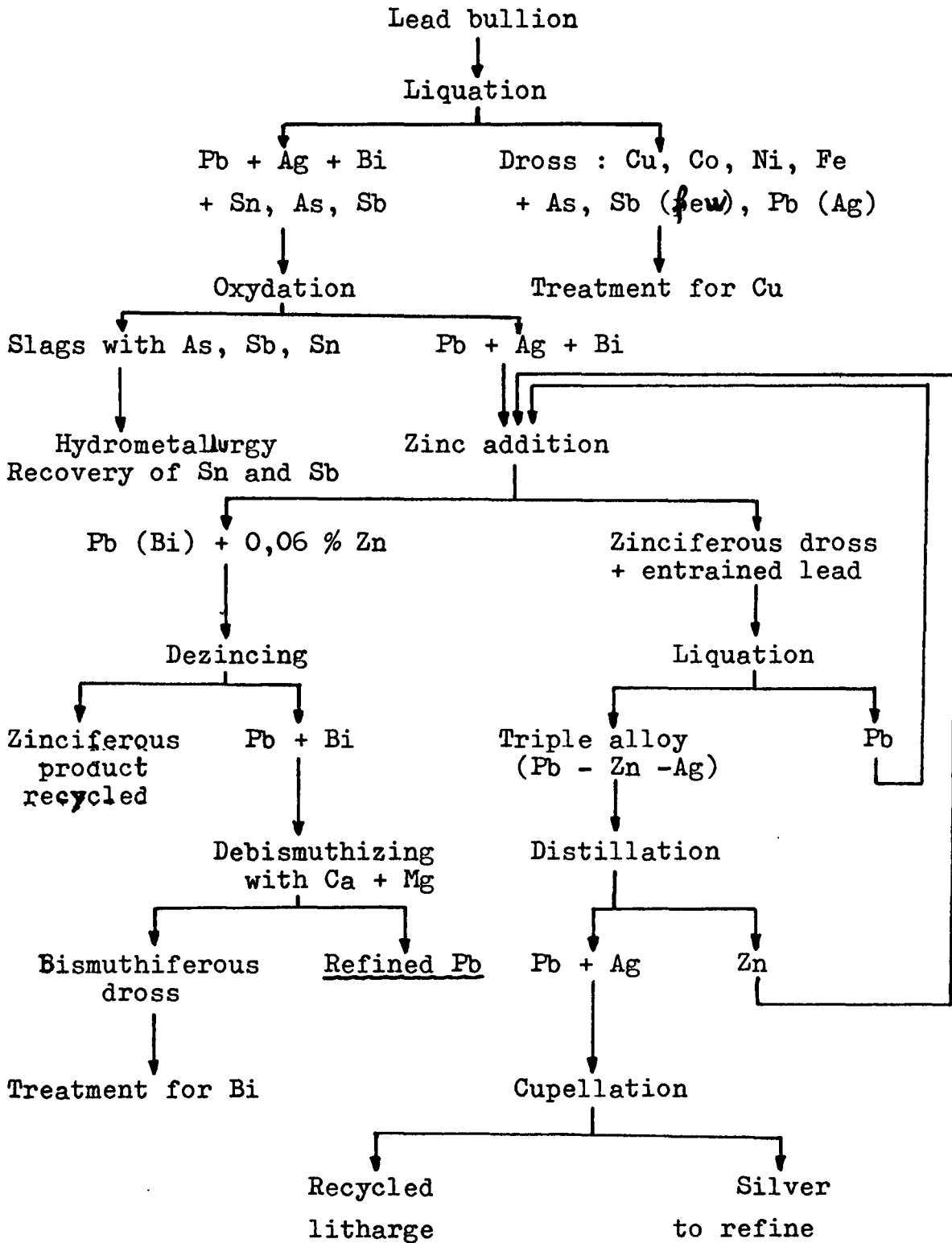
Recycled litharge       Silver to refine

Figure 13.11.3     Flowsheet of the lead refining

(from C. EK, Cours de Métallurgie des Métaux non ferreux)

and finally As In successive drosses. Softening can also be realized
In kettles with the Harris system, as shown In figure 13.11.4. The
reagents used are $NaNO_3$ (to oxidize the Impurities), NaOH (to aid
the formation of $Na_3AsO_4$, $Na_3SbO_4$ and $Na_2SnO_3$, In that order), and
NaCl (to form a fluid slag). Removal of 0.1 to 0.2 % Impurities can
take 4 to 5 hours. The sodium salts formed In the Harris process
are treated by wet techniques to separate arsenic-, antimony - and
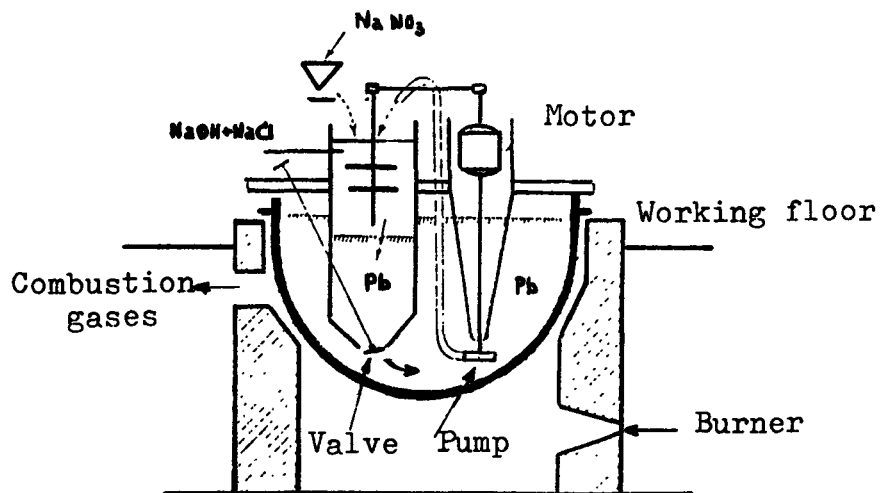tin Insoluble compounds, the last two being used for metal production.



Figure 13.11.4  HARRIS kettle for lead softening

(from a B.R.G.M. report for this dossier)

3) Third step : desliverizing. Silver as well as other precious metals
   are removed by the formation of Insoluble Intermetallic compounds,
   with lead and zinc added to the bullion In countercurrent stages.
   Crusts from the first stage, rich In silver ($\pm$ 10 %), are remelted
   to remove and recycle argentiferous lead. They are then retorted to
   volatilize zinc metal that Is condensed and recycled. The residue
   of the retorting Is a lead-silver mixture that Is treated by cupel-
   lation In a hearth furnace In which litharge Is skimmed off, leaving
   the bulk of the precious metals (known as "doré") to be refined by
   chlorine gas treatment or electrorefining. Gases from the cupella-
   tion furnace are rich In Se.

4) Fourth step : debismuthizing. When the bismuth content justifies
   treatment, this metal can be removed by two techniques :

   - The Kroll-Betterton process utilizes additions of calcium and
     magnesium (Introduced as lead alloys) to form mixed drosses Inso-
     luble In lead at about 330°;

- The electrolytic Betts process uses a fluosilicate solution
  $(PbSIF_6-H_2SIF_6)$ to refine bismuthiferous lead anodes into very
  pure cathodes.
  Electrorefining must be operated on decopperized lead, but it
  can remove Ag, Sb, Bi, As, Sn, Te, Se, etc, that are collected in
  anode muds for retreatment.

5) Fifth step : Ingot casting. A final refining step, with NaOH + NaNO₃,
   removes the last impurities, the pure lead (99.99-99.997 %) is then
   cast in ingots to market specifications.

## 13.11.F. BY-PRODUCTS OF LEAD METALLURGY

1) Copper is removed as a matte formed in the blast furnace or as a
   dross produced in the decopperizing step (most common method).
   Retreatment of that dross also gives a matte. In general, these
   mattes are sold to specialized companies where copper is produced
   by converting and refining.

2) Arsenic is transformed by the Harris treatment into sodium arsenate,
   which is finally precipitated as calcium arsenate, a compound of
   very low solubility and toxicity; arsenic metal or arsenic trioxide
   cannot be economically recovered from these products.

3) Antimony is insoluble as sodium antimonate in dilute NaOH solutions.
   It is filtered, dried and reduced in small reverberatory furnaces
   to produce antimony metal or lead-antimony alloys.

4) Tin is separated as precipitated calcium stannate; this compound
   can be added to cassiterite charges to be reduced in reverberatory
   furnaces.

5) Silver (and some other precious metals) are produced, as stated
   above, by cupellation and refining.

6) Bismuth is recovered from the dross after lead liquation. In
   general, enriched drosses are sent to specialized companies' where
   they are treated in successive chemical or pyrometallurgical refi-
   ning steps.

7) Cadmium, selenium and tellurium are sometimes valuable by -products
   of lead metallurgy.

## 13.12 - ZINC PYROMETALLURGY

### 13.12.A. INTRODUCTION

The main component of zinc concentrates is sphalerite (or blende), ZnS. Their zinc content generally varies from 48 to 62 % Zn, with an average content of 32 % S. Principal impurities are galena, pyrite and gangue minerals ; trace elements are sometimes present in valuable amounts : cadmium, germanium, gallium, thallium, indium, etc.

In some orebodies, the main zinciferous mineral is marmatite, a mixed sulphide of Fe and Zn, in which the iron present in the lattice structure cannot be separated by such physical means as gravimetric concentration or flotation. Oxidized zinc minerals, called collectively "calamine", consist essentially of carbonate, silicate, hydrosilicate, etc, which are difficult to beneficiate by physical means beyond 30-35 % Zn. The Zn assay can be further increased either by calcination, expelling combined $CO_2$ and $H_2O$, or by metallurgical concentration, producing impure zinc oxide but at a significantly higher cost.

Direct treatment of sulfide concentrates is not economical by reduction with C, $H_2$ or another metal such as Fe. Partial oxidation of the sulfide and reaction of the residual ZnS with its oxidation products (oxide and/or sulfate) can only be carried out at such a high temperature that no "roast-reaction" process has ever been applied in zinc metallurgy. Sulfide concentrates are oxidized by roasting to give ZnO that can be reduced by carbon in acceptable conditions. However, the low boiling point of the metal creates a number of problems which impeded industrial production of zinc metal until the beginning of the 19th century, when the so-called Belgian process was born in Liège in J.J. Dony's workshop.

### 13.12.B. ZnO REDUCTION BY CARBON

ZnO can be reduced by carbon or by CO at moderate temperature as follows :

$$ZnO_{(s)} + C_{(s)} = Zn_{(g)} + CO_{(g)} \qquad (1)$$

$$ZnO_{(s)} + CO_{(g)} = Zn_{(g)} + CO_{2(g)} \qquad (2)$$
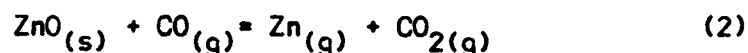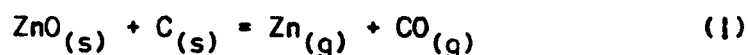
In fact, In order to obtain a good reaction kinetics, temperatures must rise to 1100-1300°C and therefore zinc metal is produced in gaseous form. To liquefy the metal, it is necessary to cool it, at which time reaction (2) takes place from right to left and zinc is oxidized back into ZnO. Zinc liquefaction is thus possible when $CO_2$ is excluded from the resulting gases. To do that, one can first separate the reduction gas circuit and the combustion gas circuit (when using carbonaceous fuel). The charge may also be reduced in an electric furnace, with an excess of carbon in the charge leading to the reaction :

$$CO_{2(g)} + C_{(s)} = 2 \, CO_{(g)} \hspace{2cm} (3)$$
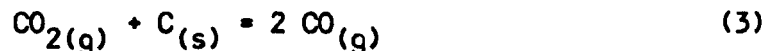
This reaction also tends to take place in the righ-left direction when the temperature decreases ; a slight reoxidation of zinc is therefore unavoidable. Losses of liquid zinc are also increased by these two phenomena :

a) a time lag for the condensation, theoretically at 906°C, results in the production of solid condensed particles;

b) a reoxidation takes place on the surface of the liquid metallic droplets and prevents their entering into the molten bath.

Another efficient solution to this problem is used in modern condensers : the condensation is made very quickly with immediate cooling, thus strongly decreasing the contact time between gaseous Zn and $CO_2$ at oxidation temperatures. Mechanically-operated systems also permit the break up of the oxidized layer on the particles by attrition and to thereby increase the amount of zinc going to the liquid phase.

ZnS and $ZnSO_4$ (immediately transformed into ZnS) are not reduced by C and must be fully oxidized before reduction. It is therefore necessary to roast the concentrates completely in order to obtain a minimum amount of residual sulfur. As zinc silicate is hard to reduce, even at temperatures of about 1250°C, it is wise to roast as quickly as possible so that the contact time at roasting temperature is decreased. On the other hand, zinc ferrite ($ZnO.Fe_2O_3$) causes only slight modifications in the reaction rate, without other drawbacks. Gangue minerals must remain solid until all the gaseous zinc has volatilized from the reduced charge.

If slag can be formed In the furnace used, Its formation temperature must be high enough for the slag to be liquid only when all the zinc Is reduced.

## 13.12.C.   ROASTING PRACTICE

Zinc blende roasting must be performed In order to :

1) obtain maximum desulfurization;
2) avoid the formation of zinc silicate;
3) produce a dense and porous sinter allowing free flow of reducing gases and release of gaseous zinc.

Dwight-Lloyd roasting allows the production of a sinter containing 0.1 % sulfide S and 0.4 % total S, and helps volatilize lead, cadmium (recovered In the dusts) and arsenic.   Gas produced contain 5-6 % $SO_2$.  Zinc concentrates with 30-32 % S, previously roasted first In multiple-hearth furnaces, can now be treated In fluidized bed reactors It Is common, however to dilute raw concentrate with recycled sinter to get the proper sulfur content In the feed.

With adequate charge preparation, It Is possible to get dead roasted sphalerite In a fluidized bed, but S assays are higher than In the D.L. practice; however, the $SO_2$ content of the gas easily allows $H_2SO_4$ production by double catalysis.

## 13.12.D.   REDUCTION PRACTICE

### I. HORIZONTAL RETORTS

The discontinuous process In horizontal retorts (Belgian process due to J.J. DONY) has initiated the Industrial zinc production and was used until recently. The charge, made up of sintered concentrates and an excess of reducer Is first put In refractory retorts having a capacity of around 100 kg  then placed In a reverberatory furnace.

At the open end of the retorts there are tightly fixed refractory condensers (outside the furnace) in which zinc vapor is condensend to liquid zinc. At the end of the condensers there are metallic tubes that collect zinc dust. The working cycle is normally 24 hrs, and sometimes 48 hrs.

This process consumes 1050 kg of coal per ton of zinc, and gives rise to an important recycling (25-30 % of the metal); total recovery is not higher than 90 %, and the zinc obtained is rather impure.

Besides requiring a large labor force, a disadvantage in countries where manpower is expensive, it cannot comply with the present environmental protection legislation. Some minor improvements have been made such as a single condenser for all the retorts on one side of the furnace, as well as machines for filling up and cleaning the retorts. However, in the E.E.C. countries the horizontal retort process no longer produces zinc ingots, but is sometimes used for the production of zinc powder or zinc oxide.

## 2. CONTINUOUS PROCESSES

The development of continuous processes for zinc production represents a significant advance. These processes require the prereduction of the charge in an external furnace, but they allow the design of better condensers which improve the direct recovery of liquid zinc,total recovery being increased to 93-96 %. The principal continuous processes are the New Jersey vertical retort and the St Joe electrothermic furnace, and, for mixed lead-zinc charges, the Imperial Smelting furnace (see below).

## 3. NEW JERSEY VERTICAL RETORT

The vertical retort (figure 13.12.1) is constructed in carborundum; it is externally heated, with combustion air preheated to 1000-1100° C; the capacity of one retort is 8-9 tpd of zinc.

Briquetted and prereduced charge is fed at the top and the residues are continuously removed at the foot of the retort. Gases are extracted through a side-port and cooled in a "splash condenser".
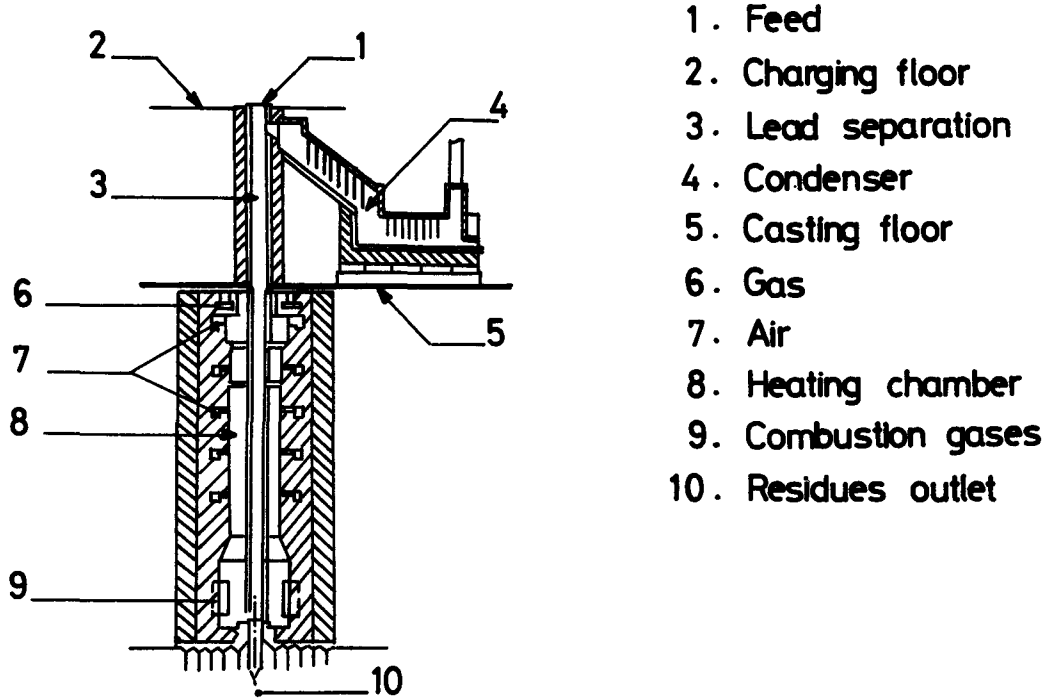
Vertical retort

1. Feed
2. Charging floor
3. Lead separation
4. Condenser
5. Casting floor
6. Gas
7. Air
8. Heating chamber
9. Combustion gases
10. Residues outlet
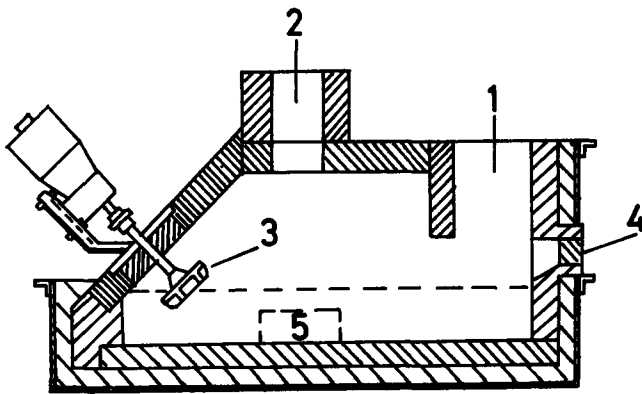


Splash condenser

1. Gas inlet
2. Gas outlet
3. Pulverizing rotor
4. Cleaning door
5. Lateral outlet

Fig. 13.12.1    NEW JERSEY vertical retort process
(from C. EK, Cours de Métallurgie des Métaux non ferreux)

The zinc rain results In a very short cooling time (zinc bath temperature
Is 500°C) and In an attrition of the oxidized layers of the zinc droplets.

## 4. ST JOE ELECTROTHERMIC FURNACE

The St Joe electrothermic furnace (figure 13.12.2.) Is a
vertical furnace fitted with 8 electrodes; its capacity Is about 90 tpd
of zinc. The sinter, prereduced at about 750° C, Is fed at the top.
Gases are vacuum extracted through an annular ring flue half-way up
the side of the furnace. Zinc Is condensed In a U-tube containing
liquid zinc and cooled by water (Weaton-NaJarIan condenser); CO gas
Is recovered. This process has never been used In E.E.C. countries.

## 5. TREATMENT OF OXIDIZED ORES AND RESIDUES

After calcination In a rotary furnace for dewatering and
decarbonating, the oxidized concentrates rich In zinc can be treated
by mixing with roasted blendes.

Most of the oxidized concentrates , however, have zinc
contents of only 20-30 % and are highly siliceous. They can be metallur-
gically beneficiated by the Waelz process, as well as certain residues
(from leaching, for Instance) containing around 20 % Zn. The Waelz
furnace Is a long rotary furnace, whose capacity can be up to
120000 tpy.

The zinciferous products are mixed with 25-30 % coke or coal
fines. The gases (Zn + CO) are burned by an excess of air and zinc Is
collected as ZnO. Residues are maintained In the solid state. Zinc reco-
very Is about 80-90 %, the dust contains 60-65 % Zn, as well as lead and
cadmium. Special types of blast furnaces (V.M.'s Philippon cubilot,
Oker's half-shaft furnace) were also used for this treatment; gases are
always oxidized at the top by air or water Injection.

## 6. TREATMENT OF ZINCIFEROUS SLAGS

Slags from lead or copper metallurgy, containing a high
amount of zinc (8 to 22 %) are treated by fuming ("slag-fuming") In order
to recover 90 % of the zinc and 98 % of the lead.

Briquettes

Coke   Sinter

Preheating

Burner

Gas washing   Rotary feeder

Vacuum
pump

CO   Upper electrodes

Liquid
zinc   Vapour ring

Cooler

Condenser
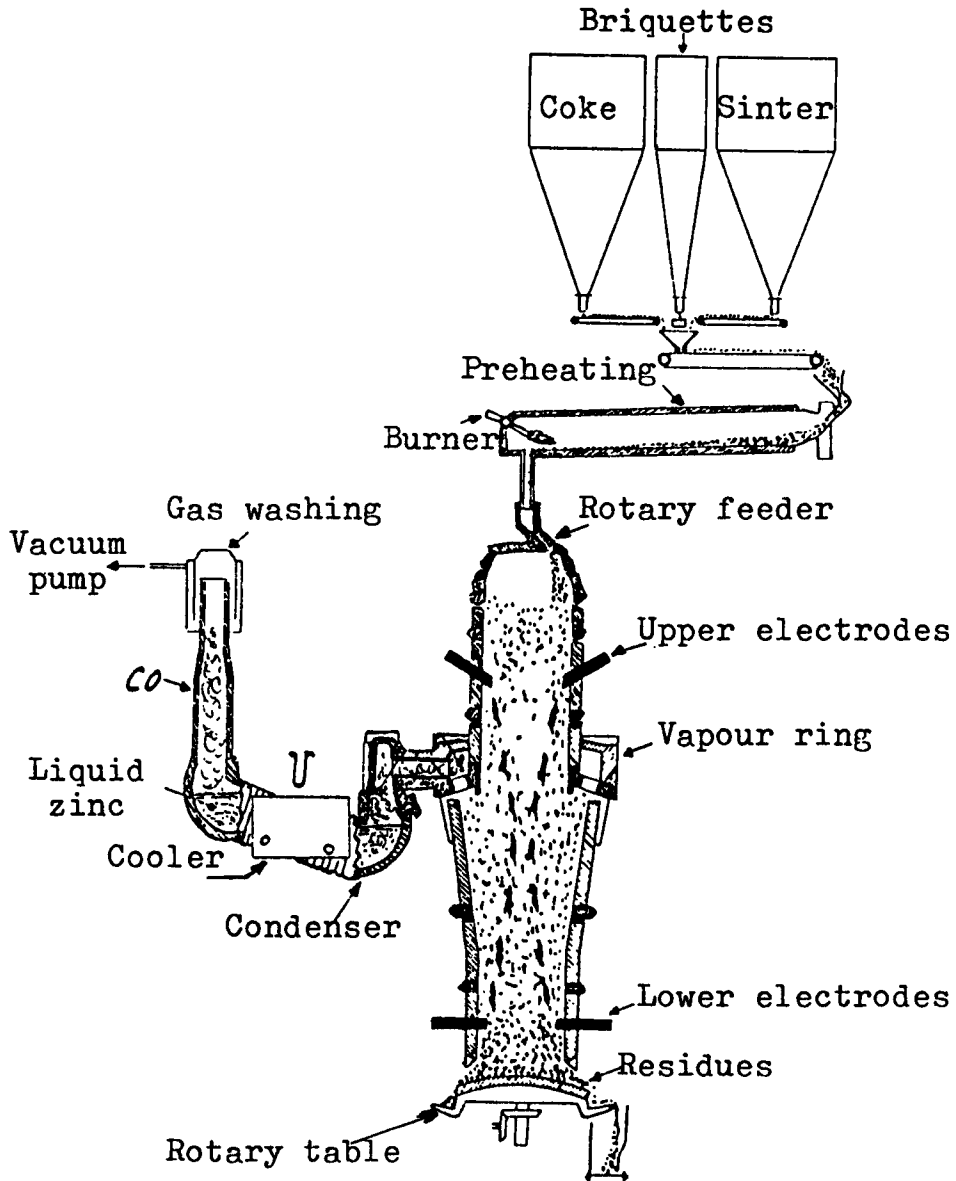
Lower electrodes

Residues

Rotary table

Figure 13.12.2 ST JOE electrothermic furnace

(from The Josephtown Story, p. 18)

Water-jacketted rectangular furnaces are followed by a large combustion chamber, waste-heat boilers, and gas cleaners. Slag is fed hot, at the liquid state, sometimes with a small proportion of granulated cold slag. The bath is fumed by a mixture of air and pulverized coal blown through tuyeres. The temperature is about 1200 C, zinc and lead are volatilized, then reoxidized by an excess of air.

Furnace capacity is about 700 tpd. Dust contains 60-70 % Zn and 7-10 % Pb. A schematic view of the furnace is shown on figure 13.12.3.

## 13.12.E. ZINC REFINING

Zinc obtained by pyrometallurgical processes is rather impure, containing 1 to 1.2 % Pb and up to 0.4 % Cd.

Partial refining can be carried out by liquation in a reverberatory furnace, where four layers are formed : zincy lead, hard ferrous zinc, liquated zinc, oxidized dross. Excellent zinc refining can only be obtained by fractionated distillation in New Jersey columns (figure 13.12.4); zinc purity is over 99.99 % and cadmium is completely recovered.

After melting, raw zinc is fed in the liquid state into the first column, which is heated at the foot; the liquid phase is rich in lead and iron, and the gaseous phase is rich in zinc and cadmium. The latter phase is condensed, the liquid is then fed into a second column whose liquid phase is very pure zinc and whose gaseous phase, assaying 10-20 % Cd, is further treated for cadmium.

Waste heat boiler

Lead furnace slag

Flue for
dust

*12% Zn*    *13% SiO₂*
*3ci3,5% Pb*  *7,5% CaO*
*23% Fe*    *4% Al₂O₃*

*15% Co*

Combustion

chamber

*1200°*

Final slag   *0,02% Pb*   after   *2h/%*
              *3,0% Zn*
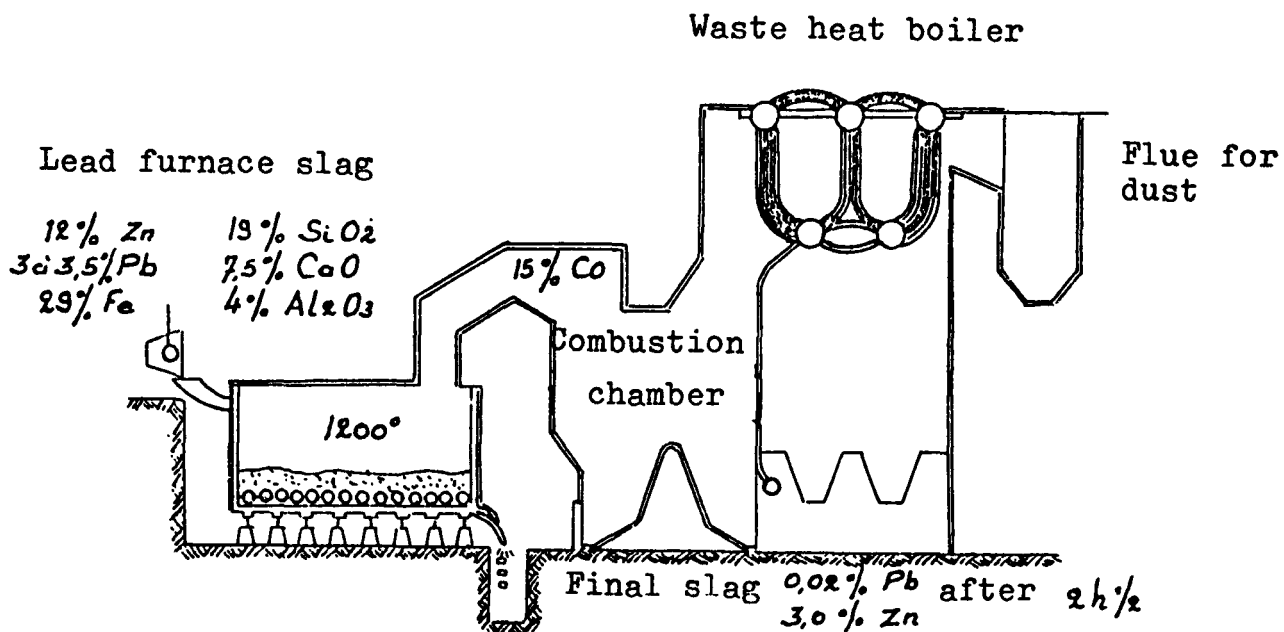
Figure 13.12.3    Slag-fuming furnace

(from C. EK, Cours de Métallurgie des Métaux non ferreux)

Condenser

*Cd+Zn*

*Zn+Cd*    Condenser

Feed of
liquid
zinc

Treatment
for Cd

Combustion
chambers

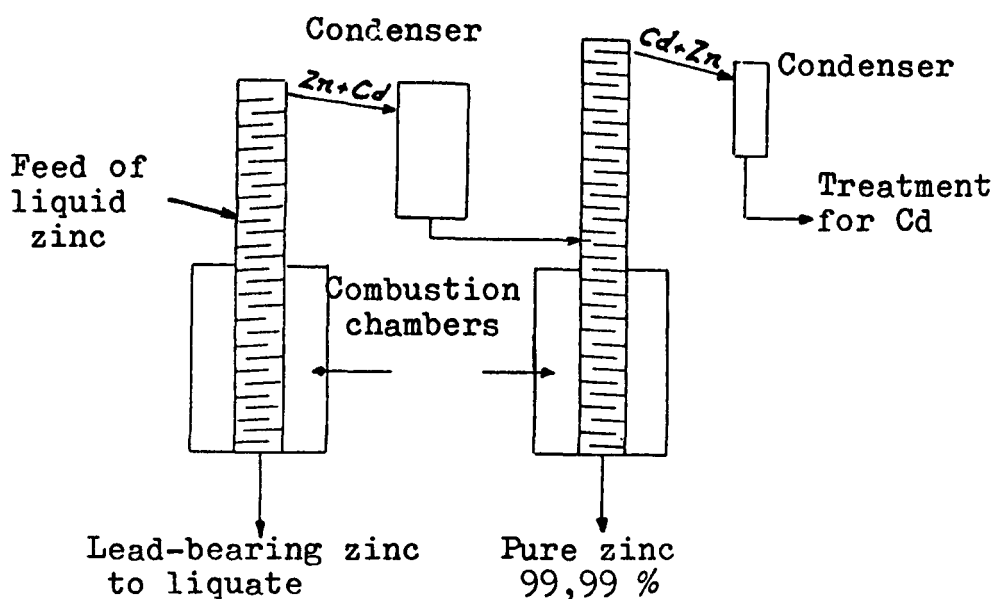Lead-bearing zinc      Pure zinc
to liquate             99,99 %

Figure 13.12.4 NEW JERSEY distillation columns

(from C. EK, Cours de Métallurgie des Métaux non ferreux)

## 13.13 - ZINC HYDROMETALLURGY

### 13.13.A. INTRODUCTION

More than 75 % of the zinc produced in the world is presently
obtained by hydrometallurgical processes, and this ratio is still slowly
increasing.

Zinc's standard electrode potential is -0.76 V; this value
is much lower than that of hydrogen. It is however possible to electro-
win zinc in aqueous solution, due to the high hydrogen overvoltage on me-
tallic zinc deposited at the cathode; this overvoltage can reach up to
1-1.2 V.

As zinc sulfide is not soluble in sulfuric acid, sulfide
compounds must be roasted before leaching and solubilization of the
zinc as sulfate.

Leaching is carried out by the recycled spent electrolyte
which is rich in sulfuric acid; to compensate for losses, however,
roasting must be made slightly sulfating. Due to contact among $ZnO$,
$SiO_2$ and $Fe_2O_3$, roasting can favor the formation of zinc silicate and
mainly, zinc ferrite. Silicate is easily soluble in sulfuric acid, but
zinc ferrite is only soluble in hot concentrated acid; iron is also
soluble in these conditions. A few years ago, leaching was giving a
residue rich in zinc ferrite (18-22 % Zn) that had to be retreated in
a blast furnace or in a Waelz kiln.

New processes (precipitation of iron as jarosite or goethite)
can eliminate the dissolved iron and filtrate the precipitate, both
previously impossible. These retreatment processes leave residues
with a content of 3 to 5 % Zn.

Several metals more noble than zinc, particularly copper,
cadmium and cobalt, are dissolved in the same way as zinc; they cannot
be present during electrowinning. The solution must be purified in seve-
ral stages with zinc powder. Although the feed solution does not
contain any free sulfuric acid, electrolysis is carried out in a
$ZnSO_4$ + $H_2SO_4$ solution, between an argentiferous lead anode and a
cathode that is, initially, an aluminium sheet.

Raw blende

↓

Partially sulfatizing roasting

↓

Calcine

↓↓↓

Neutral leaching

$\left\{\begin{array}{l}\text{ZnO excess; pH 5,5} \\ \text{oxidation (MnO}_2\text{)} \\ \text{precipitation} \\ \quad\text{(Fe, Al, Ge, As, Sb)}\end{array}\right.$

↓

Classifiers

Sands ← → Slimes + Solution

↓ Thickeners

Slimes ← → Neutral solution

Make-up acid ‐‐‐

Acid leaching

↓

Classification -Thickening
Washing

Partially
neutralized
solution        Sands and
                slimes

Precipitation
with zinc powder

↓

Filtration

Solution        Cu - Cd
                Residue

↓

Purification
for Co and Ni

Solution        Co-Ni precipitate

↓

Electrolysis

Solution        Zn cathodes
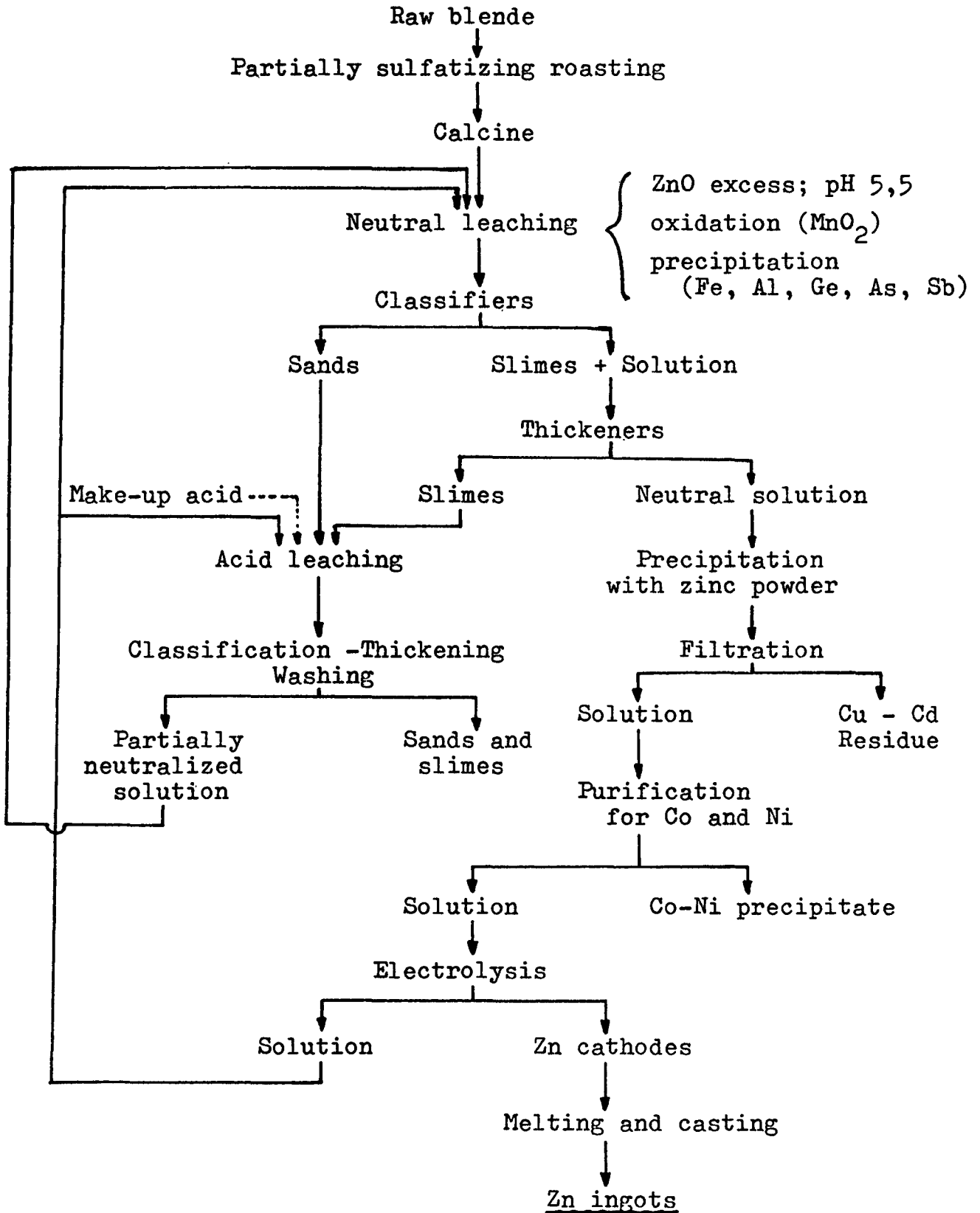
↓

Melting and casting

↓

**Zn ingots**

Figure 13.13.1    Classical flowsheet for Zn electrolysis
(from C. EK, Cours de Métallurgie des Métaux non ferreux)

It is necessary to favor a high value of hydrogen overvoltage, which increases with current density and the addition of colloids, and decreases with a rise in temperature, zinc concentration and impurity content. The influence of acidity is more complex: its increase results in an increase of the overvoltage value and of the electrolyte conductivity, but hydrogen release is favored. In the same way, an increase of current density increases not only the hydrogen overvoltage, but also the polarization losses and the ohmic drop in the cell.

Thus, acidity and current density have opposite effects on the economic results of electrowinning. Two practical processes can be envisaged :

- the first, known as the ANACONDA process, limits both the acidity (around 150-170 g/l acid) and the current density (300-400 A/m$^2$);

- the second, known as the TAINTON process, operates with both a high acidity (270 g/l acid) and a high current density (1000 A/m$^2$) to increase the hydrogen overvoltage.

Although economically it's highly efficient, the TAINTON process causes great problems of corrosion, solution viscosity, and healthiness of the electrolysis cellroom. Electrolytic plants normally use current densities of 400-600 A/m$^2$, and, rarely, 700-800 A/m$^2$.

A schematic flowsheet of an electrolytic plant is presented in figure 13.13.1.

13.13.B. INDUSTRIAL ROASTING PRACTICE

Partly sulfatizing roasting of the sphalerite concentrates is now carried out in a fluidized-bed reactor, having been made in the past in multiple-hearth furnaces and flash roasters.

The capacity can reach 500 to 600 tpd; the temperature, easily controlled, is about 950° C. Sulfate sulfur production in the dust varies from 1 to 2.25 %; remaining sulfide sulfur content is about 0.3 %. The retention time of the concentrates in the furnace is 4 to 5 hours. The gases contain 8 to 10 % SO$_2$; they are cooled in the

waste-heat boiler and are then (after dedusting) used for acid production.

Some plants that were operating Dwight-Lloyd sintering machines have saved this unit as a roaster, since the sinter appears to have better neutralizing qualities for electrolyte treatment.


13.13.C.  INDUSTRIAL LEACHING PRACTICE

Leaching is carried out with the spent electrolyte, in pachucas or mechanically-agitated tanks. It is operated continuously or in batch, and comprises 1, 2, or 3 stages.

More often than not the procedure includes a neutral leaching, the solution going to the purification step with a pH of 5.6-6. This pH is obtained by the addition of an excess of calcine that, in oxidizing conditions, precipitates iron and aluminium hydroxides, carrying also As, Sb and Ge. About 75 % of the zinc is dissolved.

After classification and decantation, the slurry is sent to the acid leaching step, where the pH is about 2.5-3 and 14-20 % of the zinc is dissolved; a slightly acid solution and the wash solutions (equal to the amount washed away with the residues ) are recycled to the neutral step. In the batch processes, the spent electrolyte is used in slight excess, then neutralized by some calcine or limestone.

After this stage, the residues still contain about 20 % zinc with the iron, lead, and gangue of the calcine.


13.13.D.  TREATMENT OF THE RESIDUES

In the most modern processes, the residues are treated by hydrometallurgy, either after the acid leach or directly as second-stage leaching. Most of the zinc in the residues (especially the zinc ferrite) is dissolved by concentrated sulfuric acid at 80-95° C. The residue of this operation contains mainly lead sulfate (15-20 % Pb) with the silver and the ore gangue; zinc content can be less than 2 %; it is decanted and filtered. In some plants this residue is

floated for lead and silver. The concentrates thus obtained (assaying 50-55 % Pb) are suitable as make-up for lead smelting.

After leaching the solutions contain 40-60 g/l sulfuric acid, 15-20 g/l Fe, as well as other impurities. They are neutralized with roasted ore (or, better, sintered ore) or zinc oxide. Iron is precipitated in a filtrable form by one of the following two processes :

- the jarosite process, where a $NH_3$ addition precipitates an easily-filtered jarosite salt,$NH_4Fe(-)(SO_4)_2.2Fe(OH)_3$, while the solution, with 2-3 g/l Fe and 3-5 g/l $H_2SO_4$. flows back to the neutral leach (figure 13.13.2 and 13.13.3);

- the goethite process, where iron is first reduced to the ferrous state with raw concentrate (ZnS), then precipitated, with the addition of finely dispersed air and calcine at 80-90°C and pH 3-4, in the form of goethite, $Fe_2O_3.H_2O$ (also easily filtered) (figure 13.13.4).

In any case, the residues obtained are rich in iron (30-50 %) and still contain 2-4 % Zn. The leaching recovery is now up to 95-97 %, instead of 88-90 %.

In plants without these retreatment processes, the residues are either dumped or treated in a Waelz furnace, in a cubilot or by a sulfatizing roasting step with the addition of pyrite.

13.13.E. SOLUTION PURIFICATION

The principal impurities to be eliminated are copper, cadmium, cobalt and nickel. Purification is generally realized in hot solutions (about 75° C), in batch, and in 3 or 4 successive stages; the reagent is usually zinc powder (sometimes scrap in the first stage). The first stage eliminates copper; the second , with addition of antimony powder, eliminates cobalt, nickel, the remaining copper, and most of the cadmium. Finally the third stage reduces the solution's cobalt content to about 0.2 mg/l. The cements are thickened and filtered, then retreated to give
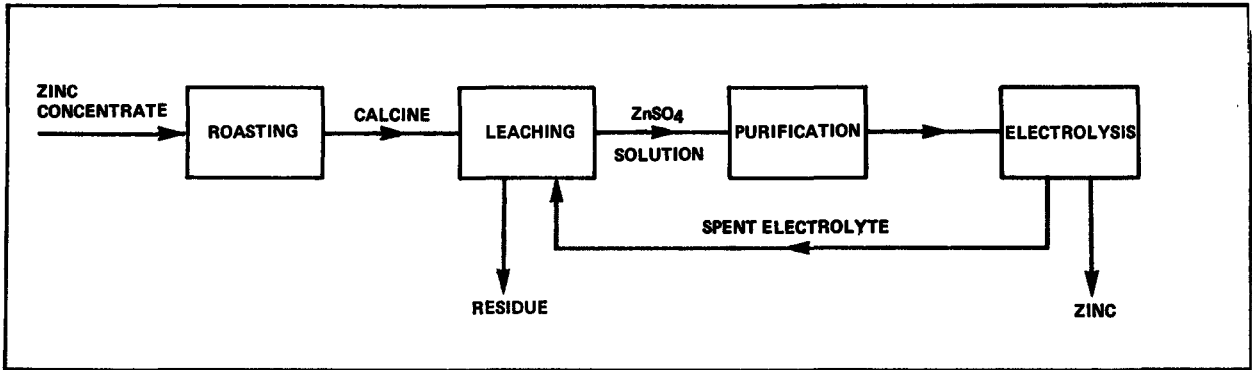
**SIMPLE FLOWSHEET** of the electrolytic zinc process which traditionally has zinc recoveries of about 85 to 93 percent from sulphide concen- trates. Zinc losses mainly result from the formation of very insoluble zinc ferrite which reports in the solid leach residue. **No. 1**
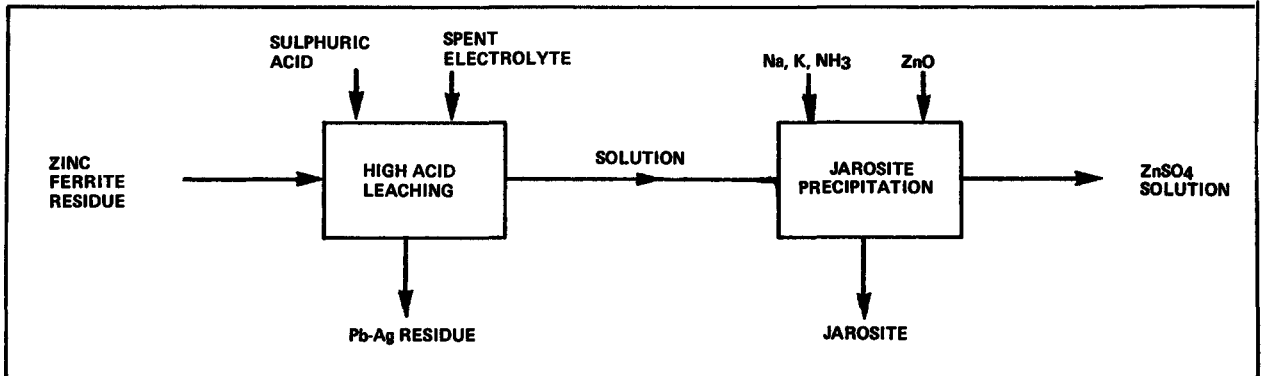


**JAROSITE PROCESS** can increase zinc recovery in electrolytic plants to 96 to 98 percent. After high acid leaching the iron is precipitated as crystalline jarosite which can be washed and discarded with far less loss of zinc than is the case with ferric hydroxide. **No. 2.**
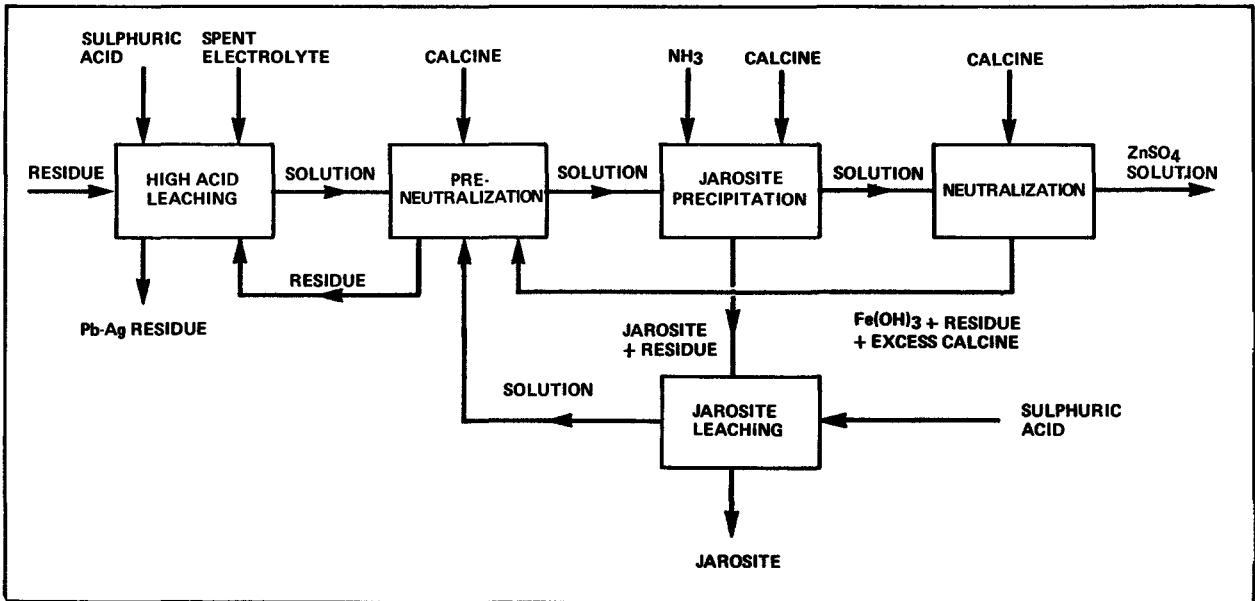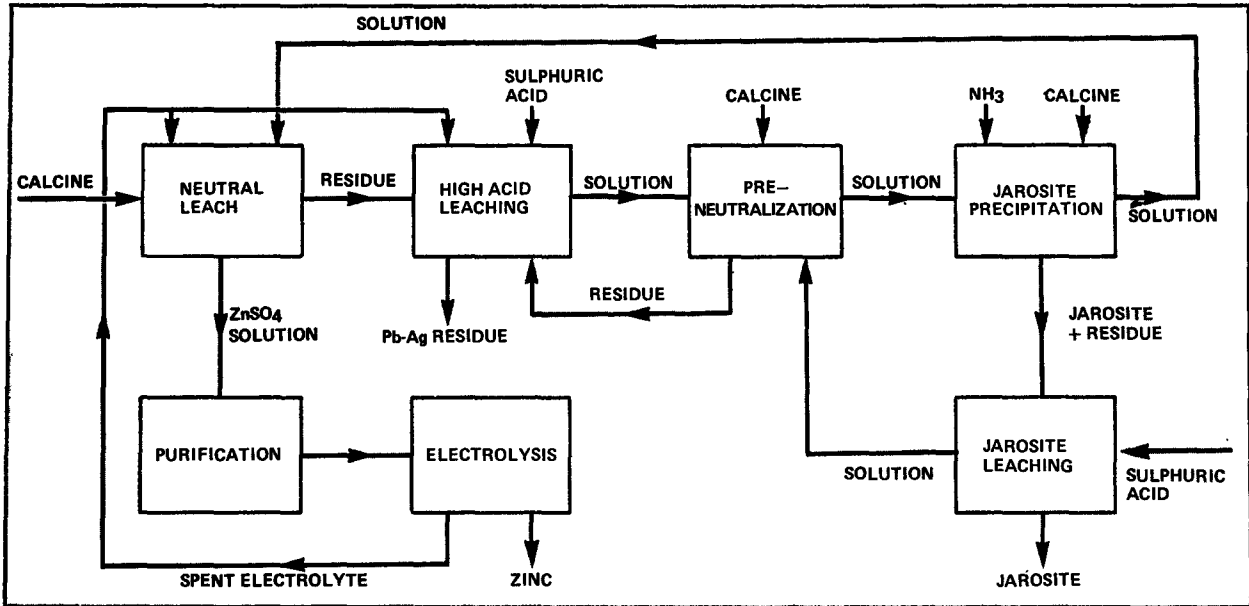


**CALCINE** may be used as neutralizing agent but in this case the residue from this calcine is lost with the jarosite unless special steps ...re taken. This flowsheet shows how these residues can be recycled and how jarosite can be leached to reduce zinc loss. **No. 3.**

Figure 13.13.2 Jarosite process

(from World Mining, september 1972, p. 35-36)

NEUTRAL calcine leaching integrated with the Jarosite Process is used at the zinc plant of Det Norske Zinkkompani at Eitrheim in Norway.

Asturiana de Zinc in Spain uses a similar flowsheet but without pre-neutralization and jarosite leaching steps. No. 4.
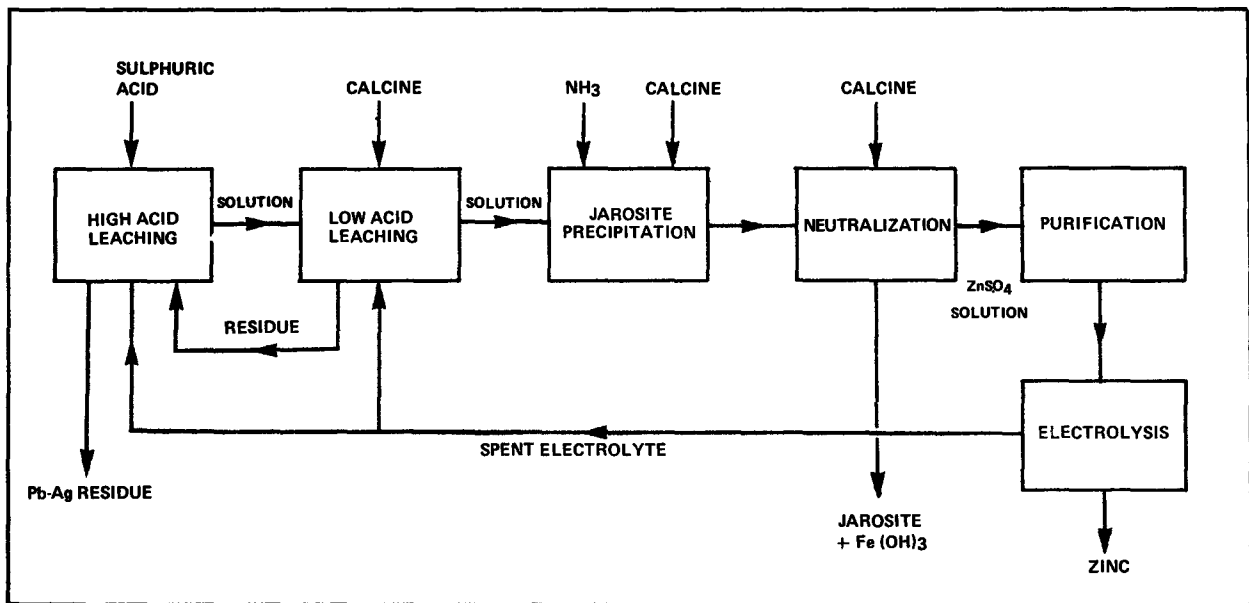


COUNTER CURRENT calcine leaching integrated with the Jarosite Process. A proposed flowsheet of a continuous system with high zinc recovery. If required the flowsheet could incorporate a low acid stage for calcine leaching and a high acid stage for ferrite. No. 5.

Figure 13.13.3 Jarosite process

(from World Mining, september 1972, p. 37-38)

Leach residue

Agitation

Decantation

Solution | Underflow

ZnS (reduces $Fe^{3+}$)

Agitation | Spent electrolyte

Agitation

Decantation | Decantation

Calcine | ZnS + S | Filtration

Neutralization | Solids | Solution

Roasting

Decantation | $PbSO_4$, Ag, S

Solution | Air | Calcine

Agitation

Thickening
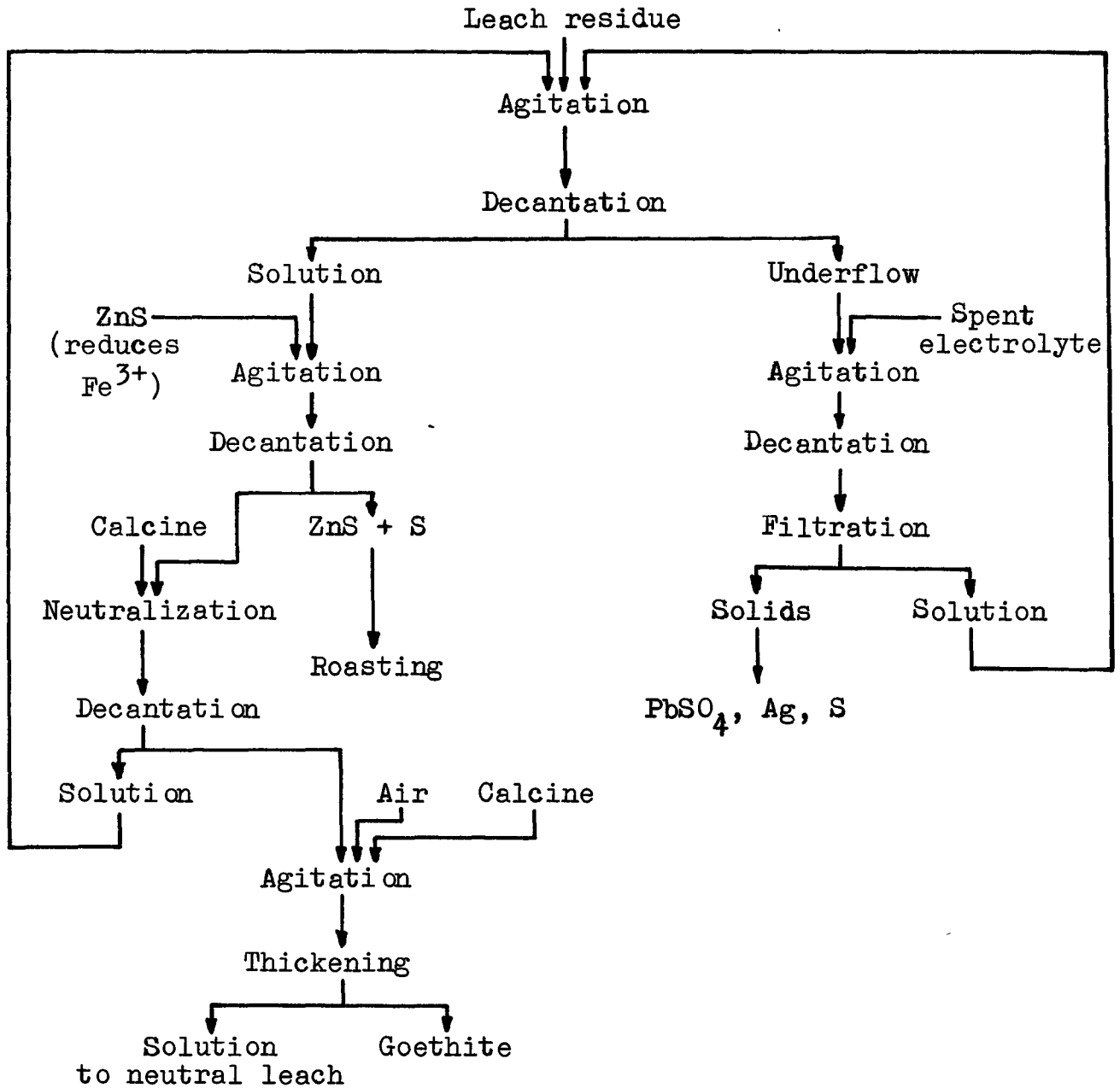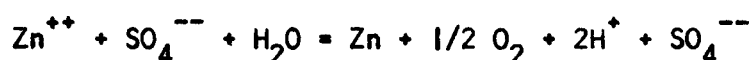
Solution to neutral leach | Goethite

Figure 13.13.4 Goethite process

(from C. EK, Métallurgie des Métaux autres que le Fer)

products rich In either copper, cadmium, or cobalt, while the excess zinc powder Is redissolved.

## 13.13.F. ELECTROLYSIS

Zinc electrolysis Is due to the following reaction :

$$Zn^{++} + SO_4^{--} + H_2O = Zn + 1/2\ O_2 + 2H^+ + SO_4^{--}$$

It Is carried out In hundreds of cells. Each contains 20 to 50 lead-silver or lead-antimony anodes, and the same number, less one, of cathodes made Initially of an aluminium starting-sheet but soon covered with deposited zinc. Electrolysis comprises two steps, for Instance :

|                | Feed  | End of step 1 | End of step 2 |
|----------------|-------|---------------|---------------|
| $H_2SO_4$, g/l | 1 - 2 | 150           | 170           |
| Zn , g/l       | 145   | 75            | 35-40         |

Solutions are cooled In atmospheric cooling-towers.

The operating cycle can vary from 12 to 72 hours, but it averages 24 to 48 hours. Electric current Is fed through silicium rectifiers at 400-600 V and about 50 000 A.

In the most modern plants, cathodes are automatically and mechanically stripped by machines In a complex computer-controlled circuit. It Is consequently possible to Increase the cathode working surface area from 1 to 2.6 m², decreasing the ground space and capital Investment for the electrolysis hall.

## 13.13.G. MELTING OF THE CATHODES

The metal obtained by electrowinning cannot be used as Is; It must be melted and cast Into Ingots.

Low frequency Induction furnaces are usually used for this. When casting zinc, It forms an oxide layer on the ingot surface; this layer Is scraped to obtain metal assaying 99.995 % Zn.

## 13.14 TREATMENT OF MIXED LEAD-ZINC MATERIALS

### 13.14.A. INTRODUCTION

In the mid-fifties, Imperial Smelting, an English Company, developed a blast furnace which could simultaneously produce lead and zinc, giving a new impetus to zinc pyrometallurgy.

This furnace can treat mixed concentrates whose dissemination of the sulfides of lead and zinc limits flotation selectivity; a single unit can produce 100 000 to 120 000 tpy of zinc and 40 000 tpy of lead.

In this furnace, the gases are moderately reducing (between lead and iron blast furnaces) by :

- maintaining the gases that leave the furnace (which contain zinc vapor and carbon oxide) at a high temperature (900-1000°C);

- quickly condensing the zinc vapor in a lead bath.

Zinc is produced by cooling the lead (where it is solubilized) from 550° (2.50 % Zn) to 440° (2.25 % Zn).

Lead of the charge appears as bullion in the furnace's crucible.

The Imperial Smelting furnace presents a number of advantages, but also some drawbacks for which it is difficult to find suitable remedies :

- very high lead circulation in the condenser, i.e. more than 400 tons per ton of zinc;

- low direct recovery of zinc (75 %) due to the drosses that clog the condenser;

- high zinc content in the slag (6-7 %) , or else iron is reduced;

- difficult control of the furnace to avoid hanging up;

- use of an expensive reducer and production of impure zinc needing refining.

## 13.14.B. INDUSTRIAL PRACTICE

The charge to sinter is composed of :

- concentrates to smelt (sulfides, oxides, mixtures) ;
- drosses, dusts, and rich slags to recycle;
- fluxes for the furnace (limestone and sometimes silica);
- recycled sinter (75 % of the charge), consisting of fines and of excessively coarse sinter which is too high in sulfur and must be crushed before recycling.

Sulfur content of this charge is strictly fixed at 7-8 %. Typical composition could be :

| Zn | Pb | S | Cu | Cd | FeO | $SiO_2$ | CaO |
|----|----|---|-----|------|-----|------|-----|
| 42 | 18 | 7 | 0.9 | 0.05 | 8 | 3 | 4.8 |

This charge is sintered on a Dwight-Lloyd machine, with an updraft that cools the lead in the charge and not on the grizzlies. Sulfur assay is decreased to 0.8 % and the gases with 6,5 % $SO_2$ are sent to sulfuric acid production.

Hot sinter (about 400°) screened between 10 and 100 mm, is mixed with -90+40 mm coke (preheated to 800°); the mixture is fed into the furnace (schematically presented in figure 13.14.1). Air blown into the furnace is preheated to about 1000° in cowpers. Outflowing gases are maintained at 800-1000° by preheated air injection to burn part of CO. Gases then contain 5 % Zn, 9-14 % $CO_2$ and 18-23 % CO.At these temperatures, zinc is not oxidized by $CO_2$.

Lead is reduced and forms a bullion collecting the copper. The slag assays 0.5 to 1 % Pb, but from 5-9 % Zn (averaging 7% ), 14-22 % $SiO_2$, 16-30 % CaO, 36-42 % FeO and 2-3 % S; the CaO/$SiO_2$ ratio must be maintained at 1.2.

The condenser has several rotors that pulverize a rain of lead which quickly condensesand solubilizes zinc vapor.

After lead cooling,zinc is removed by a weir with a content of 1.3 %
lead. Partially oxidized drosses are formed in the condenser, decreasing
the direct recovery to 75 % of the zinc.

For efficient operation of the furnace, the lead and zinc
contents in the treated charges are well established :

|    | maximum | average | minimum |
|----|---------|---------|---------|
| Zn | 50      | 40      | 34      |
| Pb | 22      | 18      | 12      |

Total coke consumption is about 0.8 t/t of zinc.

Taking into account the recycles, the total recovery in the
most modern units is : 92 % for zinc, lead and silver, and 70 %
for copper.

The zinc produced is rather impure and must be refined in
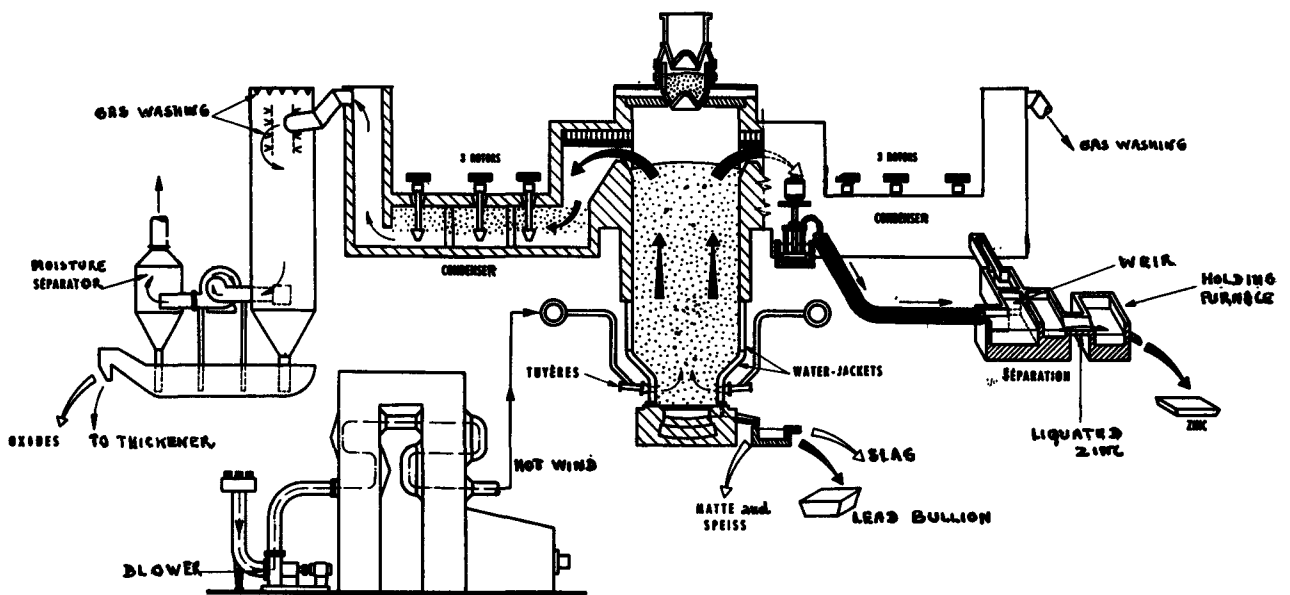New Jersey columns.



Figure 13.14.1 IMPERIAL SMELTING furnace

(from Annales des Mines, january 1965, p. 19)

## CHAPTER 13.2   PRACTICE IN E.E.C. COUNTRIES

### 13.21   INTRODUCTION

In 1973 (x), lead metal production amounted to 942 400 t in the E.E.C. countries, i.e. 22 % of world production. However, mines in these countries provided only 164 200 t, or 4.5 % of world production. The principal suppliers of concentrates are Canada, Peru, and Sweden.

In the same year, zinc metal production amounted to 1 228 400 t in the E.E.C. countries, i.e. 21 % of world production. However, mines in these countries provided only 361 600 t, or 6 % of world production. The principal suppliers of concentrates are Canada, Peru, Australia, and Sweden.

In 1974, zinc production capacity amounted to 1 625 000 t in E.E.C. countries, i.e. 31 % of world capacity; in that figure, electrolysis represented around 60 %.

Since then, capacity has slightly increased, with a higher ratio for electrolysis.

At the present time, it does not appear that production capacity could be greatly increased by building new plants   (Ireland may be an exception).

(x) Figures taken from Minemet statistics; Greenland included.

13.22  DENMARK

There Is no lead or zinc primary smelter In Denmark.

13.23    IRELAND

The following Is borrowed from a report prepared by C. Burton (1977) for this Pb-Zn dossier :

"At the present time, lead and zinc smelting facilities do not exist In Ireland. The Minister of Industry and Commerce, in the previous Coalition Government,did however announce his Intention to promote the establishment of smelter facilities In Ireland to process concentrates from the Navan Mines. This was undertaken by the Industrial Development Authority, who eventually appointed New Jersey Zinc Ltd. to carry out a 6 month study on the feasibility of building a smelter. If this report is favourable, development plans and permits could be completed by July-Septembre 1978.

"Construction of a 100-150 000 tonne/year zinc smelter would then take three years and the project would be completed by 1982 at a cost (assuming present prices) of £50 million. The Industrial Development Authority will underwrite 5-7 percent of the estimated cost, and the Irish Government will probably take a share In the project In the region of 10 percent. The smelter's profits will be tax-free until 1990".

— — —

The statement reproduced on the following page has appeared In Mining Magazine, october 1977, p. 317 :

# Irish Smelter - Refinery

Currently, zinc and lead concentrates are shipped to nine European smelting companies. However, the sales contracts contain provisions for the ultimate diversion of zinc concentrates to an Irish refinery when such a facility is established.

The study for an Irish zinc refinery undertaken by New Jersey Zinc (NJZ, the operating partner in the project) and the Irish Development Association (IDA) is expected to be completed late this year. Its terms of reference cover technical and financial requirements, plus recommendations on the optimum site.

Following the expected acceptance of this study, the next stage will be financing which it is hoped will be completed by 1978. Technical and engineering preparations having taken place in parallel, it is hoped these will have progressed sufficiently to allow planning permission to be sought in Spring 1978.

The time scale envisaged for construction is put at $2\frac{1}{2}$ years, and it is estimated that the refinery would be operational some time after mid-1981. It is hoped that the availability of refined Zn metal in Eire will give rise to spin-off industry in light engineering.

The refinery would be designed for an output of 100,000 tonne/year, employing directly some 500 people. It is considered by NJZ that the prevailing fluctuations in Zn prices do not present a major obstacle in view of the long-term nature of the project. One advantage is NJZ's marketing expertise and access to world markets. This is essential in view of the relatively small proportion of annual output which could be absorbed by indigenous demand.

Major considerations still to be assessed in detail include power requirements (there does not seem to be a marked advantage for any one site from this viewpoint) and environmental constraints. Regarding the former, cheap power is not available in Eire and power costs are among the most expensive in Europe. The proposed electrolytic smelter would use 425 million kWh. There is a possibility that natural gas might be used for power generation.

The choice of the electrolytic route indicates the extent to which environmental considerations are becoming all-important. Regarding the economics of the chosen route to Zn, processing base metal concentrates into metal is capital intensive and requires major economies of scale. The New Jersey plant will cost over £60 million, but will in fact treat only $\frac{1}{3}$ of the Navan mine's Zn output.

It is widely considered that an Irish smelter is inevitable to secure the benefits of a vertically integrated industry. NJZ is expected to have about 55% control of the smelter, 25% will be Irish Government owned and the remaining 20% to zinc producers —Tara, and possibly Bula.

## 13.24 UNITED KINGDOM

The following information is borrowed from a report prepared by R.N. Crockett (1977) as a contribution to this Pb - Zn dossier :

"In 1974 the total UK consumption and production of lead was made up as follows :

| | Tons (1974) |
|---|---|
| Total consumption | 325 300 |
| Primary production from : | |
| Imported concentrate (expressed as bullion) | 29 400 |
| Imported bullion | 137 000 |
| Secondary production of : | |
| Refined lead | 140.000 |
| Remelted lead | 59 000 |

"Therefore, of a total production of 365 400 tons in 1974, approximately 54 % came from secondary smelters. Expressed as a percentage of consumption the proportion of secondary lead is probably greater.

"The relatively small UK output of lead from concentrates is confined to that produced along with zinc at the I.S.P. smelter at Avonmouth.

"The Britannia Lead Company are the only British firm to produce refined primary lead from imported bullion. The bullion is obtained from Mount Isa in Australie. The refinery of this company is situated at Northfleet, Kent.

"The Britannia Lead Company are also currently planning to move into the secondary field by building a 25 000 tpy whole-battery smelting plant adopting the Danish Bergsoe process.

"The existing British secondary lead industry currently has a collective capacity of approximately 200 000 tpy and is dominated by three companies viz :

| | |
|---|---|
| Associated Lead Manufacturers Ltd | (approx. 80 000 tpy) |
| H.J. Enthoven and Sons Ltd | (approx. 60 000 tpy) |
| Chloride Metals Ltd | (approx. 50 000 tpy). |

A number of much smaller refineries account for the balance.

Figures for production and consumption of zinc in the UK for 1974 are as follows :

| | Tons (1974) |
|---|---|
| Consumption | 353 100 |
| Primary production from : | |
|     Imported concentrate | 84 400 |
| Scrap zinc consumption in : | |
|     brass | 45 700 |
|     chemicals | 35 500 |
|     diecast alloy | 2 030 |

"Secondary material thus contributes only 24 % of the total amount. With the exclusion of scrap brass, which does not normally re-enter the zinc circuit, this proportion falls to only 11 %. Therefore by far the great part of the United Kingdom production of zinc is met by the output of the single British primary smelter at Avonmouth owned byCommonwealth Smelting Ltd. This plant makes use of the Imperial Smelting Process perfected since the Second World War. The outstanding merit of the I.S.F. technique is its acceptance of concentrates that are note only mixtures of lead and zinc but which may vary widely in grade and in the ratio of these metals present in the furnace charge.

"The limited production of secondary zinc in the United Kingdom is divided between two companies, namely Durham Chemicals Ltd and Metals and Alloys (Birmingham) Ltd.

"It is considered that any future developments in lead and zinc metallurgical techniques in the UK are likely to be related to recent research in Italy on molten salt technology the use of which might offer considerable environmental advantages over present extraction techniques. In particular the Warren Spring Laboratory of the Department of Industry has been investigating the possibility of producing electrolytic zinc from smelter dust and wastes. No electrolytic zinc is presently produced in the UK but various companies involved in copper smelting are interested in the possibilities. At present the copper smelters produce a certain amount of zinc dust which is sold for the production of oxide and chemicals".

Further details can be obtained from the bibliography, especially for the I.S.P. furnace, for which only part of the abundant literature is mentioned here.

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13.25    FRANCE

The following is translated from a report prepared by the B.R.G.M. for the present Pb - Zn dossier.

13.25.A.    PENARROYA

Penarroya's plant at Noyelles-Godault (Pas-de-Calais), is the only French smelter producing soft lead from concentrates; it is refined to 99.9960 % .

Lead smelting and refining :

Dwight-Lloyd sintering    : 2 units, total area $37.5m^2$

Water-jacket smelting furnace : cross-section at tuyere level : $8.06m^2$

Harris refining : I unit with a capacity of 135 000 tpy.

Imperial Smelting furnace and zinc refining :

Dwight-Lloyd sintering : I unit, total area $80m^2$

Imperial Smelting furnace : cross-section at lower tuyeres : $17m^2$

New Jersey columns for zinc and cadmium.

Present capacities :

| | |
|---|---|
| Lead bullion | 140 000 tpy |
| Refined lead | 135 000 tpy |
| Zinc | 130 000 tpy |
| Sulfuric acid | 150 000 tpy |
| Silver | 200 tpy |

13.25.B.    COMPAGNIE ROYALE ASTURIENNE DES MINES

The hydrometallurgical smelter at Auby-les-Douai is the most recent in France (1975).

Equipment :

Fluo-solid roasting (S = $70 m^2$; nominal capacity : 500 tpd of raw charge)

Smulders waste heat boiler (20 tph of vapor at 40 bars)

Sulfuric acid produced by double catalysis (550 tpd)

Leaching in double cycle with iron precipitation as jarosite

Current purification with zinc powder

Electrolysis with jumbo cells (2.6m$^2$ - 120 cells with 44 cathodes each)

Vieille Montagne automatic stripping (2 units = 300 tpd)

Melting and casting (Demag - 2 1800 kW furnaces)

Present capacity :

| | |
|---|---|
| Electrolytic zinc | 100 000 tpy |
| Sulfuric acid | 175 000 tpy |
| Cadmium | 145 tpy |

## 13.25.C. VIEILLE MONTAGNE

### a) Viviez plant (Aveyron)

Fluid bed roaster (41 m$^2$ - 250 tpd of raw charge)

Waste beat boiler (7 tph at 40 bars)

Sulfuric acid produced by single catalysis (250 tpd)

Common leaching

Purification with zinc powder

Electrolysis (1.3 m$^2$ - 890 cells with 28 anodes each)

Manual stripping

Melting and casting

Present capacities : electrolytic zinc    97 000 tpy

                                 sulfuric acid      160 000 tpy

                                 cadmium          100 tpy

### b) Calais plant

Roasting plant replacing the Port-de-Bouc plant

Fluid bed roaster (70 m$^2$ - 500 tpd of raw charge)

Smulders waste heat boiler (20 tph of vapor)

Sulfuric acid by double catalysis

This plant now operates at only 50 % of capacity.

## 13.25.D. POSSIBLE EVOLUTION OF FRENCH PLANTS

### a) Lead_smelting_in_the_blast_furnace

Except in the case of a technical break-through, there should be

no specific modifications in the plants using this process. It appears that progress will be only marginal.

France's capacity for lead smelting in blast furnaces is practically saturated; and since the developing countries plan to build their own smelters, larger capacities are not forecast for France.

b) Imperial Smelting furnace

Smelting in the Imperial Smelting furnace is due for new advances, technicians claim. A significant obstacle is the cost of coke in France (450 FF/t), and research work will be aimed at savings in that field. France's capacity for Imperial Smelting is not saturated. Technicians claim that Penarroya's furnace can produce more if it can be fed with oxidized charges (Waelz furnace, for instance).

c) Zinc_hydrometallurgy

1. C.R.A.M.'s plant at Auby seems to operate at 90 % of capacity. In view of the Company's expenditures on the new plant, it does not appear that it can invest in other operations in the next few years.

2. V.M.'s plant in Viviez includes a rather old section (leaching, electrolysis and cathode stripping). It would be logical that this part's technology be brought up to date; but this could represent an enormous amount of capital investment, coming in addition to the money already assigned to the wet treatment of residues. On the other hand, the Company has built a modern roasting plant (500tpd) in Calais, and it may be tempting to add an electrolysis hall. This might also mean, however, that operations would be slowed down or stopped at the Viviez plant, which in addition suffers from its geographical location (far from sea-ports and customers).

In 1973, the Viviez plant operated at 83 % of capacity.

d) Conclusions

It seems that French metallurgists in the lead and zinc field do not forecast new capital expenditures in primary extractive metallurgy during the next few years.

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## 13.26 BELGIUM, THE NETHERLANDS, LUXEMBURG

### 13.26.A. METALLURGIE-HOBOKEN-OVERPELT LEAD SMELTER IN HOBOKEN

In its Hoboken Division, M.H.O. treats (essentially on a toll basis) a wide variety of raw materials in what might be described as a lead-copper smelter but is in fact a very complex plant. It includes the following sections :

- reception, sampling and assaying of all sorts of raw materials, concentrates, slimes, flue dust, scrap and residues; this represents about 2 000 lots per year, containing such valuable metals as Ag, Au, Pt, Rh, Pd, Pb, Cu, Sb, Sn, Bi, Se, Te, etc.)

- roasting of S-rich materials in 7-hearth Wedge furnaces; $SO_2$ gases are sent to sulfuric acid plant;

- crushing, grinding and mixing;

- sintering on two Dwight-Lloyd machines 2 m wide by 35 m long, each producing 750 tpd; downdraft two-pass method; gas recycling leading to a 99 % volatilized S recovery;

- blast furnace plant, two units smelting lead charges and the third lead-copper charges; oxygen enrichment of the blast; 10-14 % coke on charge; 1100 to 1200 tpd of charge smelted to give lead bullion, matte, speiss, and discarded slag;

- lead refinery, commissionned in 1968, capable of (monthly) :

    fine lead production : 10 000 t;
    silver extraction from lead : 50 t;
    bismuth extraction from lead : 40 t;
    arsenic + tin + antimony extraction : 400 t;
    predrossing of lead at blast furnace;
    drossing to 0.1 % Cu with pitch addition only;
    softening by Harris process to selectively give first arsenic and tin and then antimony;
    decopperizing with sulfur to 0.02 % Cu;
    desilverizing by Parkes'process;
    dezincing by vacuum distillation;
    debismuthizing by Ca + Mg Betterton process;
    caustic soda treatment and casting of fine lead;

- wet plant for retreatment of Harris salts;
- precious metals plant, able to produce :

    fine silver : 150 tpm

    fine gold : 3 000 kg/m

    platinum : 1 000 kg/y

    palladium : 6 000 kg/y

One can also find a copper converting plant, a tin smelter, an antimony smelter, selenium and tellurium production facilities, and two sulfuric acid plants (60 000 tpy and 120 000 tpy, by a contact and Petersen plant, respectively).

Lead bullion yearly production amounts to 75 000 t, although refined lead production can reach 125 000 tpy.

After long years of study, calculations of smelting and refining costs and of the metal losses are now completely automated in the lead and silver plants. Computer models contain experimental parameters which are determined twice a year for costs and less often for metallurgical problems. (Lauwers, 1977).

## 13.26.B. METALLURGIE-HOBOKEN-OVERPELT ZINC SMELTER AT OVERPELT

For many years, Overpelt operated a zinc smelter based on reduction in horizontal retorts; the company has made a number of improvements to this process, especially the single face condenser. It now operates a modern electrolytic plant that includes the following units :

- Overpelt-type fluidized-bed roasting furnaces (2 units), operating on pellets of 0.6 to 4 mm diameter; grid area of 10.75 $m^2$; 20 % dust (recycled to pelletizing); the advantages claimed are :

  a) very low sulfide and sulfate content in the calcine;

  b) high specific capacity : 20-24 t of blende/$m^2$ of grid per day compared to 6.5- 7.5 for the V.M.-LURGI furnace;

  c) greater stability of the fluidized bed;

  d) more opportunities to add various materials to the feed;

e) less sensitivity to Pb, Cu, $SiO_2$, and water contents, and to particle
   size of the concentrate;

f) calcine can be stored in the open air.

However, it appears that the necessity of preliminary pelletization is a
serious drawback. Figure 13.26.1 shows the Overpelt furnace.

- leaching in four stages : neutral leach, weak acid leach, hot leach, and
  super hot leach; after thickening, the neutral solution is feed to
  purification; the hot leach solution is submitted to goethite precipi-
  tation, according to the V.M. patent procedure; super hot leach residue
  assays 25-30 % Pb and 1 000- 1500 g/t Ag, and is sent to the Hoboken
  lead smelter;

- purification in two stages : the first one is cold, and precipitates Cu
  and Cd by zinc powder : the second one is hot and cements mainly cobalt
  by the addition of zinc powder and $Sb_2O_3$ (V.M. reverse purification);

- electrolysis at 375 A/m$^2$ under 3.3 V, in a 48-hr cycle; cathodes have an
  area of 2.6 m$^2$ ; current efficiency ranges between 90 and 93 %, with an
  energy consumption of 2 900 to 3 150 kWh/t. The electrolysis solution
  contains 45-50 g/l   Zn and 175 g/l sulfuric acid.

- cathode stripping is automated according to the V.M. system; 5 632 catho-
  des are stripped each day in 2 shifts;

- melting of the cathodes in two 1 600 kW induction furnaces at 15 t/h;

- casting of 25 kg ingots in two 15 t/h straight-line machines, or direct
  manufacture of specialty alloys.

Among a number of interesting characteristics, one can note that a
Prayon filter is used for the goethite filtration; this goethite is stored
in an impervious basin, where the discharged precipitate forms the dam.

A complete description of this plant has recently been published
(Van Den Nest, 1977).

Nominal capacity of the plant is 100 000 tpy zinc and 250-400 tpy
cadmium, obtained by electrolysis of the purification cement leach solution.

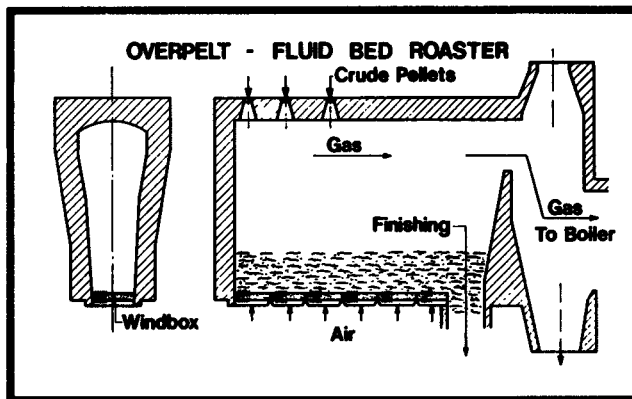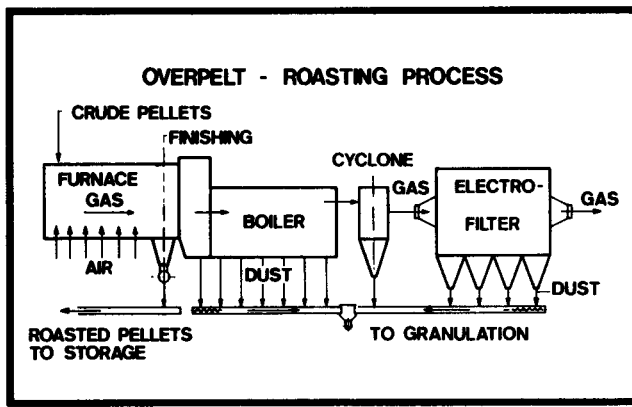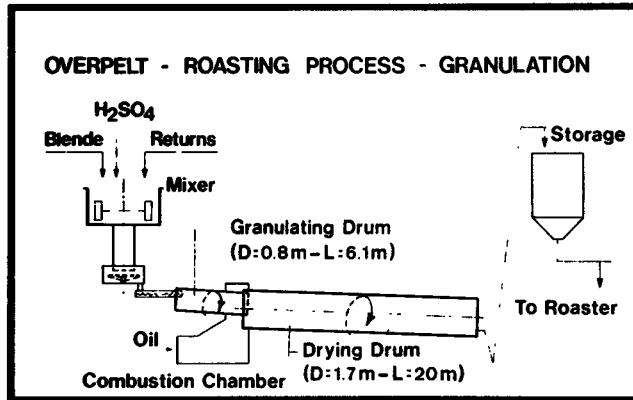Acid production amounts to 140 000 tpy.

Figure 13.26.1 Roasting furnace at Overpelt
(from CIM Bulletin, august 1977, p. 174-175)

## 13.26.C. SOCIETE DE PRAYON ZINC SMELTER

Société de Prayon operates, at Engis-Eheln ( on both sides of the Meuse river) a large chemical-metallurgical complex, including a recent electrolytic plant with a capacity of 65 000 tpy zinc. Other products are : sulfur derivatives, cadmium metal, salts, fluorated products, phosphoric acid and derivatives, and liquid and solid fertilizers.

The zinc electrolytic plant comprises :

- roasting in a V.M. -LURGI fluidized-bed reactor (80 % of the total zinc feed), and sintering on a Dwight-LLoyd machine (20 % of total zinc feed); sinter is used in the neutralization step where it dissolves better than the calcine;

- leaching in two stages : neutral and hot leach; precipitation of iron as ammonium jarosite; filtration of both residues (lead-silver and jarosite) on Prayon filters (first use of these filters in zinc hydrometallurgy);

- purification according to a reverse V.M. process (QUATPERS, 1976);

- electrolysis in a V.M. hall with 2.6. $m^2$ cathodes, with 400 $A/m^2$, and a 48-hr deposit time; automatic stripping of the cathodes;

- smelting in a 1 600 kW induction furnace with a capacity of 15 tph.

It must be stressed that Prayon is carrying out intensive research to better dispose of the jarosite.

At present, part of it is treated to produce $Fe_2O_3$; tests have been made on a lime treatment yielding a solid product "jarochaux" that can be easily stored.

Prayon also produces cadmium in its Trooz plant; the process and capacities are kept secret.

## 13.26.D. VIEILLE MONTAGNE ZINC SMELTER AT BALEN

Vieille Montagne's zinc electrolytic plant at Balen has a capacity of about 160 000 tpy; part of this capacity is from old-fashioned cellrooms, but the new automated hall now produces at least 70 000 tpy. The company

operates a number of proprietary processes, such as the V.M.-LURGI flui-
dized-bed roasting reactor, the goethite process for Iron precipitation,
the reverse continuous purification, and the automated cellroom with
mechanical cathode stripping.

Plant operations Include the following :

- fluidized-bed roasting In three 130 tpd-capacity reactors of 16 m$^2$
grate area and one 350 tpd-capacity reactor of 50 m$^2$; calcine Is pro-
duced with less than 0.25 % sulfide sulfur and about 2 % sulfate sulfur;

- waste-heat boilers, gas cleaning system, and two units producing
280 and 350 tpd sulfuric acid, respectively;

- pulping of the calcine In a mixture of spent electrolyte, cleaning solu-
tion containing MnO$_2$, and solution coming from the cement treatment; clas-
sifying at about 75 microns In a hydrocyclone, ball milling, and recycling
of the underflow;

- leaching In four steps : neutral to pH 5.1 - acid to pH 2-2.75 - hot
leach - superhot leach (100 g/l acid; 4 hours; 80°);

- treatment of the leaching residue by flotation to get first a silver con-
centrate, then a 50 % Pb lead concentrate;

- Iron precipitation by the goethite process; precipitate Is Impounded;

- continuous reverse purification; first copper-cadmium cement retreated for
copper precipitate and cadmium solution;

- electrolysis at 400 A/m$^2$, 3.3 to 3.45 V, 48 hr deposition time, 90 % cur-
rent efficiency, 3 100 - 3 250 kWh/t of zinc;

- melting In Induction furnaces consuming 110 kWh/t of cast zinc.

Other productions are 600 tpy of cadmium, 210 000 tpy of contact sul-
furic acid, and 22 500 tpy of Petersen sulfuric acid.

13.26.E. BUDELCO ZINC SMELTER AT BUDEL

The Budel electrolytic zinc smelter Is Jointly owned by Australian
Mining and Smelting Europe Ltd and Billiton N.V. Production capacities are
150 000 tpy of zinc, 500 tpy of cadmium, and 250 000 tpy of sulfuric acid.
The old horizontal retort plant was shut down In 1973.

This plant presents the following features :

- roasting in two V.M.-LURGI fluidized-bed reactors, each with a grate area of 69 m$^2$; 940°; calcine with 0.1 - 0.25 % sulfide sulfur and 2 % sulfate sulfur; grinding of the calcine in a ball mill before storage;

- two waste-heat boilers; gas cleaning system; sulfuric acid plant with double catalysis; SO$_2$ conversion efficiency of 99.5 %;

- leaching in two stages : neutral to pH 5; acid leach to dissolve 95 % of the zinc; leach residues contain lead and silver, and are discarded;

- iron precipitation as jarosite, which is impounded;

- purification by the V.M. continuous reverse process;

- electrolysis in a V.M. automatic stripping cellroom; 450 A/m$^2$ ; spent electrolyte assaying 55 g/l Zn and 195 g/l H$_2$SO$_4$ ; 40-hour cycle;

- melting of the cathodes in two 2 100 kW induction furnaces, each at 18 tph; 110 kWh/t of zinc.


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## 13.27 GERMANY

### 13.27.A. PRELIMINARY NOTE

It has been extremely difficult to get in touch with German companies; letters written to obtain permission to visit plants have been either unanswered, or answered negatively; companies have sometimes sent booklets on their plants and operations, papers on specialized subjects, and production figures.

Under these conditions, this section was based upon limited available details and a survey of several publications from 1965 on.

### 13.27.B. NORDDEUTSCHE AFFINERIE

Norddeutsche Affinerie is a lead-copper smelter that had the following production capacities in 1974 :

- copper : 370 000 tpy;
- sulfuric acid : 600 000 tpy;
- lead : 40 000 tpy;
- production of a number of metallic elements and compounds, such as precious metals, tin, nickel, bismuth, metallic powders, oxides, salts, and chemicals.

The plant is located in Hamburg, along the Elbe river.

Complex ores, by-products from this or other companies'plants, flue dust, metallic residues, old scrap, etc., are smelted in 4 shaft furnaces :

- 9.0 m$^2$ tuyere area, capacity 300-500 tpd
- 6.0 m$^2$    "       "        "      200-400 tpd
- 4.3 m$^2$    "       "        "      120-150 tpd
- 4.3 m$^2$    "       "    .

Products are lead bullion, speiss, matte and slag.

Own lead bullion, external lead bullion, old lead scrap, and other lead-containing materials are refined in a 50 000 tpy Harris-plant and, for the bismuth-rich lead, in a 8 000 tpy electrolytic plant (Emicke et al., 1971).

Principal steps of the lead refining are :

- decopperizing by liquation, dross recycled to lead smelter;
- tellurium extraction by NaOH;
- arsenic and tin extraction by NaOH + NaNO$_3$;
- antimony extraction by NaOH + NaNO$_3$;
- final decopperizing by sulfur, dross being recycled before the refining;
- desilverizing by the Parkes process;
- dezincing by vacuum distillation;
- depending on the bismuth content, debismuthizing by the Ca-Mg process
  or by electrorefining;
- final refining by NaOH + NaNO$_3$ ;
- casting of 50 kg ingots on an automatic machine.

Lead electrorefining is carried out in a fluosilicic electrolyte, at 160 A/m$^2$ and 0.4 - 0.6 V, for 6 days.

Antimony is recovered and sold as NaSb(OH)$_6$. Calcium stannate is sent to the tin plant. Tellurium is recovered as impure slimes. Precious metals are separeted by cupellation, then refined by electrolysis. Bismuth is obtained from the fused-salt electrorefining of anodic slimes.

13.27.C. PREUSSAG AG METALL SMELTERS IN GOSLAR AREA

The company supplied the following information :
"Preussag AG Metall is operating a smelting plant of its own, Hüttenwerk Harz,situated in Goslar-Oker; it is the sole property of Preussag; it has a pyrometallurgical zinc plant with an annual capacity of 100 000 tpy of zinc, as well as a lead smelting plant with an annual capacity of 40 000 tpy of lead.

"Production figures for 1976 were as follows :

      60 000 t of zinc
      31 000 t of lead

The principal by-products obtained in our plants are sulfuric acid, silver bullion, mercury and cadmium.

"Raw material supply is based :

- for lead production, exclusively on scrap;
- for zinc production, approximately 70 % on zinc concentrates and
  30 % on scrap and residues.

"Our smelting works are constantly kept on the latest technical level, no process modification or increase of capacity is intended for the time being".

It is also known that zinc smelting is done in a vertical retort plant after roasting on a Dwight-Lloyd machine; zinc metal production in 1968 was 46 500 t of zinc with a purity of less than 99.99 % and 14 700 t of purer zinc.

Lead smelting is conventional after Dwight-Lloyd sintering. ( HATCH et al., 1970).

### 13.27.D.  PREUSSAG-BOLIDEN-BLEI GmbH LEAD SMELTER

Preussag-Boliden-Blei GmbH is a 50-50 association of the two companies which operates a lead smelter at Nordenham, near Bremen. Plant capacity is 120 000 tpy of lead; with the zinc plant on the same location, there is a production of 240 000 tpy of sulfuric acid.

The company reported that 1976 production attained 111 000 t of lead working two thirds on lead concentrates, more than 20 % on work lead, and less than 10 % on scrap.

A world survey (HATCH et al., 1970) indicated that this plant was first operated in 1959; D.L. sintering is by a downdraft process, and gives 30 000 tpy of 100 % sulfuric acid; lead furnace slag is not treated; refining is by pyrometallurgical process, giving silver bullion and copper matte.

### 13.27.E.  PREUSSAG-WESER-ZINK GmbH ZINC SMELTER

Preussag-Weser-Zink GmbH is a 75 % Preussag - 25 % Penarroya partnership operating a zinc electrowinning plant at Nordenham. Plant capacity is 120 000 tpy of zinc.

Zinc is produced from imported concentrates; ships can unload directly at plant pier. Concentrates are stored under cover in amount corresponding to 3 months'production.

From storage the concentrates are automatically transported to the fluidized-bed roasting. The furnace has a roasting area of 90 m$^2$ (V.M.-LURGI process), and operates at I 000° with a 2m-high bed. Gas is cleaned and transformed into sulfuric acid in a double catalysis plant.

Leaching is carried out by the jarosite process.

Electrowinning is operated for 24 hours, and deposited zinc is stripped manually.

Melting is performed in two induction furnaces, and casting in two wheels producing 27.5 kg ingots.

## 13.27.F. RUHR-ZINK GmbH ZINC SMELTER

Ruhr-Zink GmbH is a wholly-owned subsidiary of Metallgesellschaft which has been operating a zinc electrolytic plant in Datteln since 1968.

Production capacities of the initial plant (since then enlarged) were 110 000 tpy of zinc, 700 tpy of cadmium, and 250 000 tpy of sulfuric acid.

The original plant included :

- roasting in two fluidized-bed V.M.-LURGI reactors of 55 m$^2$ each; gases were cleaned and transformed into sulfuric acid by a double-catalysis process to produce 165 000 tpy 96 % acid;

- batchwise leaching in a single hot neutral step; washing of the residue in 3 counter-current thickeners; filtering and drying of the residue for easy shipping;

- two-stage purification by the classical process;

- electrolysis at 600 - 750 A/m$^2$ for 24 hours; 91 % current efficiency; electrolyte temperature : 39-40°; energy consumption averaging 3 240 kWh/t;

- melting of the manually-stripped cathodes in a 1 800 kW induction furnace, using 105 kWh/t.

Since then, the company has initiated a new leaching process using a hot acid treatment of the residues, and iron precipitation by the jarosite process as modified by Ruhr-Zink itself.

In 1975 a new 35 000 tpy-capacity cellroom was put into service; new cathodes have a surface area of 2 $m^2$ (instead of 1.2 $m^2$ for the old ones); they are mechanically stripped on a Mitsui machine; current density is much lower, at 450 A/$m^2$.

The new unit's energy consumption has been lowered to 3 100 kWh/t.

13.27.G. "BERZELIUS" METALLHUETTEN GmbH ZINC AND LEAD SMELTERS

"Berzelius" Metallhütten GmbH is a wholly-owned subsidiary of Metallgesellschaft AG which operates a zinc-lead I.S.P. smelter in Duisburg-Wanheim, a lead smelter in Binsfeldhammer (Stolberg), and a lead refinery in Braubach (Koblenz).

In Duisburg, the Imperial Smelting Furnace plant includes :

- decopperized lead production capacity : 32 000 tpy
- total zinc production capacity : 85 000 tpy
- D.L. updraft sintering machine, LURGI system, 75 $m^2$
- sulfuric acid unit, LURGI system, double catalysis, 11 000 tpm
- hot briquetting for oxidized secondary materials, 60 000 tpy capacity
- I.S.P. standard furnace, 16,7 $m^2$
- zinc refinery, New Jersey system, 35 000 tpy capacity
- cadmium leaching (Cd content : 250 tpy)
- copper electrolysis : 1 800 tpy of cathodes
- Wälz furnace for low-grade materials, 80 000 tpy capacity

The lead smelter at Binsfeldhammer includes :

- total lead production capacity : 90 000 tpy
- sintering on a D.L. machine, LURGI system, 28.5 $m^2$

- sulfuric acid production in a contact unit, LURGI system, 110 tpd of 95 % acid

- two smelting furnaces, respective area at tuyere level : 10 m$^2$ and 7 m$^2$; capacity : 4.5 - 5.0 tp$\phi$ coke per m$^2$ of surface area at tuyere level

- decopperizing by Colcord process

- discontinuous antimony extraction in a refining furnace

- desilverizing by Parkes process

- dezincing by vacuum distillation

- debismuthizing by the Kroll-Betterton process

- two rotary reverberatory furnaces for the treatment of secondary mate-tials and by-products

- beneficiation plant for battery scraps, Stolberg Process, capacity of 150 t/shift.

The lead smelter at Braubach includes :

- total lead production capacity : 60 000 tpy

- four short rotary furnaces, 4 m long and 3 m in diameter, with gas cooling and cleaning

- decopperizing by Colcord process

- arsenic and antimony extraction in a continuous refining furnace

- desilverizing by Parkes process

- dezincing by vacuum distillation and the Penarroya process

- debismuthizing by the Kroll-Betterton process

- 1 straight-line casting machine, 25 tph capacity

- 2 lead presses.


13.27.H. DUISBURGER KUPFERHUETTE ZINC PRODUCTION


Duisburger Kupferhütte is a company specialized in the retreatment of pyrite cinders. Its shareholders are : BASF AG 31.445 %, Bayer AG 31.445 %, Hoechst AG 31.445 %, Gebr. Giulini GmbH 4.400 %, and Henkel & Cie GmbH 1.265 %.

The company does not produce any lead, but its capacity for zinc is 60 000 tpy(32 000 tpy technical grade ZnO, 10 000 tpy ZnSO$_4$ solution and 18 000 tpy Zn metal; all figures are given in zinc metal).

Pyrite cinders are roasted with the addition of sodium chloride, then leached to give a solution containing most of the non-ferrous metals. Treatment of that solution precipitates zinc hydroxide, which is calcined in a rotary furnace; the granules obtained are rich in zinc and low in gangue components.

These granules have been treated in a three-phases electrothermic furnace since 1961. The furnace is entirely closed; the gases produced flow through a splash condenser that recovers 90 % of the zinc vapor, the remaining 10 % being dust. Carbon electrodes dip into the slag containing 40 % $SiO_2$, 28 % CaO and under 1.5 % FeO, at a temperature of about 1 340°. Zinc ingots have a 99.96 % purity.

The charge, preheated to 300 °, is composed of 50 t of granules, 8 t of coke, and 6 t of other additions per day; it is fed to a resistance furnace 6 m in diameter. Production is 30 tpd of zinc, using 2 900 kWh/t.

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13.28  ITALY

The following is translated from a report prepared by our Italian partners for the present Pb-Zn dossier.

13.28.A.  AMMI S.P.A. - ELECTROLYTIC ZINC SMELTER AT PONTE NOSSA (BERGAMO)

a) Processes

The plant feed is integrated : high grade zinc sulfide concentrates, calcined calamine, low grade crude calamine. Calamine represents 40 % of the total feed.

Zinc ores are processed as follows :

- Blende desulphurization is carried out in a fluo-solid bed reactor, (capacity of 120 tpd of feed) with heat recovery and sulphuric acid production. The mixture formed by calcined calamine, crude calamine, partly desulphurized products and oxidized materials from recycling (galvanizing ashes) are roasted in a multiple hearth furnace in such a way as to completely remove chlorine and fluorine.

- Two-stage leaching : neutral and acid. Residues do not undergo hot leaching and are dumped as is. Their re-use for hot acid leaching by the jarosite or goethite process is greatly limited by the difficulties of storing the residues from these processes.

- Cold purification

- Medium current density electrolysis

- Cathode melting and production of 99.995 - 99.95 - 99.50 grade zinc slabs and Jumbo ingots.

b) Current status and trends in plant

As stated above, plant feed is of an integrated type. The total feed accounts for approx. 70 000 tpy of materials. The overall metal recovery is 98 %.    Capacity : 35 000 tpy of zinc cathodes.

Semi-manufactures products :

| | |
|---|---|
| zinc dust | 6 300 tpy |
| zinc oxides | 5 000 tpy |

c) Uses_of_by-products

Cadmium Is recovered In the form of cement and transported to the Porto Marghera plant for electrolytic cadmium production.

Yearly production of sulfuric acid : 31 000 tons.

13.28.B. AMMI S.p.A. - ELECTROLYTIC ZINC SMELTER AT PORTE MARGHERA (VENEZIA)

a) Processes

Zinc ores are processed by conventional methods as follows :

- Blende desulphurization Is carried out In a fluo-solid bed reactor, with a capacity of 230 tons per day of feed, heat recovery and sulphuric acid production.

- Two-stage leaching : neutral and acid. Residues do not undergo hot acid leaching. Residues are characterized by a 15-17 % zinc content. These residues can neither be dumped because of space limitations nor dischar- ged Into the sea because of pollution problems; they are transferred to the AMMI Sarda plant at Porto Vesme In order to be treated at the Waelz plant.

- Cold purification

- Medium-high current density electrolysis

- Cathode melting and production of 99.995 - 99.95 - 99.50 grade zinc slabs and Jumbo Ingots.

b) Current_status_and_trends_In_plant

The plant feed consists of approx. 90 000 tpy of blende. The overall metal recovery Is approx. 87 %. Plant capacity Is 45 000 tpy zinc cathodes.

Semi-manufactured products are :

| | |
|---|---|
| die-casting alloys | 40 - 45 000 tpy |
| KAYEM and ILZRO alloys | 800 tpy |
| wire | 800 - 1 000 tpy |
| rolled products | 6 - 7 000 tpy |

c) Uses_of_by-products

Cadmium bearing by-products, Integrated with those deriving from AMMI

plant at Ponte Nossa, are processed at Porto Marghera plant and converted
into electrolytic cadmium. Plant production capacity is :

  300 tpy of cadmium
 62 000 tpy of sulphuric acid.


13.28.C. AMMI S.p.A. - LEAD SMELTER AND REFINERY AT SAN GAVINO (CAGLIARI)

   a) Processes

The plant has three sections :

 1) Lead bullion production .
  Lead ore agglomeration is carried out in three downdraft sinte-
  ring machines. $SO_2$ gases are diluted and dispersed directly into
  the atmosphere. The main feed to the sintering machine consists
  of : domestic and imported high grade lead ores, low grade ores and
  low lead and high bismuth content, such as Boliden fumes. The
  production of primary antimonial lead is obtained by feeding the
  sintering machine with silver-free and bismuth-free lead ores as
  well as antimonial drosses from primary antimony smelting.

  Total capacity expressed as lead bullion : 30 000 tpy

  Overall metal recovery : 93 - 95 %.

  Blast furnace slags contain 1 - 2 % lead, 10-13 % zinc, and are
  treated at the Waelz plant of Porte Vesme. They are mixed with lead
  and zinc oxidized materials to modify the gangue characteristics.
  The oxides recovered are credited to San Gavino smelter, thus
  consistently increasing the overall metal recovery indicated above.

 2) Lead bullion refining.
  Refining is carried out in two separate plants :

  A) Electrolytic refining : fluosilicate electrolyte
       capacity : 30 000 tpy
  B) Conventional refining process
       capacity : 50 000 tpy (may increase).


 3) Semi-manufactured products.
  Shots are produced by pressing methods; section capacity is
  9 000 tpy (7 000 tpy standard shots,1 000 tpy nickel-plated shots,
  and 1 000 tpy microshots).

b) Uses of by-products

Copper drosses obtained In the decopperizing step of lead bullion are converted Into matte and speiss. This Is done In a short rotary furnace, and products are processed at Hoboken plant In Belgium. A plant for copper recovery by hydrometallurgy Is under study.

In this plant bismuth and silver are recovered by conventional methods In amounts depending on the feed.

13.28.D. AMMI SARDA S.p.A. - IMPERIAL SMELTING SMELTER AT PORTO VESME
(CAGLIARI)

a) Processes

The smelter consists of the following sections :

I) Waelz plant.
As Is well known, the purpose of the Waelz process Is to drive off zinc, lead, and other easily volatilized metals and to concentrate them as a fume.

The plant has been designed mainly for the concentration of zinc from low-grade oxidized materials. Actually, the Waelz plant Is used to treat the following materials generally mixed according to suitable ratios :

- run of mine;
- pre-concentrates by heavy-media separator (dynamic);
  desliming products from ore dressing;
- residues from zinc and lead ore smelting (leach residues from electrolytic zinc plant and slag from lead blast furnace).

This section Includes the following plants : ore crushing and mixing; two rotary kilns, each with a capacity of 500 tpd of feed with variable lead and zinc contents. The metal content in the fume Is 50-60 % zinc, 10-14 % lead and an extremely variable cadmium content.

The overall metal recovery Is 92 % or more for zinc and 95 % or more for for lead.

Slags from the Waelz kiln have an average metal content of I % zinc and 0.1 % lead; they are dumped.

Briquetting plant : some of the fumes are hot briquetted and fed directly to an IS furnace.

2) Imperial Smelting plant.

This section includes the following plants :

- agglomeration and sulphuric acid : The plant consists of the storage and handling of new materials; mixing and conditioning; 70 sq.mt. updraft sintering machine for burning approx. 130 tpd of sulphur; and a 400 tpd-capacity plant for converting $SO_2$ gases to sulphuric acid.

  The feed to the sinter plant consists of zinc ores, mixed ores, lead ores, Waelz fumes and sinter returns. Sinter analysis :zinc = 40-44 %; lead = 20-22 %; S total less than 1 %.

- IS furnace : This plant includes coke pre-heating, air pre-heating, mixing and charging. The shaft furnace has a standard section with only one condenser and melted lead cooling by means of immersible coolers. The 98.5- grade zinc is cast into slabs or jumbo ingots, the latter for sale or zinc refining. The lead bullion is cast into ingots and transported to AMMI's plant at San Gavino for refining.

3) Zinc refining.

Zinc refining by the New Jersey process, as modified by Mechim, uses 4 lead columns, 2 cadmium columns and 1 reboiler. The lead columns are fed by molten zinc, or jumbo ingots when necessary. The refined zinc's grade is 99.995.

All problems concerning gaseous and liquid effluents are under control.

b) Current status and trends in plants

The feed of the IS plant consists of high-grade lead, zinc, and bulk concentrates produced in Sardinia; Waelz fumes; lead and zinc high grade ores, and mixed sulphides. Waelz fumes make up for 30 % of the feed;they are fed partly to sintering and partly directly to an IS furnace after briquetting. Mixed ores represent a low percentage. The total feed to the plant exceeds 200 000 tpy.

The IS process'overall metal recovery is nearly 90-92 % lead and zinc.
IS furnace slags contain approx. 6-7 % zinc and 1.2 - 1.3 % lead. Slags are dumped. With the present-day technology the processing of slag for zinc and lead recovery is not convenient.

ISF plant capacity :

| | |
|---|---|
| 98.5 grade zinc | 70 000 tpy |
| refined zinc | 40 000 tpy |
| lead bullion | 30-32 000 tpy. |

c) Uses of by-products

Production capacity of sulphuric acid accounts for 120 000 tpy.Cadmium is recovered from the fumes of the sinter plant and from a cadmium-zinc alloy in the refining plant. Cadmium contained in the dusts is leached and subsequently cemented in a form which can be melted to commercial quality.
Approximate cadmium production : 200 tpy.
The recovery of silver, bismuth and copper takes place during a lead bullion refining process carried out at AMMI's San Gavino plant.

13.28.E.  PERTUSOLA S.p.A. - ELECTROLYTIC ZINC SMELTER AT CROTONE (CATANZARO)

a) Processes

The smelter has two sections :

I) Electrolytic zinc plant

Zinc ores are processed by conventional method as follows :

- Blende desulphurization is carried out in a fluo-solid bed reactor, with a capacity of 700 tpd of feed,heat recovery and sulphuric acid production.

- Two-stage leaching(neutral and acid) of desulphurized blende and oxide from the second section. Residues do not undergo hot acid leaching.

- Hot purification.

- Medium current density electrolysis.

- Cathode melting and production of 99.995 - 99.99 - 99.95 grade zinc slabs and Jumbo Ingots.

## 2) Residue fuming plant

Residues from the first section mixed in different proportions with stored residues from previous treatment as well as other oxidized materials from recycling (galvanizing ashes), are treated in a "Cubilot" type furnace for the recovery of zinc, lead, and germanium. This section includes the following steps:

- Drying
- Briquetting
- Fuming in "Cubilot" type furnace.

Capacity : 10 000 tpy of zinc contained in the fumes.
Duration of stored residues : 8-15 years, according to the Company's plans.

## b) Current status and trends in plants

As stated above, the plant feed is of an integrated type : sulphides and oxidized materials. Ore requirement consist of 170 000 tpy as blende. Overall metal recovery exceeds 97 %. Plant capacity is 90 000 tpy zinc cathodes.

Semi-manufactured products :

Die casting alloy (ZALMAC)   10 000 tpy.

## c) Uses of by-products

Cadmium bearing by-products are processed and converted into electrolytic cadmium. Lead is recovered as sulphate and sent to lead smelting. Germanium is recovered as concentrates with 30 % germanium content. Sulphur in the blende is converted to sulphuric acid. Silver and copper are recovered in the "Cubilot" matte.

By-product capacity :

| | |
|---|---|
| Cd | 400 tpy |
| Pb | 5 000 tpy (Pb contained in $PbSO_4$) |
| Ge | 20 tpy (in concentrates) |
| $H_2SO_4$ | 180 000 tpy. |

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## 13.29 GENERAL CONCLUSIONS FOR METALLURGY

### 13.29.A. LEAD PRODUCTION

In the E.E.C. countries, primary lead capacity (about 700 000 t/y) is divided into two types of plants : the blast furnace, where lead bullion is the principal product (50 % of capacity), and the Imperial Smelting furnace (I.S.P.), where lead bullion is co-produced with zinc (20 % of capacity).

Four I.S.P. furnaces exist in these countries : Avonmouth in the U.K. (Commonwealth Smelting Ltd), Berzelius Metallhütten in Duisburg-Wanheim, Germany (Metallgesellschaft), Noyelles-Godault in France (Penarroya), and Porto Vesme in Sardinia, Italy (AMMI Sarda). The application of this new type of furnace will be discussed more thoroughly under Zinc Production (13.29.B).

Most of the lead production comes from the blast furnace, a very versatile tool that can accept varying charges with good metallurgical results. European furnace practice is by no means different from standard practice, but one can observe the use of oxygen-enriched and/or preheated blast to improve the furnace's energy performance.

Many plants are fed with combined charges, sulfide and oxide ores being mixed before or after roasting; they are sometimes combined with a significant proportion of scraps and/or wastes (such as used batteries).

In any case, lead bullion is always very impure and must undergo thorough refining, in which many by-products of high value are recovered.

In the E.E.C. countries, lead refining is mainly accomplished by the Harris process, the most convenient for medium-capacity plants. It is very versatile when several different impurities must be eliminated and recovered as saleable materials and metals. A small refining capacity exits in electrorefining plants (8 000 t/y at Norddeutsche Affinerie for bismuth-rich bullion and 30 000 t/y at San Gavino of AMMI). Lead refining has been described in detail for some of the plants, such ad Hoboken in Belgium, Penarroya in France, and Norddeutsche Affinerie in Germany.

It must be emphasized here that the first and the last plants are combined lead-copper smelters,and that they specialize in the treatment of very complex charges whose smelting may require a computerized search for the best economic conditions. Such a program has been developed by Hoboken personnal.

For excellent surveys on lead sintering and blast furnace smelting, one may consult papers published in Erzmetall (Paschen, 1969 - 1970 - 1971 - 1973).

## 13.29.B. ZINC PRODUCTION

In the E.E.C. countries, primary zinc production is mainly obtained in electrolytic plants, with an installed capacity of 1 070 000 t/y.

I.S.P. capacity in comparison is 380 000 t/y; electrothermic furnace production is about 20 000 t/y (DKH, in Duisburg); and vertical retort production is 100 000 t/y (Oker, Harz).

Most electrolytic plants are rather new; they incorporate, to some extent, wet treatment of residues and/or automatic stripping of the cathodes. The characteristics of these modern plants have been recently described (Meisel, 1974); It must be observed that none of the three Italian smelters uses wet treatment of leach residues.

In the other plants, retreatment of the residues is mainly carried out by the Jarosite process; the two Vieille Montagne (V.M.) plants (Viviez and Balen) and the Overpelt plant, however use the V.M. goethite process.

For the roasting stage, most of the plants are equipped with a fluidized-bed roaster of the V.M. - Lurgi Type. Overpelt still uses its own type of fluidized-bed roaster, treating a pelletized charge, while Prayon feeds part of the process with sinter coming from Dwight-Lloyd sintering machine.

Purification is carried out in one of two procedures : the oldest

one operates batch-wise with the addition of $As_2O_3$ to precipitate the
cobalt in the second step; the newest one (developed by V.M.) is conti-
nuous, with addition of antimony to precipitate the cobalt by a system
called "reverse purification".

Current density in electrolysis is applied within narrow limits :
the present average is 400-600 $A/m^2$. Stripping of the aluminium cathodes
is still manual in a few plants; Dattein, however, uses the Mitsui mecha-
nical stripping process, Porto Marghera has its own process; and the
most wide spread one is the V.M. fully automatic electrolytic cell room.

Although surface area per cathode is on the order of 1 $m^2$ for ma-
nual stripping, it was increased to 1.7 $m^2$ in the Mitsui process and to
2.6 $m^2$ in the V.M. hall; it seems that V.M. is designing an electrolytic
hall with 3.2 $m^2$ cathodes.

Melting of the stripped cathodes is mostly performed in low fre-
quency induction furnaces. There are four I.S.P. furnaces in E.E.C. coun-
tries. The Avonmouth furnace is the only one remaining of the three built
on that site; it is the largest one, with a 27.3 $m^2$ cross-section area
(instead of the standard 17.2 $m^2$).

There appear to be no particular treatment characteristics in the
charge of a variety of scraps, drosses, oxides, etc.

The large capacity of zinc and lead production in the I.S.P. is sup-
ported by a number of advantages claimed for this process :

a) treatment of mixed or separate lead and zinc concentrates (either
   sulfides or oxides), and secondary materials (other than metal
   scraps); I.S.P. smelting is particulary appropriate for custom
   smelting;

b) recycling of materials produced by smelting : galvanisers' dros-
   ses, electrolytic zinc plant residues, Waelz oxides, and even
   steel plant dusts;

c) potential for energy conservation : energy use is slightly less
   than in electrolytic plants, with lead production as a bonus;

d) adaptation to environmental and emission standards; note that the
   only solid waste product is inert slag.

One must also mention the vertical retort zinc producing unit in Oker
and the D.K.H.'s particular electrothermic furnace.

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## CHAPTER 13.3 BY-PRODUCTS UTILIZATION

### 13.31 INTRODUCTION

Sphalerite and galena concentrates and recovered scraps, wastes and residues treated for zinc and lead contain a number of other elements. As both metals are produced at a high purity, all the other elements are found in residues or by-products after the metallurgical treatment.

Some components like gangue elements (silica, alumina, iron oxides, calcium and magnesium oxides, etc.) have no commercial value, except when gathered in compact or granulated form; in that case they can be used as road bottom or embankment, sea-walls or sand-blasting.

Other elements such as sulfur and arsenic present a poisonous hazard; sulfur transformed in $SO_2$ during roasting must necessarily be treated; arsenic must be converted into a harmless compound or stored in impervious containers.

Elements like cadmium, copper and precious metals are practically always valorized.

Some elements such as tin, bismuth and antimony are often valorized in lead metallurgy, but rarely in zinc metallurgy, and other ones like mercury are rarely valorized in either metallurgy.

There is a market for many of these elements, however, but their low average content in the charges does not justify the relatively high cost of valorization.

This could be different if the charges were treated separately by campaigns according to their various metal contents. But this process induces, in the production circuits, heterogeneities and modifications that cannot be justified economically.

### 13.32 SULFUR

Commercial forms of sulfur are distributed as follows :
$H_2SO_4$ : 90 %
$CS_2$ : 3 %

$SO_2$     :      3 %

Elemental S  :   4 %.

Most of the sulfur contained in sphalerite and galena is turned into $SO_2$ gas during roasting. $SO_2$ content of these gases (4 to 8 %) allows only the production of sulfuric acid. The old Petersen process, which had a very high efficiency, is less and less used for acid manufacturing; presently this production is carried out by catalysis on $V_2O_5$. Rich gases (6-8 %) are treated by double catalysis, which has an efficiency of 99.3-99.5 %, and poor gases (4-5 %) are treated by single catalysis, which has a 98.5 % efficiency.

A low $SO_2$ emission in the stack gases is unavoidable, and it increases when the facilities are started and stopped.

Other pyrometallurgical operations give rise to low $SO_2$ evolutions in gases much too diluted for economical recovery. In its Viviez plant, "Vieille Montagne" have developed an absorption system with lime treatment that has an efficiency over 90 %. In these conditions, stack gases are practically free from $SO_2$.

Another relatively important fraction of the sulfur from the ores appears as $CaSO_4$ after lime treatment of different effluents like washings of electro-filters, drains containing $H_2SO_4$, anode cleaning waters, etc. Calcium sulfate results in slimes which are rich in various impurities, and its transformation into commercial gypsum is not yet economical, although research is developping.

Sulfur remaining in the ores and concentrates is going into the slags and wastes in a form which cannot be valorized but is no more noxious.

13.33 CADMIUM

Cadmium is a by-product of zinc metallurgy, and to a much lesser degree, from lead metallurgy; no ore is treated only for cadmium, but the metal is practically always valorized in the ores and concentrates which contain it.

In the plants that operate a sintering on a Dwight-Lloyd roasting machine

(lead smelters, I.S.P. smelters and some zinc hydrometallurgical plants), part of the cadmium is going into the roasting dusts, recovered on the D.L. grate, in the washing towers or in the electro-filters slimes.

In the I.S.P. plants, cadmium is also recovered during the refining in the New Jersey distilling columns.

When zinc is produced hydrometallurgically, most of the cadmium is cemented with zinc powder when the electrolytic solution is purified.

Cadmium metal is obtained at a high degree of purity : 99.999 %; it is produced either by thermal processing (distillation followed by caustic melting), or by electrolysis.

Recovery of cadmium is around 85 - 90 %.

## 13.34 FREQUENTLY VALORIZED METALS

### 13.34.A. COPPER

In lead pyrometallurgy, most of the copper passes into the lead bullion, except in plants treating lead-copper mixed ores (Hoboken, Hamburg) and producing rich mattes in the smelting furnace. These two plants themselves convert the produced mattes. The other plants collect copper in drosses during lead purifying. These drosses and the little amount of matte produced in the smelting furnace are sweated to extract lead and enriched to 25-45 % copper, then they are sold.

In the I.S.P. furnace, mattes assaying 45 % Cu are obtained directly.

In zinc hydrometallurgy, plants which are still retreating the leach residues in cubilot furnaces likewise produce mattes with 10 % Cu. This copper comes from purification cements. The plants using jarosite or goethite processes retreat the cements by leaching to get slimes containing 65 % copper.

Copper recovery is generally around 80 %, except in plants treating copper-rich concentrates, where recovery can be higher.

## 13.34.B. PRECIOUS METALS

In lead metallurgy, precious metals are collected in the lead bullion, and are removed as triple alloy by zinc addition during refining. Zinc is volatilized from the triple alloy by vacuum distilling, lead is oxidized and skimmed in the cupellation furnace and precious metals form the "Dore" metal. Some plants are treating the Dore by themselves and produce different metals like silver, gold, platinum, palladium, osmium, etc. Recovery of these metals is very high, around 99 %. The extraction process is similar in the I.S.P. plants.

In zinc hydrometallurgy, precious metals are collected in the leach residue; their amount is much smaller than in lead metallurgy. When the plants are treating the leach residues by fuming in a cubilot furnace, precious metals are concentrated in the matte and valorized with the copper. In the plants using jarosite or goethite processes, the rich in lead leach residue is more and more retreated to remove the silver by flotation, or to get, through hydrometallurgy, a product which is enriched in lead and silver.

## 13.35 METALS VALORIZED IN LEAD METALLURGY

## 13.35.A. TIN

In lead metallurgy, the major part of tin is collected in the lead bullion from which it is extracted during dulcification, namely as stannate when the Harris process is used. The treatment of tin drosses gives a concentrate assaying around 40 % tin valorized in tin metallurgy.

In zinc hydrometallurgy, tin is removed in the leach residue and is not valorized.

## 13.35.B. ANTIMONY

As tin, antimony is removed from the lead bullion as antimonate and is valorized in the production of antimony metal.

` In zinc hydrometallurgy, it is likewise collected in the leach residue

and Is not valorized.


## 13.35.C. BISMUTH


Bismuth can be valorized only from some lead ores relatively rich in this metal and which are treated by campaigns.


Bismuth Is collected In the lead bullion, from which It can be removed in drosses with Ca and Mg, or In electrorefining anodic slimes.


Drosses and slimes are enriched In bismuth and sold to specialized refineries.


Zinc ores are generally very poor In bismuth, which Is found In the leach residue.


## 13.36 ARSENIC


Arsenic Is nearly always present In zinc and lead ores, and It sets a number of problems due to the toxicity of some of Its compounds. Moreover, when It Is present In acidic solutions, metallic zinc or cadmium additions can cause the evolution of very toxic arsenamine.


Arsenic Is little volatilized during roasting. The low proportion going Into gases Is neutralized by lime addition to the electro-filters wash waters; arsenic In the dusts Is recycled.


In lead metallurgy, part of the arsenic Is sometimes collected In a speiss dissolved In the lead bullion; speiss can be treated by distillation to produce arsenic economically.


The remaining arsenic Is collected In the lead bullion, removed by dulcification and transformed Into calcium arsenate.


In zinc hydrometallurgy, arsenic Is going Into the leach residue, and namely In jarosite or goethite precipitates (80 to 85 %).


Although calcium arsenate and mainly ferric arsenate are practically

insoluble, these compounds must be stored In Impervious tanks or ponds. As these compounds are not allowed to be used as agricultural phyto-products, recovering them Is uneconomical. However, research Is pursued to neutralize most of the effects of arsenic, as In tne "Jarochaux" process proposed by "Societe de Prayon"; they have It enter the most Insoluble compounds.

## 13.37 RARE METALS

### 13.37.A. GERMANIUM

Germanium Is a by-product of zinc metallurgy, and Its average content In sphalerites Is around 50 g/t.

It Is recovered In oxidized form In the roasting dusts, In the leach residue (from which It can be leached Itself) and In some condensed zinc liquids from refining columns.

Germanium can be recovered by dry processes (sublimation-roasting) or preferably by wet processes. Germanium concentrates are leached by hydrochloric acid to yield germanium chloride, which Is distilled, condensed and hydrolysed to germanium oxide. This oxide Is reduced by hydrogen, and the germanium Ingot Is refined by zone melting.

Germanium-marketing has slumped since other new semi-conductors have appeared, and only a few plants still recover germanium. Presently some germanium Is tapped from a zinc fraction produced In the New Jersey refining columns.

In hydrometallurgy, germanium Is going Into the Jarosite or goethite residues and Is no more recovered.

### 13.37.B. THALLIUM

Likewise thallium Is a by-product of zinc metallurgy. It Is collected In the copper-cadmium cements produced during zinc solution purification. It can be precipitated by hydrogen sulfide and separated from cadmium; then thallium sulfide Is leached with sulfuric acid and thallium metal Is recovered by electrolysis.

Thallium-marketing has slumped since its use as rat poison is prohibited. Very few plants are still recovering this metal.

### 13.37.C. INDIUM

Likewise, indium is a by-product of zinc metallurgy; some zinc blendes contain around 100 g/t In.

In pyrometallurgy, it is found in condenser dusts or in the lead residue of the refining columns.

In hydrometallurgy, it is going into the leach residue.

Like germanium and thallium, the indium-marketing has largely slumped since its use in electronics is neglected; very few plants are still recovering indium.

### 13.37.D. GALLIUM

Gallium is a by-product of aluminium and zinc industries. It is used in electronics and consumption is increasing.

Its content in zinc concentrates is very low, 10 to 30 g/t.

Gallium goes with germanium from which it is separated by chloride distilling. It is then electrolysed in alcaline solution.

Very few plants recover gallium.

### 13.37.E. MERCURY

Lead and zinc concentrates often contain a little mercury, around 50 g/t generally.

About 97 % of mercury is volatilized during roasting; that fraction of the metal is recovered in part as HgS or as mercury selenide in the wash waters of wet electro-filters, and partly in sulfuric acid

(average content : I to 4 g/m$^3$) where it constitutes a noxious impurity for some uses.

Few plants are recovering mercury; it frequently happens that metal-lurgical plants reject ores and concentrates which are relatively rich in mercury.

However, there are already some processes in order to valorize mercury collected in wash waters and even in sulfuric acid, and research is actively pushed in this field. This is why some plants filter the wash waters before lime neutralization and store the precipitate in impervious tanks, expecting a solution to this problem.


13.37.F. SELENIUM

Most of the selenium is recovered from anodic slimes produced in the copper electrorefining, but some zinc and lead concentrates contain a little selenium, around 50 g/t.

Selenium has a number of uses : pigments - glass manufacture - pho-tocopying - electronics - alloys - poultry feeding, and market prospects are good.

During roasting, selenium is volatilized like mercury and it can be recovered as oxide or as mercury selenide in the wash waters of wet electro-filters. Its valorization could then be parallel to that of mercury.


13.37.G. NICKEL AND COBALT

Lead concentrates generally contain very little cobalt, but some-what more nickel, the major part of which is collected in the speiss skim-med from the lead bullion, or produced when retreating copper mattes and drosses. Nickel is then recovered mainly as nickel sulfate.

On the contrary, zinc concentrates often contain more cobalt (0 to 100 g/t) than nickel ( 0 to 30 g/t).

The major part of both metals is collected in one of the cements during the purifying of zinc electrolytic solution. These cements can contain as much as 10-15 % cobalt and 5 % nickel, which represents, in big plants, some 10 tpy of cobalt. These cements are not very well valorized, and they are generally stored until an occasional buyer is found. Research made to better recover these metals should be carried out in common by the interested companies.

## 13.38 CONCLUSION

The present survey shows that the highly technicized lead-zinc plants of the European Community are able to recover with a high efficiency the by-products that have a high commercial value, either by the amount (like S or Cu), either by the intrinsic value (like cadmium or the precious metals).

However, some by-products which are present in low amounts in lead and zinc concentrates, like mercury, selenium, nickel or cobalt, are still left in the residues or badly recovered.

In order to attain a better economical recovery of these by-products, it is felt that some kind of collaboration should be set up among lead and zinc producers.

# PART 1.4.

TECHNICAL ASPECTS OF SUPPLY BY WASTE

## 14.1    NATURE OF THE AVAILABLE WASTES - PRESENT AND POTENTIAL USES

## 14.11    DEFINITIONS

An International Lead and Zinc Study Group wrote a report on Secondary Lead and Zinc in 1975. It included recommended definitions and descriptions to be used in collecting statistics.

Primary metal : lead or zinc produced mainly from ores or concentrates.

Secondary metal : metals or alloys recovered from scrap, wastes, ashes, drosses and residues. The term "secondary" applies only to the source of the metal and has no relation to the type of product recovered as to quality, degree of purity or physical characteristics.

Refined lead : lead produced by smelters or refineries - including production on toll - to meet recognised national or international specifications, regardless of the type of source material, i.e. whether ores, concentrates, lead bullion, mattes, residues, slag or scrap. It also refers to the lead content of alloys, in particular the lead content of antimonial lead, which are treated in smelters or refineries to meet a recognised national, international or customer specification. Lead and lead alloys produced by remelting are not included.

Remelted lead and lead alloys : lead or lead alloys produced by remelting secondary lead materials which are used, without refining, by the consumer.

Refined zinc : zinc produced by smelters and refineries - including production on toll - to meet a recognised national or international specification, regardless of the type of source material, i. e. whether ores, concentrates, residues, slags or scrap. Remelted zinc, zinc oxide and zinc dust are not included.

Remelted zinc and zinc alloys : zinc or zinc alloys produced by remelting secondary zinc materials which are used, without refining, by the consumer.

New and process scrap : new scrap includes process scrap generated during the fabrication of lead and zinc products and the manufacture of fully

completed equipment and products containing lead and zinc, or their
alloys, and consumed at a plant of different location from the plant
of generation. It also covers defective or reject articles returned
by purchasers to be reworked.

Internal or runaround scrap : process scrap generated during the course
of manufacture of zinc or lead products which Is remelted and consu-
med In the plant of generation.

Old scrap : old scrap Includes worn, damaged or obsolete lead and zinc
fabricated materials, usually discarded after serving a useful purpose,
and lead and zinc scrap recovered from the demolition of buildings and
from scrap machinery and equipment, e.g. zinc die cast scrap recovered
from automobiles.

Purchased scrap: new and old scrap purchased for use from outside sources
Including other works or companies within the same organisation.

On the other hand, collectors, retailers and wholesalers refer to a
common code for characterization of scrap pieces, with very precise defi-
nitions; this code Is sponsored by the International Recovery Office.

## 14.12 SECONDARY LEAD SOURCES

The main secondary lead sources are :

- batteries : most used batteries are collected for lead recovery, that
can reach 95 %. Growth In the use of lead batteries Is expected to conti-
nue (consumption of lead for batteries Increasing from 50 % of the lead
produced to 60 %), mainly because of Increasing car populations, and It
will make a bigger contribution to secondary supplies. More traction
batteries will be used, as well as batteries for peak-shaving In the elec-
tricity business. The grids of batteries are commonly made of lead-anti-
mony alloys and they can be processed to produce directly refined lead-
antimony alloys. Recently grids made of lead-calcium alloys have been
brought Into use (the so-called "maintenance-free" batteries) and, while
their processing for recycling has not so far presented any serious pro-
blems, If their use Increases significantly It may become necessary to
segregate one type of grid from another for separate recovery, or to
refine the alloy obtained from complex treatment. If these batteries last
longer or require purer lead, their use can lead to modified reprocessing.

However, it seems possible to get maintenance-free batteries based on lead antimony alloys, but with decreased Sb content (from 5-6 % to 2-3 %).

- cables : less lead sheathed cable is now being used than in the past and so the amount of lead to be recovered from this source is declining. However, in most countries, there are large quantities of lead sheathed cable in service which are still to be recovered as the old installations become obsolete.

- sheet and pipe: lead pipe and lead sheet were extensively used in the past in the older industrialised countries where are important sources of scrap lead for recycling. Although the use of lead pipe has declined strongly in recent years, and lead sheet as well to some extent, there are lots of these materials still to be recovered.

- alloys : consumption of lead in solder and bearing metal is keeping fairly constant; however, present changes in printing processes may bring more and more printing metal for recovery of secondary lead.

- drosses and residues : the quantity of drosses and residues available for the recovery of the lead in them is in proportion to the amount of lead melted and so will increase as lead consumption rises.

Most secondary lead will still come from well-established sources although there will be changes in relative importance as noted above. Because of stricter controls over emissions, more lead is likely to be collected in flue dusts and air filters both in lead works and other branches of the secondary metal industry; quantities will be small, as those coming from a potential control over lead emission from automobiles.

14.13  SECONDARY LEAD PRODUCTION

In many cases, lead ashes, lead dusts as well as particular residues, often of low lead content, are recycled in the blast furnace smelting process, sometimes after a sintering step.

The lead metallic scrap is remelted in the kettles of the lead refining process, either alone , or mixed with primary lead in order to be refined.

The major part of secondary lead is contained in scrapped batteries; they can be treated in big lead smelters, but also in plants which have

specialized in retreating old lead, and which are located in the neighbourhood of consuming areas.

Processes for the treatment of batteries must take into consideration all the problems of environment protection.

An average composition of an acid-free battery is, each for one third, a filling active mass low in antimony (lead oxide and sulfate), hard lead assaying 3 to 5 % Sb and other materials low in lead, such as casing, separators and iron handles.

Batteries can be smelted directly in the furnaces, which is a very simple process. But antimony of the hard lead will be diluted by the filling mass. Moreover, the chlorine content of the separators, often made of PVC, is troublesome.

The difference in physical properties of the various parts of the batteries can result in a beneficiation process, after which smelting can be divided in a treatment for antimony-rich parts and a treatment for the poor ones. The advantage is a more economical refining and an increase in antimony recovery, but the facilities are rather expensive; the separators must be carefully freed from any lead.

In simpler beneficiation plants, separators often give troubles. During the mechanical crushing of the batteries, they carry along with them some fine material from which they cannot be separated in the small plants.

On the other hand, chlorine from the PVC passes in the lead and gives rise to an important lead chloride volatilization. The Austrian Company Bleiberger Bergwerksunion (BBU) has found that these separators can be made unbreakable, plastically as well as mechanically, by a 8 minutes heating to 200°. It uses a rotary furnace heated with combustion gases. The motion of battery parts in the furnace also separates lead particles from the plate separators, so these can be recovered from the other parts by screening.

The following step of the treatment can be carried out on a rotating

hearth, in short rotary furnaces, in the refinery or, when fine material is concerned, in blast furnaces after possible sintering.

Any process for beneficiation and breaking of the batteries is expensive, whatever system is used, by hand or mechanically.

Numerous lead plants employ short rotary furnaces for the retreatment of battery scrap, for they offer a particularly high capacity at a relatively low cost. The resulting gases are at high temperatures, which cause complete burning of the plastics, hard rubber or wood, and in the absence of tar residues in outgoing gases.

Taking into account the chlorine content of flue dust, one must look for a careful gas purification. In short rotary furnaces, several by-products of the lead refining are treated, and they have a favourable effect on the retaining of sulfur and on slag.

On an idea of VARTA's, BERGSOE has designed a blast furnace suitable for the retreatment of entire batteries, and in compliance with the strictest environmental legislation. The breaking of used batteries is avoided. The storage hall is so designed that the acid which is still present is recovered, collected and stocked. Shovel loaders transport the batteries to the wide loading door of the blast furnace, as well as fluxes and recycled materials, such as slag and flue dust.

The furnace is heated with coke and enriched air preheated to 500°. The air preheating is made with fuel oil. The combustion heat of battery-casings, made of ebonite, hard rubber or polypropylene, as well as the heat content of the blast allow serious coke savings as compared to other processes.

Flue dust is smelted in a separate combustion chamber, together with fluxes, to obtain agglomerated blocks; the result is the production of 3 to 4 % of new dust in the blast furnace, instead of 8 to 10 %. Outgoing gases are cooled and filtered in a bag filter.

The Bergsoe process plants have a capacity of 35 000 - 45 000 tpy.

The BBU process involves drying of the batteries, the extraction of the separators on a vibrating screen with air suction; screen undersize is crushed in a hammer mill; crushed product is classified by means of a Zick-Zack air classifier into the fine filling mass and the coarser plate fragments. Capacity of the plant is around 3 tph.

The Stolberger process includes the treatment of unbroken batteries by crushing in an impact breaker, screening out the separators (which are cut in small pieces and recycled), washing out the fines, and carrying out, on the -80+5 mm, a sink-float separation in a magnetite medium recovering separators and plates in different products.

The Tonolli process is not very different from the Stolberger process, it also operates with a sink-float separation where the medium is made of battery slimes.

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## 14.14    SECONDARY ZINC SOURCES

As a world average, it is estimated that around 25-30 % of zinc
is recycled and recovered as metal or salts.

The largest use of zinc is for steel protection by galvanizing,
but presently little attention is given to the possibilities of recove-
ring zinc from galvanized steel scrap. However, zinc is concentrated in
the flue dust of the steel plants which feed galvanized steel scrap in
their furnaces, and the problem of the adequate recovery of zinc and lead
contained in these dusts is still open, although some solutions are al-
ready suggested, or piloted by some companies.

Galvanizers'ash consists mainly of zinc oxide mixed with metallic
zinc, traces of lead, iron and chlorides from the flux. Zinc can be
melted and directly re-used.

Galvanizers'dross or hard zinc is a zinc-iron alloy which is very
rich in zinc (around 95 %).

The quantities of these materials may increase with the growth of
galvanizing.

The next important use of zinc is die-casting, the major part of
which is employed in automobile production. Zinc ash is formed during alloy
making and on the melting pots. New metallic scrap appears in the form of
flash, sprues and gates, and old scrap could be recovered from motor vehi-
cules , domestic appliances, office equipment, etc; it is a large potential

source of secondary zinc, and die castings used in automobiles are already a major source as more and more cars are dismantled for metal recovery. Expansion of zinc die casting recovery seems to depend partly on advance in collecting and sorting of municipal wastes.

Techniques are being developed to sort and separate non-ferrous metals from car scrap, and zinc recovery should increase. It should be noted that zinc recovered from die castings is mainly used for galvanizing and producing zinc oxide and dust. These techniques involve shredding, magnetic separation, size reduction, further magnetic separation and separation of zinc from aluminium by density difference (pneumatic table or heavy media separation). It must be stressed here that a very efficient separation can be obtained after crushing the supercooled scrap (George process based on liquid nitrogen).

Zinc in brass scrap is the largest single source of recycled zinc, but zinc metal is usually not recovered separately. The bulk is in the form of new process scrap which is recycled between users, brass makers or ingot makers. Some ash is produced during brass making, but it is valued more for its copper content and so it is combined with old brass scrap for copper recovery.

There are no great problems in collecting and treating rolled zinc scrap : new metallic scrap appears as clippings or zinc sheet cuttings, and old scrap can arise from demolished buildings. Engravers'plates represent scrap of very high quality, except when made of sandwich zinc-aluminium-zinc sheets.

In sodium hydrosulfite production, where zinc powder is a major reagent, by-products such as zinc hydroxide or carbonate appear, which can be calcined to make chemical process zinc oxide or dissolved in acid to make zinc sulfate.

The main "new" source of secondary zinc will be die castings recovered after shredding operations. Recovery from coated steel via flue dusts and from sludges would be improved if new techniques could be developed; this could make more zinc available for use in brass, zinc oxide, zinc dust and chemicals. Another potential source is zinc cases from dry

cells, but recovery techniques have to be improved.

## 14.15 SECONDARY ZINC PRODUCTION

When handling scrap zinc bearing material, the first step is the preparation of raw material for distillation by removing metallic and non metallic impurities which physically contaminate the zinc fraction of the scrap.

Mechanical prerefining methods consist in crushing, screening and separating metallics from skimmings.

Pyrometallurgical prerefining are sweating operations in a kettle, reverberatory or rotary furnace. In most cases the produced ingots are sold to smelters for distilling. Smelters can justify the necessary expenditure for costly baghouses and collection systems to control nuisance fumes and combustion gases; they can also make use of the large quantities of skimmings produced in melting operations.

The retort distillation process, which can treat galvanizers' zinc drosses, is a batch system operated in successive cycles of metal production and slag formation. The furnace contains retorts to which are attached condensers where zinc vapor formed by oil or gas heating is condensed to be cast into ingots.

The muffle furnace process is a continuous operation consisting in a distilling furnace and a riser acting as a condenser. The slag in the furnace must be removed periodically.

Scrap generated by zinc rollers is preferentially re-used on the spot, for instance in battery dry cell manufacture.

Galvanizers'dross is generally a most economical source for making zinc dust even though it results in a lower conversion efficiency.

Galvanizers'ash can by used to produce zinc oxide by the direct process.

Galvanizers'ash and flux skimmings are used to make zinc chloride

and zinc ammonium chloride by hydrometallurgical methods.

Galvanizers'ash can also be used as feed for the production of zinc sulfate if sufficiently chloride-free.

From galvanizers'dross some zinc can be recovered by melting processes, and all the zinc could be won back by distilling at temperatures around I 200-I 300°.

Zinc oxide can be produced by chemical processes from zinc hydroxide or carbonate.

Since several years, some of the metallurgical furnaces meant for primary zinc production are used as such or slightly transformed for the treatment of zinc scrap and residues in order to produce secondary zinc. We can mention here the half-shaft furnace of Preussag at Oker, the I.S.P. furnaces at Duisburg and Noyelles-Godault, and some of the New Jersey refining columns where the feed is now zinc scrap and wastes instead of impure primary zinc.

14.2 USES OF WASTES AND RESIDUES IN THE E.E.C. COUNTRIES

14.21 INTRODUCTION

In all the E.E.C. countries, there is a trade of scraps, wastes, and residues containing lead and zinc.

At the present time, it is claimed that about 50 % of the lead and 20 % of the zinc consumed are produced from secondary sources.

The recovery of scrapped batteries represents 44 % of the. lead secondary production; this percentage will probably increase in proportion to the increasing number of cars, yet we still have to take into account the development of maintenance-free batteries produced with low antimony- or calcium -lead alloys.

Lead sheet and pipes, and cable sheathings represent 35-40 % of the secondary lead produced, but this ratio will probably decrease in the future.

Most of the metallic zinc is used for galvanizing steel, and is now recovered only in the dusts and fumes of steel mills. Zinc scrap and residues may be recycled when zinc content is of sufficient value or chlorine content very low.

There are two lead and zinc sources which may be successfully used in the next future : car scraps and domestic refuses.

In a few countries, there are dumps containing beneficiation tailings or metallurgical slags; the recovery of lead and zinc from these dumps cannot be neglected.

## 14.22 DENMARK

There is only one secondary smelter in Denmark; at Glostrup, Paul Bergsoe & Son is treating lead scrap (mostly used batteries) to produce about 15 000 tpy in a shaft furnace plant. This plant is described above (§ 14.13).

The furnace treats unbroken batteries and the input can reach 35 000 - 40 000 tpy.

Denmark is a net importer of lead scrap, yet a net exporter of zinc scrap.

14.23  IRELAND

This section is borrowed from a report prepared for this dossier
by Dr. C. Burton, of the I.I.R.S. in Dublin. The quantities mentioned
are expressed in short tons.

Mine Wastes and Unsaleable Products

The complexities of mineral flotation especially with oxide ores, fre-
quently result in the loss of metal values in the tailings product and
the production of unsaleable concentrates. Production at the two opera-
ting mines in Ireland over the past ten years has produced a considerable
tonnage of waste products which, within certain technological and econo-
mic constraints, may be processed to recover their contained metals.

Tynagh Mine

1. Tailings

Approximately 5.5 million tons of tailings have been deposited in the
tailings pond at Tynagh. The pond is divided into two; one half
(containing approximately 3 million tons) is known as the high barite
(BaSO$_4$) tailings because, when high grade barite ores were treated in
the mill, the tailings were directed into this part of the pond. The
average BaSO$_4$ grade of these tailings is 35 percent. The other half
of the pond, containing 2.5 million tons has lower amounts of barite
but the BaSO$_4$ assay is still relatively high.

The metal grade of the tailing product will vary between 5-10 % combi-
ned Pb:Zn at the base of the tailings pond to 0.4 % combined Pb:Zn in
the present primary ore tailings at the top of the pond. Losses during
flotation are most likely to be in the form of oxide rather than sul-
phide mineral and a considerable proportion of the metal values will
have a particle size below 20 microns. The absolute amount of metal in
the tailings pond is difficult to estimate. However, if conservative
assay figures are taken, a minimum amount of metal in the tailings pond
can be determined (Table 14.23.1).

TABLE 14.23.1

ESTIMATED METAL VALUES IN TYNAGH TAILINGS

|  | ASSAY | TONNAGE |
|---|---|---|
| Lead | 2 % | 110 000 |
| Zinc | 2 % | 110 000 |
| Copper | 0.3% | 16 500 |
| Barium Sulphate | 35 % | 1.75 million |

As the present primary ore mining produces only low grade tailings, any potential retreatment process would have to take into account continuing dilution of the higher grade tailings.

2. Silver Ore

Approximately 50-60 000 tons of silver rich ore has been stockpiled because it is not easily concentrated. It contains 7-10 oz/ton Ag, 0.6% Cu, 1.5 % Pb and 1 % Zn and barite is the major gangue mineral. The total metal contents of this stockpile is :

|  | tonnage |
|---|---|
| Copper | 360 |
| Silver | $4 \times 10^5$ oz |
| Lead | 900 |
| Zinc | 600 |

Pilot plant tests show the ore to be very difficult to float by conventional methods - most probably because 70-80 percent of the total is in the oxidized state. The maximum lead concentrate in these tests assays approximately 20 % Pb, which is generally unsaleable.

3. Lead and Zinc Oxide Wastes

Unspecified amounts of these low grade ores remain to be treated.

Mogul Mine

1. Tailings

Since 1968 the mill has produced approximately 6 million tons of

tailings product which is stored in a 90 acre tailings dam. Due to
the Improved efficiency of the mill flotation, the assay of the tai-
ling has gradually reduced since 1968, when it was 0.88 % Pb and
1.88 % Zn to figures of 0.65 % Pb and 1.1 % Zn at the present time.
However, these assay figures could vary depending on the mineralogi-
cal characteristics of the ore feed and other minor factors effec-
ting the efficiency in the mill. Using average assay figures of
0.7 % Pb, 1.5 % Zn and 0.7 % Oz/ton Ag, the total quantity of econo-
mically valuable metal in the tailings is as follows :

|  | Tons |
|---|---|
| Zinc Metal | 90 000 |
| Lead Metal | 42 000 |
| Silver Metal | 4.21 million oz. |

This represents a loss of approximately 30 percent of the lead,
15 percent of the zinc, and between 75-80 % of the silver by the
concentrator. The following mineralogical factors are considered
important in causing metal values to appear in the tailings :

1. The presence in the ore of oxide lead minerals -
   anglesite and plumbojarosite.
2. The fine grinding required to liberate the ore
   will result in excess zinc and lead as slimes.
3. Silver is associated with a number of other mine-
   rals besides galena, notably the sulpho-salt-
   tennantite/tetrahedrite.

Pyrite, dolomite and to a lesser extent calcite, quartz and barite
are the gangue minerals in the ore and it is estimated that pyrite
comprises 50 percent and dolomite 40 percent, of the tailings by
weight.

2. Calamine and Old Dump Deposits at Ballygown South

The calamine ore is an intimate mixture of smithsonite ($ZnCO_3$)
hemimorphite ($ZnOH_2SIO_3$) and hydrated iron oxides, with occasional
galena,quartz, sphalerite and baryte. It is present along fissures

In dolomite, sometimes partially replacing the latter, and occurs either as a friable dark brown earth or as light brown hard rock nodules.

Considerable work has been carried out in efforts to prove the extent of these deposits and to develop methods of upgrading the ore, both by Silvermines Ltd. and previous companies.

The size and grade of the deposit still remains in some doubt, due to a disparity between estimates based on drive and shaft development and those based on core analysis. In the 1930's The British Metal Corporation (BMC) estimating on the basis of 1640 ft of underground workings, stated that the probable tonnage available from part of the present lease area as

$$500\ 000 \text{ tons at } 21.4\ \% \text{ Zn}$$
$$\text{or } 4\ 000\ 000 \text{ tons at } 12.0 \text{ Zn.}$$

Drilling results have never substantiated those tonnages. This is most likely due to loss of core in high zinc sections, but even if the lost core was considered to contain 20 % Zn, some disparity would still exist. It has been suggested that the BMC shaft and adit developments were confined to high grade sections in the calamine and that to the sides of these developments large areas of low grade dolomite "horses" were to be found. Perhaps the most reliable estimate is that put forward by Consolidated Goldfields Ltd. In 1966, based on BMC results and their own drilling. This gave a total of 690 000 tons of oxidized ore assaying 21.4 % Zn for the whole calamine deposit.

It must be remembered at this point that the Silvermines calamine is a highly variable deposit which would be difficult to mine by underground methods - open cast development would be technically simpler, and it might be wise to view the deposit as 2 million tons of 7 % Zn ore.

Also present at Ballygown South are a series of dumps surrounding the old shaft workings of the 19th century. This represents material which was too low a grade for calcining at that time- there is some evidence that the cut-off grade was 30 % zinc. The original volume of this material was 15 000 tons between 12-17 % Zn, but a small tonnage was

removed during the 1950's for use In the Waelz kiln.

A further zinc deposit has also been delineated below the calamine. This is In effect an easterly extension of the Mogul sulphide ore, the ore occurring In the lower dolomite, 20' above the Junction with the mixed beds. It has been estimated that there Is a continuous zone (approximately 12' wide) containing 550 000 tons of sulphide ore assaying 4.6 % Zn, 1.6 % Pb and 0.5 oz/ton Ag.

3. Other Deposits In the Silvermines Area

(a) Knockanroe

In the area where Mogul of Ireland have proven a 0.5 million ton Zn/Pb sulphide deposit, calamine ore has been reported close to the Silvermines fault. One borehole north of the Knockanroe shaft Intersected 125 ft of calamine assaying 1.44 % Pb and 7.55 %, but the total tonnage of calamine In this area Is not known.

(b) Gortnadyne

In the plane of the fault south of the present Mogul Mine working, lead and copper have been worked by open cast methods and It Is reported that the lead contained up to 20 oz/ton of silver, but detailed Information Is sparse.

(c) Shallee Mine

Lead has been mined In the area behind Shallee village and further to the west In Devonian sandstones. It occurs as galena In fissures 6-8" wide which In certain areas have almost Joined together to form deposits 200' across. Detailed exploration would be required to determine the full extent of this deposit.

## TABLE  14.23.2

### SUMMARY OF WASTE AND UNWORKED ORES AT SILVERMINES

| Waste Product | Estimated Tonnage | Assay | Gross Metal Content (SDT) |
|---|---|---|---|
| 1. Mogul Tailings | $6.0 \times 10^6$ | | |
| (a) Zinc | | 1.5% | 90 000 |
| (b) Lead | | 0.7% | 42 000 |
| (c) Silver | | 0.7oz/ton | $4.2 \times 10^6$ ozs |
| 2. Ballygown South Calamine | $0.69 \times 10^6$ | | |
| (a) Zinc | | 21.4% | 147 660 |
| (b) Lead | | 1.9% | 13 110 |
| 3. Ballygown South Dump Calamine | $12 \times 10^3$ | | |
| (a) Zinc | | 15% | 1 800 |
| (b) Lead | | 1.5% | 180 |
| 4. Ballygown South Sulphide | $0.55 \times 10^6$ | | |
| (a) Zinc | | 4.6% | 25 300 |
| (b) Lead | | 1.6% | 8 800 |
| (c) Silver | | 0.5oz/ton | $275 \times 10^3$ ozs |
| 5. Knockanroe Calamine | | | |
| 6. Gortnadyne | Assay and tonnage figures not reliable | | |
| 7. Shallee | | | |

Total Gross Metal content  - zinc     264 760 tons
                                - lead      64 090 tons
                                - silver  4 475 000 ozs.

14.24  UNITED KINGDOM

This section is borrowed from a report prepared for this dossier by Dr. R.N. Crockett, of the I.G.S. in London.

## Nature of the available waste

In the fluorspar-producing areas several of the existing mines started up in the Nineteenth Century as lead and zinc producers. With changing demand and economic trends during the present century emphasis shifted to fluorspar and increasingly material relatively rich in galena or sphalerite was consigned to dumps or used as backfill. An additional factor is that prior to about 1850 it was not possible to separate galena and sphalerite other than by hand sorting and mixed ores not amenable to such treatment were also dumped. It can also be noted that the economics of lead mining in the early Nineteenth Century were based closely on the silver content of the galena and even if it was possible to make an effective separation of galena and sphalerite many low-silver galenas were either not mined or were dumped.

It is evident, therefore, that a considerable increase in the U.K. production of lead and to a lesser extent, zinc concentrates could be effected by encouraging the reworking of old mine dumps and perhaps also by opening up backfilled workings. One authority estimates that the national production of lead concentrates could be increased by as much as three times. Militating against such an operation at present is the widely scattered nature of the dumps, the working of which is really only an economic proposition for small concerns operating on a tribute basis. Moreover, tributers working dumps for fluorspar may only hold a concession for that mineral or are only paid by the companies owning concentrators for the fluorspar that they produce. An increase of lead concentrate production based on mine dumps might, however, be encouraged by a judicious combination of simple pre-concentration methods at the dumps themselves, premiums paid for galena produced and modification of the flowsheets of fluorspar concentrators to allow for greater galena recovery. Similar arguments apply to sphalerite although it is not believed that production of this mineral could be increased as much as that for galena.

## Present and Potential Use of the Various Types of Scrap

In 1974 it was estimated that, of a total U.K. annual consumption of lead of 325 000 tons, about 55-60 % was supplied by the secondary industry. Total consumption of lead in the U.K. appears to be static or declining. The amount of secondary lead available from year to year is a function of some conflicting trends.

Areas in which consumption of lead, and therefore the availability of scraps, has shown a marked decline include its using for sheating power transmission cables for which aluminium and plastics are increasingly substituted and also the use of lead in antiknock additives to petrol. Another important change is that less scrap will become available from old lead pipes and roofing sheets as these are progressively replaced in older buildings. Contrary to these areas of decline, scrap derived from redundant lead acid storage batteries is increasing in amount in line with a growing automobile population. Even in this case, however, the growth in demand for lead and the subsequent supply of scrap may be blunted by the introduction of batteries with improved power/weight ratio that use less lead per given amperage.

In 1974 lead end-uses in the U.K. were as follows :

| Use | % of total consumption |
| --- | --- |
| Cables | 14 |
| Batteries | 25 |
| Anti-knock compounds | 17 |
| Other oxides and compounds | 11 |
| Sheet and pipe | 15 |
| Solder | 5 |
| Alloys | 5 |
| Miscellaneous | 8 |
| | 100 |

In most of its major uses lead is potentially capable of being recovered. The largest single application, about 80 000 tons of lead and oxide being consumed in 1974, is in the production of

lead-acid batteries and here recovery is particularly efficient.

The short working life of batteries and an effective recovery system which brings about 90 % of all batteries back to the smelter results in a rapid turnover of the lead involved and a need for relatively small additions of metal from external sources. The recovery of values from batteries accounts for about half of all the secondary lead produced in the United Kingdom.

The rate of recovery is also high in the case of lead utilised for cables, sheets and pipes but here the lifetime is much longer, usually more than 30 years.

Lead in solder is largely lost to the secondary smelters as its main use is in the manufacture of consumer electrical goods. On the other hand, solder itself is an important outlet for recovered type metal, which contains a certain proportion of lead, made redundant by new printing methods.

In many of its older applications lead is non-recoverable but a possible source of lead, at present unrecovered, is domestic refuse from which it is estimated that 8 000 tons per annum would be available. Low grade slags containing perhaps 3 % lead are generated by primary and secondary smelters and/or at present dumped. More research is required as to the recovery of lead from alloys.

Total 1974 consumption of zinc in the U.K. was 353 000 tons, of which 24 % was secondary metal, a much lower proportion than for the other major non-ferrous metals. Moreover, nearly half of this recycled zinc originated from brass scrap, the recovery of which is effectively an independent operation and does not therefore enter the secondary zinc flow sheet. The independence of the secondary brass cycle is related to the fact that zinc for galvanizing must contain less than 0,25 % aluminium and no copper. Moreover the addition of secondary zinc is forbidden in the production of zinc-based die casting alloy made under British Standard BS 1004. Very little zinc is therefore recycled as metal and nearly all secondary zinc is used for the production of oxide, zinc dust and chemicals. This point is emphasised by the following table.

## Uses of Remelt and Scrap Zinc and Zinc Residues in U.K.

| Use | % of total Zn use which is attributable to scrap | % of total UK secondary Zn consumption incl. brass | % of total UK secondary Zn consumption excl. brass |
|---|---|---|---|
| Brass | 45 | 54 | - |
| Galvanizing | 1 | 2 | 4 |
| Zinc oxide | 37 | 17 | 36 |
| Zinc die-casting alloy | 3 | 2 | 5 |
| Zinc dust | 77 | 13 | 29 |
| Rolled zinc | Nil | Nil | Nil |
| Miscellaneous | 67 | 12 | 26 |
| (mostly chemicals) | | 100 | 100 |

In order to review possible sources of zinc for recycling it is first necessary to summarise the main initial market for the metal in the United Kingdom. Details are given in the following table :

### End Uses for Zinc in U.K. in 1974

| Use | % of total Zn consumption |
|---|---|
| Galvanizing | 26 |
| Brass | 28 |
| Die-casting | 20 |
| Zinc oxide | 11 |
| Rolled zinc | 6 |
| Zinc dust | 4 |
| Miscellaneous (mostly chemicals) | 5 |
| | 100 |

The zinc absorbed in some of its major uses is not usually capable of being recovered. For example, zinc used in the chemical industry, which includes much of the dust listed above, does not lend itself to recycling. Zinc oxide used in the manufacture of paint, rubber and cosmetics is also largely lost; for example, about 10 000 tons per annum of oxide dumped in waste tyres.

Galvanized steel tends to be recycled for its steel content rather than zinc. Some of the zinc covering on galvanized metal components is lost anyway during their lifetime because the basis of the galvanizing principle is that steel is protected by the preferential oxidation of zinc. It is, however, possible to recover much of whatever zinc remains from fume in the furnace fire dusts.

Zinc used in diecasting does have some ultimate scrap value but not as new diecast alloy owing to the specifications of BS 1 004.

An important loss of metallic zinc is in dry cell batteries most of which are dumped in domestic refuse.

The manufacture of brass absorbs relatively large amounts of scrap but this tends to be old brass rather than other zinc scrap and thus the brass cycle is virtually independent.

Apart from brass, only the manufacture of oxide, dust and "miscellaneous" are capable of making use of substantial proportions of scrap zinc. However, these three categories only amount to about 20 % of the total UK consumption of zinc and in consequence there is little incentive towards increasing the supply of secondary zinc.

However, for the sake of completeness the main sources of secondary zinc in the UK may be noted. The potential amount of zinc fume derived from steel may amount to as much as 15 000 tons per year. Zinc fume is also produced by secondary copper refiners. In times of high demand from the chemical industry much of this fume may be utilised.

Galvanized zinc drosses and zinc refining drosses and mattes may meet some of the domestic market for secondary zinc but variability in the supply available leads to the UK chemical industry to prefer fume. Some drosses are exported but most are dumped. Brass-making dross is sold for its copper content rather than zinc.

Zinc (and lead) refining slag are not treated for their metal values. It is estimated that 2 100 tons per year of zinc is lost in pyrometallurgical residues in the UK. At Avonmouth most is stockpiled and eventually

used as bulkfill on nearby construction projects. Zinc-bearing residues from the former smelting industry in the Swansea area were dispersed as fill during motorway construction.

14.25  FRANCE

This section is translated from a text prepared for this dossier by the B.R.G.M. :

14.25.A.  SECONDARY LEAD

Nature of the available waste

Lead wastes exist essentially in two categories (I) :

- old lead scrap, mainly lead piping (from turn-down or renovated buildings), tanks, sheets, or pipes (from turn-down or renovated industrial plants), and tinned capsules. It must be noted that the lead pipes are being progressively replaced by copper or plastic pipes, so that this type of scrap is decreasing.

- battery lead : it is a lead-antimony alloy that is mainly reused in battery manufacture.

Lead-tin alloy scraps represent a small market; their origin is the throwing away of bearings, mainly from S.N.C.F., and from big machinery; they come principally from industrial plants, and are retreated either in small refineries and foundries in France or exported.

A survey realized by Bureau d'informations et de PrévisionsEconomiques (B.I.P.E.) has determined an amount of 102 650 t of scraps and residues, when consumption is estimated at 110 300 t, which seems highly representative (93.2 %).

This survey emphasizes the fact that lead scraps principally come from collectors, and not from industrial plants, It can thus be inferred

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(I)  typing drosses, old types, oxidized and sulfated lead residues are disappearing. There is very little recovery of the lead-tin alloy residues.

that these scraps consist mainly of old metal (I).

In that respect, most garage keepers sell used batteries to small recovery dealers or to their own workers (in payment for overtime), who then sell them to retailers or semi-wholesalers; the latter prepare the batteries (by draining off the acid) and resell them to refineries that treat and transform them Into lead-ant.mony ingots or soft lead; the lead-antimony ingots are used again In manufacturing new batteries.

It Is the same for old lead : house piping,for instance,Is recovered by the plumber who sells It to recovery dealers, retailers, or semi-wholesalers; on the other hand, lead scraps recovered from plants generally go to semi-wholesalers only.

The survey has revealed that lead scraps are usually sent to refineries which produce soft lead (without antimony), hard lead (for batteries), and shot (for hunting and/or fishing), as well as to foundries and to the export market (Italy, Belgium, West Germany (2)). Contrary to the results of the survey, and according to the consumers themselves, It seems that the scraps are rarely sent to the foundries.

Thus, the survey's results seem hardly credible; the Inaccuracy could arise from a bad division at the semi-wholesaler level, and from too low a consumption figure In the foundries. Among other lead applications, one can mention lead hardening of steel wire In wiredrawing works (It Is a very rare of lead scraps), and the ballast for sailing-ships and handling trucks.

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(I) A rough estimate of the number of recovered batteries could be based on their present lifetime and on the number of cars; however, some people says that batteries might be stockpiled by garage keepers. One must also not forget that batteries are used on railroad engines, transport material, motor-boats,etc. Furthermore, the recovery of batteries takes place principally during wintertime.

(2) There Is, In a foreign country, an International super-wholesaler who works out contracts for the transformation of used batteries.

## Uses of the various types of scrap

It is necessary to sort the case of the typing alloys that are re-melted after each use. As drosses are formed, the grade is regularly restored by the addition of about 2 % of new metal.

Lead recovery is a very scattered activity; the refineries specialize according to the market. This explains why the producers of refined metal, as opposed to zinc remelters, do not control their market; recovered lead is 50 % of the world market.

The production of recycled metal of "primary metal quality" is marginal. This explains the differences between the various countries. The first use of scraps is in the production of alloys and oxides that do not require highly-refined lead. If there is an excess, it is refined. It is not possible to draw a long-term evolution on the refined proportion of the recovered metal : this proportion is stable.

## Secondary lead production in France

One can observe that the uses for remelted lead are very similar to those of primary lead, which explains the importance of lead recovery in the lead refining sector.

## Remelted to refined lead ratio

| 1000 t | 1971 | 1972 | 1973 | 1974 | 1975 |
|---|---|---|---|---|---|
| Refined lead | 158.3 | 186.9 | 186.4 | 177.7 | 150.7 |
| Remelted lead | 24.8 | 26.8 | 28.6 | 27.8 | 29.0 |
| Remelted lead, % of refined lead | 15.7 | 14.3 | 15.3 | 15.6 | 19.2 |

This table shows a significant increase in remelted lead. It must be observed that soft lead production represents only a small part of recovered lead.

Conclusion :  Lead recovery is an important activity. This situation explains the impossibility, for lead producers, of finding an agreement comparable to that existing for zinc : they do not control their market.

14.25.B. SECONDARY ZINC

Nature of the available waste

Zinc wastes (figure 14.25.1) are composed of :

- new zinc scrap (from manufacture), rarely put on the market (1)
- old scrap from house roofing, gutters, and outer pipes; this scrap Is rather clean, but contains a little oxide and carbonate; sometimes however, the zinc has been coated with tar.
- residues from galvanizing bathes, zinc powder spraying and zinc refining (ashes and mattes).

In fact, new scrap represents only a small part of the market residues (under 25 %). A survey made by dealers concerned 23 800 t of zinc scrap out of 67 100 t consumed, i.e. a ratio of 35 %. The remainder consists mainly of old scrap from collectors,(who are customers of the plumbers), roofers and junkyards (the repair of zinc roofs yields very little scrap). One can observe the important part of the scraps coming from the Public Properties'Administration.

As far as scrap destination is concerned, the validity of the survey is questionable, since it claims a foundry consumption much higher than that reported by the Industry (21 000t vs. 200 t) and a much lower consumption by chemical works (1 300 t vs. 16 000 t); in fact, dealers term "foundries" the refineries making zinc plates. Moreover, it seems that the dealers term "refiners" those who produce primary Ingots, and that their consumption according to the survey may be too low. The survey confirms, however, that there is no more use of scrap by zinc semiproduct makers.

Some dealers are specialized : 80 % of business is realized from house wrecking, plants, collectors or import.

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(1) In fact, plants now sell the roofers ready-to-use prefabricated elements. Shaping is thus reduced. It is done by the makers, dealers, or roofers themselves. New scrap obtained when making semi-products is directly recycled by the producers.

Figure 14.25.1  RESULTS OF A SURVEY ON ZINC SCRAP MARKET (1)
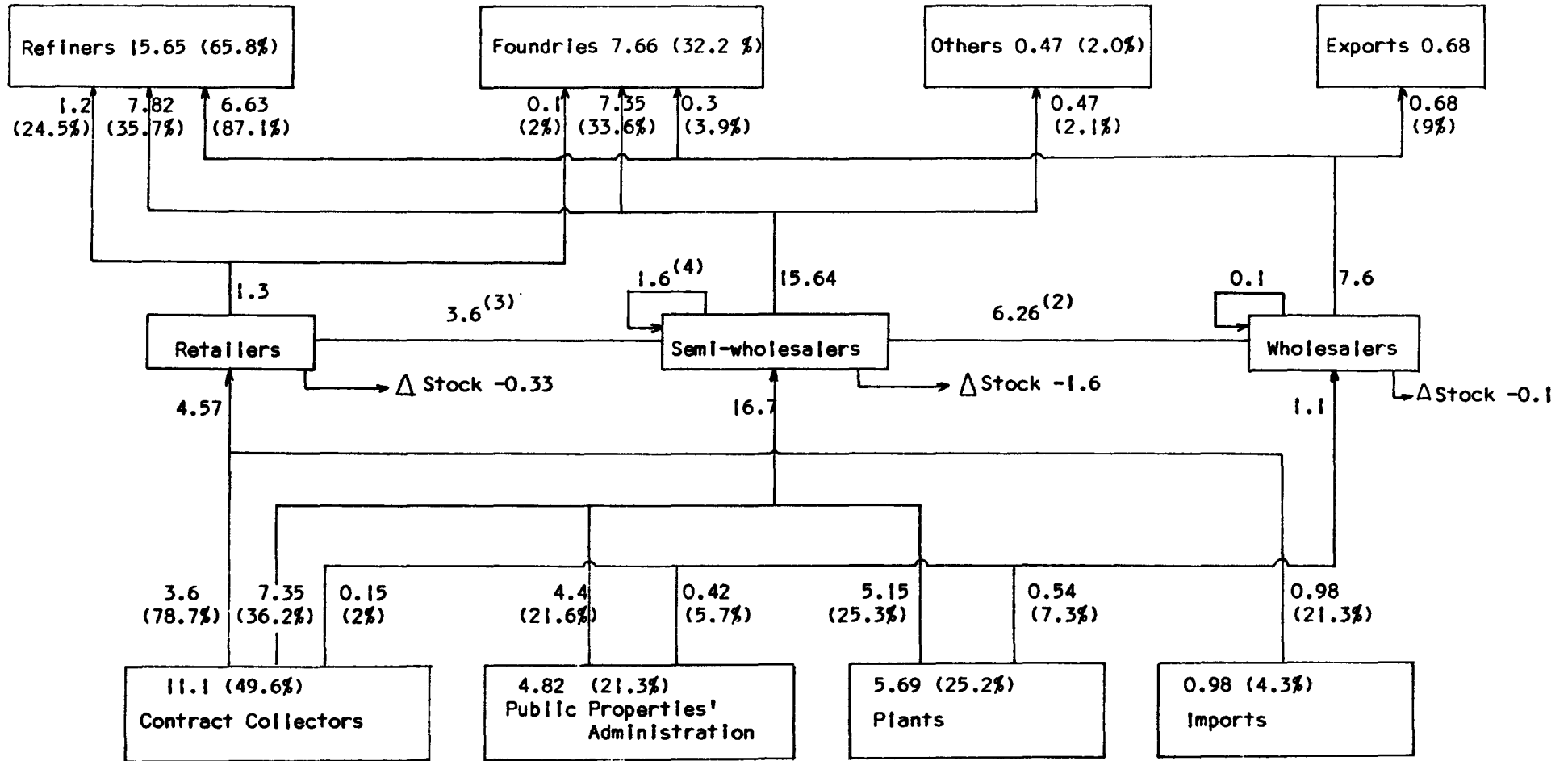
(Legend on next page)

Legend of Figure 14.25.1.

—————————————

(1) Extrapolated to the semi-wholesalers'level (from results of the survey on wholesalers) and to the retailers'level (from the results calculated for semi-wholesalers).

Survey concerning 23.78 x $10^3$ tons sold (exports excluded) and 22.59x $10^3$ tons bought. Relative representativity ratio : 35.1 %.

(2) Relative representativity ratio for the survey semi-wholesalers compared to the survey wholesalers : 6.4 %.

(3) Relative representativity ratio for the survey retailers compared to the survey semi-wholesalers : 3.06 %.

(4) Assumption for the recycling ratio : 5 %.

Results expressed in thousands tons. Percentages calculated in terms of the total supply or total sales of retailers, semi-wholesalers and wholesalers.

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Each scrap's origin is specific. Electricians provide 80 % of scraps of copper electrical wires and cables; garage keepers 80 % of used batteries; roofers 80 % of old zinc scrap; plumbers the lead pipe scraps, and aviation 80 % of old aluminium scraps.

Likewise, scrap is treated differently according to its origin. Recovered old scrap goes to the refinery; plant scraps are sent to foundries, semi-products makers, or export trade. This is the result of technical considerations based upon the quality of the different scraps and the needs of each consumer.

Uses of the various types of scrap

Zinc recovery is less significant than lead recovery, either by tonnage either by the market differences : recovered zinc is used primarily for the production of copper alloys and chemical products (lithopone) : nearly 2/3 of recovered zinc is used in applications where refined zinc is not required (copper alloys, chemicals). Recovered zinc represents about 20 % of the total zinc supply, but only 8 % of the raw metal supply (remelted or refined), compared to nearly 50 % for lead.

This is an estimate of the uses of recovered zinc in France in 1974 ( thousands tons) :

- BOUGHT BY ZINC PRODUCERS                                              75.8

    primary smelting from ashes

    primary smelting from mattes                          37.2

    refined integrated in primary smelting

    refined non integrated in primary smelting            35.6

    powder produced in zinc metallurgy                    3.0

- BRASS SCRAPS BOUGHT BY COPPER REFINERS                                4.5

- SCRAPS BOUGHT BY PRIMARY MANUFACTURE                                  59.3

    chemicals                                             25.0

    brass semi-products                                   29.4

    brass foundry                                         4.75

TOTAL                                                                   139.6


About 40 % of the zinc is directly recovered by the chemical or brass Industries; 47 % is simply refined and probably used in the same Industries.


14.25.C. LEAD AND ZINC RECOVERY FROM URBAN REFUSE


Treatment of raw urban refuse

One can consider urban refuse either in the raw state, where metals are diffuse, or after incineration; in the latter case, metals are more concentrated (3to 4 times in weight).

There are two ways to sort the raw urban refuse : at home by the housewife herself, or by general sorting of plastics,paper and cardboard (representing together 40 weight-% of the products).

In France, this type of recovery is still in the pre-development stage. There are three pilot-plants located at :

- Tournan-en-Brie (Seine-et-Marne)

- Laval (Mayenne)

- Orleans-la-Source (Loiret) (B.R.G.M.).

Paper and plastics are recovered either for reuse as derived fuels,

or for recycling : the Laval pilot plant is specialized in the transformation of paper and plastics into derived fuels, whereas the Tournan-en-Brie plant is directed to their recycling.

In the B.R.G.M. plant, both types of recovery are possible :

- organic materials can be recovered either for making compost (fertilizer), or for the manufacture of agro-alimentary products for animal feeding;

- paper, plastics,and organic materials represent 65 - 70 weight-% of the raw urban refuse; glass represents 5 - 10 %; and the total is about 70-80 % of the bulk.

The remainder, representing 20-30 % of the bulk, contains the non- ferrous metals.

Aluminium can be largely recovered and represents about 2 kg/t; it comes principally from packaging.

Lead appears rarely, and zinc is present in small quantities as brass associated with iron scraps or household materials.

In conclusion, practically no lead or zinc can be directly recovered from raw urban refuse.

Treatment of incinerated urban refuse.

After incineration of urban refuse, one obtains inert phases consisting only of slags and metals; slags are brittle whereas metals are ductile; their separation is possible by differential grinding followed by screening and magnetic separation on the screen oversize.

After these different treatments, one can obtain about 2 kg/t of heavy non-ferrous metals, including lead and zinc.

By smelting, one can recover :

- 5 to 15 % of lead
- 8 to 20 % of zinc.

Incineration is done at 800°; chlorides, i.e.those coming from the PVC, are released; and a little zinc and lead are also volatilized. They appear in the quick ashes at contents of about 10 - 20 kg of lead and zinc per ton of ashes.

It is now technically possible to obtain the metals, but this is not economical because :

- there is relatively little ash, 10 times less than clinker;
- the ash is very fine, less than 40 microns;
- recovery is limited to 60-70 %.

In the incineration clinker, lead and zinc recovery is limited since the total resources are low : about 500 000 tpy of clinker for the Paris area and 150 000 tpy for the cities of Lyon, Lille and Strasbourg. This could represent 1 300 tpy of heavy non-ferrous metals containing 5 - 15 % lead and 8 - 20 % zinc (or 65 - 200 tpy of lead and 100 - 260 tpy of zinc).

The returns from the treatment of incineration clinker come at an 80 % level from the selling of the other non-ferrous metals; 80 % of the materials are in the form of slag that can be used in construction.

In conclusion, lead and zinc recovery from incinerated urban refuse can account for only a few hundreds tons of metals per year.

## Future outlook

While lead and zinc exist in only minute amounts in the urban refuse, these metals are present in the fragments of household materials and of cars. It seems that the recovery of these metals should be considered, not from urban refuse, but from widely used materials such as stoves, refrigerators, water-heaters, cupboards, mattress springs, etc. They represent a secondary source that could be tested for the beneficiation of the metals. Car shredding could also be an important source of recovery of non-ferrous metals.

The amount of zinc used in galvanizing corresponds roughly a quarter of French zinc consumption, i.e. about 100 000 tpy. When steel scraps are smelted in blast furnaces, volatilized zinc goes into the fumes and is not

recovered. This point is important, and a number of companies are giving their attention to this problem.

About 15 000 tpy of zinc are used in vulcanization; zinc could also be recovered (for example, from used tires).

## 14.26 BELGIUM, THE NETHERLANDS, LUXEMBURG

### 14.26.A. BELGIUM-LUXEMBURG

Although two scrap trading companies exist in Luxemburg, there is no recorded production of either secondary lead or zinc in this country.

In Belgium, many companies are working in the secondary non ferrous metals business; there are a few big wholesalers in this market.

Metallurgie-Hoboken-Overpelt is the major metallurgical company treating lead scrap in Belgium. Lead scrap and residues (used batteries excluded) are sent to the Hoboken lead smelter where the lead enters the general treatment at several points (sintering, blast furnaces, refining). Secondary lead production is thus integrated into the primary production.

Several small companies remelt lead scrap (sheet, pipe, cable, sheathings, bottle capsules), yet the main lead secondary smelter is the Compagnie Metallurgique de la Campine's plant at Beerse. This company produces 6 000-9 000 tpy hard lead, about 15 000 tpy lead oxides and 6 000-7 000 tpy antimony.

Feed for the plant includes old lead scrap (poor in cadmium, arsenic, mercury, and chlorine, in order to avoid the release of noxious dusts and gases) and used batteries (breaking and casing separation are still made by hand). Treatment in a short rotary furnace gives a hard lead bullion and a discarded slag assaying 1-2 % Pb.

Lead bullion is refined by liquation (removing Cu, Fe, S, etc.) and by oxidation in a reverberatory furnace (removing tin by air blowing, excess antimony by addition of lead oxides and arsenic by addition of caustic soda).

The small production of remelted zinc is carried out for instance in Overpelt, where scrap zinc is fed to the New Jersey refining plant.

Part of the zinc ashes and residues are treated in some Belgian plants to produce zinc chemicals.

14.26.B.  THE NETHERLANDS

The major company producing secondary lead Is the Hollandse Metallur-
gische  Industrie Billiton whose plant Is located In Arnhem.

Two sections out of six In this plant are treating lead materials.
Feed for the secondary soft lead production Includes lead scrap, hard lead
from battery scrap smelting,and remelted lead. All these materials are mel-
ted and refined.

By-products containing antimony are treated with battery scrap; by-
products containing tin are treated separately to produce  solder;
by-products containing gold and silver are treated to produce gold-silver
alloy which Is sold as It Is; by-products containing copper are sold as
such too.

Battery scrap Is melted In a reverberatory furnace to produce raw
metal (used for soft lead production) and rich drosses assaying about
67 % lead and 7 % antimony. These drosses are remelted In another reverbe-
ratory furnace In order to obtain antimony-lead alloy and slag. Typing
residues are melted In a rotary furnace.

Total production (metal and alloys) amounted to 26 400 t In 1974.

## 14.27 GERMANY

In Germany, eleven plants smelt secondary zinc and twenty-five plants smelt secondary lead.

Lead
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In 1974, 158 300 t of lead scrap and residues were fed in the plants; 58 900 t were simply remelted and used as such; 99 400 t were refined with primary lead bullion.

Remelting plants have a capacity varying from 2 000 tpy to 30 000 tpy (Varta's battery retreatment plant at Krautscheid). Most plants melt old lead scrap, drosses and residues; four only retreat scrapped batteries.

Metallgesellschaft's Binsfeldhammer plant has a production capacity of 75 000 tpy; It includes a retreatment section for used batteries employing the Stollberg Zink's process. Lead bullion is refined in the Company's refinery at Braubach, which has a capacity of 60 000 tpy.

Norddeutsche Affinerie's plant in Hamburg includes secondary smelting and refining sections with a capacity of 40 000 tpy.

Preussag's plant in Oker (Hüttenwerk Harz) has a capacity of 40 000 tpy; It produced 31 000 t of lead in 1976 working only on scrap.

Zinc
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In 1974, 139 600 t of zinc scrap, ashes and residues were fed in the plants; 45 500 t were recycled directly to be marketed;23 700 t were simply remelted and the remainder was included in the charges of the primary plants.

Details about the small remelting plants are not available.

Duisburger Kupferhütte treats pyrite cinders by hydrometallurgical processes (1 000 000 tpy), mixed with 60 000 tpy zinc leach residues and 120 000 tpy other residues and by-products.

Zinc production capacity is nearly 60 000 tpy of zinc under different forms:

| zinc metal | 18 000 tpy |
| technical zinc oxide | 32 000 tpy |
| zinc sulfate solution | 10 000 tpy. |

Preussag's Hüttenwerk Harz in Oker-Goslar has a capacity of
100 000 tpy of zinc; it produced 60 000 t of zinc in 1976, 70 % of which
came from concentrates and 30 % from scrap and residues. The plant has
developed a proprietary shaft furnace, called "half-shaft", where zinc
and lead are fumed as oxides.

Metallgesellshaft's Berzelius plant in Duisburg feeds the I.S.P.
furnace with Waelz oxide, produced from lead blast furnace slag, zinc
smelter residues (from an old slag dump), and also from iron-blast fur-
nace flue dust. Galvanizers'ashes can be treated after dechlorinization
and hot briquetting. Steelworks dusts are now treated first in the
Waelz furnace to fume more than 95 % of the zinc in a product containing
40-50 % combined Zn + Pb. The Imperial Smelting Process offers the best
opportunity to deal with these materials, in particular when the smelter
affords a Waelz kiln and a hot briquetting unit.

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14.28  ITALY

This section is borrowed from a report prepared for this dossier by our Italian partners.

14.28.A.  SECONDARY LEAD

In Italy, re-cycled lead originating from residues, new scrap, and old scrap (including their respective imports) represent 45 % of total lead consumption.

New scrap comprises drosses and ashes from lead transformation processes. Old scrap includes used batteries, cable sheathings, sheets, tubes, and alloys. The table shows the supply of scrap.

The supply of single types of scrap generally depends on the level of consumption during the previous period and on the average life of the various products.

The following table shows the typical life span in years of the main scrap-producing products :

| Starter batteries | 3 |
|---|---|
| Traction batteries | 5 |
| Stationary batteries | 20 |
| Cable sheathings | 40 |
| Sheets (chemical installations) | 15 |
| Tubes | 50 |

Under present circumstances it is possible to establish the following contribution of scrap in the production of various items :

| Batteries | 60 % |
|---|---|
| Cable sheathings | 8 -10 % |
| Tubes | 80 % |
| Shot | 80 % |

Taking into consideration the average life span of certain lead

# LEAD SCRAP FLOW CHART
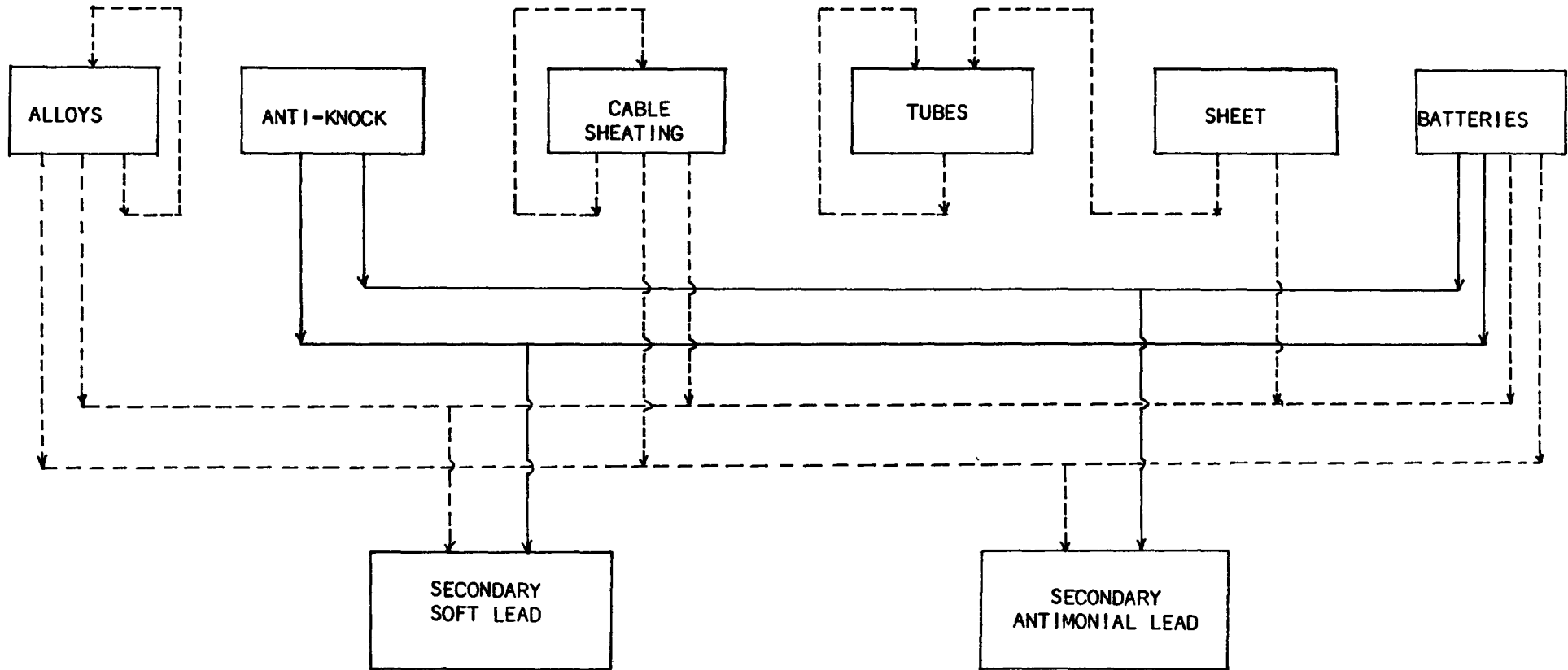


——— NEW SCRAP    — — — OLD SCRAP

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products, the most significant reserves, which, in Italy, could contribute to the re-cycling process, are, in order of importance :

Batteries

Cable sheathings

Tubes and sheets.

Important technical factors make some scrap more suitable for re-cycling than other. In the present state of technology the lead content of alkylene products, pigments, and lead shot is not considered to be reclaimable. The reclaiming of soldering alloys is scarcely taken into consideration for economic reasons.

Nature of available residues

### Residues of the primary metallurgy of lead and zinc

Primary production of lead by traditional process (Blast Furnace) :

Slag from the S. Gavino plant is treated in the Waelz furnace at Porto Vesme for the reclaiming of lead and zinc. Considerable quantities of slag are available in Sardinia for re-cycling. A check is being carried out on quantity and characteristics.

Pertusola metallurgical plant at Crotone :

The quantities of $PbSO_4$ produced, a residue of the leaching of Cubilot produced fumes, are assigned to the primary metallurgy of lead.

### Residues from the chemical industry

Preliminary research will be carried out on residue coming from the ceramics industry.

Present and potential use of the various types of scrap

I. Present use of the various types of scrap.

As shown in the enclosed lead scrap flow chart present uses of the various types of scrap are the following :

New scrap

New scrap include lead bearing ashes, slags, drosses from lead manufacturing processes. These products are usually re-cycled in secondary me-

tallurgy.

Old_scrap

Old scrap consist primarily of : obsolete batteries, cable sheathings, sheets, tubes, and printing alloys. These products are completely recycled In secondary metallurgy. As regards batteries, there Is a technical problem concerning the safety aspect of the operation. Detailed instructions are therefore necessary concerning the responsability for handling.

It appears that studies commissioned by the EEC authorities are currently being undertaken.

Alloys-soldering,_antifriction_and_others

Marginal recovery and products are diminishing continuously.

Scrap from cars, houseshold appliances, and solid town refuse - see chapter on zinc.

2. Potential use of the various types of scrap.

The current use of scrap has been described above. The potential use of scrap will be examined and described In the second report.

14.28.B. SECONDARY ZINC

The recycling of zinc In highly Industrialized countries Is considerably lower than that of other non-ferrous metals, as can be seen In table 14.28.1 mainly for two reasons :
a) the great quantity of zinc employed In dissipative uses;
b) the vast dispersion of scrap, with resultant problems of uneconomical recovery.

Dissipative uses of zinc are represented by galvanization and the chemical products wich form, as can be seen In statistical data, a very high percentage of the total consumption of zinc. The remaining consumption of zinc Is represented by sectors In which recovery presents some difficulties (die casting, brass, rolled zinc).

Table 14.28.1 METAL SALVAGED FROM NATIONAL SCRAP AS % OF CONSUMPTION (1970)

| Countries | % Metal | | | |
| --- | --- | --- | --- | --- |
| | Aluminium | Lead | Copper | Zinc |
| Australia | 19 | 48 | 40 | 16 |
| Germany | 25 | 14 | 34 | 14 |
| Japan | 25 | 24 | 34 | 12 |
| United Kingdom | 34 | 66 | 40 | 24 |
| U.S.A. | 20 | 40 | 50 | 18 |
| World | 22 | 35 | 42 | 20 |
| Italy (°) | 24 | 28 | 30 | 22 |

Source :   - European Zinc Producers Technical Committee

Stockholm, October 1-2, 1975

(°) Average 1973-1975. Our estimation.

The following tables, taken from the European Zinc Producers Technical Committee- Stockholm, October 1-2, 1975, are significant when studying the problem under review. Table 2 reports the amount of recycled zinc obtained from scrap or possible recycling. This is a theoretically ideal reference because it is extremely difficult, if not impossible, as in the case of old scrap, to establish the amount of residual zinc left in the present situation concerning the recovery and salvage technology of zinc.

The state of technological knowledge for the salvaging of zinc from scrap, residues, and by-products can be summarized as follows :

Distillation of galvanization ashes, castings and head metals, rolled zinc, etc., to produce rough zinc, oxides and dusts.

Recycling of brass scrap in brass foundries.

Transformation of galvanization ashes and flue dusts of non ferrous metals into zinc salts.

Refining of die casts and head metals for the production of zinc alloys.

Recovery of lead and zinc in volatilization products from flue dusts in plants producing shaft furnace and electric furnace steel (experimental or semi-industrial stage).

Table 14.28.2

ACTUAL AND ESTIMATED ZINC SCRAP RECYCLING IN THE USA IN 1970

| Scrap Sources | Tonnes of zinc available for recycling | Tonnes of zinc recycled | Percent recycled | Tonnes of zinc not recycled |
|---|---|---|---|---|
| New Scrap (a) | | | | |
| Galvanized clippings | 45 000 | - | 0 | 45 000 |
| Process residues (b) | 170 000 | 150 000 | 88 | 20 000 |
| Old Scrap (c) | | | | |
| Zinc base alloys | 325 000 | 54 000 | 17 | 271 000 |
| Old galvanized | 365 000 | - | 0 | 365 000 |
| Oxide & chemicals | 225 000 | - | 0 | 225 000 |
| Brass | 145 000 | 29 000 | 20 | 116 000 |
| Rolled zinc | 53 000 | 11 000 | 21 | 42 000 |
| Other old scrap | 46 000 | 2 000 | 4 | 44 000 |
| Total | 1 374 000 | 246 000 | 18 | 1 128 000 |

(a) New scrap is process scrap which is not recycled in plant, but is sold for further processing.

(b) Process residues include galvanisers'drosses and ashes,flux skimmings, diecast drosses, non-ferrous flue dusts, swarf, effluent treatment residues, etc.

(c) Old scrap is articles which are obsolete and are available for recycling.

Table 3

PRESENT SITUATION CONCERNING COLLECTION AND RECOVERY TECHNIQUES FOR ZINC SCRAP

| Scrap Source | Collection | Suitable Recovery Techniques |
|---|---|---|
| Galvanized clippings | Good | As steel furnace flue dust, at experimental stage In US Plant operating In Japan |
| Process residues | Good | Yes |
| Zinc base alloys | Poor | Yes |
| Old galvanized | Poor | As for galvanized clippings |
| Brass | Poor | Yes |
| Rolled zinc | Poor | Yes |
| Oxides and Chemicals | Poor | No |

## Nature of available residue

- Residue from (the enrichment of mineral ores) ore concentrates.

They concern only oxidized or very fine ores (Sardinia and Raibl). Residues can also be considered as those oxidized rough ores that cannot be enriched economically with conventional technology: a preliminary investigation is being carried out into the possibility of recovering them and estimating their quantity.

- Residues of primary metallurgy.

Imperial Smelting process.

Cinders have a total metal content of 7 % zinc and 1.2 % lead. Their nature makes recovery difficult. Nevertheless, the possibility of recovering the metal in a blend with other materials is being studied.

- Residues of treatments for the production of electrolytic zinc.

Residues can be found at the Ponte Nossa dump, but their wet-way recovery presents big problems concerning the dumping of residues that are difficult to collect following jarosite and goethite treatment. In Sardinia, large quantities of residues from the lixiviation treatment of ferruginous calamine can be found. Considering the quantities involved, the problem is worth looking into and preliminary investigations are under way.

Residue from Porto Marghera is shipped to Sardinia for the recovery of lead, zinc, and cadmium by means of the Waelz process.

In the Pertusola's Crotone plant, residue from the primary cycle is treated in a Cubilot furnace. To this is added old residue that was already dumped and whose zinc products are sent back to the main cycle.

- Dust and sediments recovered from the iron metallurgy industry.

Generally speaking the situation in Italy can be summarized as follows : extreme care is taken to avoid the treatment of lead-zinc

materials in metallurgical plants for the production of cast iron and conversion into steel. An exception is represented by the use of pyrite pellets, made by Solmine, with lead and zinc impurities, which are introduced in controlled quantities in some of the iron metallurgy plants (Piombino and Cogne).

The problem of the recovery of zinc and lead in the production of steel concerns, in Italy, the production of steel by electric furnace including lead steel. A careful study is to be made of the evolution of the Italian steel industry and its effects on the recovery of lead and zinc.

Italian production of electric furnace steel is currently put at 8.5 million tons a year, with a total amount of dust produced and retained on the order of 60 000 tons a year. These powders are dumped or used as such for particular uses. The zinc and lead content of dust is put, respectively, at 13-15 % and 6-7 %. This material presents certain characteristics which make it possible for it to be treated in rotary furnaces for the recovery of lead and zinc, as well as for the recovery of iron in the form of reduced sponge. From a technological point of view, there exists, as an alternative, the possibility of producing a pre-reduced pellet, to be treated by an electric furnace for the recovery of lead and zinc as oxide. The Italian situation is subject to change in relation to the introduction on the market of pyrite pellets with a greater lead and zinc content.

The most important aspect of the problem is the economic feasibility of setting up a centralized plant for the treatment of dust from steel works.

Present and potential use of the various types of scrap

I. Present use of the various type of scrap.

- New scrap
  ----------

This include the following materials :

Hot-dip galvanizing

The ashes from general galvanizing are made to undergo a mechanical treatment for the separation of the metal contained which is then turned over to the production of re-melted zinc, generally used for

hot-dip galvanizing; very fine ash, in a mixture with spent fluxes, is put through a de-chlorination process, normally in a roasting furnace, then put into the production cycle of either primary zinc or salts.

Galvanizing mattes are presently used in the production of zinc oxide, even if the possibility of their being recycled in zinc pyro-metallurgy is acknowledged.

Dust obtained from the blowing of tubes is largely used as a purifying agent in the production cycle of electrolytic zinc.

Die-castings

Dross from die-casting is recycled in some plants for the production of die-casting or employed in the production of alloys.

Non-ferrous flue dusts

They mainly concern the dusts from smoke traps in the casting of brass; these materials are partly exported, but technology is available for their being recycled for the production of zinc salts and the recovery of copper.

Rolled sheets

New scrap from the production of coffins is entirely used up in the production of zinc spheres employed in electrolytic galvanization.

- Old scrap

Brass

Old scrap originating from this sector is recycled directly by brass producers.

Die-castings

At present they are salvaged by hand from demolished motor vehicules and domestic appliances. For the time being it is impossible to establish the extent of this practice or the destination of the scrap. It is believed that part is use in die-castings,for which there is not much need of purity or quality. It is also possible that it is

used, after distillation and purification, for the production of metal and oxides, but certainly near plants for the production of primary metal.

2. Potential use of the various types of scrap.

The potential use of scrap can come from an improvement in the salvaging of scrap, increased perfection in the processes employed, or the recognition of new technologies.

Economically-viable recycling could be obtained in this way.

Galvanized clippings and old galvanized articles

The problem is essentially that of recovery of zinc from steel fumes. Galvanized clippings can amount to 20 % of the zinc use in the galvanization of sheets. The evaluation of residual zinc on the steel article at the end of its useful life is, on the other hand, extremely uncertain.

The demolition of an article manufactured with galvanized steel can, at times, take place while the article is still protected by zinc; in this case the recycling of zinc is possible. This should be quite a normal fact for reasons of safety and appearence. The article should be demolished before its state of preservation impairs its functionality, or it should be treated by other methods (painting) which protect at least part of its original zinc covering. The opinion of galvanizers and utilizers is contradictory on this matter, therefore, making it very difficult to quantify this aspect.

Brass and rolled sheets

The best use to which recycling can be put, in these two sectors, depends almost exclusively on an improvement in the collection of scraps, since an adequate processing technology is already available.

Zinc base alloys

This is the sector of greatest technical and economic interest

and feasibility. It consists of the problem of separating the alloy : a technology to perfect or define as regards solid urban waste and vehicle scrap, Inasmuch as the collection of this type of scrap forms part of a process involving other products it contains and that have to be salvaged; it also concerns a problem of process technology because there are various criteria to adopt in choosing the finished product that is obtained (pure metal, alloys, derived products).

As for the problem of recovering zinc oxide, studies are being carried out on the matter, and conclusions will be presented in upcoming reports.

As for zinc powder used in paints, the same applies here as applied to the recovery of galvanized articles that have come to the end of their useful life.

## 14.28.C. TYPICAL COMPANY

A. TONOLLI & C. S.p;A.
Paderno Dugnano (Milano)
Marcianise (Caserta)

## Processes

The Tonolli Company is in a position to treat profitably any lead residue having an economically recoverable content, as its plants include: the necessary equipment for breaking and classification of batteries according to their components, three basic means of reduction (shaft, reverberatory, rotary furnaces); as well as conventional and electrolytic lead refining plants.

Particularly, Tonolli's process for battery scrap handling and treatment (mechanical breaking and sink-float separation) makes it possible to obtain, separately, the inert part (cases and separators), the active mass (oxide and lead sulphate), and the grids and connections (antimonial lead).

Soft and antimonial lead are obtained respectively, from the active

mass or the grids and connections, treated separately. In addition, the inert part offers an economically significant recovery, due to the increase of the use of polypropylene for the cases. No by-products or non-reusable residue are obtained from the Tonolli cycle. Fumes are collected and recycled, while dross is utilized for specific purpose.

## Current status and trends in plants

Raw materials consist of disc;rded batteries (or battery plates) which account for 65-70 % of the whole input. Oxide and various dross (including sludge from tetraethyl lead production) account for 10-15 %. Scrap from cable breaking represents 5 %. The balance is represented by either crude or refined lea( slabs.

Metal recovery is up to 96-98 %; maximum recovery is obtained from batteries, whereas minimum recovery is from poor dross (e.g. tetraethyl lead dross).

Yearly production capacity :

| | |
|---|---|
| - Tonolli plant at Paderno | 60 000 tons |
| - Tonolli Sud plant at Marcianise | 40 000 tons |

The plants are operated on average at 70-80 % of their capacity.

Expansion programs
Increase of the two plants production to meet the requirements of the eighties.

## Uses of by-products

Due to the raw materials used for the feed, no by-products are obtained.