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CAC DOCUMENT NO. 217

STOCKPILE OPTIMIZATION: Energy and  
Versatility Considerations for Strategic  
and Critical Materials

by

Peter Penner

Jaap K. Spek

Stockpile Optimization Project

Bruce M. Hannon, Director

May, 1976

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May, 1976

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## ABSTRACT

The Energy Research Group was retained by the Federal Preparedness Agency "to formulate recommendations for the optimization of the stockpile mix of basic and upgraded materials so that the stockpile can better serve as an inventory of stored energy in an emergency." The document first determines the energy cost per physical unit for twenty-one metals and minerals, including aluminum, copper, lead, nickel, titanium and tin. In some cases secondary production (recycling) is considered. These costs are computed from a compilation of previous research, industry statistics, and the results of the Energy Research Group Input-Output Model. The resulting energy costs and other data are used to formulate stockpile policy recommendations for each material.



TABLE OF CONTENTS

<u>PART I.</u>	Page
<u>I.A. Introduction.....</u>	1
1. General .....	1
2. Scope of Work.....	1
3. Limitations to Research.....	2
4. Organization of Report .....	3
<u>I.B. Energy Accounting Methodology.....</u>	5
1. Dollar and Energy Accounting.....	5
2. Energy Measurement Conventions.....	7
3. Allocation Convention .....	11
<u>I.C. Optimization Methodology.....</u>	13
1. Introduction and Definition.....	13
2. Other Factors to Consider.....	14
3. Linear Optimization .....	17
 <u>PART II: DATA AND RECOMMENDATIONS</u>	
1,7,8 Aluminum and Metallurgical Grade Bauxite.....	26
Overview	
Process Description	
Figure 1,7,8 a	
Table 1,7,8: Production of Aluminum	
Secondary Aluminum: Process Description	
Table 1,7,8 b: Production of Secondary Aluminum	
Energy-Versatility Considerations for Aluminum	
Figure 1,7,8 a	
Footnotes to Section 1,7,8	
 <i>The remaining materials in Section 2 follow the format listed above:</i>	
2,3,73 Abrasives.....	38



PART II (continued)

	Page
4 Antimony.....	47
6 Chrysotile Asbestos.....	58
9 Refractory Bauxite.....	64
13 Bismuth.....	69
14,91 Cadmium, Zinc.....	78
16...22 Chromium.....	100
28 Copper.....	120
35,36 Fluorospar.....	134
42 Lead.....	143
43...52 Manganese.....	155
53 Mercury.....	179
59 Molybdenum.....	186
60 Nickel.....	197
62,63,64 Platinum Group.....	209
70,81 Titanium and Rutile.....	219
74 Silver.....	228
79 Thorium.....	239
80 Tin.....	248
82...86 Tungsten.....	263
87 Vanadium.....	277

PART III: SUMMARY AND CONCLUSIONS 287

Bibliography and References.....	291
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## I. A. INTRODUCTION

### 1. General

For the past year, the Energy Research Group has conducted a project on stockpile optimization for the Federal Preparedness Agency, General Services Administration. Quoting from the original scope-of-work statement:

"The purpose of this study is to formulate recommendations for the optimization of the stockpile mix of basic and upgraded materials so that the stockpile can better serve as an inventory of stored energy in an emergency."<sup>1</sup>

It is the purpose of this final report to furnish these recommendations along with supporting data and analyses information.

### 2. Scope of the Work

The original scope of this project included some time for examination of those factors which, in addition to energy use, ought to be included in an optimization of energy storage in the stockpile. The original proposal suggested that industrial capacity and obsolescence were the two most important additional elements. In our response to the proposal,<sup>2</sup> we stated that these considerations and most of the other important ones could be described by a single parameter called the *versatility* of the material. Examination of this parameter and energy use form the backbone of the optimization analyses in this report. Many other refinements and suggestions are discussed in Section I. C.

Throughout this project, a great deal of effort has been spent on compiling complete data on energy use for the production of strategic and critical materials. This is far from a simple, straightforward task, and much of the first two phases of the project (and their accompanying reports)

concerned various aspects of energy accounting in materials production.<sup>3</sup> Our conclusions regarding these subjects are presented in the following Section I.B.

### 3. Limitations to Research

It is always tempting to state that the greatest limitation to any study is time. Though this is true here, a number of other unique and important limitations were encountered and, in some cases, were self-imposed.

In the area of energy accounting, problems begin right at the very sources of data. Worldwide production of primary materials is in the hands of relatively few producers. Most of these companies feel that revealing any details about their operation puts them at a commercial disadvantage. This applies to domestic and foreign companies alike. Information on precisely what makes their processing unique (i.e. different from the average) is the hardest to obtain and yet often critical to an accurate energy accounting. Some costs, such as long-term expenditures on mine exploration and development and capital improvements, are very difficult to allocate on a per-unit-output basis because, for example, the total lifetime output of a working mine is not yet known and may be changing with the concentration of the material in the ore. Finally, a lack of standardization in accounting and allocation techniques contributes to discrepancies in energy use figures. In several cases, such difficulties preclude gathering data that reliably reflect average worldwide practices and resource balances. Usually data is compiled for one or several producers in a few countries and then modified to resemble practices in the rest of the world.



Many of these problems may affect optimization studies because they, too, are based on precise details of materials production. In contrast to energy accounting, which traces most processes *vertically* (in the sense of vertical integration), versatility research is *horizontal* -- the flow of the final product to other industries and consumers. A fair number of cartels exist for controlling the production of various materials but, to date, none control or even keep track of the various end uses of their products. Fortunately, the Federal Preparedness Agency need only consider the strategic and critical end uses for a material, which limits the investigation to a relatively well-known area, namely defense industries. Additional limitations to the examination of versatility are discussed in Section I.C.

#### 4. Organization of Report

This document is in two main parts. Part I contains this introduction and the two sections mentioned previously: energy accounting methodology and optimization methodology. These sections serve several purposes. First, they explain the theoretical basis for the techniques used and assumptions made in Part II of this report. They also discuss certain abstract concepts which are relevant to policymakers trying to assess the role of basic materials in the world.

Part II contains the actual energy use data and optimization recommendation organized by material or group of materials. Each small section begins with an overview of concentrated fundamental information on the material considered. Aside from being a valuable aid to understanding the figures which follow, the overview is the essential starting point for a detailed study of versatility and other important optimization factors.

After the overview, every section contains a process description. This is a summary of the industrial processes required to produce a material in its stockpiled form from naturally-occurring minerals. Such a description proves essential in trying to analyze the energy use in the individual stages of a complete manufacturing sequence. In many cases, a graphical flowsheet is also included for the same purpose. Following this is tabular energy data and a discussion of energy and versatility considerations for the materials.

In some cases, our energy research revealed little basis for an optimization of a particular commodity. This was true of the materials which either required little energy to produce or else offered little opportunity for changing practices.

Note that each section has its own footnotes, but that the list of references is at the end of the report.

## I.B. ENERGY ACCOUNTING METHODOLOGY

### 1. Dollar and Energy Accounting

For the greater part of economic history, the production and consumption cost of energy, materials, goods and services was measured on a monetary scale. The elaborate technique of dollar accounting for industrial processes has only recently been expanded by energy accounting and the determination of environmental impacts. The motivation for this lies in the fact that the volume of the earth's finite resources is beginning to appear inadequate for the world's current population and industrial growth. Specifically, severe restrictions are anticipated in the foreseeable future regarding the supply of non-renewable energy sources: the fossil fuels coal, oil, gas, as well as uranium. Since energy runs the economy, it has become necessary to take a more detailed look at the energy requirements for selected industrial sectors or processes.

Basically, two methods of energy accounting exist: process or vertical analysis and I/O analysis. To find the energy cost of a product by process analysis, one first obtains the energy bill of the manufacturer of that product. Next, the non-energy inputs to this final manufacturing stage are listed, and, via the energy bills of producers of these inputs, an actual energy cost for each one of them is allocated. Theoretically, this process has to be repeated until inputs to an industrial process solely consist of minerals extracted from the earth. It is clear that such an approach would yield accurate results, yet be prohibitively tedious, especially if one wanted to assess the energy cost of a whole spectrum of products.

For practical purposes, the analysis is truncated after a number of steps, namely when the resulting error is assumed to be reasonably small.

Rather than laboriously perform a process analysis for each product of the U.S. economy, one can treat them all simultaneously by applying the methods of I/O analysis [0-200, 0-201, 0-202]. The Bureau of Economic Analysis makes available comprehensive data on the \$-value of inter-industry transactions and final demand of goods and services. From this data, a matrix of technological coefficients can be derived, defining the dollar amount of a given industrial sector K's output sold to another sector L per dollar of L's output. The total output of industry K consists of that sold to other industries plus that sold to final demand. Both the Census of Manufactures and the Bureau of Mines provide data allowing for the calculation of the output of the energy sectors in terms of energy [0-212]. The Census of Manufactures also gives direct data on energy consumption for a great number of non-energy sectors; for remaining non-energy sectors dollar flows in the total transaction matrix mentioned earlier are converted to energy flows. The energy embodied in a sector output enters that sector from other sectors, imports and domestic energy production.

Thus a complete matrix of energy I/O coefficients of the U.S. economy is composed, with the aid of which the energy cost of an arbitrary transaction can be found in the following simple manner:

$$\begin{array}{ccc}
 \text{(Dollar Transaction)} \cdot \left( \begin{array}{c} \text{I/O energy coefficient} \\ \text{for transaction} \end{array} \right) & = & \left( \begin{array}{c} \text{energy required for} \\ \text{transaction} \end{array} \right) \\
 \$ & & \text{Btu} \\
 & \text{Btu/\$} &
 \end{array}$$

## 2. Energy Measurement Conventions.

It is obvious that for the purpose of determining the energy cost of explicitly identified materials, due to its generalizing character, I/O analysis is not suitable. This leads automatically to the choice of process analysis tailored to details of material production.

As explained above, process analysis looks at a chain of industrial processes, each of which represents a production stage of the material or commodity under investigation. The chain starts at the point where a (fuel or non-fuel) material is extracted from the earth and usually ends with final use consumption and/or disposal of the end product containing that material. In this report, however, the chain is terminated when the form of a material satisfies the National Stockpile Purchase Specification

A single industrial process, schematically represented in Figure 0-1, can be described in terms of energy flow: the inputs require materials and energy, and at the output appear upgraded materials, main products, by-products, scrap and waste products. The energy obtained onsite at an industrial facility, from direct conversion by combustion of coal, petroleum, gas or dissipation of electricity is called direct, actual or caloric energy and is expressed in Btu per ton, per bbl, per cu. ft. of fuel or per kWh of electricity used. After combustion or dissipation, it is considered to have become embodied in the product leaving the facility; thus fulfilling the law of conservation of energy.

Embodied energy, measured in Btu per ton of specified material, consists of the sum of all direct and indirect energy used to run the process.

Indirect energy encompasses:

- A. The energy embodied in main and ancillary materials, imports;

- B. Energy due to transportation, which can be seen as a special kind of industrial process;
- C. Capital energy, also called industrial services or factory overhead. This is the energy required to manufacture and build the tools, installations and offices defining a given industrial process.

Data concerning the energy industry, using primary fuels, coal, petroleum, gas and uranium, as well as electricity derived from either these fuels or from hydro-power are taken from available literature [0-201, 0-206].

It is obvious that production of energy requires energy itself. In order to have a common base for all energy accounting, the concept of primary energy is used. It is defined as the sum of all forms of direct energy required since extraction from the earth, to deliver one unit of a form of energy to the consumer, plus the caloric value of that energy form. Inverse delivery efficiency is then the ratio:

$$\text{Btu (primary)} = \frac{\text{Btu (embodied)} + \text{Btu (caloric)}}{\text{Btu (caloric)}}$$

The following table lists conversion factors together with corresponding delivery efficiencies of some of the most frequently used energy types. In a few particular cases values may differ, at which point the relevant figure will be given in a special footnote.

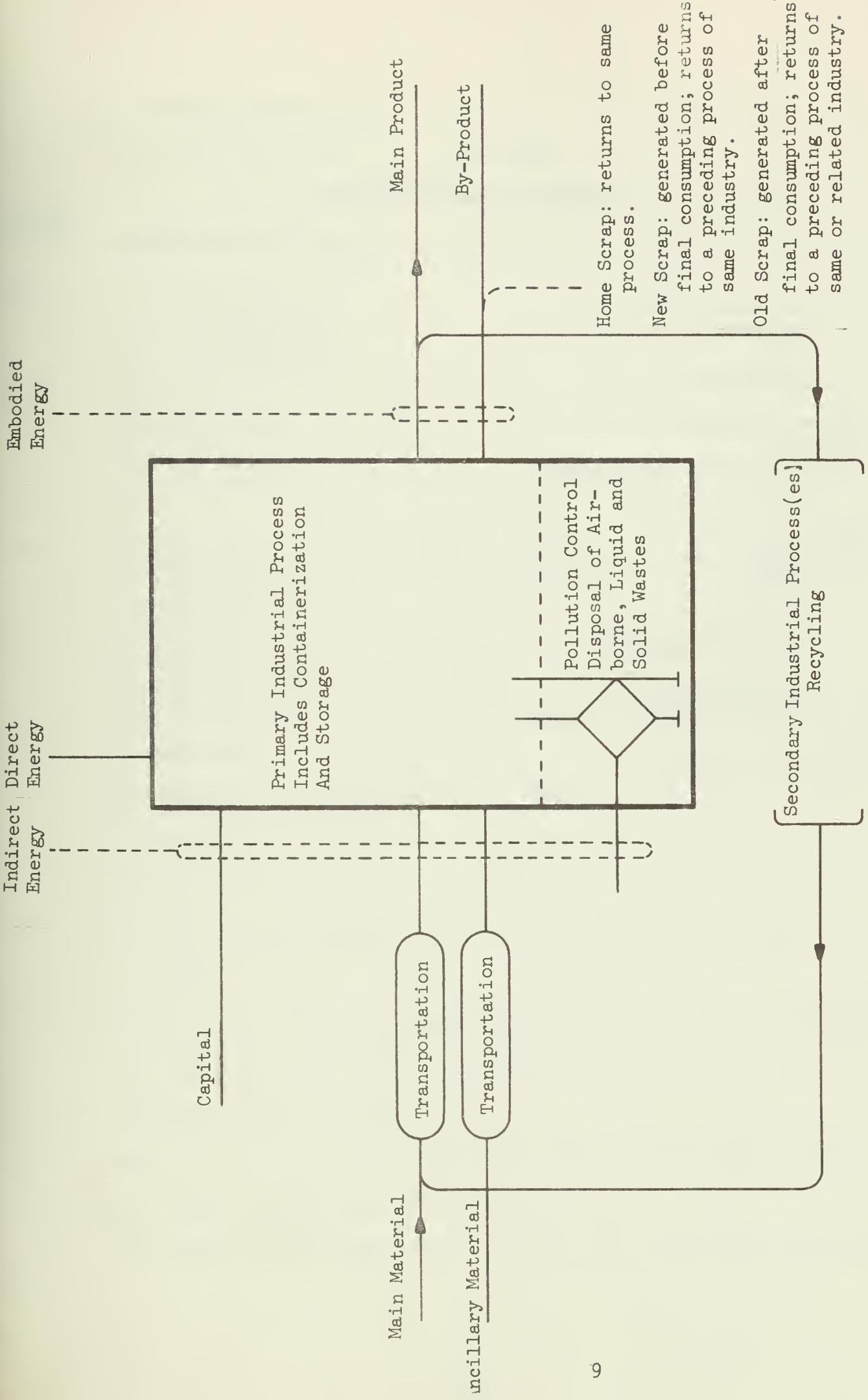


Fig. 0-1. ENERGY FLOW IN AN INDUSTRIAL PROCESS

Table 0-1

CONVERSION FACTORS EMPLOYED

	<u>10<sup>3</sup> Btu per Unit</u>	<u>Delivery Efficiency</u>
Coal:		
Anthracite (Penn.)	25,400,000 Ton	0.993
Bituminous	26,200,000 Ton	
Coke	24,800,000 Ton	
Coke Breeze	20,000,000 Ton	
Natural Gas (Dry)	1,035 Cu. Ft.	0.91
Still Gas	1,500 Cu. Ft.	
Natural Gas Liquids (Average)	4,011,000 Bbl.	
Propane	3,843,000 Bbl.	
Petroleum:		
Coke	6,024,000 Bbl.	0.83
Crude Oil	5,800,000 Bbl.	
Diesel	5,806,000 Bbl.	
Distillate Fuel Oil	5,825,000 Bbl.	
Gasoline, Motor Fuel	5,253,000 Bbl.	
Kerosene	5,670,000 Bbl.	
Heavy Fuel Oil	6,287,000 Bbl.	
Liquified Petroleum Gases	4,011,000 Bbl.	
Electricity (direct)	3,412 kWhr	0.26



### 3. Allocation Conventions

#### - Regarding Feedstocks:

Fossil fuels, not used as fuel or the source of electricity, but as material inputs instead, are assumed to contribute their primary energy to the process.

#### - Regarding Imports:

The energy cost of an imported material is determined in the country of origin. Where this appears to be difficult or impossible, we consider the cost same as if it were produced domestically, or, secondly substitute data from similar domestic operations. Thirdly, if a special derivation is required, it will be described at an appropriate point in the production table.

#### - Regarding an Industrial Process With Several Outputs:

Find for as many products as possible a "replacement" cost (i.e., the energy needed to produce them by some other process), and distribute remaining input energy according to one of these 3 criteria:

- attribute it in full to the "principal product."
- partition according to some physical parameter.
- partition according to contributions to the total \$ value of the output.

It should be noted that in many studies these distinctions are not made, all energy is implicitly allocated to the main product.

#### - Regarding Scrap Materials:

Home scrap has the same energy cost as the output at which it arises.

New scrap is attributed zero energy cost.

Old scrap has zero energy cost as long as it is not being transported.

- Regarding Waste Treatment:

Energy cost due to ancillary materials and processes are calculated for a normalized output and added to main cost.

- Regarding Transportation:

Ton-mile figures are dependent on mode, vary from case to case, and will therefore be given in specific footnotes.

- Regarding Factory Overhead:

Although this term is often considerable, it had to be omitted in this study, except in instances where I/O analysis provided data. The determination of relevant figures would have complicated the task unnecessarily.

## I.C. OPTIMIZATION METHODOLOGY

### 1. Introduction and Definition

In this section, an energy optimization model for strategic and critical materials is developed. The word optimization here means maximizing an objective function by adjusting variables are often inversely related. Other variables in the objective function affecting the stockpiling of the material but not considered in the optimization must be assumed constant.

An objective function allows one to establish a quantitative ranking of policy options under a given set of constraints. In this case it is the optimum combination of maximum energy stored and maximum versatility preserved for a given material. Energy stored, also called energy "used," "consumed," "invested," or "required," means the cumulative energy expenditure to process a material from its naturally occurring state and location to the desired form and location. Versatility is not a strict scientific concept: it refers to the choice of available applications for a material in a certain form. A useful definition for versatility of material A in form  $(c_j, p_j)$  might be:

$$V(A, c_j, p_j) = \frac{\text{number of uses for material A in form } (c_j, p_j) \text{ including combinations with other materials}}{\text{number of all uses for Material A (starting with naturally occurring form } c_0, p_0 \text{ and including combinations)}} \times 100 [\%]$$

where c indicates chemical and p the physical properties of a form. Note that the maximum value is 100, whereas the lower bound can never reach zero.

Computing such a number for any material requires gathering data that are difficult to access. However, specifying the form for which a versatility is desired suffices, once the complete V function as a look-up table is known.

It is clear that the variables energy use and versatility are inversely related. Every processing step which a material undergoes increases the energy embodied in it; each step also decreases the versatility by bringing it closer toward its final use as a specialized manufactured item. Thus optimization in this case consists of balancing these two opposing factors while considering other factors to be discussed later in this section.

As an example of a sort of first order optimization has been presented previously and is repeated here in Figure 0-2. This example shows a plot of versatility vs. energy consumption for a sample commodity, 12 oz. aluminum beer cans. Note that all other factors in beer can production, such as the price of energy or the political control of Surinam's bauxite mines, are assumed constant. It should be noted that in this plot a weighting factor has been applied to energy use. To obtain primary Btu's, this amounts to weighting of actual energy-use ("on-site") by a factor of 3.33 for electricity, 1.09 for natural gas, and so on. In many cases the conversion to primary energy is implicit and, therefore, seldom considered a weighting as such.

## 2. Other Factors to Consider

There are a number of factors other than energy use and versatility which affect the production sequence of a material. These factors should

be examined for several reasons. First, considering them constant may be incorrect, as in the case of energy prices. Knowing that some factors are changing, in particular the direction and magnitude of the changes, is very important for understanding and extrapolating these results. This may point out factors which should be varied in the optimization rather than held constant.

A third important factor is scarcity, the number of independent sources for a material. This has been complicated recently by the formation of producers' alliances, such as the International Bauxite Association. Their purpose is to increase scarcity, decrease market competition, and raise prices.

These effects are somewhat countered by other factors to consider: substitution (and complementation) of materials, international monetary, political, and trade agreements, even domestic price controls and other laws. The political situation in trading countries plays a role because it usually determines the sources' selling policy and may have market effects based on the strength, stability, and influence of the government in other areas.

It is equally vital to recognize that this optimization is performed for the National Stockpile. Accordingly, it should serve the purposes of the Federal Preparedness Agency and particularly the policy objectives of the stockpile currently being considered. For example, reference [0-125] identifies eleven possible stockpile objectives, including one described as "Advancing New Technology for Materials Supply." An objective such as this would definitely enter into an energy/versatility optimization.

If advanced technology is to be encouraged, then most materials should be stockpiled at a high versatility level to be available to new processing techniques.

Finally, the element of processing time must be considered. This relates both to transportation time (mainly from foreign sources) and to actual processing time in each step upgrading the material. It is clear that the lower the versatility, the faster the material can be brought to its final form. This might be of prime importance considering the national defense applications for the stockpile. Inclusion of this factor would necessitate a weighting inverse to that used for advancing newer technology, that is a weighting which favored more advanced forms of the material.

Factors related to energy accounting might also be included in this optimization. One consideration is scarcity of energy forms used. This means that aside from determining the actual form and amount of energy originally required from the earth, a weighting be included to favor those forms for which there is a large or easily substitutable supply. The ranking of several current energy forms, from least to most scarce is listed in Table 0-2. This ranking indicates that a weighting favoring solar energy most and oil least should be employed. Such a factor might be similar to an energy "credit" of .5 Btu for every Btu of solar, similar to the factors used now to convert Btu figures to primary.

A second element of energy accounting is the amount used in energy form by the materials industry, as opposed to energy received in ancillary materials, or "indirect" use. This is important because it is

much more difficult to control indirect energy usage than direct, and often efforts at altering direct energy use have adverse effects on indirect energy use.

Energy also enters into relationships of substitution and complementation with other factors of production. These relations involve labor, capital energy forms, and raw materials, with the former two most common. Such substitutions may be considered as alternative sources of energy, and therefore tend to offset the severity of energy shortages.

Fourth, a consideration of marginal energy cost might be useful in stockpile policymaking. Marginal energy cost is the amount of energy required to produce an additional unit of output of a given form of a material. For some materials, in some stages of production, this marginal cost might differ greatly from the average energy cost figures commonly used.

### 3. Linear Optimization

The simplest mathematical model useful for treating the many factors named above is a linear optimization model. This model requires that all factors which contribute to its objective be independent of each other or nearly so. Under this assumption the following procedure can be adopted:

1. For the optimization, define an objective function.
2. Identify all factors which relate to the objective function, which are independent, and for which data are available.
3. Assign a weight to each factor in 2.

This procedure yields an equation of the form:

$$F_{obj}(F_1, F_2, F_3, \dots) = W_2 F_2 + W_3 F_3 \dots + W_n F_n$$

where  $F_a$  = an independent factor (such as energy use in Btu's)

$W_a$  = subjective weight applied to this factor. The sum of all W's should be 1.

The value of this function might be maximized, minimized, or targeted to achieve a particular value, depending on the purpose of the optimization. As an example of this sort of optimization, consider the environmental impact measurement technique used by Midwest Research Institute (MRI) in reference [0-324]. In their research, MRI called the objective function "composite (environmental) impact index." In a particular application the following independent impact categories are considered: Raw Materials, Water Use, Energy Use, Atmospheric Emission, Waterborne Wastes, Industrial Solid Wastes, Post-Consumer Solid Wastes. For a given collection of environmental input data  $I_{ij}$ , the mean  $I_{i0}$  for each impact category is computed.

The next step is conversion of this collection of physical into dimensionless quantities, combined with weighting by category:

$$CII = \sum_i W_i \frac{I_{ij}}{I_{i0}} \cdot 100, \text{ for each } j$$

Finally, the  $j$  sums are ranked in ascending order, so that a higher number signifies a higher environmental impact.

It is appropriate to ask here whether the factors identified previously in this report are sufficiently independent to allow for a linear



optimization. Some are and some are not; Table 0-3 lists the factors grouped according to their independence. The entries in a single group in this table would have to be considered as one term and weighted by one factor in an optimization equation. Note that many of these terms are not strictly quantifiable in the sense that terms in the above MRI CII function are. If they are not, the separation of the term and the weighting factor is redundant; the term added to the function is itself a weighting factor and should be specified with this in mind.

In this report, no objective functions have been specified. We have not done this because it is our opinion that the decision as to which factors are to be included in the optimization, and particularly the choice of numerical weighting factors, is strictly a policy decision on the part of the Federal Preparedness Agency. We do in each case present graphically the results of a first order optimization of primary energy and versatility because such an analysis is straightforward and policy-free. This section is intended to form the basis for a possible complete stockpile optimization by FPA, and all findings in this section may be construed as direct recommendations from E.R.G. to F.P.A. concerning such an optimization.

Finally, it should be remembered that this procedure as well as the strategy implied by such a procedure is only one possible course for F.P.A. to follow. F.P.A.'s same objectives might be achieved, for example, by stockpiling only the basic ores of the materials and large amounts of energy in energy form. In general, policies and planning should not be formulated on the basis of a single objective function or optimization procedure alone.

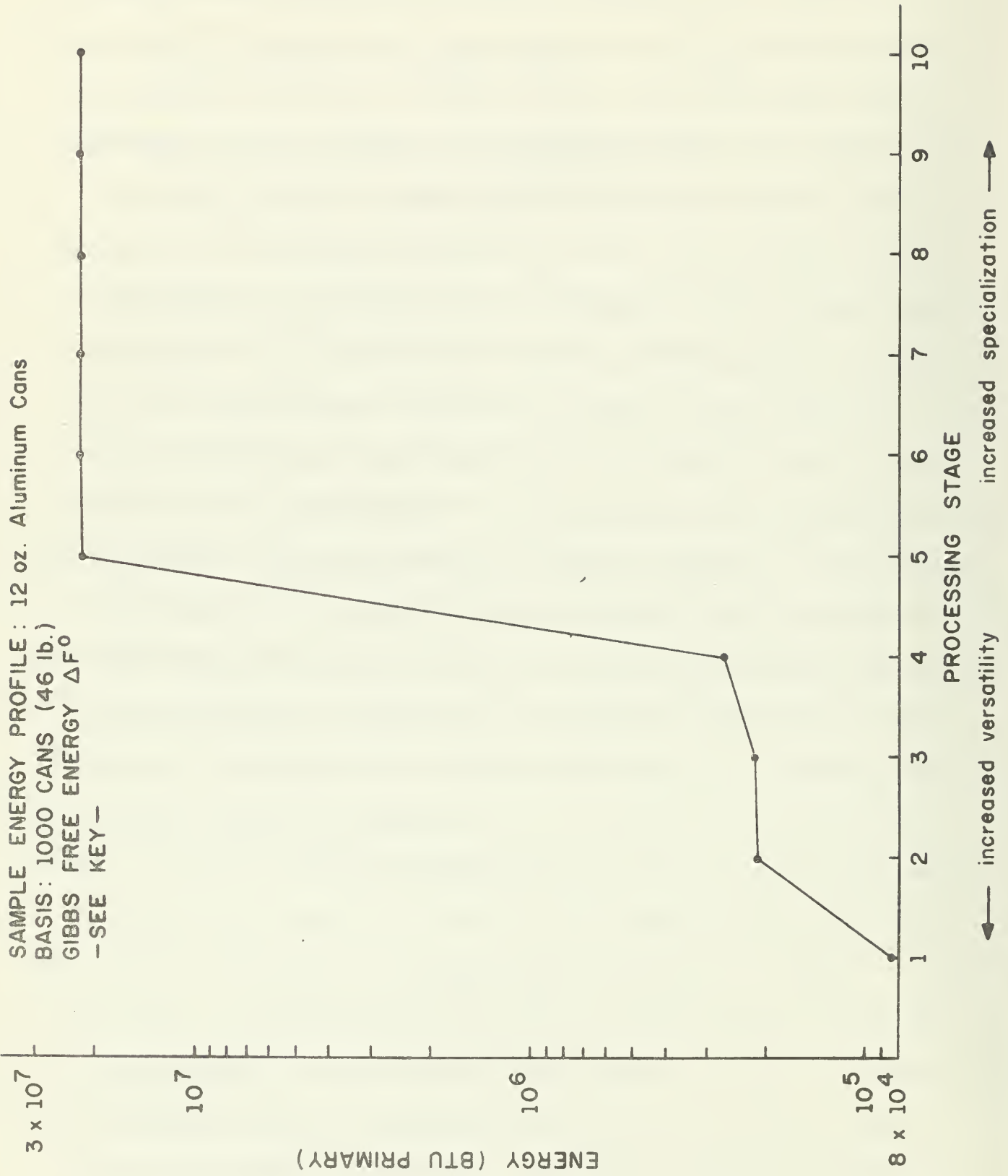


FIGURE O-2: First Order Optimization

Notes to Figure 0-2

ASSUMPTIONS

- A. 50%  $Al_2O_3$  Bauxite Ore
- B. Electric energy converted to Btu's at 3412 Btu/kwh and efficiency of electrical generation considered to be 30%.
- C. The aluminum is produced by the Bayer Process. 181 lb. of ore produces 76 lb. ingots, 62 lb. can sheet, and 46 lb. cans.

KEY TO PRODUCTION STAGES

- 1. Bauxite minining, crushing, grinding and washing
  - 2. Steam for evaporation and digestion
  - 3. Pumping, clarification, and filtration
  - 4. Calcination of  $Al_2O_3 \cdot 3H_2O$
  - 5. Electrolysis
  - 6. Melting, casting, good ingot, scalping, and hot rolling
  - 7. Sheet fabrication
  - 8. Can fabrication
  - 9. Can filling
  - 10. Storage
- } Bayer Process

SOURCES

- 1. Bravard, J. C. et al. The Production and Recycle of Metals. ORNL-NSF-EP-24, Oak Ridge National Laboratories, Oak Ridge, Tennessee, November 1972.
- 2. Makino, H. and Berry, R. S. Consumer Goods - A Thermodynamic Analysis of Packaging, Transport, and Storage. Illinois Institute of Environmental Quality, June 1973.

TABLE 0-2

Rank	Energy Form	Comments
1	Solar heat or Solar electricity	Very little commercial use but definitely the most <b>renewable</b> energy form.
2	Electricity by other fuels	Not necessarily plentiful or efficient but fuel sources are very substitutable.
3	Coal	Very plentiful and somewhat substitutable.
4	Natural gas	The ranking of these two may change with political policies or development of new sources.
5	Oil	

TABLE 0-3

General Factors

Natural Scarcity, U.S. and Global

Substitution and Complementation

Cartel or Unilateral Political Actions Affecting Price or Supply;  
International Trade and Monetary Policies;  
Domestic Trade Policies

Non-Political Import Disruptions

Stockpile Factors

Objective of Stockpile

Transportation and Processing Time

Energy Factors

Scarcity, Substitution and Complementation of Energy Type

Ratio Direct to Indirect Usage

Marginal Energy Cost

FOOTNOTES TO PART I

- <sup>1</sup> RFP to contract AP-75-4, 5/23/75.
- <sup>2</sup> "Stockpile Energy Optimization," Price Proposal to the Office of Preparedness, Energy Research Group, 6/4/76.
- <sup>3</sup> Phase 1 and Phase 2 Progress Report to the Federal Preparedness Agency, General Services Administration, Energy Research Group, 9/1/75 and 2/7/76.

SECTION II:

DATA AND RECOMMENDATIONS

## 1,7,8 ALUMINUM AND BAUXITE, METAL GRADE

### Overview

Aluminum, atomic number 13, is a metallic element comprising about 7% of the earth's crust.<sup>1</sup> Most of this is present in aluminum silicates (clays) and aluminum oxides (bauxite rock). Aluminum clays contain about 30% basic aluminum oxide ( $Al_2O_3$ ) and are in abundance in many regions of the world.<sup>2</sup> Bauxite contains approximately 50%  $Al_2O_3$  and is the only current commercial source for aluminum due to demand, available technology, and cost.<sup>3</sup> World bauxite reserves are estimated at 5760 million tons (.86% domestic)<sup>4</sup>; commercial deposits used for aluminum production are found mainly in Australia, Jamaica, Surinam, the U.S.S.R., and Guinea.<sup>5</sup> Bauxite is classified according to the purpose for which the aluminum is used: metallurgical, refractory, or abrasive. Metallurgical grade is often further specified by country of origin, though this practice will not be used in this section. Refractory and abrasive grade bauxite are discussed in other sections.

U. S. production of aluminum is handled by twelve domestic producers who import either raw or concentrated bauxite from foreign mines which are usually company-owned or nationalized. In 1973, the United States imported 3,419,000 short tons of raw bauxite, 1,712,000 tons of alumina, and produced a total of 4,893,000 short tons of pure primary aluminum (66.4% from the major three producers).<sup>6</sup> Secondary production of aluminum has been profitable on a commercial basis since around 1954 and in 1973, 1,400,000 tons of scrap were reprocessed to yield 1,230,000 tons of metal,<sup>7</sup> 25% of all demand.



Manufacturing aluminum by the Bayer process yields several significant coproducts and byproducts. Foreign companies have recovered pit iron, iron oxide, vanadium and chromium from bauxite ore. In the U. S., Reynolds Aluminum produces gallium from its domestic bauxite. Byproducts of bauxite refining are used for cement-making and as a de-acidifier for land and industrial waste. There is an extremely high concentration of titanium in the "red mud" byproduct of bauxite refining, but to date no economical means of recovery has been found.<sup>8</sup>

Aluminum metal is extremely versatile, light, and strong. The number of applications for aluminum has grown steadily since its introduction in the 1890's and consumption has grown at a yearly rate of 6.9% in the last decade.<sup>9</sup> Major markets for aluminum are (in order of 1973 consumption) building and consumption, transportation, containers and packaging, and electrical equipment.<sup>10</sup> There are several substitutes for aluminum, notably plastics, steel, fiberglass, and wood.

## PROCESS DESCRIPTION

This excellent description of the aluminum production sequence is taken from a recent Battelle/Columbus report for the U.S. Bureau of Mines [0-325a]:

"Aluminum production may be subdivided into four major steps: mining, handling, and drying of bauxite at the mine site, transportation, refining the bauxite into alumina, and smelting the alumina into aluminum.

Most bauxite lies near the surface where it is surface mined. It is then crushed, ground, and kiln dried to remove excess moisture.

The method used to separate alumina from impurities in the bauxite is the Bayer process. In this process, the bauxite is mixed with caustic soda and 'digested' under heat and pressure so that the alumina in the bauxite is dissolved in the caustic soda as sodium aluminate, leaving behind the impurities as insoluble solids which are filtered out in a series of pressure reducing tanks and filter presses. The solution containing alumina is cooled and 'seeded' with fine crystalline alumina hydrate to precipitate alumina trihydrate which is then filtered, washed, and heated in kilns to drive off chemically attached water and yield commercially pure alumina. The dry alumina is then shipped to the aluminum smelter.

At the smelter the electrolytic reduction cell (or "pot as it is known in the trade) breaks alumina down into its components, aluminum and oxygen. The alumina is dissolved in a molten

cryolite (sodium-aluminum fluoride) electrolyte. High-amperage, low-voltage direct current passes through a suspended carbon anode located at the top of the pot and deposits aluminum on the bottom carbon lining, which, covered with a molten layer of aluminum, acts as a cathode. As the aluminum builds up in depth, it is siphoned off. The separated oxygen plates out on the anode, where it combines with carbon, and is released as carbon dioxide."

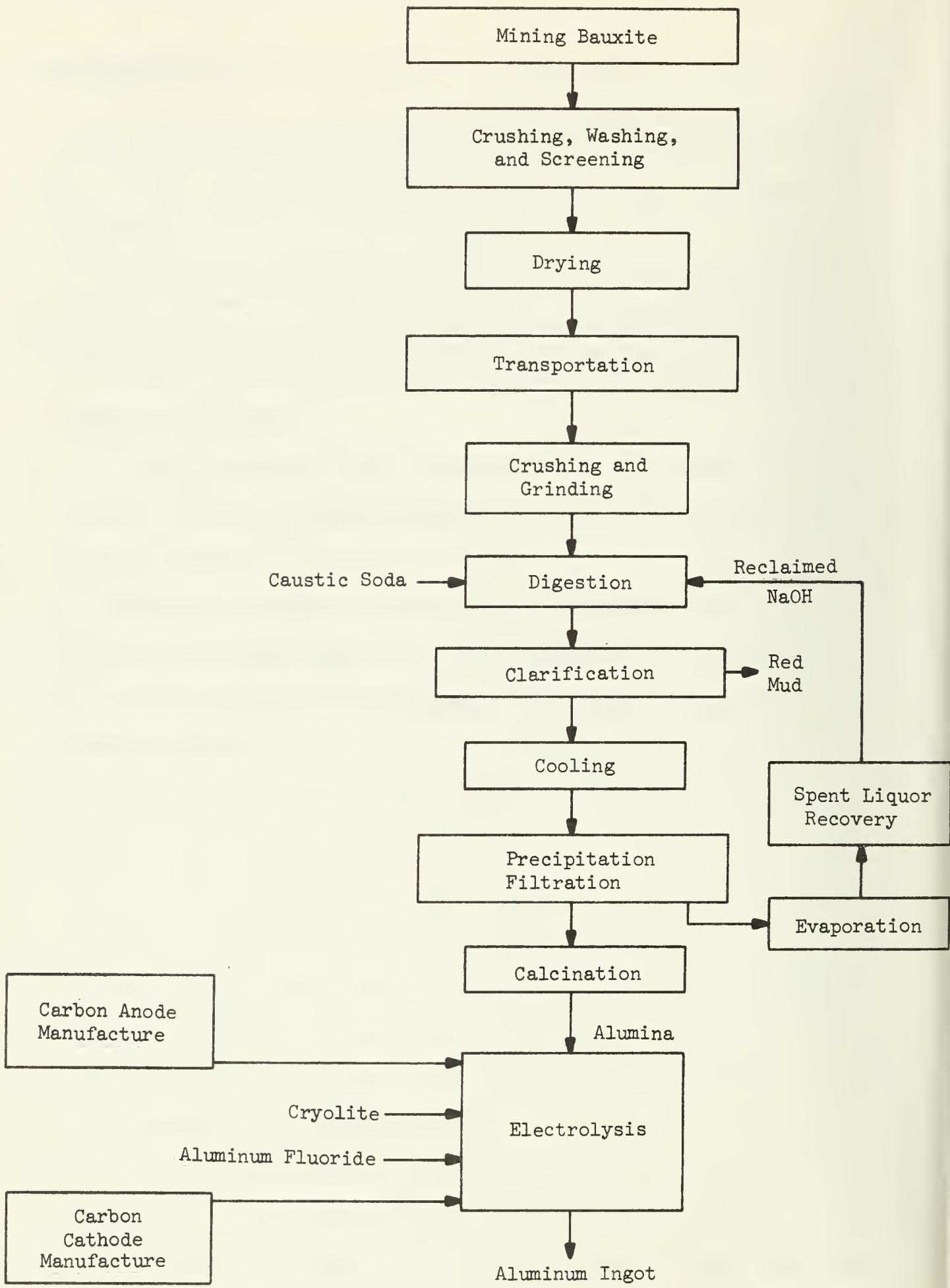


Figure 1a: PRODUCTION OF ALUMINUM

Source: [0-325b]

Table 1,7,8. PRODUCTION OF ALUMINUM  
 (Basis: 1 ton pure primary aluminum ingot to federal specifications)<sup>c</sup>

STAGE	BATTELE/COLUMBUS <sup>a</sup>			ATKINS <sup>b,f</sup>		
	Type	Amount	10 <sup>3</sup> Btu	Type	Amount	10 <sup>3</sup> Btu
1. Mining, Processing and Transport <sup>g</sup>	electric	30.15 kWh	396	electric	21 kWh	275
	diesel oil <sup>f</sup>	.70 gal.	2,375	fuel oil	8.4 gal.	1,404
	materials <sup>e</sup>	.80 lb.	24	diesel oil	9.2 gal.	1,532
	heat energy <sup>d</sup>	-	1,970	natural gas	1,071 ft <sup>3</sup>	1,341
<i>Subtotal</i>			<u>4,765</u>		<u>4,552</u>	
Total Energy required per ton Processed metallurgical bauxite			1,065		1,011	
2. Refining <sup>h</sup>	electric	203.81 kWh	2,675	electric	423 kWh	5,551
	natural gas <sup>i</sup>	7,720.0 ft <sup>3</sup>	8,483	natural gas	12,680 ft <sup>3</sup>	15,885
	steam	19,565 lb.	27,391	fuel oil	51.0 gal.	8,522
	materials <sup>j</sup>	-	5,350	diesel oil	10.1 gal.	1,682
<i>Subtotal</i>			<u>43,899</u>		<u>31,640</u>	
Cumulative Subtotal			48,664		36,192	
3. Smelting (including carbon anode and cathode manufacture)	electric <sup>p</sup>	16,973 kWh	210,927	electric	16,450 kWh	215,874
	natural gas <sup>i</sup>	2,094 ft <sup>3</sup>	2,301	natural gas	3,562 ft <sup>3</sup>	4,462
	transportation <sup>l</sup>	292 net TM	196	LNG	3.0 gal.	314
	materials <sup>m</sup>	.503 tons	19,727	fuel oil	2.3 gal.	384
	materials <sup>n</sup>	29.18 gal.	4,669	fuel oil	.8 gal.	134
				materials <sup>k</sup>	-	18,660
<i>Subtotal</i>			<u>237,820</u>		<u>239,828</u>	
Cumulative Subtotal			286,484		276,020	
4. Ingot Manufacture <sup>o</sup>				electric	55 kWh	722
				natural gas	4,820 ft <sup>3</sup>	6,038
				LNG	.2 gal.	21
<i>Subtotal</i>			<u>-</u>		<u>6,781</u>	
TOTAL			286,484		282,801	

NOTES TO Table 1,7,8

- <sup>a</sup> Source: [0-325a], p. 9.
- <sup>b</sup> Source: [1-121], pp. 11-17.
- <sup>c</sup> See [1-140].
- <sup>d</sup> Type unspecified, probably natural gas.
- <sup>e</sup> Energy equivalents for materials and explosives. Includes 9,500 Ton Miles of water shipping @ 250 Btu/TM.
- <sup>f</sup> Caloric values of fuels assumed: 130,000 Btu/gal. diesel oil, 140,000 Btu/gal. fuel oil, 1,120 Btu/ft<sup>3</sup>.
- <sup>g</sup> Includes mining (energy and materials) loading, intramine transport, crushing, washing, screening, drying, and transportation from mine to plant.
- <sup>h</sup> Includes crushing, grinding, lime, digestion, clarification, cooling, precipitation-filtration, evaporation, spent liquor recovery, and calcination.
- <sup>i</sup> Caloric values used: 1,000 Btu/ft<sup>3</sup> natural gas, 1,400 Btu/lb. steam.
- <sup>j</sup> .15 ton caustic soda @  $30.0 \times 10^6$  Btu/ton and .1 ton lime @  $8.5 \times 10^6$  Btu/ton.
- <sup>k</sup> "average for pitch, coke, coal, and gilsonite materials"; aluminum fluoride and cryolite are included elsewhere.
- <sup>l</sup> All are by rail @ 670 Btu/TM.
- <sup>m</sup> 425 tons petroleum coke @  $30 \times 10^6$  Btu/ton, .02 tons anthracite @  $25.94 \times 10^6$  Btu/ton, .035 ton cryolite @  $155.0 \times 10^6$  Btu/ton, .02 ton aluminum fluoride @  $51.4 \times 10^6$  Btu/ton, and .003 ton fluorospar @  $1.59 \times 10^6$  Btu/ton.
- <sup>n</sup> Pitch binder, caloric value: 160,000 Btu/gal.
- <sup>o</sup> Not specified separately by Batelle/Columbus.
- <sup>p</sup> Actual electric energy delivery efficiency to aluminum smelters assumed to be 30.7%.

## SECONDARY ALUMINUM - PROCESS DESCRIPTION

Secondary aluminum is produced from six classes of nonferrous scrap: clippings, borings, and skimmings (new scrap) and sheet, wire, and iron (old scrap). Each type requires a different type of preparatory cleaning and grinding. Some types also require a magnetic separation step to eliminate large ferrous impurities in the scrap. When processed, all scrap is fed into an electric reverberatory furnace and then poured into ingot forms.

## ENERGY-VERSATILITY CONSIDERATIONS FOR ALUMINUM

The energy/versatility graph for primary aluminum indicates that the optimum form for stockpiling is probably primary aluminum ingot. If advanced forms beyond aluminum ingots are considered, this conclusion becomes even more evident. If stockpiling ingots does not prove feasible or desirable, the next best form is refined alumina. See Figure 1-b.

Table 1b. PRODUCTION OF SECONDARY ALUMINUM<sup>a</sup>

(Basis: 1 ton pure secondary aluminum ingot)

STAGE	ENERGY	UNIT	10 <sup>3</sup> Btu
1. Transportation	Unspecified	-	169
<i>Subtotal</i>			<u>169</u>
2. Crushing (drying, baling, separation, etc.)	Unspecified <sup>b</sup>	-	1,523
<i>Subtotal</i>			<u>1,523</u>
<i>Cumulative Subtotal</i>			<u>1,692</u>
3. Smelting and Ingot Production	electricity and natural gas <sup>c</sup>	-	9,055
<i>Subtotal</i>			<u>9,055</u>
<b>TOTAL</b>			<u>10,747</u>



NOTES TO TABLE 1b

<sup>a</sup> weighted by type of scrap recovered in United Kingdom [1-123] p. 318

Clippings	17%
borings	19%
skimmings	9%
<hr/>	
Subtotal new scrap	45%
<hr/>	
sheet, etc.	27.5%
wire	5%
"irony"	22.5%
<hr/>	
Subtotal old scrap	55%

According to the data, 1.29 tons of the average scrap yields one ton pure secondary aluminum. Source for figures in table 1b: [1-123] p. 318.

<sup>b</sup> For crushing only ( $532 \times 10^3$  Btu/ton scrap) energy use is 94% fuel for electricity and 6% indirect energy for machinery, building and maintenance.

<sup>c</sup> data from Alcoa's unique recycling process indicates the energy breakdown (for one ton secondary aluminum) [1-121] p. 15:

	<u>TYPE</u>	<u>AMOUNT</u>	<u>10<sup>3</sup> Btu</u>
remelt .....	natural gas	-	4,000
	electricity	6 kWh	79
ingot production.	electricity	55 kWh	722
	natural gas	4,820 ft <sup>3</sup> @ 1,120 Btu/ft <sup>3</sup>	5.032
	L.N.G.	.2 gal @ 91,900 Btu/gal	22
<hr/>			
TOTAL for this stage (slightly higher than [1-123])			10,755

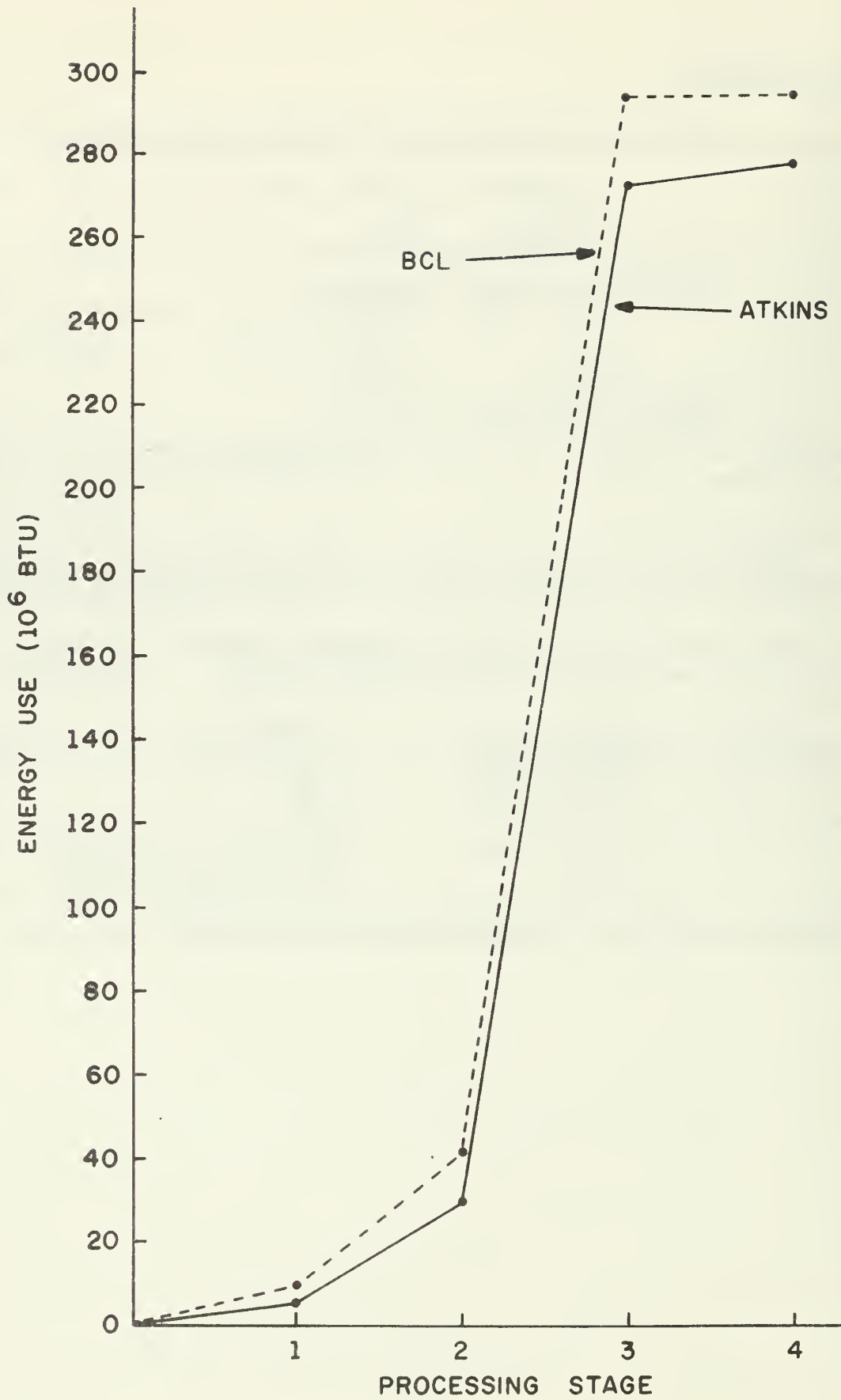


Figure 1b: Production of Aluminum

FOOTNOTES TO SECTION 1,7,8

- <sup>1</sup> [0-300] p. 11
- <sup>2</sup> Ibid. p. 14
- <sup>3</sup> [0-149] p. 437. One exception is Reynolds Aluminum mine at Hurricane Creek, Arkansas. This mine is about 2/3 the size of large foreign mines and produces metallurgical-grade bauxite, though not of the same chemical composition as foreign ores. [9-205] and [9-206]
- <sup>4</sup> [0-300] p. 11
- <sup>5</sup> [0-145] p. 4
- <sup>6</sup> Ibid. and [1-120] p. 33.
- <sup>7</sup> [1-120] p. 38.
- <sup>8</sup> [0-149] p. 449
- <sup>9</sup> [1-120] p. 30.
- <sup>10</sup> Ibid. p. 2

## 2,3, 73 ABRASIVES

### Overview

Three abrasives are currently stockpiled by the Federal Preparedness Agency: Aluminum oxide, abrasive grain; aluminum oxide, fused/crude; and silicon carbide. These materials are manufactured from domestic and foreign abrasive-grade bauxite ores and silica sand.<sup>1</sup> There is a plentiful supply of silica sand in many countries of the world, including the U.S. Abrasive-grade bauxite is produced both in the U.S. (Georgia and Alabama) and foreign countries such as Surinam. It has the following approximate composition: min. 55%  $Al_2 O_3$ , max. 5%  $Si O_2$ , max. 6%  $Fe_2 O_3$ , and min. 2.5%  $Ti O_2$ . Several ancillary materials are also required in the production sequences for these materials.<sup>2</sup>

Numerous foreign and domestic companies are engaged in manufacturing abrasives. In 1967, SIC Industry 3291, producing 85% of all domestic abrasives consumed, contained 361 companies producing 625.4 million dollars worth of products.<sup>3</sup> Some abrasive products are imported, notably from Canadian manufacturers. The major products produced by the abrasives industries are loose grain abrasives, bonded or coated abrasive products (such as grinding wheels or sandpaper), and metal abrasive products.<sup>4</sup> Other uses for these materials include refractories production, catalyst carriers, some metallurgical processing, and as porous media for filtration and diffusion.<sup>5</sup>

There are several substitutes for these materials, depending on the specific application: corundum, diamonds, garnet and emery.<sup>6</sup> There are no significant coproducts from current manufacturing practice and there is no secondary production.

## PROCESS DESCRIPTIONS

### 2,3. Oxide

Abrasive grade or "brown" bauxite is mined, dried, beneficiated, and calcined by the bauxite producer.<sup>7</sup> These producers, operating at the mine site in most countries, sell their products on the open market. Companies making abrasives buy this processed bauxite and produce aluminum oxide in a one-step process by combining the ore, metallurgical coke, and iron borings in an electric furnace.<sup>8</sup> The resulting "fused crude" aluminum oxide can then be crushed, screened, and graded to produce an "abrasive grain" product.<sup>9</sup>

### 73. Silicon Carbide

The manufacture of silicon carbide begins with the mining of glass sand. Commercial deposits of sand and sandstone exist in New Jersey, the Allegheny Mountains, and the Mississippi Valley.<sup>10</sup> Aside from being transported, the sand may have to be quarried, crushed, washed and screened.<sup>11</sup> Abrasives manufacturers buy the processed sand and combine it with petroleum coke, sawdust, and salt in an electrical (graphite core) resistance furnace. The resulting crude crystal is crushed, cleaned and graded.<sup>12</sup>

Table 2,3 PRODUCTION OF ALUMINUM OXIDE

(Basis: One ton abrasive grain aluminum oxide (to stockpile specifications)<sup>j</sup>)

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>a</sup>	electric	5.03 kWh	66
	diesel fuel oil	.116 gal.	19
	unspecified <sup>b</sup>	-	721
	materials <sup>c</sup>	.8 lb.	24
<i>Subtotal</i>			<u>830</u>
2. Calcining <sup>d</sup>	No. 6 fuel oil	40 gal	6,684
<i>Subtotal</i>			<u>6,684</u>
<i>Cumulative Subtotal</i>			<u>7,514</u>
3. Electric Arc Furnace	electric <sup>e</sup>	2350 kWh	30,839
	metallurgical coke <sup>f</sup>	140 lb.	1,400
	iron borings <sup>g</sup>	175 lb.	12
<i>Subtotal</i>			<u>32,251</u>
<i>Cumulative Subtotal</i>			<u>39,765</u>
4. Crushing, Grinding Sizing	electric <sup>h</sup>	6kWh	79
<i>Subtotal</i>			<u>79</u>
<b>TOTAL</b>			<u>39,844</u>

NOTES TO Table 2,3

- a Based on mining and metallurgical bauxite and corrected for new basis assuming a yield of 1 ton Aluminum from 9,000 lb. dry bauxite ([0-149] p. 443). Includes mine transportation, drying, crushing, and transportation to the U.S. from foreign source. Source: [0-325a] p. 9.
- b For materials, repairs, tires and maintenance of transportation equipment, drying, and transportation.
- c Explosives, considered to have an energy content of  $30 \times 10^3$  Btu/lb.
- d Done at mine site [2/3-204]. Caloric Value of 5,825,000 Btu/bbl. applies to average fuel oil [0-206] Table B1.
- e [2/3-300].
- f Average use of -3/6" metallurgical coke "breeze." [2/3-304]. Caloric value of coke is  $20 \times 10^6$  Btu/ton [0-206] Table B1.
- g New scrap assumed to have zero energy embodied, but transportation energy as follows: 4.37 ton-miles (50 miles) by truck @ 2.760 Btu/TM [0-208].
- h Estimate of energy required to meet federal size specifications (see [3-143]) [3-304].
- j See [2-140] and [3-143].

Table 73: PRODUCTION OF SILICON CARBIDE

(Basis: One ton of Silicon Carbide to federal specifications)<sup>a</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Glass Sand Mining <sup>b</sup>	electric	13.9 kWh	182
	natural gas	431 ft. <sup>3</sup>	490
	coal	.0058 ton	150
	fuel oil	.31 gal.	52
	residual fuel oil	.11 gal.	19
	gasoline	.076 gal.	11
	unspecified <sup>c</sup>		257
<i>Subtotal</i>			<u>1,161</u>
2. Electric Furnacing <sup>f</sup>	electric	7000 kWh	91,862
	furnace oil for drying coke <sup>e</sup>	2.70 gal.	451
	petroleum coke <sup>g</sup>	1.1 ton	27,280
<i>Subtotal</i>			<u>119,593</u>
<u>Cumulative Subtotal</u>			<u>120,754</u>
3. Crushing, Screening, Grading <sup>h</sup>	electric	2.0kWh	26
	<i>Subtotal</i>		
<u>TOTAL</u>			<u>120,780</u>



NOTES TO Table 73

<sup>a</sup> See [73-143]

<sup>b</sup> Includes sand processing and transportation; data originally applied to bottle manufacturing [0-324] p. 35.

<sup>c</sup> Transportation as follows:

<u>TYPE</u>	<u>TON-MILES</u>	<u>ENERGY INTENSITY [0-208]</u>	<u>ENERGY (Btu)</u>
Rail	90	1980	178,200
Barge	3	1590	4,770
Truck	27	2760	74,520

<sup>d</sup> Sawdust, salt, and graphite resistance bar; energy content neglected.

<sup>e</sup> Average of two cases drying coke from 9% and 11% moisture to a nominal 3%. Furnace oil caloric value assumed to be 5,825,000 Btu/bbl. [0-206] Table B1.

<sup>f</sup> Source [2/3/73-205] and [2/3/73-304].

<sup>g</sup> Delivery efficiency assumed to be unity.

<sup>h</sup> Estimate of crushing energy. [73-304].

## ENERGY-VERSATILITY CONSIDERATIONS FOR ABRASIVES

Figure 2/3/73b shows that for both abrasives, the optimum point for stockpiling is immediately following the furnacing stage. In the case of aluminum oxide, a material at this stage is already considered a strategic and critical material (fused, crude) and there is, therefore, no reason from the standpoint of the consideration of energy and versatility to stockpile any aluminum oxide as abrasive grade. The same is true of silicon carbide, where much more energy is required for the furnacing step.

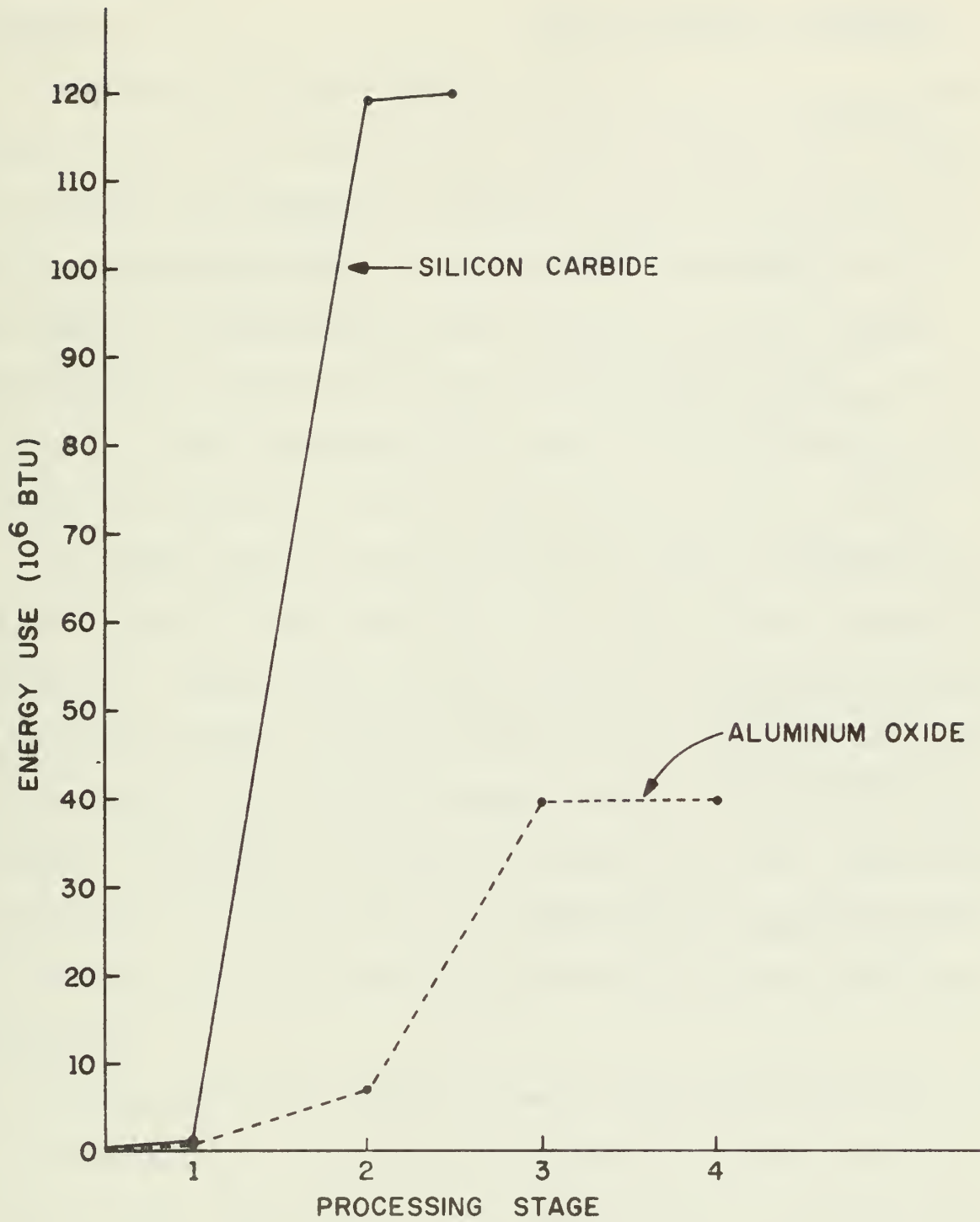


Figure 2/3/73b. PRODUCTION OF ABRASIVES

FOOTNOTES TO SECTION 2,3,73

<sup>1</sup> [2-205]

<sup>2</sup> [0-149] p. 440.

<sup>3</sup> [0-112] Vol. II, p. 32E1.

<sup>4</sup> Ibid.

<sup>5</sup> [0-122] pp. 2, 3, 68.

<sup>6</sup> Ibid.

<sup>7</sup> [2-205]

<sup>8</sup> Ibid.

<sup>9</sup> [0-122] p. 2.

<sup>10</sup> [0-324] p. 34

<sup>11</sup> Ibid

<sup>12</sup> [2-205] and [0-122] p. 68.

#### 4. ANTIMONY

##### Overview

Antimony is the 51st element, a brittle metal used by man since ancient times.<sup>1</sup> It is found in over a hundred mineral forms but only the stibnites, or sulfides, are commercially useful.<sup>2</sup> One useful ore form tetrahedrite stibnites has the form  $(\text{Cu, Fe, Zn, Ag})_{12} \text{Sb}_4 \text{S}_{13}$ .<sup>3</sup> Most deposits are small, on the order of 1,000 tons of ore, and are found in Mexico, Bolivia, Red China, Peru and other countries. Ore is sold by the (mainly independent) mine owners on the open market. World reserves are estimated at 2,000,000 tons ore, much of it in China.<sup>4</sup>

Currently, about 25 countries produce elemental antimony, with 80% of all output coming from South Africa, China, Bolivia, the U.S.S.R., and Mexico.<sup>5</sup> Domestically, virtually all ore is produced by two companies in Idaho and Montana; a handful of large companies also process various forms of imported antimony into antimony oxide, pure metal, and other products. According to the Bureau of Mines, "The antimony metal and oxide producers are essentially large vertically integrated companies with a wide scope of activity in marketing and manufacturing base metals and chemicals."<sup>6</sup>

World production of primary antimony rose steadily until 1964, when it began to level for a few years, rising again to a total production of 76,413 short tons in 1973.<sup>7</sup> For this year the U.S. produced only 22.5% of this or 17,206 short tons, while consuming 34,542 short tons of primary antimony (45.2% of world total).<sup>8</sup> About 50 metal-producing companies and 112 oxide-producing companies consume the bulk of this demand.<sup>9</sup>

Since antimony is produced only from ore containing other valuable metals, by-product production is extremely important, both economically and metallurgically. For the former, the U.S. Bureau of Mines reports that:

"in some ore bodies, the antimony content shares total value equally with one or more other metallic constituents of the ore.<sup>10</sup> As to the latter, it is important to note that the processing required depends directly on the other minerals present in the ore, and whether they are to be recovered or not. By far the two most important by-products (which are in some cases the major products) are lead and/or silver. Other minerals found in both domestic and foreign ores are gold, tungsten, arsenic, and copper. In the U.S. virtually all the above by-products are recovered.

Secondary production is of major importance to U.S. antimony users. In 1973, for example, 20,473 short tons or fully 46.1% of all antimony demand was from secondary production. This metal was recovered mainly from lead storage batteries (60%), metal type (20%), and bearing metal, babbitt, and other metal scrap."

Antimony is produced in three major forms which in turn determine the final use for the material, almost always in combination with other materials. Pure metal, produced in 60 lb. ingots called "pigs," accounts for about 14.5% of total use and is alloyed into solder, type metal, ammunition, and storage batteries. Antimony oxide, 21% of demand, is a chemical used in the ceramics, textile, plastic, chemical and other industries. Antimony sulfide (.17%) is used in pigments and plastic, while the remaining antimonial lead (both primary and secondary) is used mainly for storage batteries, type, and ammunition.

Several substitutes are available for various end uses of antimony.

Mercury and Zirconium are adequate substitutes in pigments while plastics and other processes act as substitutes in the communications industry. Some organic compounds have equally good flameproofing capabilities, and tin and calcium can be used as alternate alloying agents for lead, mainly in storage batteries.<sup>12</sup>

## PROCESS DESCRIPTION<sup>13</sup>

The process described is for a major domestic antimony mine and associated smelter operating in the Coeur d'Alene district of Idaho. This producer also recovers (for one pound of pure antimony) 1.75 lb. copper, .34 lb lead, and .375 lb. silver, partly using other companies' smelters. The silver produced is considered at least as valuable as the antimony.

Ore is delivered from the underground mine veins in large (15") chunks. Four separate stages of grinding are required to reduce the ore to the size 60% -200 mesh. This ore is fed to a large, complex flotation circuit which separates most of the silver, antimony and copper from the waste minerals (96% of the silver). Several retreatment circuits are connected to the first and alternately produce two concentrates, with the following approximate compositions:

Conc #1 (silver): 4.94% Ag, 25% Cu, 18% Sb, 4% Pb.

Conc. #2 (pyrite): .34% Ag, 1% Cu, 1.4% Sb, 5% Pb.

The second concentrate is sold to another company which produces silver, copper, lead and iron from it. The silver concentrate is trucked to an electrolytic antimony plant where it is first leached to dissolve the antimony and separate it from the lead, silver and copper. The latter are recovered as solids, processed further, and shipped to the company's silver smelter. The clear antimony (thioantimonate) solution is pumped to a large electrolysis cell. In this, 96 cells operating at 1,500 Amperes and flushed by several chemical solutions deposit metallic antimony on the cathodes. When the metal is stripped, washed and weighed, it is sent to the refinery. There the antimony is remelted to a purity of 99.5% antimony and less than .1% arsenic.



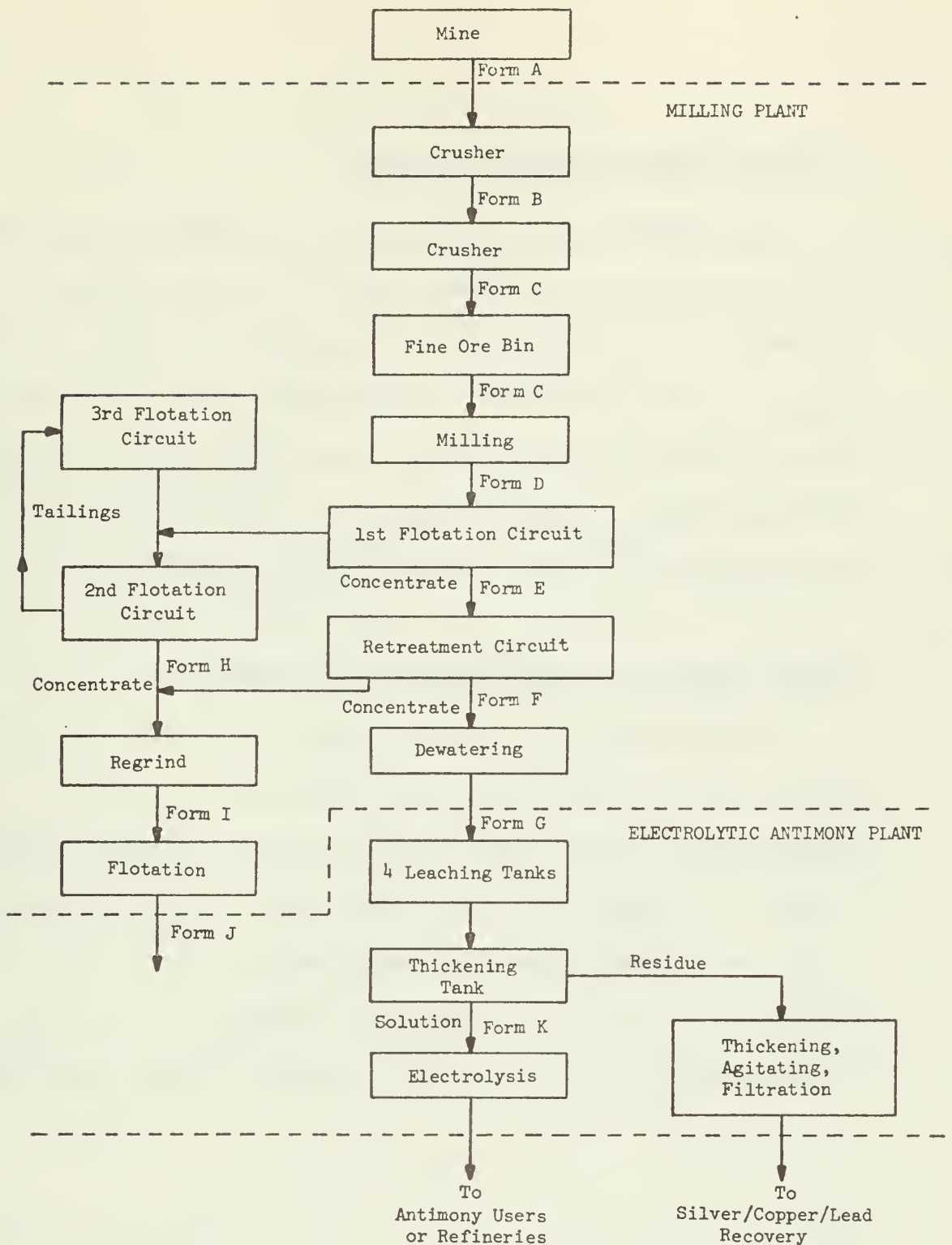


Figure 4a. PRODUCTION OF ANTIMONY\*

FORMS

- A - Siderite quartz, pyrite, tetrahedrite, galena chalcopryite, and sphlaterite. 15" max. size.
- B - 3" pieces.
- C - .5" pieces
- D - 60% minus 200 mesh.
- E - 94-97% of silver tetrahedrite recovered (600-800 oz Ag./T.)
- F - 1300 oz. Ag./T.
- G - Silver tetrahedrite concentrate, typically: 1300 oz Ag./T., 25% Cr, 15% Sb, 4% Pb.
- H - 40-60 oz Ag./T.
- I - 95% minus 325 mesh.
- J - Pyrite Concentrate, typically: 40 oz. Ag./T., 10% Cu, 1.4% Sb, 5% Pb.
- K - Pregnant solution.

\* Sunshine Mining Co., Kellogg, Idaho. Source: [4-122].

## A NOTE ON ENERGY ALLOCATION METHODS

The companies considered here produce small amounts of many metals but are generally acknowledged to have two major outputs: silver and antimony. Of these two, silver is considered to be far more valuable. Thus for processing stages involving both metals, allocation is on the basis of total value and is explained in the notes to the table. Care has been taken to separate processing stages which involve only one metal and energy use for these stages is not allocated jointly.

## ENERGY-VERSATILITY CONSIDERATIONS FOR ANTIMONY

Antimony metal is a classic example of the electrolysis stage consuming most of the manufacturing energy-- 65% in this instance. Before electrolysis, another 31% of total energy use is consumed. This makes the post-electrolysis stage the obvious choice for stockpiling. This is especially true because there are definite versatility advantages to having the unrefined metal available. Versatility considerations might, in some cases, call for either stockpiling the ground ore, which contains contains several other metals. See figure 4b.

Table 4. PRODUCTION OF ANTIMONY

(Basis: 1 ton of antimony to federal specifications)<sup>a,c</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>c</sup>	Electric <sup>b</sup>	166 kWh	2,178
	Materials <sup>h</sup>	-	37
<i>Subtotal</i>			2,215
Allocated energy use for antimony production <sup>c,d</sup>			56,991
2. Crushing and Grinding	electricity <sup>e</sup>	6.02 kWh	79
	Subtotal of allocated energy use for antimony production <sup>c,d</sup>		2,033
	Cumulative subtotal of allocated energy use for antimony production		59,024
3. Flotation Beneficiation	electricity <sup>f</sup>	6,160 kWh	80,838
	materials <sup>g</sup>		1,328
<i>Subtotal</i>			82,166
Cumulative Subtotal			141,190
4. Antimony Electrolysis	electric <sup>i</sup>	8,569 kWh	112,453
	natural gas <sup>i</sup>	87,460 ft <sup>3</sup>	99,474
	materials <sup>j</sup>	-	85,262
<i>Subtotal</i>			297,189
Cumulative Subtotal			438,379
5. Antimony Refining	natural gas	11,600 <sup>k</sup>	13,193
	transportation <sup>l</sup>	-	7,414
<i>Subtotal</i>			20,607
TOTAL			458,986

NOTES to Table 4

<sup>a</sup> See [4-141].

<sup>b</sup> 1974 average power consumption in mine was 166 kWh/ton ore [4-123].

<sup>c</sup> Ratio of mill concentration is 56:1 [4-120], yielding a 15% Sb concentration of which 90% is recovered. Thus about 415 tons of ore are required for a ton of antimony. Figures listed are per ton ore.

<sup>d</sup> Energy is allocated according to the techniques described in section 14/91. Relevant data for 1974 for this producer are [4-124]:

METAL	AMOUNT	REVENUE	PERCENTAGE
Silver	2,161,000 oz.	\$9,655,960	86.2%
Copper	838,000 lb.	846,489	7.6%
Antimony	572,439 lb.	700,292	6.2%

Thus 6.2% of total energy for mining and milling is allocated to antimony.

<sup>e</sup> Based on plant equipment:

MACHINE*	MOTOR <sup>†</sup>	POWER <sup>†</sup>	ENERGY <sup>#</sup> (kWh/Ton)
Traylor 3' TZ Crusher	200 h.p.	460 v. @ 312.5A.	1.20
Symons 4' Shorthead Cone Crusher	125 h.p.	385 v. @ 150 A.	.48
Two 4x8' (Denver) Mills	50 h.p.	460 v. @ 64 A.	1.96
8x8' (Denver) Mills	300 h.p.	460 v. @ 344 A.	7.91
			} 4.34

\* Atkins classifier, ore bin transfer system, etc. estimated to be negligible.

<sup>†</sup> [4-203], [4-204], [4-205], [4-206].

<sup>#</sup> First two machines assumed to produce at 120 Tons/hr; third at 15 Ton/hr. and last at 20 Ton/hr.

<sup>f</sup> Derived from the difference between operating statistics for mining and milling from producer and estimates in stage 2. Allocated on usual basis of energy use per ton of final antimony output, but then charged for only 6.2% of energy use per foot note d.

<sup>g</sup> A total of 8.06 lb. industrial chemicals are used on the average per ton of concentrate inputs @ 23,330 Btu/lb. (Na<sub>2</sub>CO<sub>3</sub>). [0-321] p. 92 and [4-121]. Since concentrate averages 15% antimony and metal is 96% (with 10% waste), 7.07 tons of concentrate are needed for 1 ton of metal.

- h 1.24 lb. dynamite per ton ore [4-124] @ 30,000 Btu/lb [0-325b] p. 37.
- i Identified as allocated to "antimony plant only"; figures reflect basis of one ton antimony.
- j 43% of caustic soda used (225 g. soda/l. soln. x .0166 l./gram Sb) [4-121] and [4-120].
- k [4-304].
- l Transportation energy for truck transit from Kellogg, Idaho to Laredo, Texas ([4-122]) derived as follows: One ton @ 2220 miles ([0-113] p. 114) with truck circuitry factor 1.21 and energy intensity of 2760 Btu/TM [0-208].

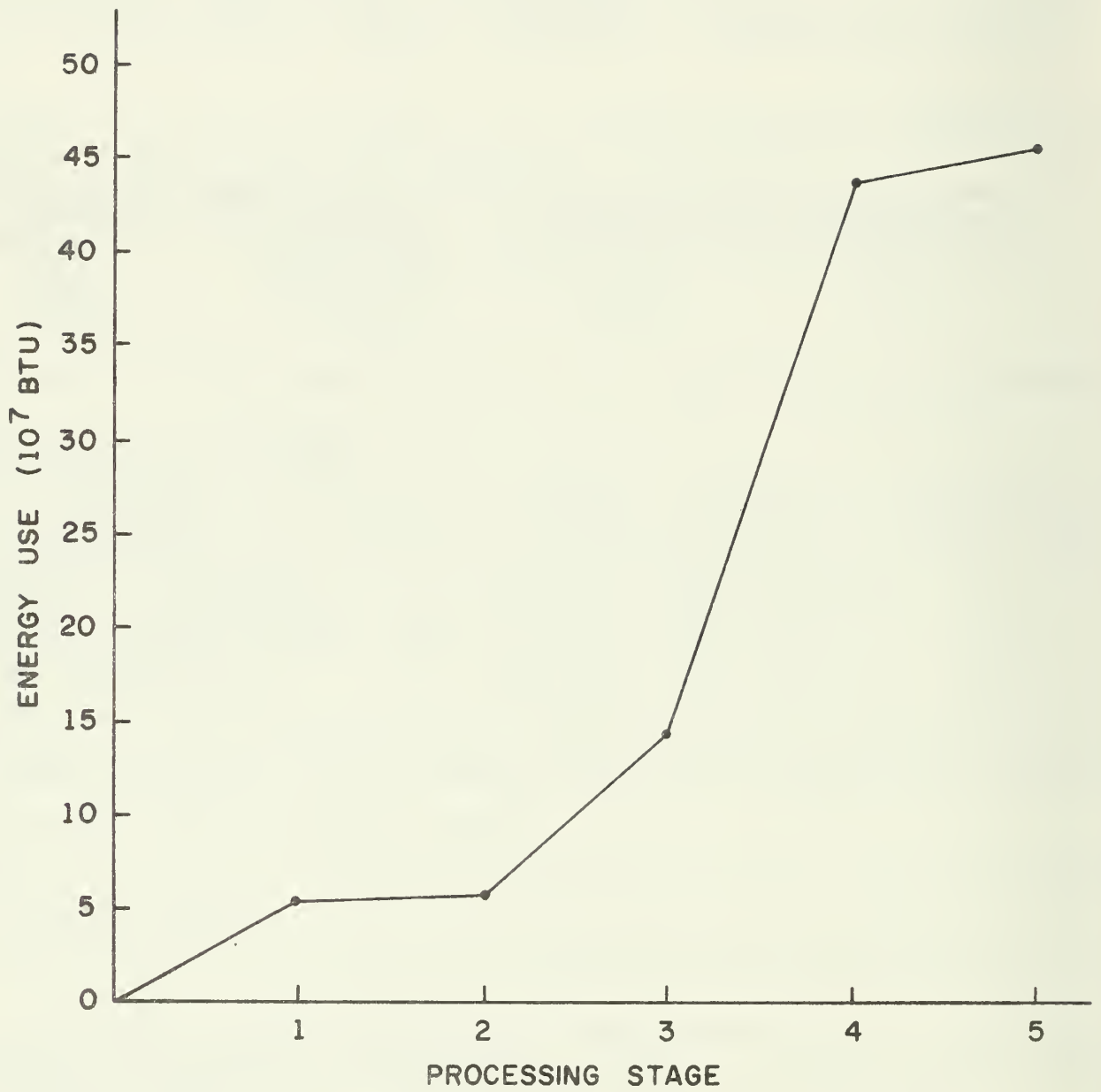


Figure 4b: Production of Antimony

FOOTNOTES TO SECTION 4.

- <sup>1</sup> [0-149] p. 465 and [0-122] p. 4.
- <sup>2</sup> Ibid.
- <sup>3</sup> [4-120] p. 1.
- <sup>4</sup> [0-149] p. 465 - 466.
- <sup>5</sup> Ibid.
- <sup>6</sup> Ibid.
- <sup>7</sup> [0-145] p. 7.
- <sup>8</sup> Ibid.
- <sup>9</sup> [0-149] p. 465 - 466.
- <sup>10</sup> Ibid.
- <sup>11</sup> Ibid, p. 469.
- <sup>12</sup> Ibid, p. 470 and 4-140.
- <sup>13</sup> Sources: [4-141], [4-120], [4-121], [4-122] and [4-201].

## 6. CHRYSOTILE ASBESTOS

### Overview

Chrysotile asbestos is one form of a naturally fibrous mineral having the formula  $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .<sup>1</sup> It is found in several massive deposits in Vermont, Quebec, British Columbia, Rhodesia, South Africa, the U.S.S.R., and elsewhere.<sup>2</sup> In addition, many smaller and less concentrated deposits are present around the world. About 95% of all asbestos produced in the world today is of chrysotile form, and about 46% of the free world's supply of this fiber comes from the Jefferey region of Quebec, Canada.<sup>3</sup> This region contains eight major asbestos producing companies, six of them owned by U.S. corporations. A handful of small producers also operate domestic mines. In 1973, U.S. chrysotile demand was approximately 868,000 short tons, 91% of which was imported.<sup>5</sup> U.S. reserves are estimated at several hundred million short tons.<sup>6</sup>

In 1967, 138 companies consumed 93% of the U.S. asbestos demand, producing 575 million dollars' worth of products.<sup>7</sup> The most important final products made from chrysotile are thermal and electrical insulation, brake linings, heat-resistant clothing, electrical and aircraft insulators, cement, and floor tile. There are no important byproducts of asbestos production; one producer recovers magnesia from mill waste, while other minor uses have been found for the waste.<sup>9</sup> In terms of strategic uses for asbestos, no satisfactory substitute has been found. Some applications of asbestos have substitutes such as glass wool and other mineral fibers, plastics and aluminum.<sup>10</sup>



## PROCESS DESCRIPTION

Chrysotile asbestos ore is mined from large open pit mines (200 to 1200' deep) using standard pit-mining techniques. Often before a ton of ore can be mined up to 6 tons of waste must be drilled, blasted, and hauled away.<sup>11</sup> The ore proceeds through two stages of crushing and concentrating and is then dried to remove the chemically attached water. Finally, the fiber undergoes a complex milling, cleaning and grading operation. Each grade is pressure-packed in 100 lb. 5-ply paper bags occupying about two cubic feet.<sup>12</sup>

## ENERGY-VERSATILITY CONSIDERATIONS FOR ASBESTOS

As the accompanying table shows, the energy requirement for asbestos production is a relatively smooth function of processing stage. This leaves several significant options for stockpiling. Generally, the more advanced the material can be, the more energy will be stored, so such a form should be favored. It seems here that the final product, graded asbestos fiber, does not cause any decrease in versatility, so this is the proper form for stockpiling (as well as the most convenient. However, the results of this simple analysis show that the forms just prior to it are also worthy of consideration. See Figure 6.

Table 6. PRODUCTION OF CHRYSOTILE ASBESTOS

(Basis: One ton of cleaned, graded and packaged chrysotile asbestos to federal specifications)<sup>a</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu	
1. Mining <sup>b,c,d</sup>	electric	38 kWh	499	
	diesel fuel oil	10.09 gal	1,680	
	bunker 6C oil <sup>e</sup>	1.32 gal.	245	
	kerosene	.04 gal.	7	
	gasoline	0.46 gal.	70	
<i>Subtotal</i>			<u>2,501</u>	
2. Primary crushing <sup>b</sup>	electric	6 kWh	79	
	<i>Subtotal</i>			<u>79</u>
<i>Cumulative Subtotal</i>			<u>2,580</u>	
3. Secondary crushing	electric	68 kWh	892	
	<i>Subtotal</i>			<u>892</u>
	<i>Cumulative Subtotal</i>			<u>3,472</u>
4. Drying <sup>c</sup>	electric	38 kWh	499	
	No. 2 fuel oil <sup>f</sup>	.49 gal.	82	
	bunker 6C oil <sup>e</sup>	13.97 gal.	2,593	
	propane <sup>f</sup>	.11 gal	12	
<i>Subtotal</i>			<u>3,186</u>	
<i>Cumulative Subtotal</i>			<u>6,658</u>	
5. Milling and grading <sup>g</sup>	electric	226 kWh	2,966	
	<i>Subtotal</i>			<u>2,966</u>
<i>TOTAL</i>			<u>9,624</u>	

NOTES TO Table 6

a See [6-141]

b Figures apply to, and are dependent on, a large Quebec mine with the following characteristics:

- a) 3:1 waste/ore ratio
- b) 6% fiber per ton ore
- c) 25-30" mine precipitation per year

Source: [6-300] and [6-201].

c Liquids converted from imperial gal. using the factor 1.200949 U.S. gal./1 mp. gal. [0-100] p. F231.

d Mine-plant transportation neglected

e Caloric value assumed to be 154,045 Btu/gal. [6-300]

f Fuel oil average caloric value assumed to be 5,825,000 Btu/Bbl.  
Propane average caloric value assumed to be 3,843,000 Btu/Bbl.

g Packaging not included.

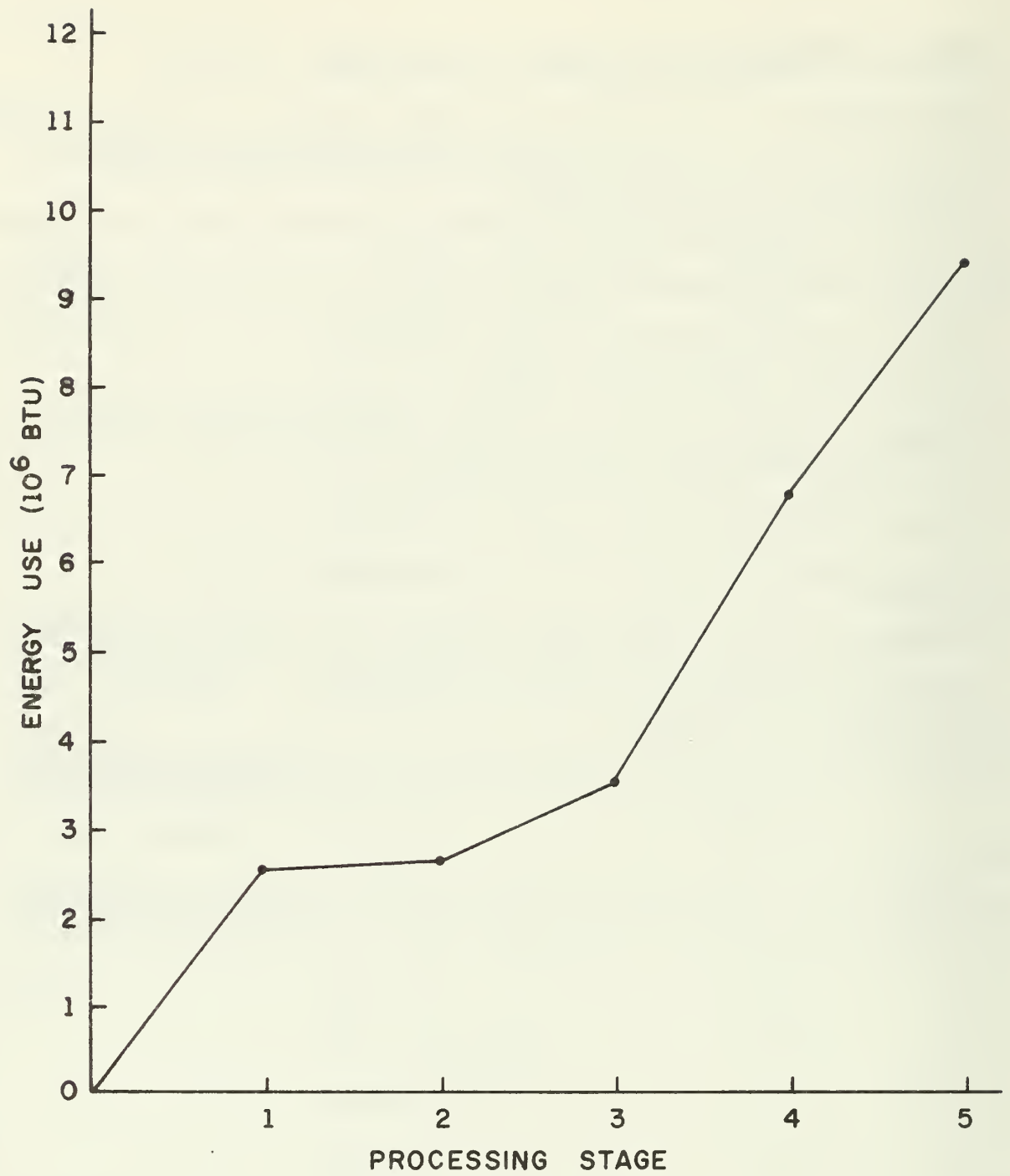


Figure 6: Production of Chrysotile Asbestos

FOOTNOTES TO SECTION 6

- <sup>1</sup> [0-149] p. 852.
- <sup>2</sup> Ibid, p. 851 and [0-145] p. 10.
- <sup>3</sup> [0-149] p. 851 and [6-200].
- <sup>4</sup> Ibid, p. 852.
- <sup>5</sup> [0-145] p. 10.
- <sup>6</sup> [0-149] p. 854.
- <sup>7</sup> [0-112] p. 32E-2.
- <sup>8</sup> [0-112] p. 32E-17 and [0-122] p. 6.
- <sup>9</sup> [0-149] p. 836.
- <sup>10</sup> Ibid, p. 856 and [6-140]
- <sup>11</sup> [6-300].
- <sup>12</sup> Ibid and [0-149] p. 853.

## 9. REFRACTORY BAUXITE

### Overview

Refractory bauxite is one form of aluminum oxide ore used solely for manufacturing high-alumina bricks and cementing compounds.<sup>1</sup> It occurs in large deposits in Arkansas, Georgia, Alabama, Surinam, British Guyana, and the Republic of Ghana,<sup>2</sup> and is a mixture of hydrated aluminum oxide, silica, iron oxide, titanium dioxide, and other impurities.<sup>3</sup> Though more than eight domestic refractory bauxite producers once operated in the U.S.,<sup>4</sup> only one large minerals company (C-E Minerals) now mines and calcines domestic refractory bauxite, which is sold on the world market. The other large aluminum and refractory companies import their refractory ores precalcined from Guyana, Ghana, or Surinam.<sup>5</sup>

In 1973, domestic production of nonmetallurgical bauxite was 193,000 long tons (dried equivalent).<sup>6</sup> For the same year, total refractory bauxite and alumina consumed in the U.S. (in SIC sector 3297) was 245,000 short tons.<sup>7</sup> In the last year for which complete figures are available, 1968, the refractory industry used a total of 162,000 short tons of which 102,000 tons (63%) was refined bauxite.<sup>8</sup> There are no significant byproducts or co-products from the production of refractory bauxite.<sup>9</sup> To date, no secondary uses or substitutes have been found.

## PROCESS DESCRIPTION

Refractory bauxite is strip-mined from large surface deposits in Georgia, Alabama, Surinam, Ghana, and several other locations.<sup>10</sup> The overburden of 3-25 ft. is first stripped off and discarded by steam shovels. Ore beds are typically 25-300 ft. long, about 50 ft. deep, and must often be drilled or blasted to remove the ore. Loose ore is shovel-loaded onto steam unit trains or trucks and shipped several miles to the processing plant. The large ore chunks are ground, either by gyrators or disintegrators, and then dried and "calcined" to drive off all chemically-bonded water in the ore.<sup>11</sup> Calcining is done in gas or oil-fired rotary kilns at a temperature of 1,700°-2,900°F for 1 to 1.5 hours.<sup>12</sup>

NOTE: No optimization section is included for this material. Only one a single step consumes significant energy, calcining. Since this does not significantly decrease versatility, bauxite should be stockpiled after calcining.

Table 9. PRODUCTION OF REFRACTORY BAUXITE

(Basis: One ton of calcined refractory bauxite<sup>a</sup>)

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining, loading and transportation	electric	1.9 kWh	25
	diesel fuel oil	.116 gal.	21
	unspecified <sup>c</sup>	----	726
	materials <sup>d</sup>	.8 lb.	24
<i>Subtotal</i>			<u>796</u>
2. Crushing, washing and screening <sup>b</sup>	electric	kWh	41
	unspecified <sup>e</sup>	----	3
<i>Subtotal</i>			<u>44</u>
<i>Cumulative Subtotal</i>			<u>840</u>
3. Calcining	either:		
	fuel oil <sup>f</sup>	70.5 gal.	11,780
	or:		
	natural gas <sup>g</sup>	8600 ft. <sup>3</sup>	9,451
<i>Subtotal<sup>h</sup></i>			<u>10,616</u>
<b>TOTAL</b>			<u>11,456</u>



NOTES TO Table 9

- <sup>a</sup> It is assumed that the weight of calcined bauxite is equal to the weight of raw bauxite minus the water loss (from 33% to .5%), i.e. 1.5 tons of raw ore yield 1 ton of calcined ore. [0-140] p. 192. See [9-141].
- <sup>b</sup> Based on mining of metallurgical bauxite and corrected for new basis assuming a yield of 1 ton Aluminum from 9000 lb. of dry bauxite. ([0-149] p. 443) Source: [0-325a] p. 9. Includes mine transportation, drying, crushing, and transportation to the U.S.
- <sup>c</sup> For materials, repairs, tires, and maintenance of transportation equipment; drying, and transportation.
- <sup>d</sup> Explosives, considered to have energy content of  $30 \times 10^3$  Btu/lb.
- <sup>e</sup> "Machinery wear and service energy." [0-325a] p. 9.
- <sup>f</sup> Average of domestic operations (using No. 1 to No. 4 fuel oils) and foreign Alcoa operations (using No. 6 fuel oil). Caloric value used is for average fuel oil ( $5.825 \times 10^6$  Btu/Bbl.) [9-300] and [9-203].
- <sup>g</sup> Domestic producer can alternatively use gas (assumed caloric value 1000 Btu/ft.<sup>3</sup>)
- <sup>h</sup> Average of all cases in stage 3.

FOOTNOTES TO SECTION 9

- <sup>1</sup> [0-122] p.7. See [0-112] v.II p.32E-23 for a list of products made with refractory bauxite.
- <sup>2</sup> [0-122] p.7, [9-140] p. 228 and [9-204].
- <sup>3</sup> [9-141]. Bureau of Mines specifications for refractory bauxite are: minimum  $\text{Al}_2\text{O}_3$ , 59-61%, max.  $\text{SiO}_2$ , 1.5-5.5%, max.  $\text{Fe}_2\text{O}_3$ , 2% and max.  $\text{TiO}_2$ , 2.5%. [0-149] p. 440. Stockpile purchase specifications are similar, see [9-141].
- <sup>4</sup> [9-140] p.229.
- <sup>5</sup> [9-204] and [9-205].
- <sup>6</sup> [9-143]. Figure quoted is all Alabama and Georgia bauxite production, none from Arkansas.
- <sup>7</sup> [0-145] p.4.
- <sup>8</sup> [0-149] p.448.
- <sup>9</sup> Note that this is not true of metalurgical grade bauxite or alumina.
- <sup>10</sup> [9-140] p.228, [0-122] p.7, and [9-204].
- <sup>11</sup> [9-140] p.231-236 and [9-300].
- <sup>12</sup> [0-149] p.440 and [9-300].

### 13. BISMUTH

#### Overview

Bismuth is a metallic element with a number of unique properties and uses. It is found in small concentrations throughout the world-- average concentration in the earth's crust is .1 p.p.m., almost a million times smaller than the most plentiful metal, Aluminum.<sup>1</sup> Due to this low concentration, virtually no ore is mined solely for its bismuth content; it is usually produced along with lead, copper, tungsten, and gold. Of these co-products, lead is by far the most important, because most bismuth metal is recovered during lead beneficiation and smelting.<sup>2</sup>

Bolivia, Japan, Mexico and Peru each contribute about 18% of world mine output of contained bismuth; the remainder comes from 16 countries, including an estimated 8% from the U.S.<sup>3</sup> Similarly, only a score of countries produce bismuth metal in many nonferrous metal smelters, with Peru producing 25% of world output and Bolivia, Canada, Japan, Mexico and Peru producing most of the rest.<sup>4</sup> Only a single U.S. company produces significant bismuth concentrates from a mine and only the American Smelting and Refining Company in Omaha, Nebraska, produces primary bismuth metal. There are two domestic secondary producers.<sup>5</sup> Total estimated domestic production of pure bismuth was estimated at 850,000 lbs. in 1968, while consumption was about 2,348,000 lbs. and imports were 1,266,000 lbs., mostly from Peru.<sup>6</sup>

Bismuth is used primarily in the pharmaceutical industry, which consumes about 40% of domestic demand in the production of stomach remedies, antiseptics, and the like.<sup>7</sup> A large portion is used for producing aluminum, steel, iron, and other fusible alloys and much of the rest is used with lead in

temperature control devices.<sup>8</sup> Some substitutes exist for the medicinal and alloying uses for bismuth, but none are as desirable.<sup>9</sup>

### PROCESS DESCRIPTION<sup>10</sup>

The ore beneficiation processes used depend on the metals from which bismuth must be separated. In some cases liquation in cast iron pipes is employed, in others it is carbon reduction in reverberatory furnaces. If the bismuth is present in an oxide or carbonate form, as in tin concentrate, wet extraction may be used. The most common practice is "debismuthizing" lead mine concentrates. Because bismuth behaves much like lead, great care must be taken to separate them in both the major metal flows and the wastes such as flue dusts. Over 90% of this separation is accomplished using the Betterton-Knoll process.<sup>11</sup>

In the Knoll process, the bismuth must first be "desilvered." Then enriched calcium and magnesium is added to an ore bath. The bismuth forms a dross of  $\text{Ca}_3 \text{Bi}_2$  and  $\text{Mg}_3 \text{Bi}_2$  which is skimmed off the top, leaving a bismuth concentration of about .025% in the lead and 2 - 4% in the dross.<sup>12</sup> The dross is melted in large kettles, after which the following processing occurs in one prominent bismuth refinery:<sup>13</sup>

"When the kettle is filled and now contains approximately 1.5% Bi, calcium and magnesium are added to remove bismuth in the bullion to less than 0.6%; the crust that forms is then skimmed off and cast into 20 lb. patties or 1-ton jumbos, containing 8 to 10% bismuth.

This lead-bismuth alloy is melted in the bismuth refinery, in two, 20-ton and two, 10-ton kettles, and chlorinated. The lead chloride produced is removed and utilized in exchange reactions with calcium and magnesium.

Chlorination is continued until the charge contains approximately 65% bismuth, when it is de-silverized. The zinc-silver crusts are

recycled within the refinery. The bismuth lead alloy (65% Bi) is cast into pigs. A second charge is treated similarly, but after de-silverizing, the charge is chlorinated to pure bismuth; the level in the chlorinating kettle is kept topped up by adding the 65% alloy cast previously.

The metal is then cast into bars, and transferred to the final refining section, where absorbed chlorine and trace metals are removed by caustic and niter. The bismuth metal produced is 99.99% pure."

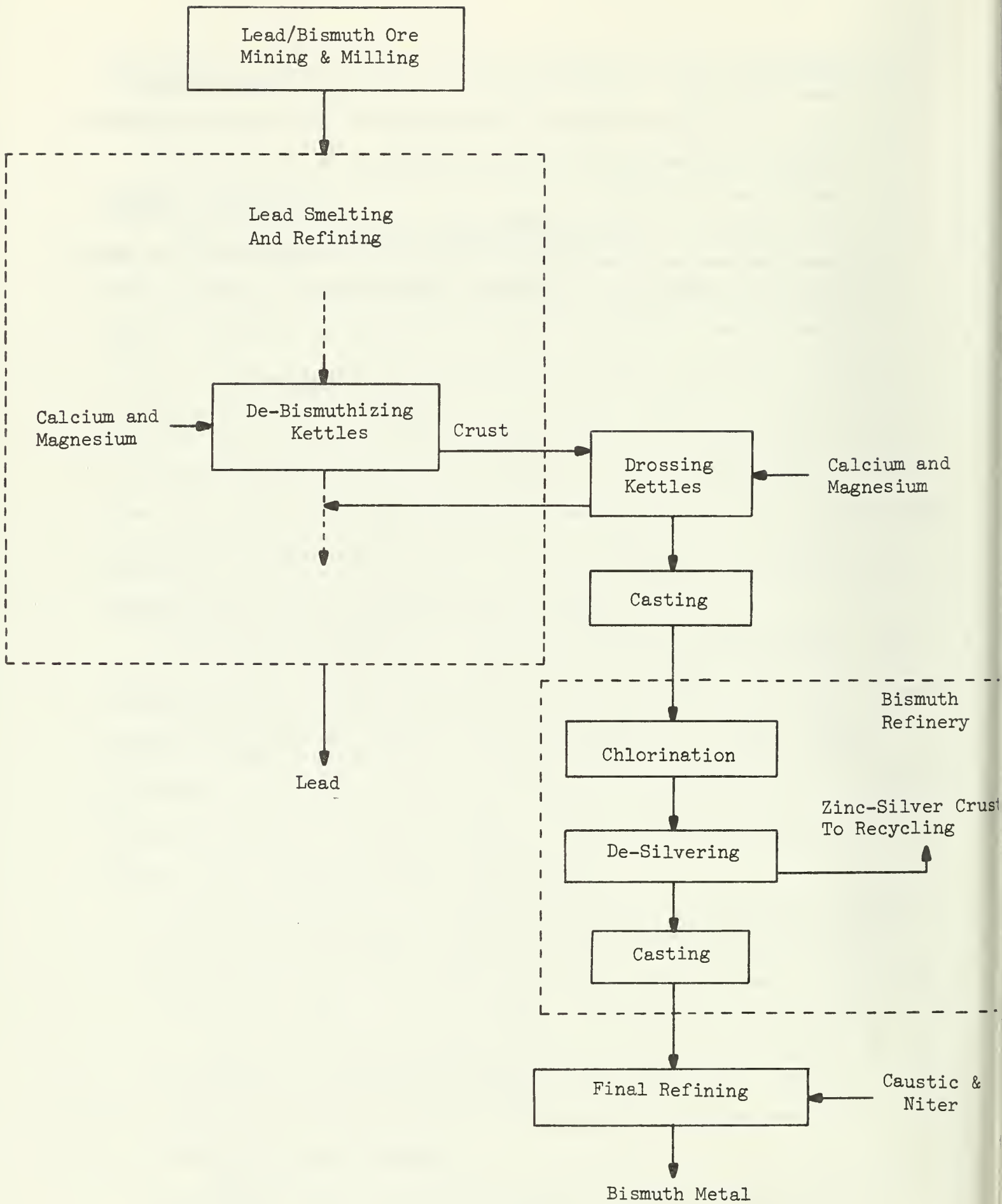


Fig. 13 : Production of Bismuth

## A NOTE ON ENERGY ALLOCATION TECHNIQUES

Under normal circumstances, the production of bismuth and lead should be considered jointly. In such a case, the most probable technique for energy allocation would be on the basis of final value of metal output, as is done in section 14/91 of this report.

However, the circumstances here are rather unique. The ore from which lead and bismuth are produced contains in concentrate form only .05% bismuth and an average of 140 times as much lead (in addition to a number of other products).<sup>14</sup> The price of bismuth in 1973 was about \$6/lb. while the price of lead was about \$.16/lb., yielding a ratio of about 37:1.<sup>15</sup> Thus the lead revenue from this producer was about four times his revenue from bismuth. Furthermore, it would be necessary to remove all bismuth from lead even if it were of no value because refined lead must be virtually bismuth-free. Finally, it is generally accepted in the industry that any costs associated with bismuth begin with the dross removed from the lead concentrate. For example, one prominent producer states: "In fact, in our process I think it would be true to say that they (bismuth and silver) 'get a free ride' up to the stage of removal from the bullion."<sup>16</sup>

Because of all these factors, this report will conform to industry practice and consider bismuth only from the point where it is removed from the lead concentrate, or more specifically, from the 8 - 10% slab crust coming off the second drossing stage.

Table 13. PRODUCTION OF BISMUTH<sup>a</sup>

(Basis: 1 ton of bismuth metal to federal specifications)<sup>a</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Refinery remelting <sup>b</sup>	electric	100,000 kWh	1,312,308
	materials <sup>c</sup>	-	2,259,830
	transportation <sup>c</sup>	-	<u>1</u>
<i>Subtotal</i>			<u>3,572,139</u>
2. Final refining <sup>d</sup>	Fuel oil <sup>e</sup>	7,200 gal.	1,203,094
	materials <sup>g</sup>	-	<u>13,220</u>
<i>Subtotal</i>			<u>1,216,314</u>
<b>TOTAL</b>			<u>4,788,453</u>



NOTES TO Table 13

- <sup>a</sup> See [13-140]. Source: [13-300].
- <sup>b</sup> 8 - 10% bismuth dross in 20 lb. or 1 ton pieces.
- <sup>c</sup> Transportation from lead refinery to bismuth refinery estimated to be .5 TM by truck @ 2760 Btu/TM ([0-208]).  
Materials used are .5 ton calcium @ 8.5 million Btu/ton ([0-325a] p. 16),  
6 tons magnesium @ 358.16 million Btu/ton ([0-325b] p. 86) and  
6,000 lb. chlorine gas @ 17,770 Btu/lb.
- <sup>d</sup> Treating 65% Bi bars.
- <sup>e</sup> Converted from imp. gal. at 1.2 gal./imp. gal ([0-100] F-223) and  
caloric value assumed to be 138,690 Btu/gal ([0-206]).
- <sup>f</sup> Based on information from [14-200].
- <sup>g</sup> .1 ton caustic soda @ 47.7 million Btu/ton and .2 ton sodium nitrate @  
42.25 million Btu/ton ([0-325a] p. 109).

## ENERGY-VERSATILITY CONSIDERATIONS FOR BISMUTH

No versatility graph is included in this section due to the limited nature of bismuth production. From the point at which it separates from its coproducts, only two processing stages are required to bring it to refined metal form. Though each is a significant energy user, there is probably very little change in versatility between semi-refined and pure bismuth. Therefore all bismuth should be stockpiled in finished form as present specifications stipulate.

FOOTNOTES TO SECTION 13

- <sup>1</sup> [0-149] p. 504.
- <sup>2</sup> Ibid, p. 503.
- <sup>3</sup> [0-140I] p. 215.
- <sup>4</sup> [0-149] p. 504.
- <sup>5</sup> [0-140I] p. 211.
- <sup>6</sup> [0-149] p. 507.
- <sup>7</sup> [0-122] p. 9.
- <sup>8</sup> [0-149] p. 506.
- <sup>9</sup> [0-122] p. 9.
- <sup>10</sup> Source: [13-141] and [13-120] unless noted.
- <sup>11</sup> [0-149] p. 505.
- <sup>12</sup> [13-121] p. 20.
- <sup>13</sup> Ibid.
- <sup>14</sup> Ibid.
- <sup>15</sup> [0-101]p.168 and [0-110] p. 131.
- <sup>16</sup> [13-300]

## 14,91 CADMIUM, ZINC

### Overview

Cadmium and zinc are considered together in this section because they occur together in every commercial ore deposit in the world today. In an early U.S. Bureau of Mines document, it is flatly stated that "The entire output of primary metal is recovered as a byproduct in smelting and refining zinc-bearing ores; hence, cadmium reserves are related to zinc-ore reserves and the cadmium content of such reserves."<sup>1</sup> Later Bureau documents agree and add that if it were not for an excessively high cadmium demand prices of cadmium would also be dependent on zinc production.<sup>2</sup>

Cadmium/zinc ores are found in moderate underground deposits or "pitches and flats" above ground.<sup>3</sup> Large reserves exist in Mexico, Canada, Australia, Peru, Southwest Africa, and many other countries. All but one commercial domestic zinc deposits contain cadmium in concentrations of about .01% to 1%, as compared to an average zinc content of 4%.<sup>4</sup> Most of these deposits are in the Coeur d'Alene district of Idaho, Washington State, and the upper Mississippi. The one major deposit of zinc not containing significant cadmium is at Franklin and Sterling Hill, N.J.<sup>5</sup> World reserves of cadmium are estimated at 2 billion pounds and zinc at about 90 million tons; U.S. reserves are about 100 million pounds and 29 million tons respectively.<sup>6</sup>

Zinc is an important metal in world trade, ranking fourth among all metals on the basis of annual world production. Numerous companies in twenty-five countries produce zinc metal with Canada by far the largest producer.<sup>7</sup> In the U.S. in 1968, 18 companies produced 1.075 million tons of primary metal.<sup>8</sup> These smelters are almost all owned by large diversified nonferrous-metal corporations with many ties to foreign mines and companies.

Nine of these firms also produce cadmium metal on-site while two smaller firms produce cadmium only from zinc-smelter flue dust, scrap, or residues.<sup>9</sup>

Production of zinc has grown rapidly worldwide, but has declined slightly in the U.S. to a level of 678,000 tons. U.S. demand has continued to grow steadily to 1,649,000 tons in 1973, requiring imports amounting to 37%. In the same year domestic cadmium metal demand was 6,228 tons, production was 3,714 tons, and imports were 1,946 tons or 31%.<sup>10</sup>

As mentioned, cadmium is considered to be almost entirely a byproduct of zinc production. Most zinc ore contains many other valuable minerals, such as copper, gold, fluorospar, lead, manganese, silver, and others. In some deposits in Missouri and the West, more lead, manganese and silver are recovered than zinc, making zinc a byproduct. In most other operations the major byproduct of zinc production are sulfur, germanium, thallium, indium and gallium.<sup>11</sup>

Though technology exists for recovering both zinc and cadmium, presently only a small proportion of zinc metal is recycled, about 6% of demand in 1973.<sup>12</sup> Secondary cadmium was produced in the 1950's in the U.S., reaching the highest level of 427,000 lbs. in 1950 (4% of 1950 consumption).<sup>13</sup>

Zinc is used mainly for metallurgical work, being either alloyed to produce die-cast parts, used to galvanize steel, or alloyed with copper to produce brass. About 60% of all cadmium is used for electroplating metal parts such as aircraft body sections. The remaining major uses are in nickel-cadmium batteries, as pigments in chemical compounds, and in various other alloys.<sup>13</sup> Substitutes to cadmium exist for most

of its applications; Zinc and nickel-chrome for plating and galvanizing; lead, zinc and barium chromates for pigment compounding, etc. The major substitutes for zinc metal are aluminum and magnesium, while steel can in some cases replace brass.<sup>15</sup>

## PROCESS DESCRIPTIONS

### 91. Zinc

An excellent description of the various metallurgical processes used for zinc production is published by Battelle/Columbus Laboratories:<sup>16</sup>

Zinc is produced by three processes, two pyrolytic and one electrolytic. The pyrolytic processes, electrothermic and vertical retort, provide about 35 and 20 percent, respectively, of the U. S. zinc producing capacity, and the electrolytic process provides about 45 percent. The operational sequence for the electrothermic, vertical retort and electrolytic processes are shown in Flowsheets 22, 23, and 24, respectively.

The zinc concentrates are obtained principally from zinc, lead-zinc, and lead ores although some are derived from copper ores. The domestic ores are predominantly sulfide ores from underground mines except for an insignificant amount of open pit ore. The ore treatment involves crushing, grinding, and beneficiation by flotation to produce a concentrate containing 50 to 60 percent zinc before shipping to the zinc plants.

For the electrolytic process, the concentrate is roasted and the roaster gases are passed through waste heat boilers, cleaned, and used to produce sulfuric acid. The soluble oxides produced by roasting are leached with spent electrolyte. Manganese dioxide is added during this operation to oxidize the ferrous sulfate to ferric sulfate to facilitate iron removal as the solution is neutralized. The spent electrolyte and calcine are added to the leaching tanks under conditions of controlled acidity to avoid dissolving too much iron while dissolving all possible zinc.

After leaching, the neutral, or pregnant solution, is filtered in large drum or Oliver filters, or in the case of hot, concentrated solutions, Burt filters are used. The residue may be processed further to recover the

remaining zinc, and the final residue is dried and sent to a lead smelter to recover the lead and other metals.

The filtrate is purified in a series of steps by adding controlled amounts of zinc in each step to replace metals which occur below zinc in the electromotive series. The purified solution then goes to the cell room where the zinc is plated out on aluminum cathodes as the electrolyte flows slowly through the cells. The rate of zinc deposition is governed primarily by the current density used. Common practice is 70 amp/square foot but one plant uses up to 105 amp/square foot. The heat generated in the bath is removed by cooling coils or in one case by a flash cooler under reduced pressure. Strontium carbonate or barium hydroxide may be added to reduce lead contamination of the zinc, and glue or gum arabic are among the agents added to obtain a smoother deposit of zinc.

The electrolytic zinc process has the advantage of directly producing Special High Grade zinc which is much used in die casting and where very high purity is needed. Zinc from the pyrolytic plants is normally somewhat less pure and constitutes grades such as prime Western (much used in galvanizing), Brass special, Intermediate and High Grade.



#### 14. Cadmium

There are three major methods for producing cadmium as a byproduct of lead, copper and zinc production. Two of these--horizontal and vertical zinc-retort processes, make use of the fact that cadmium has lower melting and boiling points, and is more easily reduced.<sup>17</sup> The third process involves leaching and precipitating cadmium prior to the electrolysis of zinc. The process described applies to the mining and milling of lead-zinc ores in several locations and the production of cadmium as a byproduct of zinc leaching and electrolysis at the Flin Flon plant of the Hudson Bay Mining and Smelting Co.<sup>17</sup>

Lead/zinc ore is mined underground using the "room and pillar" system of mining. The ore is blasted, drilled, bulldozed, and shovel-loaded into trucks for hauling to the mill. At the mill, the zinc ores are processed by any of several methods. For example, the "volatilization" method begins by washing, screening, mixing, and heating the ore to produce small nodules. These are inserted in a volatilization furnace operating at extremely high temperatures, around 1,000°C, for several hours. The atmosphere in the furnace is either an inert gas, a vacuum, or a "reducing atmosphere."

Starting with zinc ore concentrate, Chizhikov [14-101] has written this description of the plant from which energy data has been obtained (see Fig. 14a):

The average cadmium content of the zinc concentrate is 0.12%. During the purification of the roasted concentrates from copper and cadmium a residue is obtained which contains 55.2% cadmium, 24.4% zinc, and 0.4% copper. The production of a copper-cadmium residue with such a high cadmium content and a low copper content

is brought about by the purification system used for the zinc solution in the electrolytic zinc works.

Purification of the zinc solution from cadmium is carried out by a continuous method in two stages.

The neutral solution from the thickeners passes into a tank, 3.66 m in diameter, fitted with a rubber covered, three blade stirrer on a wooden shaft. The solution passes successively through five tanks (agitators). Zinc dust is added continuously to each of the five tanks by means of a vibratory feed. The consumption of zinc dust in the first stage of purification amounts to 32 kg for 1 ton of electrolytic zinc.

When the copper content of the solution becomes less than 150 mg/l a solution of copper sulphate is added to the feed channel.

To avoid cementation the underflow from the first agitator flows into the second and so on. The overflow is filtered and the filtrate is directed to the second purifying operation which is also carried out successively in five agitators.

Here a small amount of copper sulphate is added continuously to the first agitator. Zinc dust is added continuously to all the agitators at the rate of 32 kg per ton of electrolytic zinc. On completion of the second purification the solution is filtered.

The cadmium residues from both stages of purification are ground in pebble mills and leached with acid electrolyte (heated to 75° by steam) in agitators, 3.66 m in diameter and 6 m high, lined with acid resistant brick on a layer of rubber. The tanks are covered and provided with separate ventilators, each with a capacity of 700 m<sup>3</sup> per minute. The cases are ejected into an 18 m high chimney.

During the leaching of the copper-cadmium residue, zinc, cadmium and iron go into solution while copper remains in the deposit. The final solution contains up to 1 g/l sulphuric acid.

The cadmium residue contains about 27% zinc, 29.4% copper and 3.85% cadmium. The cadmium content is reduced to 1% and the zinc content to 8% by subsequent treatment of the residue with an acid

solution of copper sulphate containing 40 g/l copper. The product is sent to the copper works.

The solution from the acid leaching of the copper-cadmium residue, which contains 115 g/l zinc, 0.016 g/l copper, 2 g/l iron and 3.9 g/l cadmium is treated with zinc dust until it contains 0.08 g/l cadmium or less.

The amount of zinc dust added in this operation must be the minimum necessary to ensure a high cadmium content in the cadmium residue. The final cadmium residue contains up to 55.2% cadmium, 24.4% zinc and 0.4% copper. The residue is passed to a special cadmium plant where it is treated with spent acid electrolyte (at 75° in lead-lined tanks provided with paddle stirrers). After neutralisation the solution is analysed for copper. If the copper concentration exceeds 5 mg/l the minimum amount of zinc dust for the precipitation of the copper is added to the solution.

The solution after filtration, which contains 114 g/l cadmium, 68.0 g/l zinc, 0.012 g/l copper and 0.004 g/l cobalt, is passed for electrolysis.

The cadmium electrolysis plant consists of four cascades of five baths each. The solution in the cascade is circulated by gravity. Each bath contains 13 aluminium cathodes (1016 x 610 mm) and 14 lead anodes (1000 x 584 x 8 mm). The cathodes are provided with strips of plastic. The baths operate without cooling. The current density at the cathode is 30 A/m<sup>2</sup>. Gum is added to each bath at the rate of about 30 kg per ton of electrolytic cadmium.

Satisfactory results are obtained if the cadmium content of the solution is greater than the zinc. An excessive reduction in the cadmium content leads to the formation of a spongy cadmium deposit and a low current efficiency. The spent cadmium electrolyte contains 58 g/l cadmium, 64 g/l zinc, 0.025 g/l copper, 0.025 g/l cobalt and 42 g/l sulphuric acid. The temperature of the bath is maintained at about 21° during electrolysis. The average current efficiency is 80%.

The cadmium is stripped from the cathodes every 24 hours. The cadmium deposits are washed with water, rolled tightly and dried in a steam drier. The dried cadmium is melted in a thermostatically controlled, electrically heated, cast iron furnace of 180 kg capacity. The pot is covered and is provided with an exhaust system for the removal of the gases. The cadmium is melted under a layer of caustic at 400°. The alkali layer protects the metal surface from oxidation and assists the removal of zinc from the cadmium. The alkaline dross which contains cadmium oxide and beads of metal is leached with water. The solid residue is returned to the beginning of the process and the molten cadmium is cast in cast iron moulds as rods, spheres or slabs.

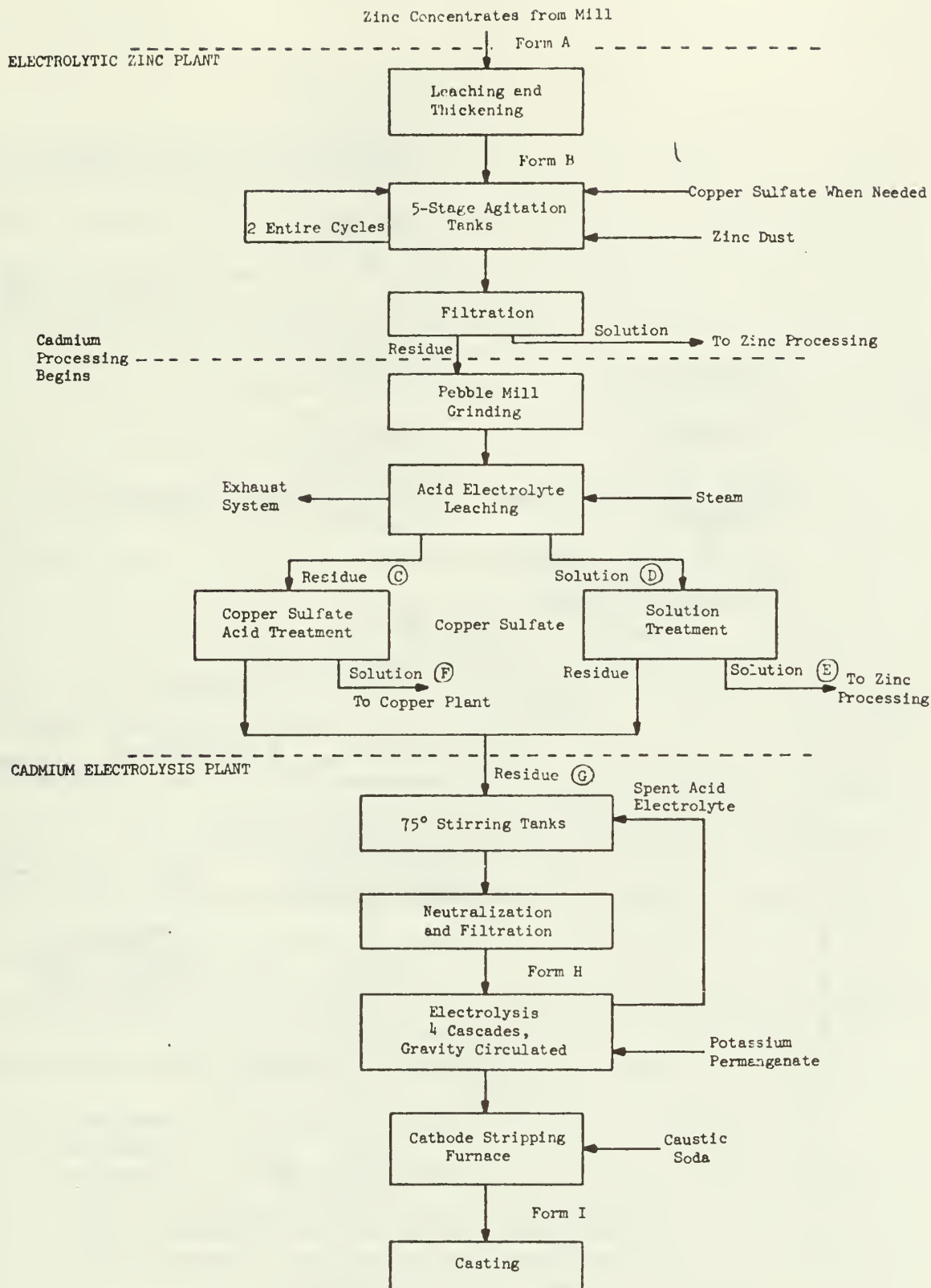


Figure 14a: PRODUCTION OF CADMIUM\*

Source: Energy Research Group

- FORMS: A .12% Cd  
 B Neutral solution  
 C 27% Zn, 29.4% Cu, 3.85% Cd  
 D 115 g/l Zn, .016 g/l Cu, 2 g/l F3, 3.9 g/l Cd, 1 g/l H<sub>2</sub>SO<sub>4</sub>  
 E Less than .08 g/l Cd.  
 F 1% Cd, 8% Zn  
 G 55.2% Cd, 24.4% Zn, .4% Cu  
 H 114 g/l Cd, 68.0 g/l Zn, .012 g/l Cu.  
 I Molten metal, 99,9871% Cd, .0028% Zn, .0019% Cu, .0082% Pb, trace of iron.

\* Describes Cadmium production at Flin-Flon Plant, Canada.  
 See text for prior mine and mill processing.  
 Source: [14-101] and [14-301]. 27

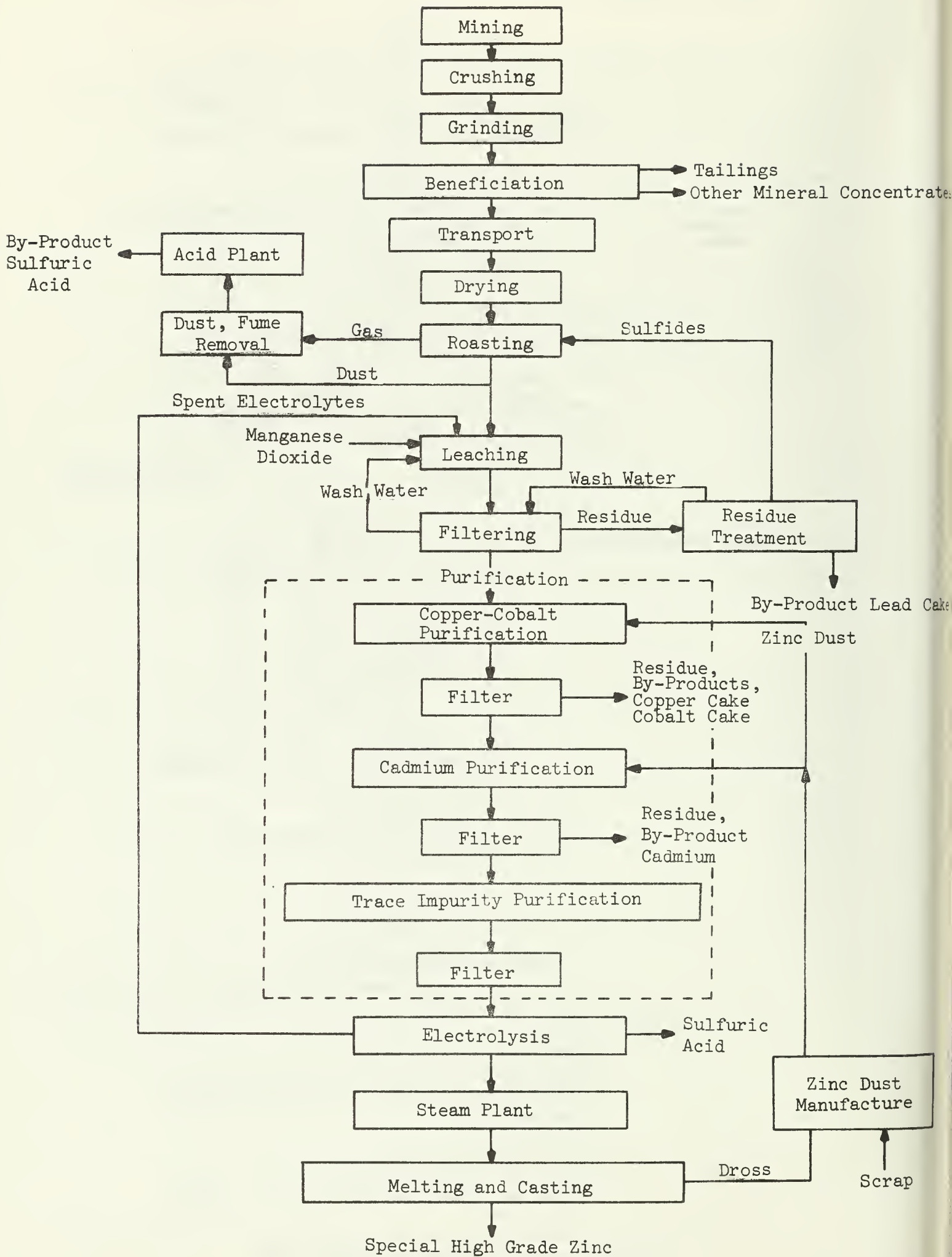


Figure 91a: PRODUCTION OF ELECTROLYTIC ZINC

## A NOTE ON ENERGY ALLOCATION METHODS

Zinc, Cadmium, and other metals produced by the mines and smelters described here may certainly be considered as coproducts. In order to attach an energy cost to the individual outputs, some means is required for allocating energy use in these processes among the outputs.

Such a question has long been considered by economists, who have given it the name of "the joint products question." It is generally agreed among them that any solution is a hypothetical construct useful only for accounting purpose. However, the question takes a slightly different form when viewed from the standpoint of energy accounting. Rather than seeking a scheme for allocating costs, a solution is desired which indicates the relative economic importance of these joint outputs to society. This relative scaling can then be applied to energy consumption to, in effect, charge society for the energy use required to fulfill its desires.

This type of solution is possible in only two situations -- either a perfectly competitive marketplace for all joint products or markets for which extensive economic data are available. We assume the former in this case, though it is recognized that even the worldwide markets for these metals are not perfectly competitive. If perfect competition exists, all producers are price-takers and economic value is described perfectly by the exogenous price level. A similar measure will be used in this analysis: the ratio of relative total revenue due to one metal to another. In 1974, the producer's relative revenues appear as below:

METAL	ANNUAL OUTPUT (lbs.)*	PRICE (\$/lb.)**	"REVENUE"(\$)	REVENUE %
Copper	108,152,000	.5953	64,382,886	65.78%
Zinc	154,046,000	.2084	32,103,186	32.79%
Cadmium	386,768	3.61	1,396,232	1.43%

\* [0-107] p. 190

\*\* [0-101], 1973 Avg. N.Y.

Therefore 1.43% of all energy use from the concentrate stage to the cadmium plant will be allocated to cadmium. The same system can be used to allocate energy use for zinc/cadmium mining and milling. These data come from a different producer, having this financial breakdown:

METAL	ANNUAL OUTPUT (lbs.)*	PRICE (\$/lb.)**	"REVENUE"(\$)	REVENUE %
Lead	38,922,000	.1629	6,340,394	34.71%
Zinc	40,560,000	.2084	8,440,200	46.20%
Silver	87,652	33.71	2,954,749	16.17%
Cadmium	146,841	3.61	530,096	2.90%

\* [14-303]

\*\* [0-101] and [0-110], 1973 Avg. N.Y.

For mining and milling cadmium ores, 2.90% of total energy use will be allocated to cadmium.



Table 91. PRODUCTION OF ZINC<sup>a</sup>

(Basis: 1 ton of zinc to federal specifications)<sup>a</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	electric	369.3 kWh	4,846
	diesel oil	7.4 gal	1,232
	gasoline	16 gal.	90
	materials <sup>b</sup>	-	<u>836</u>
<i>Subtotal</i>			<u>7,004</u>
2. Crushing and Grinding	electric	350.6 kWh	4,601
	materials <sup>c</sup>	-	<u>551</u>
<i>Subtotal</i>			<u>5,152</u>
<i>Cumulative Subtotal</i>			<u>12,156</u>
3. Beneficiation	electric	141.1 kWh	1,852
	materials <sup>d</sup>	-	273
	transportation <sup>e</sup>	-	<u>704</u>
<i>Subtotal</i>			<u>2,829</u>
<i>Cumulative Subtotal</i>			<u>14,985</u>
4. Drying and Roasting	electric	266.8 kWh	3,501
	natural gas <sup>f</sup>	1,769 ft <sup>3</sup>	1,944
	propane <sup>g</sup>	8.14 gal.	773
	credit <sup>h</sup>	-	<u>- 1,345</u>
<i>Subtotal</i>			<u>4,873</u>
<i>Cumulative Subtotal</i>			<u>19,858</u>
5. Leaching, Purification and Electrolysis	electric	3,681.8 kWh	48,317
	natural gas <sup>f</sup>	601 ft <sup>3</sup>	660
	materials <sup>i</sup>	-	<u>575</u>
<i>Subtotal</i>			<u>49,552</u>
<i>Cumulative Subtotal</i>			<u>69,410</u>
6. Melting and Casting	electric	100.064 kWh	1,313
	natural gas <sup>f</sup>	2780 ft <sup>3</sup>	<u>3,055</u>
<i>Subtotal</i>			<u>4,368</u>
<b>TOTAL</b>			<u><b>73,778</b></u>

NOTES TO Table 91

- <sup>a</sup> By the electrolytic process. This process produces any grade zinc including Special High Grade, which meets all federal specifications [0-101], p. 307 and [0-325a] p. 158.  
SOURCE FOR FIGURES IN AMT. COLUMN IS: [0-325a] p. 169, 170 UNLESS NOTED.
- <sup>b</sup> 18.84 lb. Steel/ton Zinc @ 17,500 Btu/lb. and 16.87 lb. explosives/ton zinc @ 30,000 Btu/lb.
- <sup>c</sup> 31.5 lb. steel/ton zinc @ 17,500 Btu/lb.
- <sup>d</sup> 2.89 lb. organic reagents @ 20,000 Btu/lb. and 42.9 lb inorganic reagents @ 5,000 Btu/lb.
- <sup>e</sup> 1,050 ton-miles @ 670 Btu/TM.
- <sup>f</sup> Caloric value assumed 1,000 Btu/ft<sup>3</sup>.
- <sup>g</sup> Caloric value and delivery efficiency assumed to add to 95,000 Btu/gal.
- <sup>h</sup> Energy credit for byproduct production of 1.62 tons sulfuric acid @ 830,000 Btu/ton.
- <sup>i</sup> 85.0 lb. manganese dioxide @ 5,000 Btu/lb.; .084 ton sulfuric acid @ 830,000 Btu/ton; 16.0 lb. inorganic reagents @ 5,000 Btu/lb.

Table 14. PRODUCTION OF CADMIUM

(Basis: 1 ton cadmium metal to federal specifications)<sup>a</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining Lead/Zinc/Silver/ Cadmium Ores <sup>b</sup>	electricity	49.28 kWh	647
	natural gas <sup>e</sup>	121.4 ft <sup>3</sup>	137
	diesel fuel	.0595 gal.	10
	gasoline	.0399 gal.	6
	materials <sup>c</sup>	-	19
<i>Subtotal</i>			<u>819</u>
Energy allocated to Cadmium production <sup>d</sup>			<u>248,744</u>
2. Milling and Concentrating <sup>b</sup>	electricity	26.38 kWh	346
	<i>Subtotal</i>		
Energy allocated to cadmium production <sup>d</sup>			<u>105,086</u>
Cumulative Subtotal (cadmium production)			<u>353,830</u>
3. Zinc Plant Separation	electricity <sup>g</sup>	131.754 kWh	173
	materials <sup>h</sup>		2,293
<i>Subtotal</i>			<u>2,466</u>
Energy allocated to cadmium production <sup>f</sup>			<u>67,022</u>
Cumulative Subtotal (cadmium production)			<u>420,852</u>
4. Cadmium Plant	electricity <sup>i</sup>	2,000 kWh	26,246
	materials <sup>j</sup>		2,108
<i>Subtotal</i>			<u>28,354</u>
TOTAL ENERGY REQUIRED TO PRODUCE 1 TON CADMIUM			<u>449,206</u>

NOTES TO Table 14

<sup>a</sup> See [14-141]

<sup>b</sup> Ore contains (relative proportions) 48.8% Pb, 50.9% Zn, .1% Ag, and .2% Cd. Total energy used in mining at Bunker Hill Mining Co., Kellogg, Idaho, per ton ore produced. [14-303].

<sup>c</sup> Applies to Tri-State Zinc, Inc., Illinois, mines with zinc/lead ratio in the ore by weight .83; cadmium content unknown. [91-141]. Materials used are:

MATERIAL (\$/ton output)	[91-141]	BEA Sector [0-210]	Deflator [0-211]	Energy Coefficient [0-201]*
\$.0188	drill steel	45.02	1.0768	73,560 Btu/\$
\$.3461	repairs and supplies	75.00	1.1398	36,056 Btu/\$
\$.106 lb/ton	explosives	-	-	30,000 Btu/lb [0-325a] p. 9

\* Neglects difference in purchasers and producers prices.

<sup>d</sup> Assumes a recovery efficiency of 90% from ore. If 73.4 tons of Cd. metal were contained in the 691,849 tons of ore mined, then 9,426 tons of ore are required for 1 ton of cadmium contained and 10,473 tons of ore are required for one ton of final cadmium output. [14-303]. Only 2.9% of the energy required to produce the 10,473 tons of ore is allocated to cadmium (see preceding section on allocation).

<sup>e</sup> Caloric value used: 1,027 Btu/ft<sup>3</sup>.

<sup>f</sup> In this step energy figures listed are per ton zinc output. To allocate to cadmium, the following production statistics are used:

total 1975 zinc production: 65,463 tons  
total energy use in stage: 161,431,758,000 Btu  
2.9% of total: 4,681,521,000 Btu  
total 1975 cd production: 79.85 tons  
allocated energy use per ton cadmium: 67,022,000

<sup>g</sup> Source: [14-305]. Figure listed is energy use per ton zinc output and will be allocated to cadmium when cumulated.

<sup>h</sup> 32 kg. zinc/ton zinc are consumed ([14-301]). Zinc has an energy intensity of  $65.0 \times 10^6$  Btu/ton. [0-325a] p. 157. Figure listed is per ton zinc output. Copper sulfate use is neglected.

<sup>i</sup> For electrolysis and cathode stripping. [14-301].

j 10 lb. potassium permanganate/ton cd. @ \$5.15/lb @ 281,962 Btu/\$1967  
[14-204], [0-201], [0-209], [14-301]. 39 lb. caustic soda/ton cd.  
@ 23,950 Btu/lb. [14-301] and [0-325a] p. 109. Deflator used is 1.2370  
(1967-1975 II) from [0-209].

### ENERGY/VERSATILITY CONSIDERATIONS FOR ZINC

Zinc is the more or less standard case in which a single refining step late in the manufacturing sequence requires most of the energy. In this case the major step is electrolysis, which consumes over two-thirds of total energy use. As with copper, the metal should probably be stockpiled after this stage. Again, unless there is no difference in versatility, there is little reason to require the cathodes to be remelted and recasted. See Figure 91b.

### ENERGY/VERSATILITY CONSIDERATIONS FOR CADMIUM

Cadmium poses a dilemma in optimization. Due to the by-product nature of production and low electrolysis energy use, cumulative energy use grows gradually and steadily similar to many non-metals (Fig. 14b). In this case there is no optimum from the standpoint of energy use and stockpiling decisions should be made on the basis of strategic and versatility considerations.

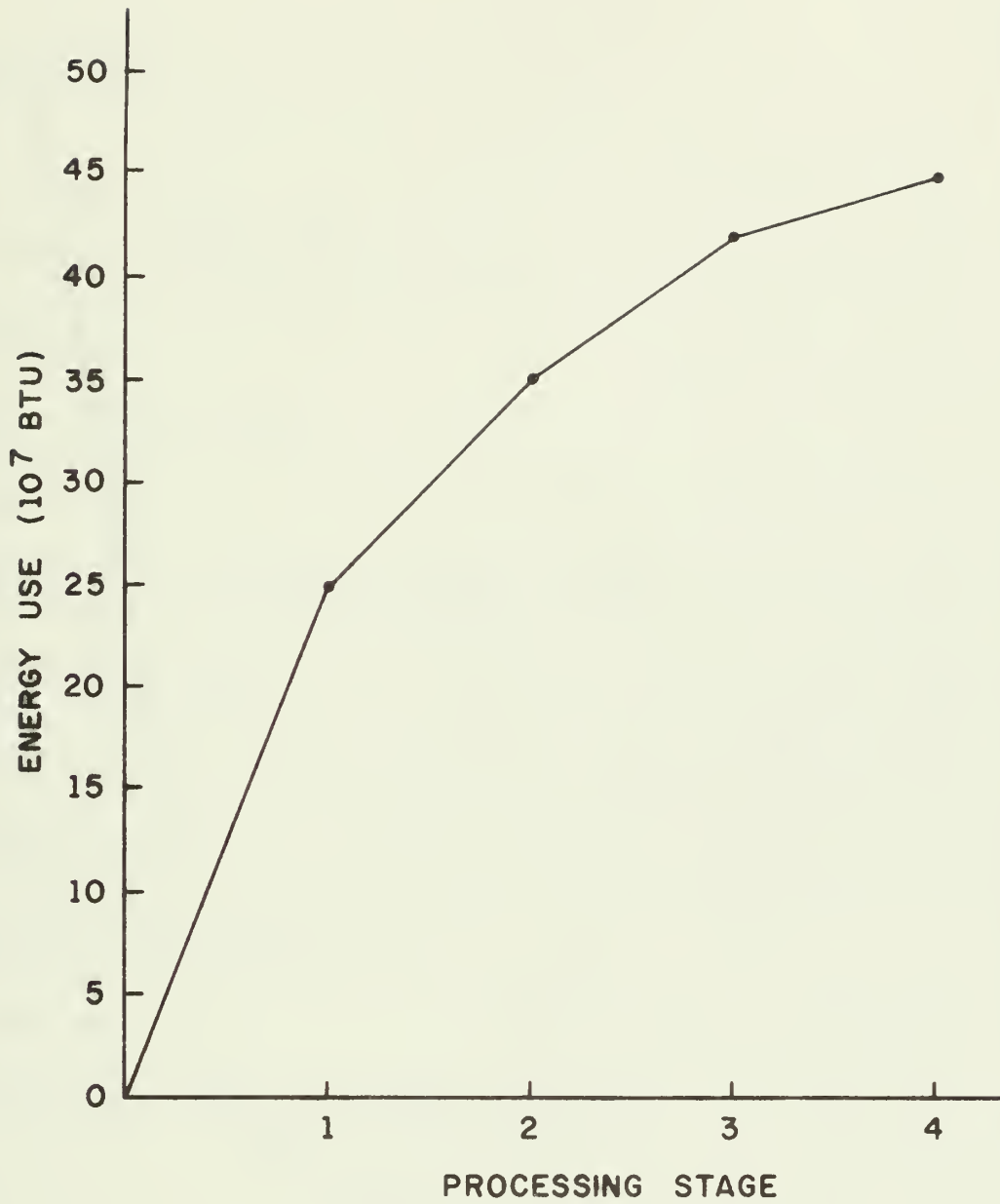


Figure-14b: Production of Cadmium



Figure 91b: Production of Zinc



FOOTNOTES TO SECTION 14,91.

- <sup>1</sup> [14-140] p. 1.
- <sup>2</sup> [0-149] p. 515.
- <sup>3</sup> Ibid.
- <sup>4</sup> [14-140] p. 4 and [0-149] p. 811.
- <sup>5</sup> [14-140] p. 4.
- <sup>6</sup> Ibid and [0-149] p. 811.
- <sup>7</sup> [0-149] p. 806.
- <sup>8</sup> [0-112] Pt. II p. 33C-7 and [0-149] p. 764.
- <sup>9</sup> [0-149] p. 516, 806.
- <sup>10</sup> [0-145] p. 17, 94.
- <sup>11</sup> [0-149] p. 814.
- <sup>12</sup> Ibid and [0-145] p. 94.
- <sup>13</sup> [14-140] p. 28.
- <sup>14</sup> [0-149] p. 520, 815 and [0-122] p. 89, 90.
- <sup>15</sup> Ibid.
- <sup>16</sup> [0-325a] p. 156
- <sup>17</sup> [14-140] p. 6.
- <sup>17</sup> Sources: [91-141, [4-100], [14-301], [14-140].
- <sup>18</sup> [0-149] p. 811 and [14-140] p. 4.

## 16...22 CHROMIUM

### Overview

Chromium, atomic number 24, is an important component in a great variety of heat and corrosion resistant materials, mainly stainless and alloy steels. It occurs in a large number of minerals, but the only commercially important one is chromite, a mineral oxide ore of chromium and ferrous iron.<sup>1</sup> Average concentration in the earth's crust is 200 ppm, about the same as zirconium but considerably higher than zinc, nickel, copper.<sup>2</sup> Although the U.S. has some low grade ore deposits in Montana, California, Oregon and Alaska, practically none of it has been processed by the industry since 1961.<sup>3</sup> From the three useable ore groups: metallurgical grade, chemical grade and refractory grade chromite, the first has the highest chromium content, a minimum of 48%  $\text{Cr}_2\text{O}_3$ , a maximum of 8%  $\text{SiO}_2$  and a minimum Cr : Fe ratio of 3:1.<sup>4</sup> All of the U.S. demand is imported, the four most important sources being the U.S.S.R., Turkey, Philippines, Southern Rhodesia and the Republic of South Africa.

- Metallurgical grade chromite is the basis for production of Low-Carbon, Silicon- and High-Carbon Ferrochromium. The latter is an input to electrolytic processes yielding pure chromium metal.
- Chemical grade chromite has 44.5 ...46 weight-percent  $\text{Cr}_2\text{O}_3$  and 4... 1.25%  $\text{SiO}_2$ .<sup>5</sup> It is imported from the world's largest known deposits in the Bushveld Igneous Complex of the Transvaal in South Africa and goes into the production of primary sodium bichromite and chromate from which chemicals for pigments and plating are derived. By aluminothermic process it can be reduced to pure chromium metal.
- Refractory grade chromite has the lowest chromium content: a

minimum of 31%  $\text{Cr}_2\text{O}_3$ , an average 58% of  $(\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)$  and maximum 12% of Fe. This ore comes from the Philippines, Turkey and the Republic of South Africa.

This mineral is used alone or in combination with other materials to make refractories which are capable of resisting high temperatures in (steel making) furnaces or kilns. Such linings are provided as mortars and cements, as well as in the form of bricks or shapes, either fired or chemically bonded.

Not only the U.S. but other major Western consuming nations, such as Great Britain, France, Germany, Sweden and Japan, have no remaining indigenous chrome. The trend towards greater control of chrome by the producing countries is likely to be enhanced as the nations with ore expand into production of the more profitable ferrochrome products. Major expansion of internal ferrochrome capacity is known to be under way in the Soviet Union, Turkey, South Africa, Rhodesia, Finland, France, New Caledonia, and possibly India.<sup>7</sup>

The U.S. industry consumes about 25% of the world's supply of chromium as alloys, chemicals and refractories. In 1968, seven companies with plants in 12 locations produced essentially all of the chromium metal and alloys used as additives in steelmaking and other alloy production. In addition, there were four large chemical producers and 11 principal refractory producers.<sup>8</sup> In 1973 domestic consumption was 1,387,000 tons of chromite ore and concentrate containing about 429,000 tons of chromium. The metallurgical industry used 66.3%, that is 920,000 tons of chromite containing 303,000 tons of chromium in producing 417,745 tons of chromium alloys and metal.

The chemical industry used 14.9%, that is 206,000 tons of chromite containing about 64,000 tons of chromium in producing 159,000 tons of chemicals (sodium bichromate equivalent). The refractory industry used 18.8% which amounts to 261,000 tons of ore containing about 63,000 tons of chromium.<sup>9</sup>

From the total U.S. supply in 1973 of 864,000 tons of chromium, 239,000 tons were industrial stocks. An estimated 16,000 tons was exported as alloys and chemicals, an estimated 13,000 tons was exported as refractories and the U.S. demand of 596,000 tons was distributed over the following sectors:<sup>10</sup>

CONSTRUCTION AND FABRICATED METAL PRODUCTS 28%: Stainless steel products for industrial and residential buildings, highway and bridge construction, stainless steel fabricated into trim and wheel covers for vehicles, panels for trailers, railroad cars;

TRANSPORTATION 18%: Steel and iron castings for motor vehicles, railroads and ships; high temperature and special alloys, chiefly jet engine component parts;

MACHINERY 15%: Alloy and stainless steel pumps, tanks, pipes and tubes, oil and gas refinery equipment, mining and chemical plant equipment, tools;

REFRACTORIES 13%: Furnace linings and other products for both ferrous and nonferrous melting and smelting;

CHEMICALS 8%: Pigments and paints (yellow traffic paints), coatings for metal on bridges and other exposed surfaces, treatment of hides and tanning operations for leather products;

OTHER 17%: various industrial purposes such as plating from

solutions, plasma-arc deposition to form wear resisting surfaces, corrosion inhibitors, catalysts, textile dyes, ductile metal for surgical use, special alloys for defense needs, chromite sands for mold and core making in foundries.<sup>11</sup>

Although chromium occurs in a number of minerals, chromite is the only source for industrial use. This ore is treated for recovery as ferrochromium but not for the other metals that may be substituted for iron in the general chromite formula. Iron is not objectionable in the chromium alloys produced for use in iron and steel production. However, iron is not considered as a coproduct or by-product, but is present because of production techniques. As the percentage of iron increases, the value of the chromium alloy is correspondingly decreased. Slag resulting from the smelting operation is often crushed and sold for road ballast or similar low-value by-product uses.<sup>12</sup>

Secondary chromium accounts for about 6% of U.S. supply, stainless steel scrap being the only sizable source. It is normally consigned to melts of the same or similar composition and recycled through regular electric steelmaking furnaces. For all practical purposes, home scrap acts as a permanent circulating load. Better separation of stainless steel and chrome-plated parts from junked vehicles and appliances prior to final disposal would result in additional chromium. Similarly, improved methods of recovery from liquid and solid industrial waste now under study by the Bureau of Mines could save much chromium now discarded or partially recovered in many industrial operations. Fully automated steelmaking would eliminate other causes of inaccurate use.<sup>13</sup>

- The lack of a possible alternate for chromium among alloying elements is unique: chromium cannot be adequately replaced in

corrosion-resistant, high temperature alloys. One could replace stainless steel, but stainless steel cannot be made without chromium. Substitution for chromium is much more limited than for molybdenum and nickel as far as achieving hardenability is concerned. About 5% of total stainless steel capacity may be replaced by copper, nickel, or titanium alloys at a cost penalty.

For iron and steel plating and many corrosive resistance purposes of this kind, nickel, zinc or one of several other metals can be substituted. Aluminum and high impact plastics can have the same effect.

- In some paint applications, lead, iron oxide and cadmium can be used instead of chromium pigments. Sodium bichromate for leather tanning can hardly be substituted: vegetable tannins give only acceptable results in specific cases. Plating and metal protection for engine parts and other metal uses are not easily obtained by any other way, unless alternate design solutions are applied.
- Refractory chromite may be replaced by magnesite and dolomite: changes in steelmaking methods resulted in shifting away from "chrome-magnetic" type bricks in which chromite was the larger constituent.<sup>14</sup>

## PROCESS DESCRIPTION

Chrome ore is mined by both the open-pit and underground methods and only minor beneficiation is done such as hand sorting, heavy-media separation or screening for lump ores. For the production of high-carbon ferrochromium,<sup>16</sup>

"The ores are smelted in three-phase submerged arc electric furnaces. The charge to the furnace, which is continuously operated, consists of one or more types of chrome ore, silica fluxes for slag and metal control, coke which is the reductant, wood chips to keep the charge open for flow of gases produced in the pyrometallurgical reactions, and recycled ferroalloy scrap and/or slag concentrates. About every two hours the furnace is tapped at a bottom hole and, after slag-metal separation, the alloy is cast. After cooling it is crushed, sized, and shipped (Figure 17 / 18).

"A considerable part of the chromium units in stainless steels which were derived from high-carbon ferrochromium are recycled as stainless scrap which is collected and graded not only for chromium content, but also for the nickel in austenitic grades. Chromium which was consumed in the production of low alloy steels is not recoverable because such scrap is mixed with other common grades of steel and when remelted in steelmaking the chromium is oxidized and lost in the slag."

About 75% of the U.S. production of pure chrome metal is obtained electrolytically. Experimental electrowining of chromium metal was undertaken by the U.S. Bureau of Mines in the Fifties.<sup>17</sup> Various existing industrial processes<sup>18,19</sup> follow this scheme:<sup>20</sup>

"The chrome alum feed solution is made from high carbon ferrochromium using depleted anolyte as the leaching agent. The electrodeposition of chromium is conducted in a diaphragm cell with

cathodes of stainless steel and anodes of lead - 10% silver. The composition of the catholyte and anolyte must be held within narrow limits; the same applies to pH and temperature of the catholyte.

Feed solution enters the catholyte compartment; a portion of this solution leaves the cell from the catholyte compartment and the remainder flows through diaphragms into the anolyte and then passes out of the cell. Because they control several important aspects of the process, diaphragms of the proper porosity are essential." (Figure 21).

A second method of producing pure chromium metal consists of aluminothermic reduction of chromic oxide by means of finely divided aluminum. Particle size, admixture of reagents and oxygen balance are important parameters in this exothermic process. Chromic oxide of acceptable purity (low sulfur content) is made of chromite ore in the following way: a mixture of finely ground chemical grade chromite with sodium carbonate and some carrier such as limestone or iron oxide, is roasted and agitated at a high temperature. With water, sodium chromite is leached out of the roasted mass, filtered, concentrated and acidified to form sodium bichromate solution. The liquor is filtered again, concentrated and then crystallized out. After reduction with sulfur or carbon in an open furnace, washing and re-washing of the mass results in pure green chromic oxide.<sup>21</sup>

"The process for the production of low-carbon ferrochromium is somewhat complex. A ferrochromium-silicon alloy is produced in a submerged-arc electric furnace, while in another open-arc electric furnace, chrome ore fines and lime are melted. The chrome silicide operations are shown in Figures 17, 19, 20. Then in a series of ladle reactions and repourings of mixtures of chrome silicide and ore-lime melt, a low-carbon ferrochromium



and a waste slag are produced. The net metallurgical reactions of the series of reladlings is to reduce the  $\text{Cr}_2\text{O}_3$  and  $\text{FeO}$  in the chrome ore with the silicon contained in the chrome silicide and to end up with a waste slag low in  $\text{Cr}_2\text{O}_3$  and a low-carbon ferrochromium product.

Another process, which is proprietary, consists of the solid state decarburization of high carbon ferrochromium under vacuum conditions. High carbon ferrochromium is crushed and ground and then the surface of the metallic particles are oxidized to the desired extent at elevated temperatures. The oxidized ferrochrome is then mixed with cereal binder and water and briquetted in a roll type press. The briquettes are then loaded on a flat-bed car and moved into a long horizontal cylindrical furnace. The door is closed and heating (internal graphite resistance elements) and evacuation started. The charge is held at about 2500 F and a vacuum of less than 3 mm of mercury. The net reaction is that between the carbon and the oxides in and on each of the ferrochromium particles. Carbon contents of below 0.025 percent can be obtained.

The average chromium content of low-carbon ferrochromium produced in the United States during 1973 was 70 percent. Carbon content is usually below 0.05 percent and silicon is about 0.2 percent."<sup>16</sup>

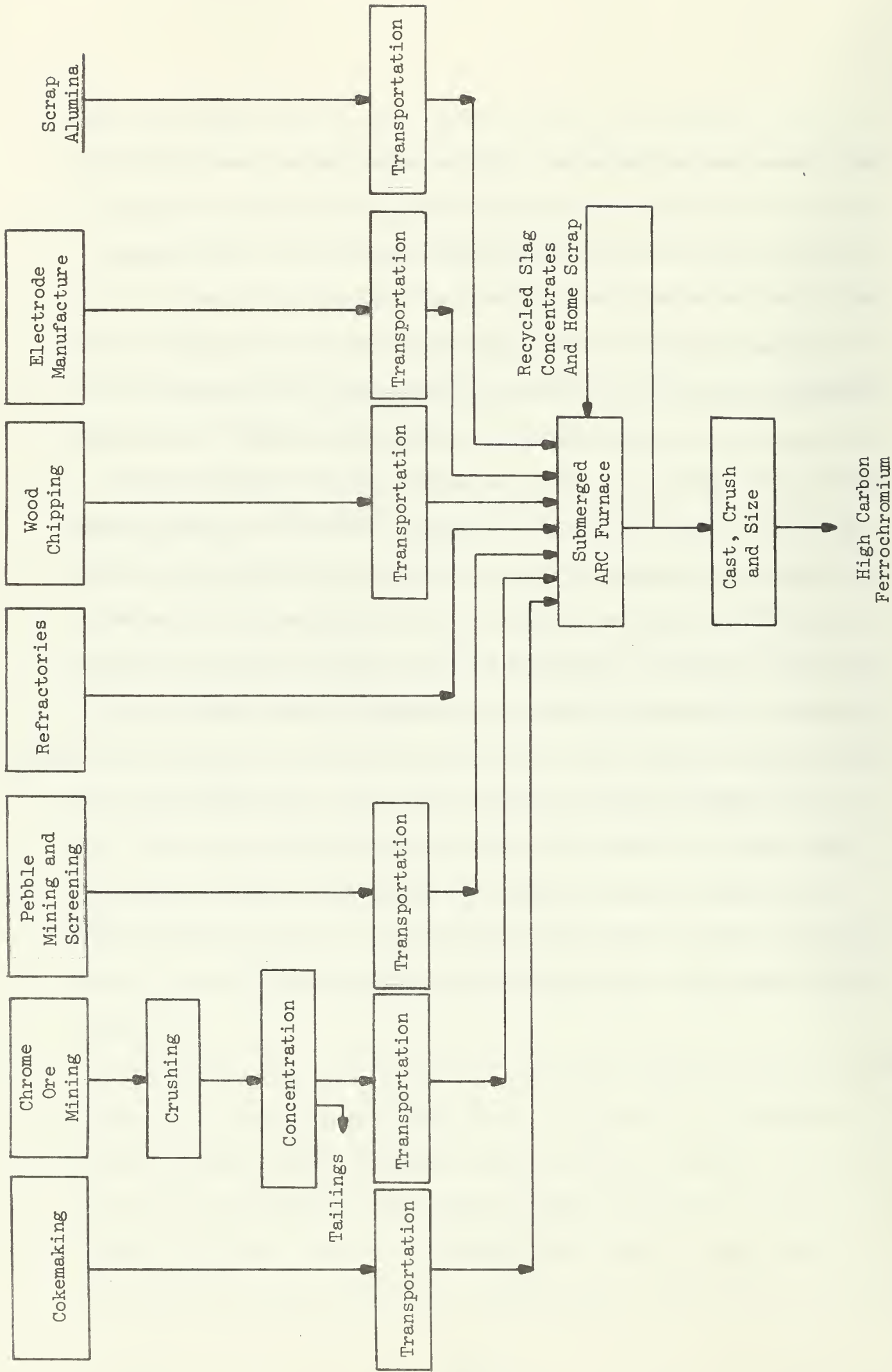


Figure 17,18: Production of High-Carbon Ferrochromium

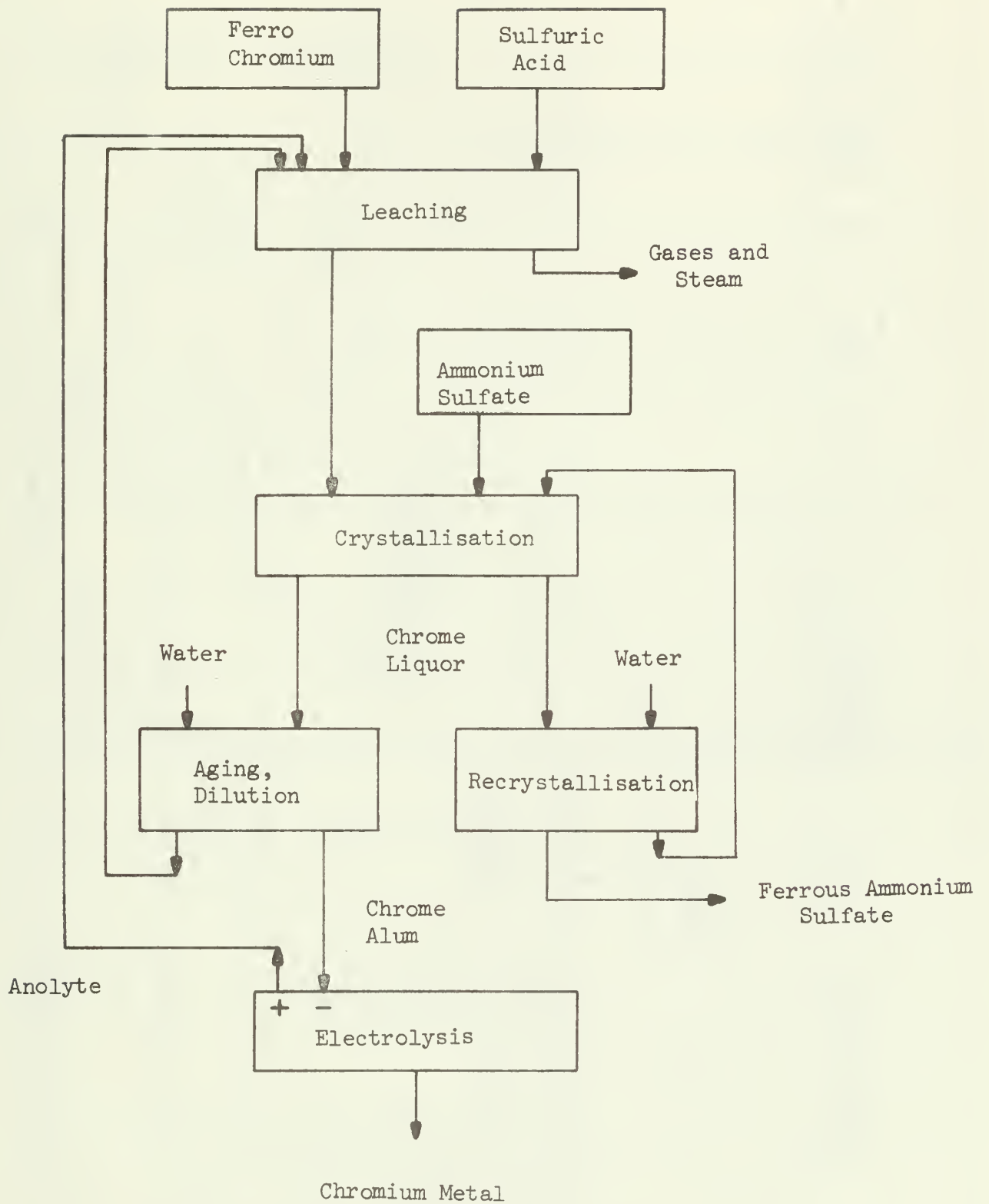


Fig. 21: Production of Electrolytic Chromium Metal

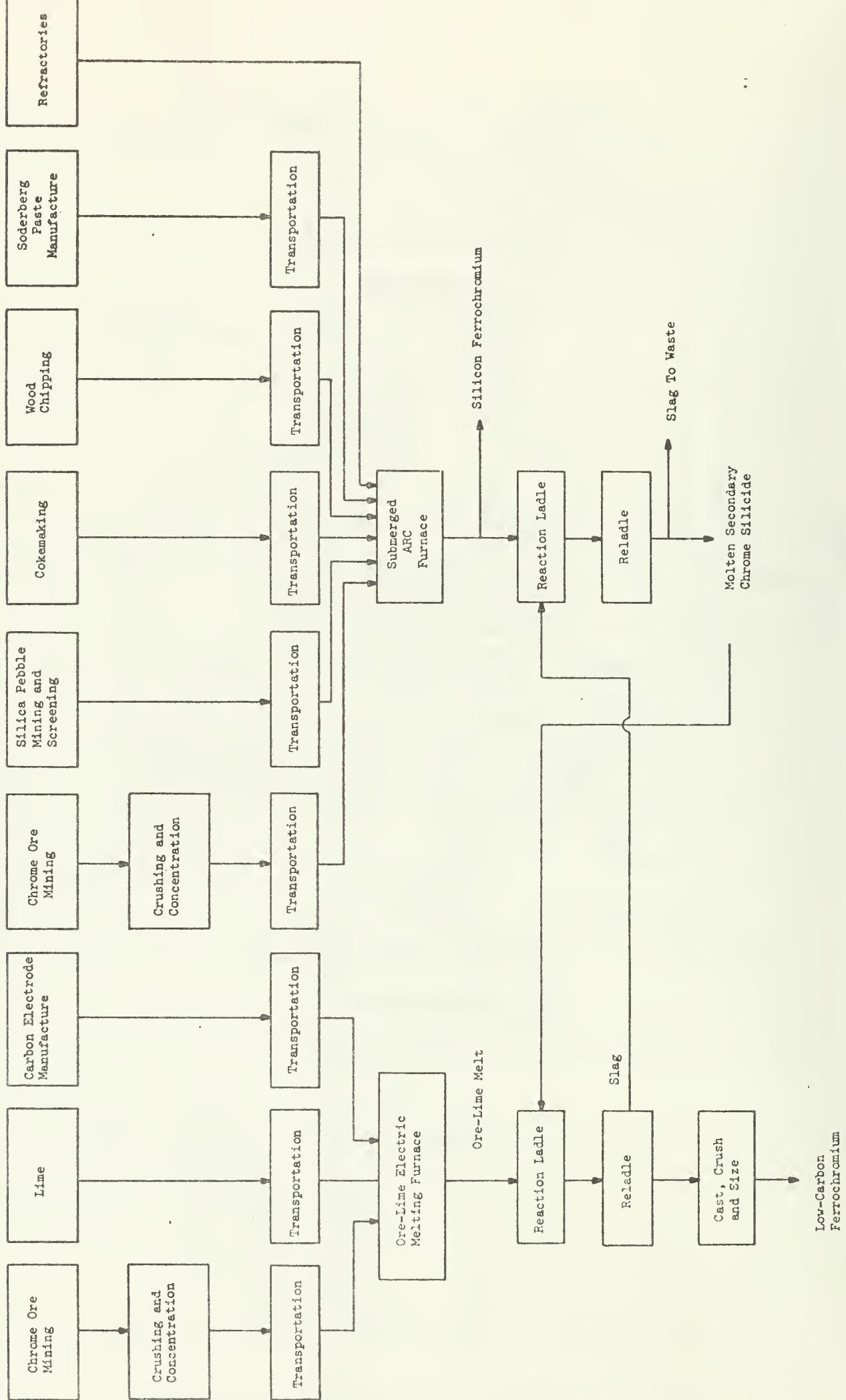


Fig. 17,19,20: Production of Silicon Ferrochromium and Low-Carbon Ferrochromium

Table 17, 18, 21. PRODUCTION OF HIGH-CARBON FERROCHROMIUM AND PURE CHROMIUM METAL<sup>a</sup>

(Basis: 1 ton of HC Fe Cr, Cr metal, to federal specification)<sup>a</sup>

HIGH CARBON FERROCHROMIUM		PURE CHROMIUM METAL <sup>m</sup>	
STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining, Crushing Concentration	ore <sup>b</sup>	2.50 net ton	625
	materials <sup>c</sup>	-	53
	electricity	12.325 kWh	162
	transportation <sup>d</sup>	-	5,140
	<i>Subtotal</i>		5,980
Total energy required per ton metallurgical chromite			
2. Preparation of Furnace Charge	silica pebble <sup>e,f</sup>	0.213 net ton	64
	coke <sup>e,g</sup>	0.375 net ton	11,889
	Wood chips <sup>e,h</sup>	0.0975 net ton	728.
	refractories <sup>i</sup>	0.023 net ton	562
	carbon electrodes <sup>e,j</sup>	0.022 net ton	1,811
	alumina scrap <sup>k</sup>	0.179 net ton	24
<i>Subtotal</i>		15,078	
Cumulative Subtotal			
3. Smelting	electricity <sup>l</sup>	3,831 kWh	50,274
<b>TOTAL</b>			
			71,332

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Initial Material	high carbon ferrochromium	1.537 net ton	109,638
	<i>Subtotal</i>		109,638
2. Preparation of Cellfeed	sulfuric acid	0.768 net ton	638
	amonium sulfate	1.117 net ton	45,227
	reducing sugar	0.179 net ton	6,537
	filter media	0.026 net ton	50
	steam	0.025 net ton	50
	general plant energy <sup>o</sup>	-	30,912
3. Electrolysis	electricity	11,200 kWh	146,978
	<i>Subtotal</i>		230,392
<i>Total</i>			340,030
Total energy required for 1 ton electrolytic chromium <sup>p</sup>			
			255,022

NOTES TO Table 17,18,21

- <sup>a</sup> Reference: [0-325b] pp. 34-38, [18-21-204]. See [17-140], [18-140], for specifications. 1 ton of raw ore yields on the average .92 ton of concentrate.
- <sup>b</sup> Estimate of 250,000 Btu/net ton based on data for mining of coal and similar materials.
- <sup>c</sup> 1.75 lb. of explosives @ 30,000 Btu/lb.
- <sup>d</sup> 7,500 miles @ 250 Btu/TM by ship (40,000 ton ocean-going ore carrier), and 500 miles @ 670 Btu/TM by rail.
- <sup>e</sup> Leeper, R.A., "Smelting of High-Carbon Ferrochromium in a Three-Phase Electric Furnace," Address at the Ferroalloys meeting of the AIME Electric Furnace Conference, Pittsburgh, December 1, 1965.
- <sup>f</sup> Estimated from analogous mining operations at 0.1 million Btu per ton of gravel mined as a surface deposit and average transportation of 300 miles by rail ( $0.213 \times 300 \times .67 = 43,000 \times 10^3$  Btu).
- <sup>g</sup> See [0-325b] Appendix A, Table A2, energy consumption to manufacture metallurgical coke:  $31.50 \times 10^6$  Btu/ton; 300 mile transportation by rail @ 670 Btu/TM included.
- <sup>h</sup> Sawing and chipping of wood estimated at 5 kWh per net ton, transportation distance estimated at 50 miles by truck @ 2,400 Btu/TM. Caloric value of 7,280,000 Btu/net ton from National Coal Association: "Bituminous Coal Data," 1972 Edition.
- <sup>i</sup> A major U.S. producer's estimate of average refractory consumption in ferro alloy production. Energy cost of refractories Battelle estimate:  $25 \times 10^6$  Btu/ton.
- <sup>j</sup> See [0-325b] Appendix A, Table A3, Energy Consumption to Produce Electrode Graphite Here a value of 82,000,000 Btu/net ton based on average energy consumption in several plants is used. Includes 500 miles of rail transportat  
@ 670 Btu/TM.
- <sup>k</sup> 200 miles @ 670 Btu/TM. Scrap itself has zero energy cost.
- <sup>l</sup> 3,575 kWh for smelting. See note e. The following three items are proprietary data from a major producer obtained by Battelle: 75 kWh for pollution control, 180 kWh general plant energy, 1 kWh for crushing and sizing.

- <sup>m</sup> Private communication from a major manufacturer. The by-products of 1 ton of electrolytic chrome are -  
2.054 ton of ferrous ammonium sulfate and 0.054 ton of leach residue.
- <sup>n</sup> Sulfuric acid @ 831,000 Btu/ton [0-325a] p. 154.  
Ammonium sulfate @ 40,490,000 Btu/ton [0-321] p. 94.  
Reducing sugar @ 36,520,000 Btu/ton [0-321] p. 96.  
Filter media, plastic impregnated maple [16-22-101] @ 20,000,000 Btu/lb. (E.R.G. estimate),  
Steam @ 2,000,000 Btu/ton [0-325a] Appendix A.
- <sup>o</sup> Estimated by same manufacturer: about 10% of total energy cost.
- <sup>p</sup> Based on 1973 average prices of \$1.53 /lb of chromium and \$0.25/lb. of ferrous ammonium sulfate.

Table 17, 19, 20. PRODUCTION OF SILICON AND LOW-CARBON FERROCHROMIUM<sup>a</sup>

(Basis: 1 ton of SiFeCr, LC FeCr to federal specification)<sup>a</sup>

SILICON FERROCHROMIUM		LOW-CARBON FERROCHROMIUM	
Stage	Type	Amount	10 <sup>3</sup> Btu
1. Mining, Crushing and Concentration	chromite ore <sup>b</sup>	1.25 net ton	312
	materials <sup>c</sup>	-	27
	electricity	6.15 kWh	81
	transportation <sup>d</sup>	-	2,541
<i>Subtotal</i>			<i>2,961</i>
2. Preparation of Furnace Charge	silica pebble <sup>e</sup>	1.7 net ton	512
	coke <sup>f</sup>	.95 net ton	30,116
	wood chips <sup>g</sup>	.17 net ton	1,269
	soderberg paste <sup>h</sup>	.0675 net ton	2,583
	refractories <sup>i</sup>	.023 net ton	575
<i>Subtotal</i>			<i>35,055</i>
<i>Cumulative Subtotal</i>			<i>38,016</i>
3. Smelting	electricity <sup>j</sup>	8,360 kWh	109,709
	<i>Subtotal</i>		
<i>TOTAL</i>			<i>147,725</i>

LOW-CARBON FERROCHROMIUM		LOW-CARBON FERROCHROMIUM	
Stage	Type	Amount	10 <sup>3</sup> Btu
1. Mining, Crushing and Transportation	chromite ore <sup>b</sup>	1.70 net ton	425
	materials <sup>k</sup>	-	36
	electricity	8.35 kWh	110
	transportation <sup>d</sup>	-	3,156
<i>Subtotal</i>			<i>4,327</i>
2. Preparation of Furnace Charge	carbon electrodes <sup>l</sup>	0.02 net ton	1,643
	lime <sup>m</sup>	1.45 net ton	12,374
<i>Subtotal</i>			<i>14,017</i>
<i>Cumulative Subtotal</i>			<i>16,344</i>
3a	Ore lime melting	2.750 kWh	36,089
3b	molten silicon ferrochromium	0.625 net ton	90,477
	electricity <sup>n</sup>	295 kWh	3,871
<i>Subtotal</i>			<i>130,436</i>
<i>TOTAL</i>			<i>148,180</i>



NOTES TO Table 17, 19, 20.

- <sup>a</sup> Reference [0-325b] pp. 39-47; See [17-140], [19-140], [20-140] for specifications.
- <sup>b</sup> Estimate of 250,000 Btu/net ton based on data for mining of coal and similar materials.
- <sup>c</sup> .9 lb. of explosives @ 30,000 Btu/lb.
- <sup>d</sup> 7,500 miles @ 250 Btu/TM by ship and 500 miles @ 670 Btu/TM by rail.
- <sup>e</sup> Estimated from similar mining operations at 100,000 Btu/ton of gravel mined as a surface deposit; includes average of 300 miles of rail transportation.
- <sup>f</sup> See [0-325b] Appendix A, Table A2, energy consumption to manufacture metallurgical coke:  $31.50 \times 10^6$  Btu/ton, 300 miles of rail transportation included.
- <sup>g</sup> Sawing and chipping of wood at 5 kWh/net ton, calorie value of 7,280,000 Btu/net ton from National Coal Association: "Bituminous Coal Data," 1972 Edition. Transportation distance estimated at 50 miles by truck @ 2,400 Btu/TM.
- <sup>h</sup> See [0-325b] Appendix A, Table A4, energy consumption to manufacture Soderberg paste:  $37.92 \times 10^6$  Btu/ton. Included are 500 miles of rail transportation @ 670 Btu/TM.
- <sup>i</sup> A major U.S. producer's estimate of average refractory consumption in ferroalloy production. Energy cost of refractories:  $25 \times 10^6$  Btu/ton (Batelle-estimate).
- <sup>j</sup> 7,200 kWh for smelting, 800 kWh for pollution control and 360 kWh for general plant energy. Proprietary data from a major manufacturer.
- <sup>k</sup> 1.2 lb. of explosives @ 30,000 Btu/lb.
- <sup>l</sup> 82,000 Btu/net ton, private communication from a major manufacturer, includes 500 miles of rail transportation @ 670 Btu/TM.
- <sup>m</sup> See [0-325a] p. 20, energy consumption in the production of quicklime: 8,487,000 Btu/ton. Includes 70 miles of rail transportation @ 670 Btu/TM.
- <sup>n</sup> 150 kWh for pollution control, 140 kWh for general plant energy, 5 kWh for casting, crushing, and sizing.

Table 16, 22. PRODUCTION OF CHEMICAL AND  
REFRACTORY GRADE CHROMITE ORE<sup>a</sup>

STAGE	CHEMICAL GRADE CHROMITE			REFRACTORY GRADE CHROMITE		
	Type	Amount	10 <sup>3</sup> Btu	Type	Amount	10 <sup>3</sup> B
1. Mining Beneficiation	ore <sup>b</sup>	1.0 net ton	250	ore <sup>b</sup>	1.0 net ton	250
	materials <sup>c</sup>	-	21	materials <sup>c</sup>	-	21
	electricity	5.0 kWh	66	electricity	5.0 kWh	66
	transportation <sup>d</sup>	-	<u>2,585</u>	transportation <sup>e</sup>	-	<u>3,835</u>
<b>TOTAL</b>			<b>2,922</b>			<b>4,172</b>

NOTES TO TABLE 16,22.

<sup>a</sup> Reference [0-325b] p. 37, [16-140], [22-140].

<sup>b</sup> Estimate of 250,000 Btu/net ton based on data for mining of coal and similar materials

<sup>c</sup> .7 lb. of explosives @ 30,000 Btu/lb.

<sup>d</sup> 9,000 miles at 250 Btu/TM by ore carrier, and 500 miles by rail at 670 Btu/TM.

<sup>e</sup> 14,000 miles at 200 Btu/TM by ore carrier and 500 miles by rail at 670 Btu/TM.

## ENERGY-VERSATILITY CONSIDERATIONS FOR CHROMIUM

Although smelting and electrolysis are major energy consuming steps in the processing of chromium, a small percentage of chromite ore should be kept in the stockpile to meet versatility requirements. For the same reason, the remaining percentage of contained chromium should be partitioned over the following forms: low carbon ferrochromium, high carbon ferrochromium, silicon ferrochromium, chromium metal.

A possible partitioning based on current national demand would approximately have these ratios: 2 to 5 to 2 to 1, respectively.

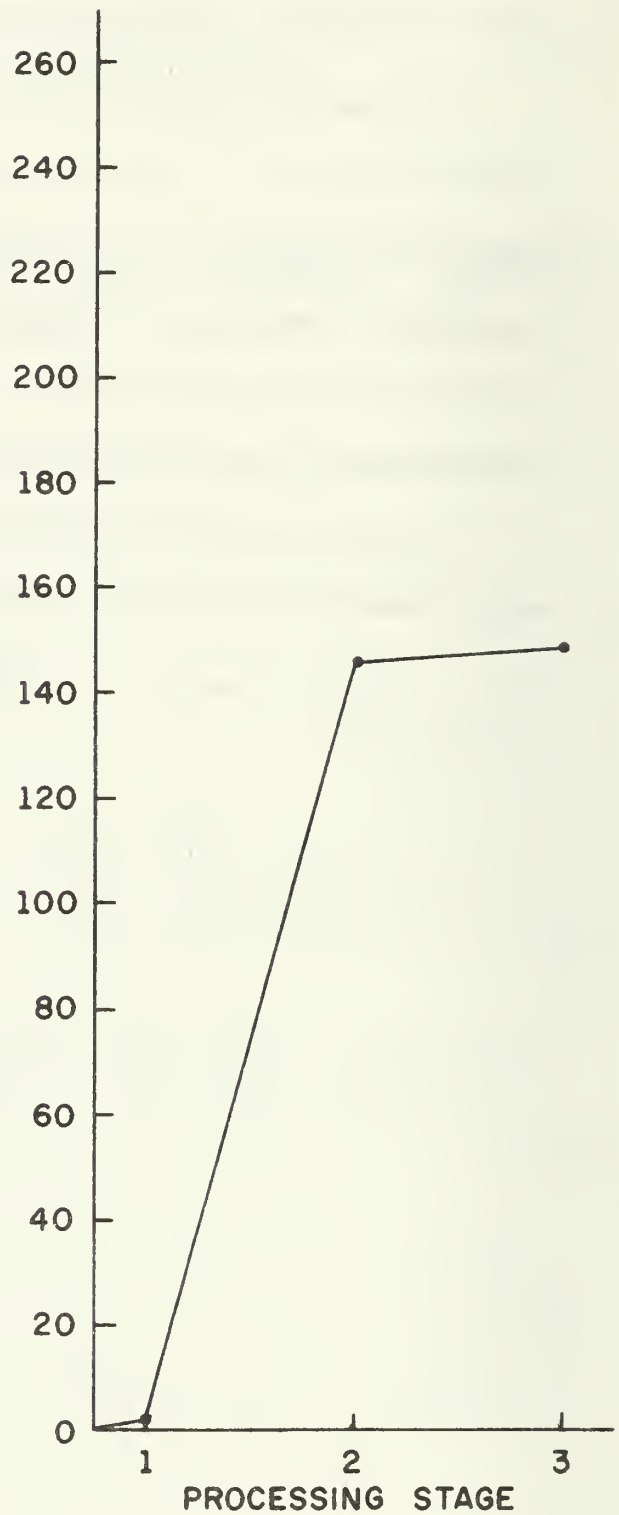
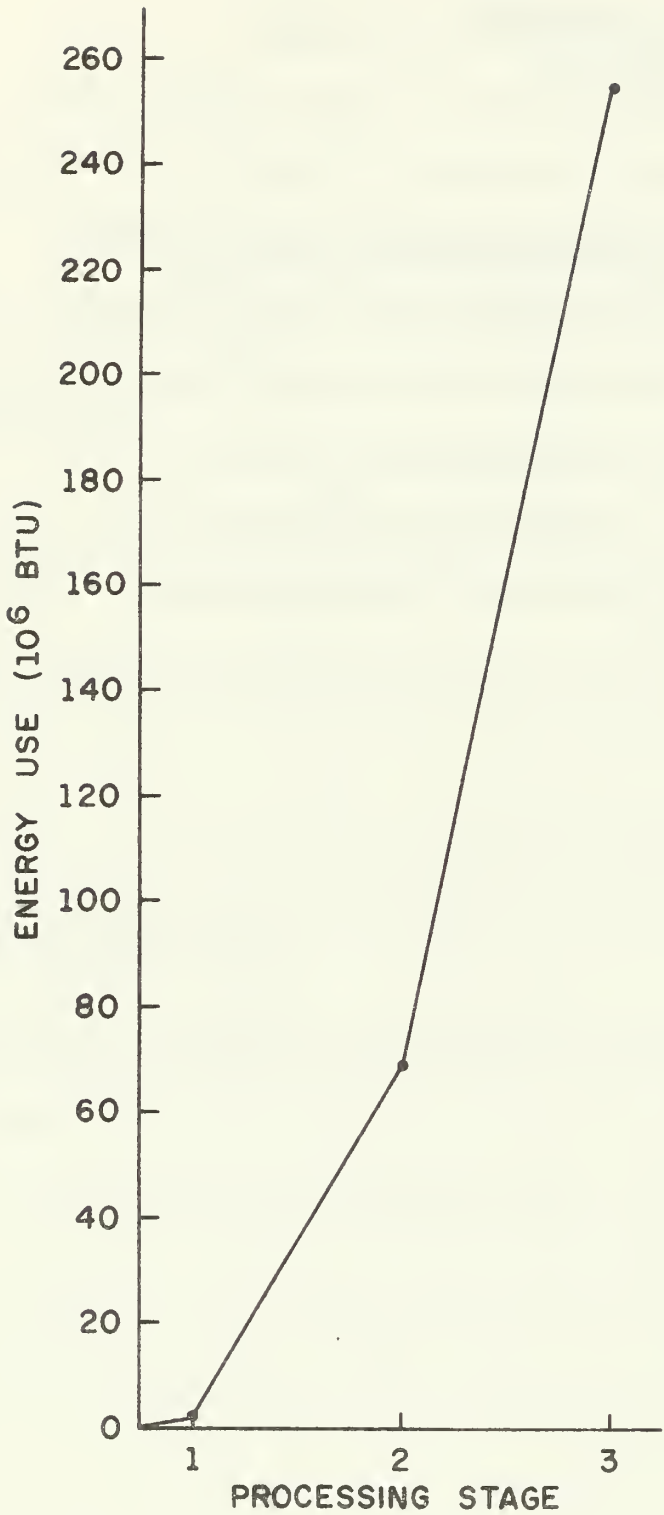


Figure 17,18,21b: Production of HC FeCr and Cr Metal

Figure 17,19,20b: Production of SiFe and LC FeCr

FOOTNOTES TO SECTION 16...22

- <sup>1</sup> [16...22-101] p. 7-10.
- <sup>2</sup> [16...22-100] p. 304.
- <sup>3</sup> [0-149] p. 249, [18...21-203] and [18...21-141].
- <sup>4</sup> [17-140].
- <sup>5</sup> [16-140].
- <sup>6</sup> [22-140].
- <sup>7</sup> [16...22-121] p. 5.
- <sup>8</sup> [0-149] p. 249.
- <sup>9</sup> [0-140I] p. 279.
- <sup>10</sup> [0-145] p. 21.
- <sup>11</sup> [0-149] p. 255.
- <sup>12</sup> [0-149] p. 254.
- <sup>13</sup> [18...21-203], [0-149] p. 252
- <sup>14</sup> [0-122] p. 12-17.
- <sup>15</sup> [16...22-101] p. 20.
- <sup>16</sup> See [0-325b].
- <sup>17</sup> See [18...21-142].
- <sup>18</sup> [16...22-100] p. 323.
- <sup>19</sup> [16...22-101] p. 38.
- <sup>20</sup> [16...22-102] p. 512.
- <sup>21</sup> [16...22-101] p. 25-29.

## 28. COPPER

### Overview

Man has used copper since prehistoric times, and continues to use it in unprecedented amounts. It is a highly versatile metallic element found in the earth's crust in an average concentration of 55 parts per million.<sup>1</sup> There are only six major commercial copper ore deposits in the world: the Western U.S., the State of Michigan, central Africa, the Western Andes, parts of the U.S.S.R., and West-central Canada.<sup>2</sup> Though there are many copper mineral forms, only a handful are commercially mined, mainly sulfide and oxide forms. World ore reserves were estimated at 308 million tons of metal in 1970 while U.S. reserves were set at approximately 166 billion pounds in 1973.<sup>3</sup>

Though about 64 countries produce copper ore, much of the world's copper metal production is controlled by large, integrated North American companies.<sup>4</sup> The United States has almost always been the largest single producer and currently accounts for 22% of world metal production; other important sources include Japan (12%), the U.S.S.R (9.8%), Zambia (9.7%) and Chile (8.9%).<sup>5</sup>

In the U.S. in 1968, twenty-five copper mines operated into 19 smelters and about 16 refineries, with 46% of the mining and almost 85% of all smelting controlled by four main companies.<sup>6</sup> In 1974, total U.S. copper consumption was 3.1 million tons, including 545,100 tons of metal imported in various forms.<sup>7</sup> U.S. refined copper consumption, equal to 2.1 million tons in 1974, has grown 140% since 1955.<sup>8</sup>

Secondary production is also a very important source of copper. In 1973, 1,291,241 tons of copper were recovered, about one-third from old

scrap and two-thirds from new, accounting for about 43% of total domestic supply.<sup>9</sup> By-products and co-products are also of major importance to the copper industry. According to the Bureau of Mines, "98% of the U.S. mine production of copper was recovered from ores mined primarily for their copper content."<sup>10</sup> However, in Canada and the Congo, nickel and cobalt are considered equally important products. Significant amounts of lead, molybdenum, iron, zinc, gold, silver, nickel, platinum, selenium and tellurium were recovered from copper ore processing in 1968.<sup>11</sup>

The largest use for copper is as a conducting metal in the electrical and electronics industries. This industry used about 50% of all domestic copper demand in 1968. Other important uses for copper are in transportation, equipment, plumbing, appliances, coinage, ammunition, and miscellaneous construction industry uses.<sup>12</sup> Some very good substitutes exist for copper in some cases -- aluminum and plastics substitute in many construction uses while steel, brass and aluminum are often alternate choices in heavy industry.<sup>13</sup>

## PROCESS DESCRIPTION

Battelle/Columbus Laboratories has previously published a detailed study of the copper industry. The following is an excerpt from their account of the copper-refining process:<sup>14</sup>

"Domestic copper is mined, with few exceptions, from sulfide ores. The commercially important ores are sulfides of copper, copper-molybdenum, copper-zinc, and copper-lead-zinc. Most ores contain small quantities of silver, gold, platinum, selenium, and tellurium, which are recovered as by-products.

Ore grade has declined over the years to the point where most ores now contain less than 1 percent copper. Generally, ore that contains more than about 0.4 percent copper is concentrated; ore having less than this amount is deposited in waste rock dumps, from which some copper is recovered by dump leachings. In this study energy estimates were based on data from eight open pit mines. Tons of ore and waste rock mined and the quantities of contained copper were provided by the companies in some cases, and were estimated in others. The ore grades ranged from 0.55 percent copper to 0.92 percent copper and averaged about 0.7 percent copper.

In underground mines essentially all of the material removed contains more than about 0.3 percent copper, and it is all sent to the concentrators. In the large open-pit mines, the source of most of our copper, stripping ratios (ratio of waste rock to ore) vary from about 1:1 to as high as 12:1. Thus, much of the energy required for mining is consumed in the excavation and hauling of overburden.

The ore from the mines is sent to the concentrators, which include crushing, grinding, and flotation operations. Crushing is done usually in gyratory and cone crushers, which consume relatively little energy. By comparison, grinding, carried out in rod mills and ball mills, requires most of the energy consumed in ore concentrating.

The concentrate, which contains about 25 percent copper, is sent to the smelter charge preparation plant and is mixed with



cement copper produced by leaching and precipitation operations. In most smelters this mixture is furnace dried and charged directly into green-charge reverberatory furnaces. In the present study a green-charge reverberatory furnace was used for the flowsheet and energy estimation.

In some plants the concentrate is roasted to convert some of the sulfides to oxides and to eliminate some of the sulfur. In roasting, most of the energy is derived from the burning of the sulfur in the concentrate. Roasted concentrate, or calcine, is then charged into the reverberatory furnace. In addition to concentrates and cement copper, the reverberatory furnace charge includes silica rock, lime rock, and ore as fluxing agents, and copper-bearing dust collected from the Cottrell precipitators in the smelter.

The product of the reverberatory furnace is matte, a mixture of copper sulfide and iron sulfide which contains from 30 to 60 percent copper. This is tapped from one side of the reverb into ladles, in which the liquid matte is held until it can be transferred into converters. Slag is tapped from the opposite side of the reverberatory furnace. The slag contains very little copper and is sent to the slag dump.

The converters (usually Pierce-Smith design) are cylindrical furnaces into which compressed air is blown through tuyeres below the surface of the liquid matte. The sulfur and iron in the matte are oxidized, leaving an impure blister copper containing between 98 and 99 percent copper. Most of the heat in the converter operations is provided by the oxidation of the sulfur and iron. A little fuel is needed to keep the converters hot between charges. Electrical energy or process steam is consumed by the blowers, which provide air for the oxidizing reactions. Slag from the converters is recycled to the reverberatory furnaces.

The last operation in the smelter is the fire refining of blister copper to anode copper and the casting of anodes. Although this is a refining operation, it is carried out in the smelter because the blister copper is transferred in the molten state to the anode furnaces. The latter are fuel fired and may be reverberatory furnaces

or cylindrical furnaces very similar to the converters. In this operation air is blown through the blister copper to complete the oxidation of iron and to oxidize minor impurities, e.g., nickel. After the oxidation step the slag is removed and returned to the reverberatory furnace. At this point the copper is saturated in oxygen, and this is reduced by bubbling reformed natural gas through the melt. The deoxidation used to be carried out by submerging green tree trunks (poles) into the metal. Although natural gas is now used, the operation is still called "poling". Poling is continued until the oxygen content of the copper is lowered to about 0.17 percent. A 200-ton heat in the anode furnace may require about 1.5 hours for blowing and slag skimming and about three more hours for "poling". Thus, the operation consumes a significant amount of petroleum fuel, natural gas for "poling", and electricity for blowing. Anodes are cast directly from the anode furnaces into coated copper molds which are moved into position on large rotating, horizontal, casting wheels. In one recent installation each wheel is fed automatically by two furnaces. Castings are poured alternately from each furnace, and a measured quantity of molten metal is cast into each mold as it rotates on the wheel.

The anodes, which contain 99+ percent copper, are shipped to the refinery. The major operation of the refinery is the electrolytic refining of anode copper to cathode copper, which contains 99.8+ percent copper. The tankhouse is a large consumer of energy. The cells use electrical energy for electrolysis and natural gas or oil for heating the copper solution.

The finished cathodes are either sold or are melted and cast into refinery shapes, e.g., wirebar and cakes, or continuously cast wirerod."

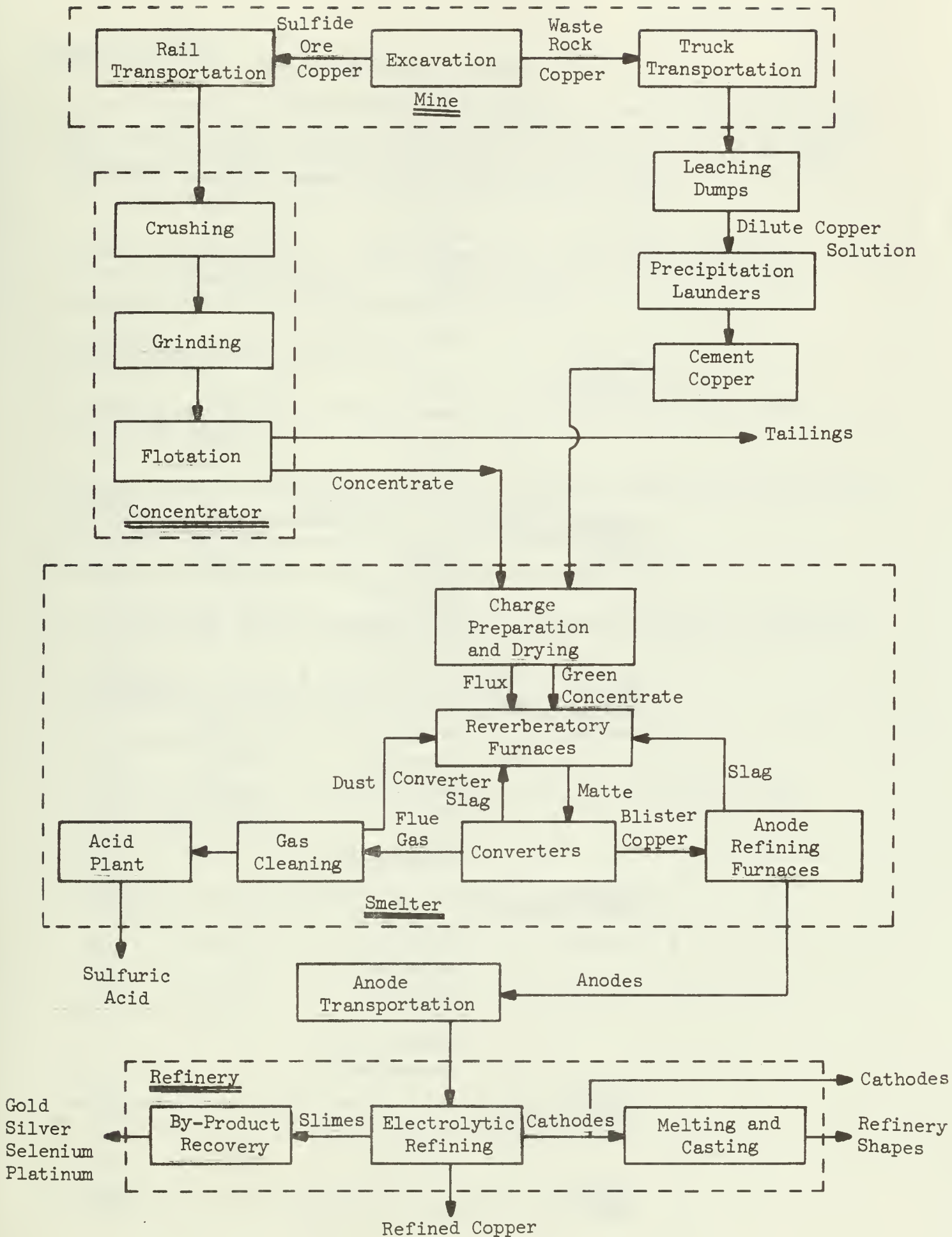


Figure 28a. PRODUCTION OF REFINED COPPER

Source: [0-325a]

Table 28. PRODUCTION OF COPPER<sup>a</sup>

(Basis: 1 ton of refined copper)<sup>a</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	electric	788.8 kWh	10,351
	natural gas	220.5 ft <sup>3</sup>	250
	diesel oil	38.62 gal.	6,432
	coal <sup>b</sup>	.0013 ton	33
	materials <sup>c</sup>	-	4,650
	transportation <sup>d</sup>	-	3,055
	<i>Subtotal</i>		<u>24,771</u>
2. Concentration	electric	2930 kWh	38,451
	natural gas	2465 ft <sup>3</sup>	2,804
	petroleum <sup>b</sup>	1.62 gal.	293
	steam <sup>b</sup>	366.6 lb.	513
	materials <sup>e</sup>	-	8,052
	<i>Subtotal</i>		<u>50,113</u>
	<i>Cumulative Subtotal</i>		<u>74,884</u>
3. Smelting <sup>f</sup>	electric	439.28 kWh	5,765
	natural gas	16,556 ft <sup>3</sup>	18,830
	petroleum <sup>b</sup>	75.092 gal.	13,571
	net steam <sup>g,b</sup>	3,410 lb.	- 4,774
	materials <sup>h</sup>	-	8,684
	<i>Subtotal</i>		<u>42,076</u>
	<i>Cumulative Subtotal</i>		<u>116,960</u>
4. Anode Refining	electric	6.44 kWh	85
	natural gas	3,139 ft <sup>3</sup>	3,570
	petroleum <sup>b</sup>	1.5 gal.	271
	coal <sup>b</sup>	.005 ton	126
	steam <sup>b</sup>	169.22 lb.	237
	transportation <sup>i</sup>	-	612
	<i>Subtotal</i>		<u>4,901</u>
	<i>Cumulative Subtotal</i>		<u>121,861</u>
5. Refining	electric	307.49 kWh	4,035
	natural gas	1,165 ft <sup>3</sup>	1,325
	petroleum <sup>b</sup>	19.92 gal.	3,600
	coal <sup>b</sup>	.007 ton	177
	materials <sup>j</sup>	-	14
	transportation <sup>j</sup>	-	2
	<i>Subtotal</i>		<u>9,153</u>
	<i>Cumulative Subtotal</i>		<u>131,014</u>
6. Cathode Melting	electric	7.37 kWh	97
	natural gas	1,869.7 ft <sup>3</sup>	2,127
	<i>Subtotal</i>		<u>2,224</u>
	<b>TOTAL</b>		<u>133,238</u>

NOTES TO Table 28

- <sup>a</sup> Source: [0-325a], p. 51 for all figures listed in amount column and these notes unless noted. Basis is implied to be one ton of refined copper. Since it is electrolytically produced, it is expected to meet the usual electrolytic grade standards of 99.90% Cu, which conforms to most federal specifications for copper. [28-140] and [0-101] p. 145.
- <sup>b</sup> Caloric values assumed: coal (bituminous) 25.27 million Btu/ton (100% delivery efficiency); unspecified petroleum, 150,000 Btu/gal.; steam 1,400 Btu/lb (100% delivery efficiency).
- <sup>c</sup> 155 lb. explosives @ 30,000 Btu/lb.
- <sup>d</sup> Including waste; 921.4 TM by truck @ 2,400 Btu/TM and 1,261.3 TM by rail @ 670 Btu/TM.
- <sup>e</sup> 273 lb. steel @ 17,500 Btu lb., 541 lb. inorganic chemicals @ 5,000 Btu/lb. and 28.5 lb. organic chemicals @ 20,000 Btu/lb.
- <sup>f</sup> Includes gas cleaning, acid production, and converter.
- <sup>g</sup> Steam produced in reverberatory furnace less steam consumed in converter.
- <sup>h</sup> .1 ton cement copper @ 86.84 million Btu/ton
- <sup>i</sup> 912.5 ton-miles by rail @ 670 Btu/TM
- <sup>j</sup> .0165 ton sulfuric acid @ 830,000 Btu/ton and 3.5 ton-miles by rail @ 670 Btu/TM.

## SECONDARY COPPER

### PROCESS DESCRIPTION<sup>15</sup>

Figure 28b shows the natural flows associated with the recycle of all types of copper scrap. The figure shows that, in contrast to most primary metal manufacturing, the amount of processing required for a unit output is very much a function of the input. All scrap must first be transported from the user or producer to the recycling industry. Most of this comes from scrap dealers by truck or rail car and must be unloaded by crane. Then, all scrap except wire is crushed and baled, the wire being processed by a special machine which removes the insulation. The bales are about 3 feet x 2 feet and weight 1,500-3,000 lbs. At this point, the bales are classified and either processed and fed to a refining furnace or first blast furnaceed and converted, as natural copper concentrates are, before refining. The final stage for all forms of scrap (which is omitted if the desired secondary product is a brass alloy) is electrolytic refining.

Because the steps leading up to the refining furnace are uncertain, they cannot be separated into discernable stages applying to all scrap, except using hypothetical, mathematical allocation techniques. However, this is no reason to disqualify this process from an energy analysis, it merely reduces the detail in the processing stages as considered in this report.

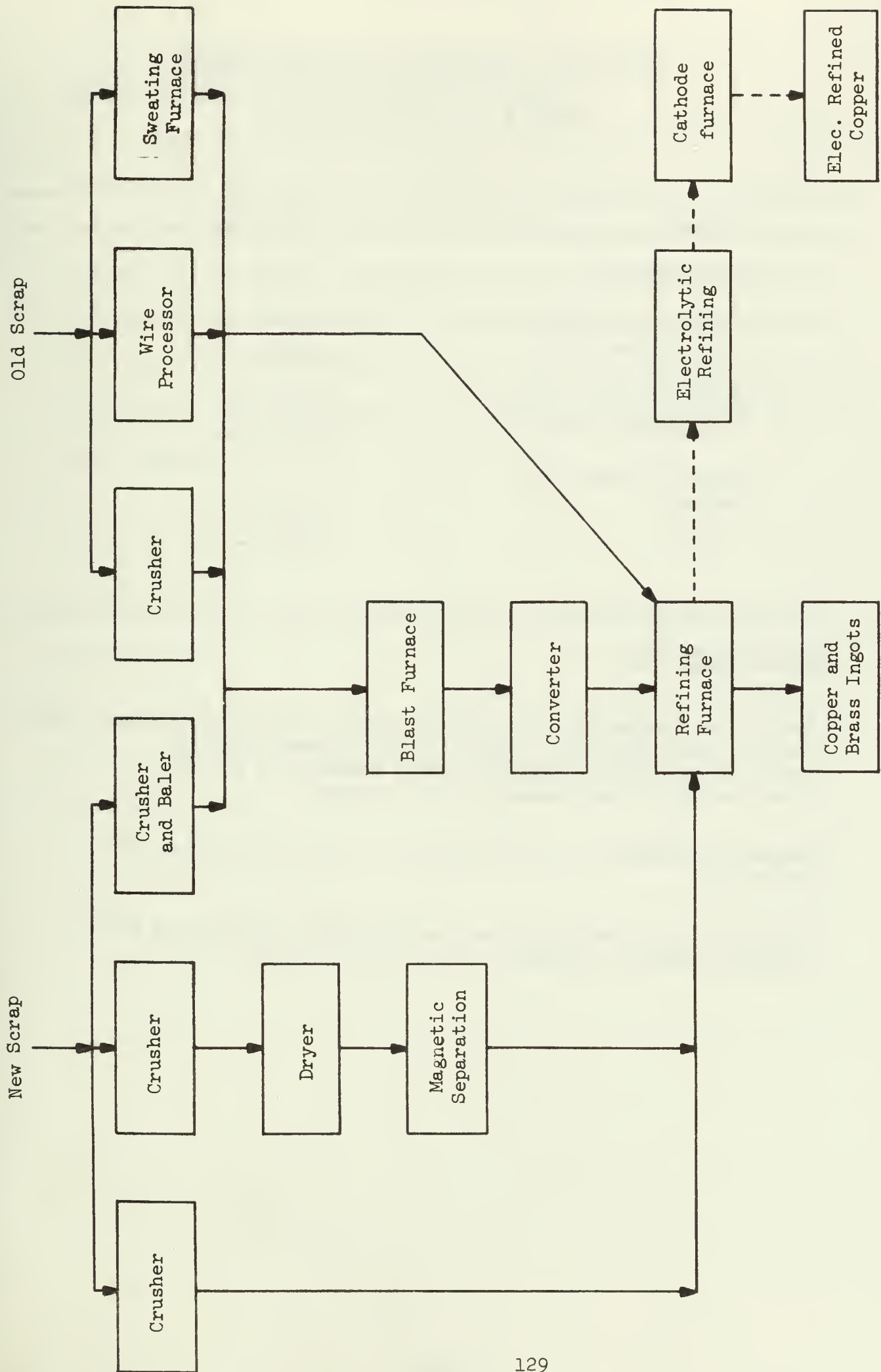


Fig. 28b. PRODUCTION OF SECONDARY COPPER

Source: [28-123]

Table 28b. PRODUCTION OF SECONDARY COPPER<sup>a</sup>

(Basis: 1 ton refined copper)<sup>a</sup>

STAGE	10 <sup>3</sup> Btu
1. Transportation <sup>b</sup>	122
2. Crushing to Refining <sup>c</sup>	<u>9,159</u>
<i>Cumulative Subtotal</i>	<u>9,281</u>
3. Electrolytic Refining	<u>4,152</u>
<i>Cumulative Subtotal</i>	<u>13,433</u>
4. Cathode Furnace and Casting	<u>498</u>
<i>TOTAL</i>	<u>13,931</u>

NOTES TO Table 28b

<sup>a</sup> Product is electrolytically refined copper expected to conform to most federal specifications. Source for all figures: [28-123].  
 Note: ALL FIGURES ARE PRIMARY ENERGY UNSPECIFIED BY TYPE.  
 Converted from 1 kWh thermal @ 3,412 Btu/kWh.

<sup>b</sup> weighted according to the distribution of 34% old scrap and 66% new scrap.

<sup>c</sup> Includes all processing between and including crushing and first refining furnace, averaged over all types of scrap.



## ENERGY-VERSATILITY CONSIDERATIONS FOR COPPER

Copper is rather unique in that it has a long series of processing steps each requiring a large proportion of energy use. Though the largest increment occurs very early in concentration, significant increments are added in later stages. We, therefore, feel that the optimum form for stockpiling in this case will depend very strongly on versatility considerations. Unless there are significant versatility differences, there is certainly no reason to stockpile recastings rather than cathodes. See figure 28c.

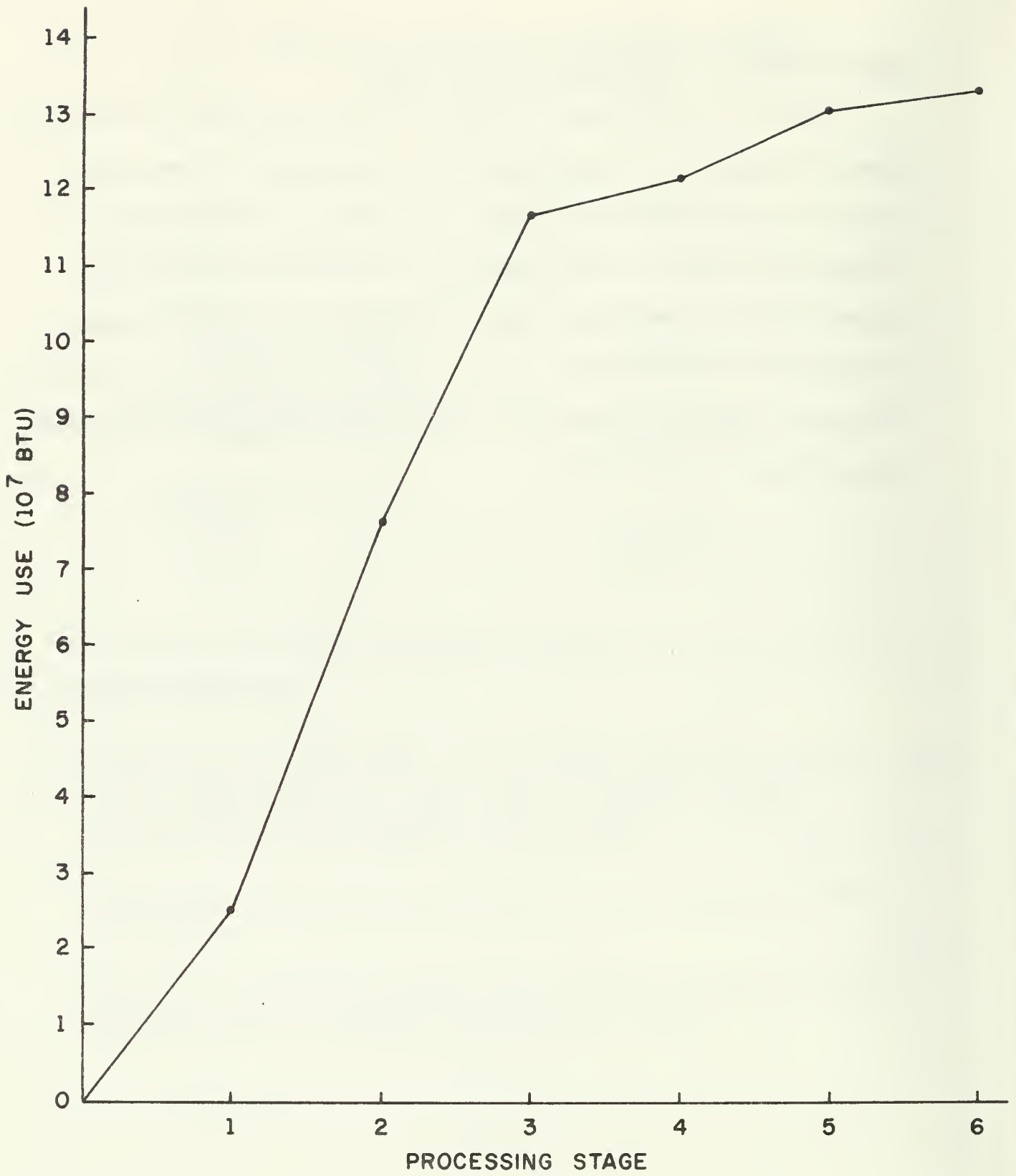


Figure 28c: Production of Copper

FOOTNOTES TO SECTION 28

- <sup>1</sup> [0-149] p. 538.
- <sup>2</sup> Ibid.
- <sup>3</sup> Ibid
- <sup>4</sup> Ibid and [0-140I] pp. 494-496.
- <sup>5</sup> [0=140I[ p. 496.
- <sup>6</sup> [28-120] p. 10 and [0-300] p. 31.
- <sup>7</sup> [0-149] p. 537 and [28-121] p. 4.
- <sup>8</sup> [28-121] p. 6.
- <sup>9</sup> [0-140I] p. 480 and [0-145] p. 25.
- <sup>10</sup> [0-149] p. 543.
- <sup>11</sup> Ibid.
- <sup>12</sup> [28-121] p. 5, [0-149] p. 545, [0-145[ p. 25, [0122] p. 24.
- <sup>13</sup> [0-122] p. 24 and [0-149] p. 545.
- <sup>14</sup> [0-325a] pp. 46-49.
- <sup>15</sup> Source: [28-123] and [28-200].

Overview

Fluorospar is the name given to minerals containing high concentrations of fluorite, or calcium fluoride ( $\text{CaF}_2$ ). Depending on the amount of calcium fluoride present, the fluorospar is classified as metallurgical grade (60-72.5% effective  $\text{CaF}_2$ ) or acid grade (more than 97%  $\text{CaF}_2$ ).<sup>1</sup> Domestic deposits of this mineral are found in Illinois and Kentucky as veins in bodies of sedimentary rock and in igneous formations all over the western United States.<sup>2</sup> The U.S. Bureau of Mines estimates that all U.S. Fluorospar reserves contain 5.4 million tons of elemental fluorine.<sup>3</sup> Because the production technology is not complicated and mineral deposits are very common, many countries all over the world are producers. Among foreign ones, Mexico is by far the largest, followed by the U.S.S.R., Spain, Thailand, and France.<sup>4</sup> Total world production in 1973 was 4,927,849 tons, almost a quarter from Mexico. The United States produced 248,601 tons and imported about 1,200,000 tons in this year, about half metallurgical and half acid-grade.<sup>5</sup> By 1973, most domestic output came from 23 mines and 7 plants.<sup>6</sup> Strong competition from cheaper imported fluorospar forced the closing of many domestic producers in the early 1970's.

As the ore names imply, most fluorospar is used either to produce hydrofluoric acid or as a metallurgical flux. Acid production is the single largest use, accounting for 49% of all domestic consumption and almost all acid-grade consumption.<sup>7</sup> Similarly, virtually all metallurgical-grade fluorospar was consumed in the metals industry, mainly in steelmaking furnaces and in the removal of impurities into the slag.<sup>8</sup> The hydrofluoric acid produced from fluorospar is in most cases only an

intermediate product leading to the production of fluorine and fluorocarbon gases, chemicals, medicines, nuclear materials, and fluoridated drinking water.<sup>9</sup>

There are no adequate substitutes for any type of fluorospar, though several materials are being considered. A very small amount of fluorine is recovered from scrap aluminum and from phosphate rock in fertilizer plants.<sup>10</sup> Small amounts of several precious and more common metals are recovered in fluorospar production. For example, in 1968 the fluorospar industry produced as byproducts 1,000 tons of lead, 5,000 tons of calcium, and 12,000 tons of zinc.<sup>11</sup>

#### PROCESS DESCRIPTION

Battelle/Columbus Laboratories has published this concise description of fluorospar production processes:<sup>12</sup>

"Most fluorspar deposits are mined by underground methods. The two most common types of deposits are steeply inclined fissure veins and horizontal bedded replacement deposits. After mining, the crude ore is put through primary crushers, washed, and screened. The large-size fraction is further concentrated by means of heavy-media plants or similar processes. The under-size material is sent directly to flotation plants. The mill feed is ground and then treated by froth-flotation methods. First, the sulfide minerals (galena and sphalerite) are removed and recovered to yield minor amounts of by-product lead and zinc concentrates. Next, the fluorspar concentrate is filtered and dried. Part of concentrate is further processed into fluorospar pellets for sale to special markets. In recent years, with the increased shortage of barites, some producers are also recovering barite from the fluorspar ores."

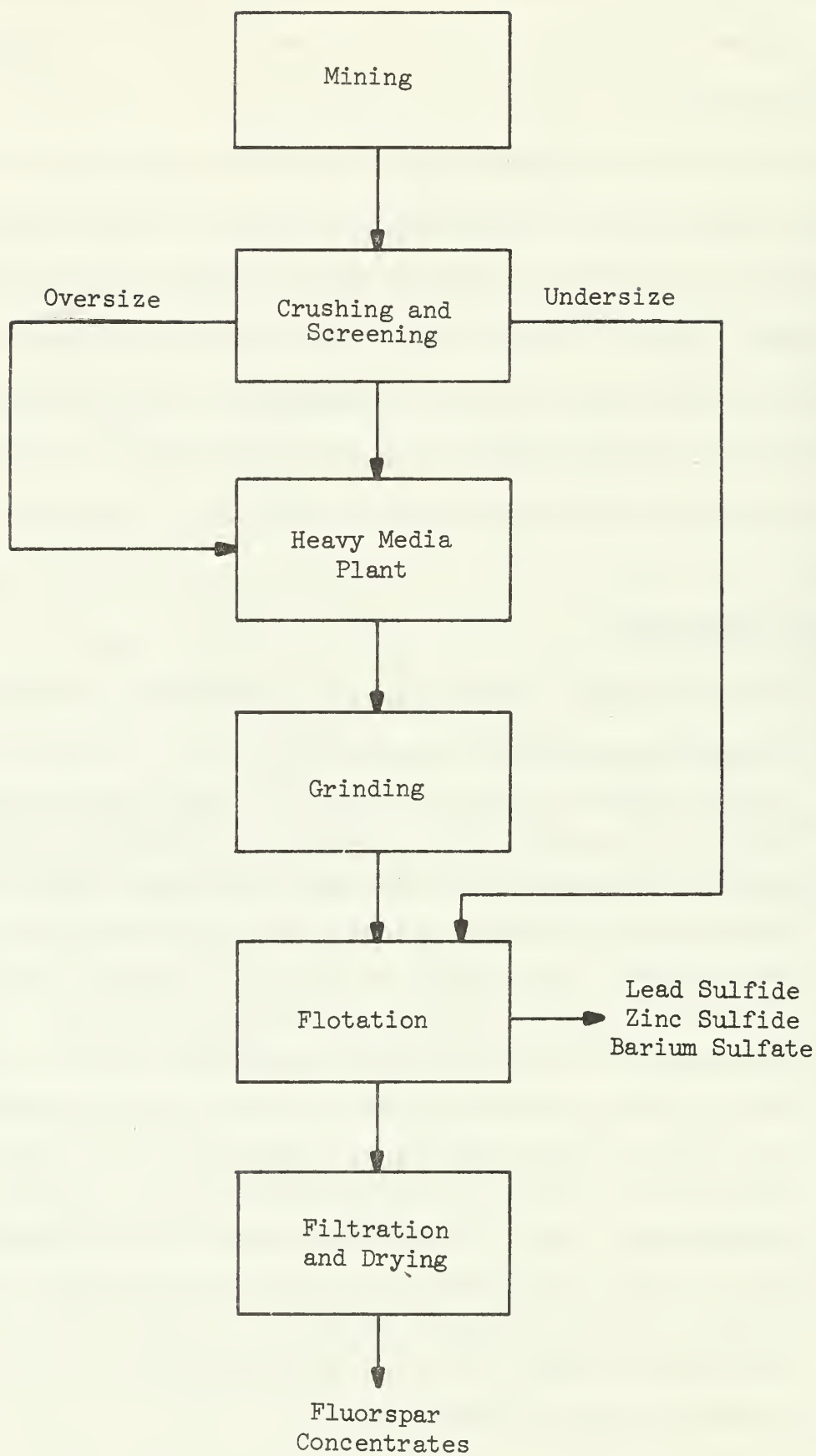


Figure 35,36 : PRODUCTION OF FLUORSPAR  
Source: [0-325b]

Table 35. PRODUCTION OF ACID GRADE FLUOROSPAR<sup>a</sup>

(Basis: 1 ton of concentrate fluorospar to federal specification)<sup>b</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	electric	46.94 kWh	616
	diesel oil	.67 gal.	111
	gasoline	.65 gal.	98
	propane	.35 gal.	39
	materials <sup>c</sup>	-	278
<i>Subtotal</i>			<u>1,142</u>
2. Crushing and Screening	electric	11.28 kWh	148
	<i>Subtotal</i>		
<u>Cumulative Subtotal</u>			<u>1,290</u>
3. Heavy Media Plant	electric	41.28 kWh	542
	materials <sup>d</sup>	-	27
	<i>Subtotal</i>		
<u>Cumulative Subtotal</u>			<u>1,859</u>
4. Grinding	electric	87.74 kWh	1,151
	materials <sup>e</sup>	-	44
	<i>Subtotal</i>		
<u>Cumulative Subtotal</u>			<u>3,054</u>
5. Flotation	electric	58.56 kWh	768
	natural gas <sup>g</sup>	175.0 ft <sup>3</sup>	192
	materials <sup>f</sup>	-	196
	<i>Subtotal</i>		
<u>Cumulative Subtotal</u>			<u>4,210</u>
6. Filtration and Drying	electric	24.12 kWh	317
	natural gas <sup>g</sup>	1,352 ft <sup>3</sup>	1,485
	distillate fuel oil <sup>g</sup>	.23 gal.	38
	<i>Subtotal</i>		
<u>TOTAL</u>			<u>6,050</u>

NOTES TO Table 35

<sup>a</sup> Source: [0-325b] p. 76.

<sup>b</sup> See [35-140].

<sup>c</sup> 7 lb. explosives @ 30,000 Btu/lb. and 3.88 lb. roof bolts @ 17,500 Btu/lb.

<sup>d</sup> 1.78 lb. ferrosilicon @ 15,400 Btu/lb.

<sup>e</sup> 1.88 lb. grinding balls and .604 lb. liner @ 15,400 Btu/lb

<sup>f</sup> 49.02 lb. industrial chemicals @ 4,000 Btu/lb.

<sup>g</sup> caloric values assumed to be: 1,000 Btu/ft<sup>3</sup> natural gas  
138,690 Btu/gal. distillate oil  
([0-325b] p. 76 and [0-206] Table B1)



Table 36. PRODUCTION OF METALLURGICAL-GRADE FLUOROSPAR

(Basis: 1 ton of metallurgical pellets)<sup>a</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>b</sup>	electric	80.40 kWh	1,055
	diesel oil	.17 gal.	29
	propane	.11 gal.	12
	materials <sup>c</sup>	-	<u>278</u>
<i>Subtotal</i>			<u>1,364</u>
2. Milling <sup>d</sup>	electric	586.59 kWh	7,698
	natural gas <sup>e</sup>	1,920 ft <sup>3</sup>	2,110
	diesel oil	.56 gal.	95
	materials <sup>f</sup>	-	<u>71</u>
<i>Subtotal</i>			<u>9,974</u>
<i>Cumulative Subtotal</i>			<u>11,348</u>
<i>Total energy required per ton concentrated metallurgical fluorospar</i>			<u>11,348</u>
3. Pelletizing <sup>g</sup>	electric	11.97 kWh	157
	natural gas	497.3 ft <sup>3</sup>	564
	diesel oil	.01 gal.	<u>2</u>
<i>Subtotal</i>			<u>723</u>
<b>TOTAL</b>			<u>12,071</u>

NOTES TO Table 36

- <sup>a</sup> Metallurgical pellets are made from fluorospar concentrates which conform to federal specifications [35/36-200] and [35/36-201]. However, pelletizing is one processing step beyond the form specified as a strategic and critical material. See [36-140].
- <sup>b</sup> Per ton crude metallurgical grade fluorospar. Source: [36-300] unless noted.
- <sup>c</sup> 3.88 lb. roof bolts @ 17,500 Btu/lb. and 7.00 lb. explosives @ 30,000 Btu/lb. Source: [0-325b] p. 76.
- <sup>d</sup> Per ton concentrate; Source: [36-300] unless noted.
- <sup>e</sup> Caloric value assumed to be 1,000 Btu/ft<sup>3</sup> and allocated as follows: 65.1% to drying kilns and 34.9% to boiler.
- <sup>f</sup> 1.78 lb. ferrosilicon @ 15,400 Btu/lb. and 2.484 lb. mill parts @ 17,500 Btu/lb. [0-325b] p. 76.
- <sup>g</sup> Source: [36-300].

ENERGY-VERSATILITY CONSIDERATIONS FOR FLUOROSPAR

No figure is necessary for examining these commodities. Neither consumes much energy in its manufacture and all energy use is very evenly distributed. Furthermore, there is no versatility advantage to any pre-final forms of the materials. Therefore both materials should be stockpiled in their current, finished forms.

FOOTNOTES TO SECTION 35,36

- 1 [0-149] p. 990.
- 2 Ibid.
- 3 Ibid.
- 4 [0-140I] p. 532.
- 5 Ibid.
- 6 Ibid p. 525.
- 7 Ibid p. 527.
- 8 [0-122] p. 34.
- 9 [0-140I] p. 528
- 10 [0-149] p. 993.
- 11 Ibid.
- 12 [0-325b] p. 73.

## 42. LEAD

### Overview

Lead, atomic number 82, is an extremely versatile and useful element for many industries. It is found in several mineral forms, with galena or lead sulfide being the most common one in the United States.<sup>1</sup> Domestic commercial lead deposits can be found mainly in Missouri (producing 81% of all U.S. lead ore), Coeur d'Alene district of Idaho (10%), and several other locations in the West.<sup>2</sup> Worldwide, the United States leads the world in mine production with 603,000 tons or 15.6% of world total, while the U.S.S.R., Canada, Australia, and Peru all contribute slightly less.<sup>3</sup>

According to the U.S. Bureau of Mines, "Lead mining and refining is a major basic industry and, in tonnage of metal produced in 1968, ranked fifth. Some 53 countries, well distributed over all of the continental areas have smelted lead from mined ore."<sup>4</sup> In the U.S., twenty-five mines produced 99% of all domestic ores in 1973 and in 1967, nineteen companies produced 304 million dollars worth of primary lead products.<sup>5</sup>

Historically, lead use in the United States has grown steadily; since 1964, the growth rate has been 2.5%/year. Even though we have been the world's largest producer, imports are usually required to meet our growing demand.<sup>6</sup> In 1973, the U.S. consumed 1,598,000 tons of lead, with 178,000 tons or 11.2%<sup>6</sup> imported. Secondary production of lead, commercially practiced since 1907, is an extremely important source of lead and supplied 539,000 tons or 33.7% of domestic demand in 1973.<sup>7</sup> Most secondary lead, about 73% comes from storage battery antimonial lead and is thus also a source of secondary antimony.<sup>8</sup>

Lead is used in hundreds of commercial applications in several major areas. One major use, as a gasoline additive, is expected to diminish as Environmental Protection Agency regulations concerning gasoline go into effect.<sup>9</sup> The largest single user industry is transportation, with the main product being storage batteries. Each battery requires about 20 lbs. of lead and this use alone accounted for 35% of all lead demand in 1968.<sup>10</sup> Other major uses are in plumbing pipes, paint pigments, vibration and nuclear absorption, communication cables, ammunition, printer's type, lead bearings and solder.<sup>11</sup>

Several substitutes exist for lead in specialized uses, but most have one or more problems. Nickel-cadmium batteries cost more than the lead-acid type. Titanium dioxide is useful in some chemical applications, and some plastics may be used as cable coverings.<sup>12</sup> "Lead ranges from the major product, as in the Missouri ores, to a co-product, as in the complex Western ores," to a by-product in the Eastern ores."<sup>13</sup> According to the Bureau of Mines, 1968 production of lead also yielded all commercially produced bismuth, over half of all antimony, 10.7% of all zinc produced, 29.7% of tellurium, 17% of all silver, and 5.1% of all gold.<sup>14</sup>

## PROCESS DESCRIPTION

The following description of lead production has been published in reference [0-325a]:

"The production of lead involves three major steps: (1) mining, crushing, grinding, and beneficiation to produce lead concentrates; (2) smelting of the concentrates to produce lead bullion, and (3) refining the bullion to separate other metal values and remove impurities.

Insofar as possible, lead is separated from other values in an ore as lead concentrates in the beneficiation steps. In the smelter, lead concentrates are mixed with fluxes and recycle products such as dust from collection systems and slags. The mixture is then pelletized and sintered on a traveling grate furnace to remove sulfur as  $SO_2$  and also some of the impurities and values such as arsenic, antimony, and cadmium. The sinter produced is charged to the blast furnace with coke, fluxes, and recycled material from associated operations to yield bullion and slag. The bullion contains lead and the easily reduced metals which may be present in the sinter, i.e., copper, antimony, arsenic, bismuth, gold, and silver. The slag will contain silicates from the original charge, and zinc. Where the zinc content of the ore is high enough, the molten slag is treated in a "zinc fuming furnace" to recover zinc as zinc oxide.

The bullion is then subjected to a series of refining operations. The first one, drossing to remove copper is usually performed at the smelter. If antimony, arsenic, or tin are present, the decopperized bullion is then "softened" by oxidizing the molten bullion to remove these elements. The softened lead is then treated with zinc dust (Parke's Process) to remove any gold and silver which may be present as precious metal compounds. The zinc remaining in the "desilvered lead" is removed in a "vacuum dezincing" process. If bismuth is present, it is removed by the "Betterton" process. Calcium and magnesium, remaining after the debismuthizing step, are removed along

with traces of zinc, antimony, and arsenic in a final refining step which involves treatment with caustic soda, to which sodium nitrate is sometimes added."



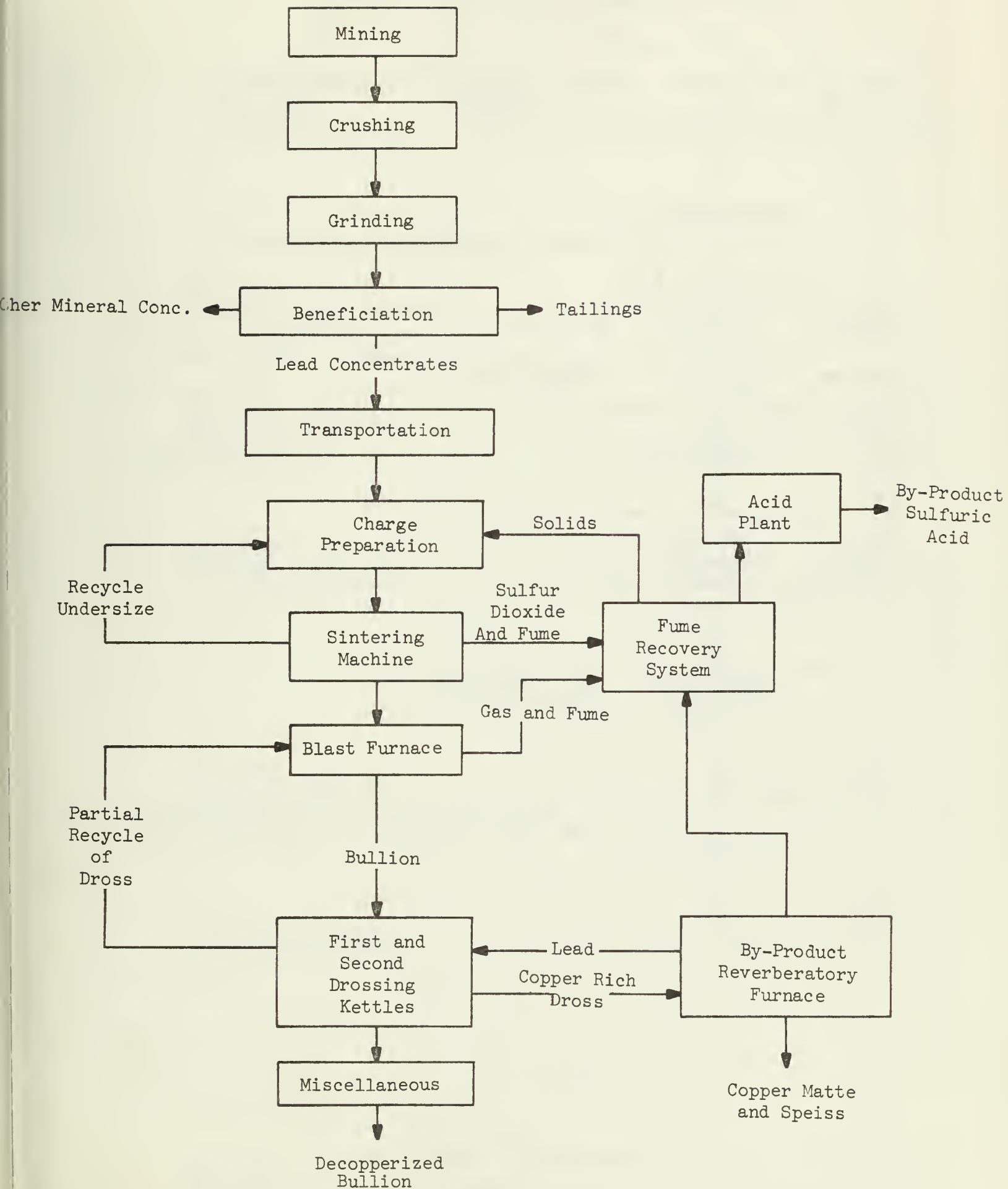


Figure 42a. PRODUCTION OF LEAD

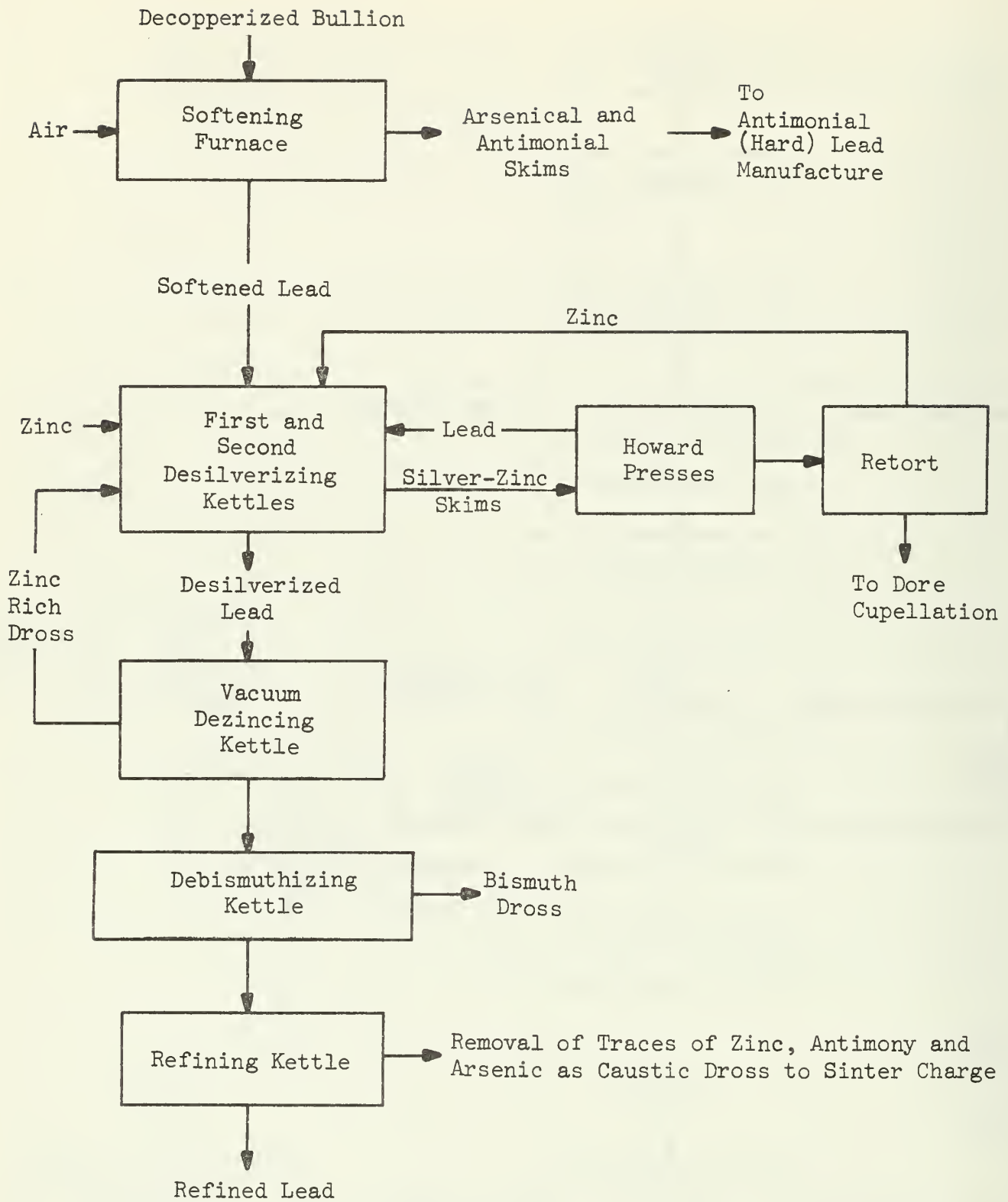


Figure 42a. PRODUCTION OF LEAD (continued)

Source: [0-325a]

Table 42. PRODUCTION OF LEAD

(Basis: 1 ton refined lead)<sup>a</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	electric	274.7 kWh	3,605
	diesel oil	5.51 gal.	918
	gasoline	.44 gal.	66
	materials <sup>b</sup>		620
<i>Subtotal</i>			<u>5,209</u>
2. Crushing, Grinding, Beneficiation	electric	273.1 kWh	3,584
	materials <sup>c</sup>	-	410
<i>Subtotal</i>			<u>3,994</u>
<i>Cumulative Subtotal</i>			<u>9,203</u>
3. Ore Beneficiation	electric	105.0 kWh	1,378
	materials <sup>d</sup>	-	76
	transportation <sup>e</sup>	-	340
<i>Subtotal</i>			<u>1,794</u>
<i>Cumulative Subtotal</i>			<u>10,997</u>
4. Sintering	electric	49.8 kWh	654
	natural gas	614.05 ft <sup>3</sup>	698
	metallurgical coke	.019 ton	458
	materials <sup>g</sup>	-	88
	transportation <sup>h</sup>		12
<i>Subtotal</i>			<u>1,910</u>
<i>Cumulative Subtotal</i>			<u>12,907</u>
5. Blast Furnace	electric	42.5 kWh	558
	natural gas	220.0 ft <sup>3</sup>	250
	petroleum coke <sup>f</sup>	.23 ton	6,872
<i>Subtotal</i>			<u>7,680</u>
<i>Cumulative Subtotal</i>			<u>20,587</u>
6. Dressing	electric	109.93 kWh	1,443
	natural gas	1,989.19 ft <sup>3</sup>	2,262
	diesel oil	.4 gal.	66
	metallurgical coke <sup>f</sup>	.006 ton	145
	materials <sup>i</sup>	-	195
	energy credit <sup>j</sup>	-	606
<i>Subtotal</i>			<u>3,505</u>
<i>Cumulative Subtotal</i>			<u>24,092</u>

Table 42. PRODUCTION OF LEAD (continued)

(Basis: 1 ton refined lead)<sup>a</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
7. Softening	electric	2.6 kWh	34
	natural gas	754 ft <sup>3</sup>	858
<i>Subtotal</i>			892
Cumulative Subtotal			24,984
8. Desilvering and Dezincing	electric	21 kWh	276
	natural gas	900 ft <sup>3</sup>	1,024
	materials <sup>k</sup>	-	364
<i>Subtotal</i>			1,664
Cumulative Subtotal			26,648
9. Debismuthing	electric	14 kWh	184
	natural gas	1,300 ft <sup>3</sup>	1,479
	materials <sup>l</sup>	-	766
<i>Subtotal</i>			2,429
Cumulative Subtotal			29,077
10. Refining and Casting	electric	3 kWh	39
	natural gas	220 ft <sup>3</sup>	250
	materials <sup>m</sup>	-	60
<i>Subtotal</i>			349
TOTAL			29,426

NOTES TO Table 42

- <sup>a</sup> Source: [0-325a] p. 107 for all figures in amount column. This reference does not list a basis for the figures directly, but it can be inferred from the accompanying text that the basis is one ton of lead which probably meets federal specifications (see [42-140]). Note: Plant heating and lighting (1.1% of energy use) is neglected.
- <sup>b</sup> 13.98 lb. steel @ 17,500 Btu/lb. and 12.55 lb. explosives @ 30,000 Btu/lb.
- <sup>c</sup> 23.44 lb. steel @ 17,500 Btu/lb.
- <sup>d</sup> 1.46 lb. organic chemicals @ 5,000 Btu/lb.
- <sup>e</sup> 507 ton-miles by rail @ 670 Btu/TM.
- <sup>f</sup> Caloric value of metallurgical coke "breeze" assumed to be 20,000,000 Btu/ton, and petroleum coke, 24,800,000 Btu/ton [0-206] Table B1; delivery efficiency is 83% [0-210] and [0-201].
- <sup>g</sup> .12 ton limestone @ 240,000 Btu/ton; .07 ton iron ore @ 715,000 Btu/ton; .09 ton silica sand @ 100,000 Btu/ton.
- <sup>h</sup> 18.5 ton-miles @ 670 Btu/TM.
- <sup>i</sup> .002 ton sulfur @ 5,800,000 Btu/ton and .01 ton soda ash @ 18,300,000 Btu/ton.
- <sup>j</sup> energy credit for by-product sulfuric acid production of .73 ton @ 830,000 Btu/ton.
- <sup>k</sup> .0056 ton zinc spelter @ 65 million Btu/ton.
- <sup>l</sup> .00066 ton calcium @ 243 million Btu/ton and .00173 ton magnesium @ 350 million Btu/ton.
- <sup>m</sup> .001 ton caustic soda @ 47.7 million Btu/ton and .00025 ton niter @ 42.25 million Btu/ton.

## ENERGY-VERSATILITY CONSIDERATIONS FOR LEAD

As figure 42b shows, the major energy-consuming step in lead production is furnacing, which is common among most smelted metals. In the case of lead, however, this stage is not as close to the end of processing as is usual. The post-smelting steps are all moderate energy users and probably change the versatility considerably. A close examination of these stages is required before a decision is made as to which one is optimal for stockpiling.

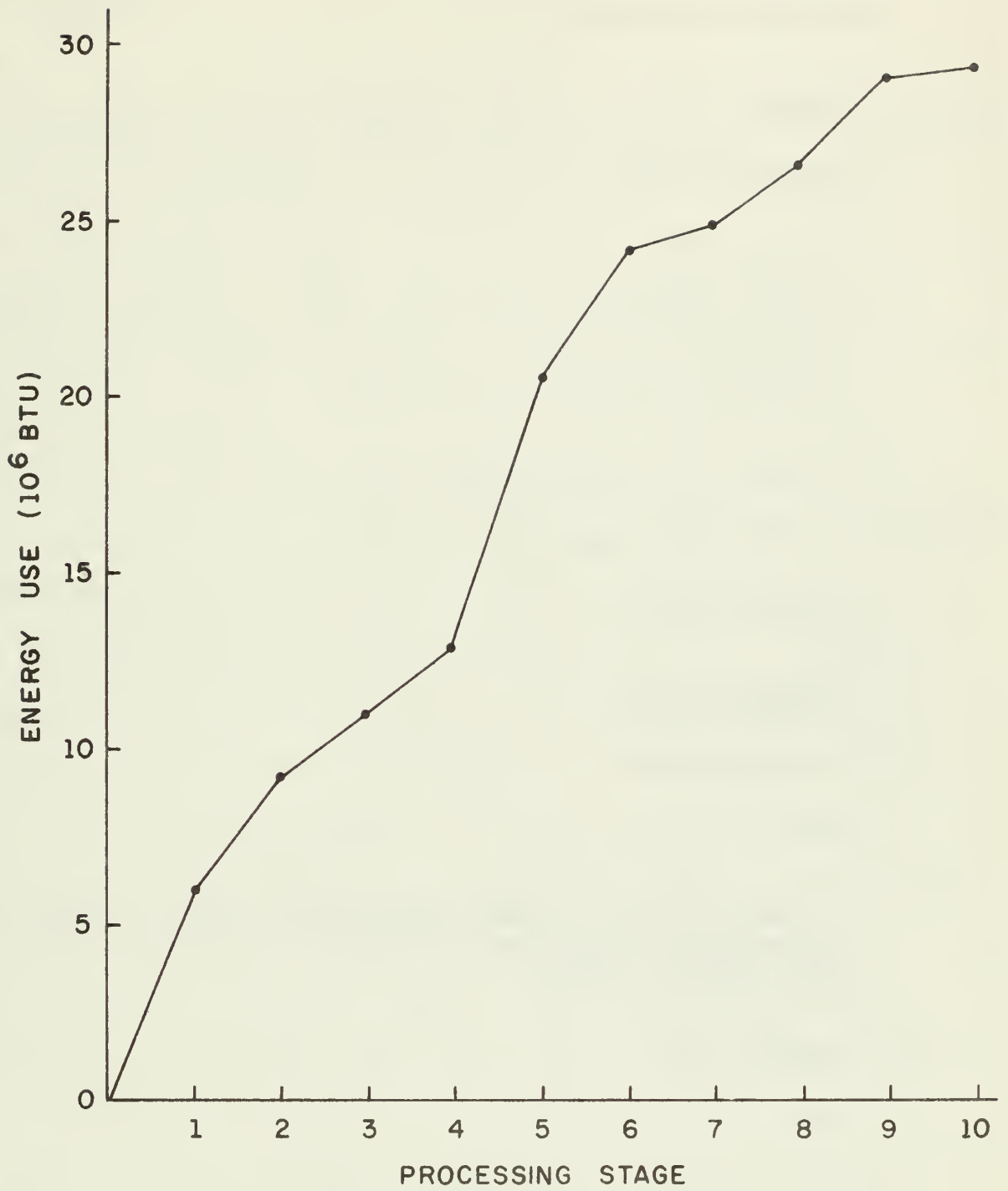


Figure 42b: Production of Lead

FOOTNOTES TO SECTION 42

- <sup>1</sup> [0-149] p. 605.
- <sup>2</sup> [0-140I] p. 688
- <sup>3</sup> Ibid, p. 711.
- <sup>4</sup> [0-149] p. 604.
- <sup>5</sup> [0-140I] p. 688 and [0-112] p. 336-7.
- <sup>6</sup> [0-149] p. 604 and [0-140I] p. 692.
- <sup>7</sup> [0-149] p. 604 and [0-145] p. 44.
- <sup>8</sup> [0-149] p. 609.
- <sup>9</sup> [0-140I] p. 686.
- <sup>10</sup> [0-149] p. 686.
- <sup>11</sup> Ibid.
- <sup>12</sup> [0-122] p. 41 and "stockpile materials for which 'Plastics' were specified in the April, 1973 Review." Office of Preparedness, General Services Administration, 3/18/75.
- <sup>13</sup> [0-149] p. 611.
- <sup>14</sup> Ibid.



## 43...52 MANGANESE

### Overview

Manganese is a brittle, gray-white metal similar to iron and chromium. As an element known to mankind, it is just over two-hundred years old. Its most important characteristic is that it is essential for the economic production of steel with current technology -- slightly less than fourteen pounds of manganese are needed to remove the sulfur from one ton of molten steel.<sup>1</sup>

Manganese is the twelfth most common element in the earth's crust, present in concentrations of about .1%. The main natural forms of manganese are oxides, carbonates, and silicates. From a commercial standpoint, by far the most important ore is manganese dioxide, or  $MnO_2$ .<sup>2</sup> Manganese deposits occur close to the surface in Africa, Asia, South America and Europe, and are mined using either standard open-pit or room-and-pillar methods. Due to expected shortages of ore, many world producers and consumers are actively investigating the mining of manganese nodules from the Pacific ocean floor. The main ore producing countries and their share of 1973 production are the U.S.S.R. (36%), South Africa (19%), Brazil (10%), and Gabon (9%), India (7%), Australia (7%), and Red China (5%).<sup>4</sup>

Classification of the many mineral forms of manganese ore is a complex process. According to the U.S. Bureau of Mines<sup>5</sup>:

"For statistical-reporting purposes, the Bureau of Mines classifies domestic manganese ores, on the basis of manganese content, as manganese ores, ferruginous manganese ores, and manganiferous iron ores...The manganese ores, and in some instances the manganiferous ores, are classified into three principal use categories as

metallurgical, battery, and chemical grade. The determining factor usually is the suitability of the ore for the particular use. Synthetic ore...refers to material which is produced by methods other than ordinary concentration, calcining, sintering or nodulizing."

The most precise U.S. physical and chemical standards for ore are those produced for the national stockpile.<sup>6</sup>

As with tin, several countries smelting manganese ores into various products are not ore producers and must buy manganese concentrates on the world market. Most producers are large companies specializing in ferroalloys. The major metal-producing operations are SEDEMA, Belgium, seven plants in India, several smelters in Japan, EMCOR in the Republic of South Africa, and fifteen plants owned by ten businesses in the United States.<sup>7</sup> Of the 10,738,000 tons of manganese consumed in all forms in 1973, the United States consumed 1,554,000 tons or 14%.<sup>8</sup> For that year, imports of manganese alloys and metals contained 336,000 tons while imported ores contained 722,000 tons of the element.<sup>9</sup>

About three-fourths of all manganese consumed in the United States is used in ferroalloys, most of which in turn are used in the production of iron and steel. About one-third of this manganese-produced steel (amounting to about 25% of all manganese use) goes to the construction industry. The remaining manganese-embodying steel is used in transportation equipment, industrial and agricultural machinery, containers, appliances, pipe and tubing, fertilizer and brick manufacture, ordnance materials, nuts, bolts, and many other fabricated metal products.<sup>10</sup> Ferromanganese is usually classified as high-, medium-, or low-carbon. High-carbon is most commonly used in steelmaking.

Manufacture of high-silicon ferromanganese or siliconmanganese, not to be confused with ferromanganese, accounts for about 9% of all elemental manganese consumed. This particular form of manganese ends up in construction and transportation products and industrial and agricultural machinery.<sup>11</sup> Pure electrolytic manganese metal, rather than a ferro- or silico-alloy, is also used in some alloying processes, such as those making stainless steel, bronze, nickel-chrome, aluminum, and other metals.<sup>12</sup> All in all, 91% of all manganese is consumed in one of the three major metallic forms.

The remaining 9% of domestic demand is consumed directly in ore (or dioxide) form, either for dry-cell battery manufacture (1%) or a variety of chemical uses:<sup>13</sup>

"Important chemical uses include the production of...photographic developer, a dye intermediate, a stabilizer in painting...a powerful oxidizing agent,...and as a catalyst."<sup>14</sup>

The most important co-product of manganese is iron, but since the two are almost always used together they are seldom separated in the manufacturing sequence. Some mines also recover small amounts of lead, zinc, copper, gold and silver.<sup>15</sup> Because manganese is widely disseminated in the many stages of ferrous metal processing, insignificant amounts are recovered for secondary use.<sup>16</sup>

There are very few effective substitutes for manganese in its various end uses. Virtually no feasible substitutes exist for some form of manganese in iron and steel-making. Various materials can replace manganese in some of its chemical uses, and titanium, zirconium, and other rare-earth metals can sometimes take the place of pure manganese metal.<sup>17</sup> An alternate dry-cell battery using no manganese is now being made.<sup>18</sup>

## PROCESS DESCRIPTIONS

### 43. Natural Battery - Grade Dioxide<sup>19</sup>

Battery-grade manganese dioxide is strip-mined. The overburden is about 100 feet and must be bulldozed off, exposing the orebody. Most deposits are relatively pure and clean and the ore is hand-shoveled into a dump truck. This allows for some visual sorting of waste from ore. Trucks deposit the ore at a plant which begins by washing and drying the raw ore. The dry ore is crushed from its natural size down to roughly the size of a #60 sieve and is packed for shipment by rail.

### 44. Synthetic Battery - Grade Dioxide<sup>20</sup>

In the United States, the major starting material for this end product is a metallurgical-grade concentrate imported from Africa. (Refer to process description, commodity 47, below). The concentrates are received by rail, unloaded, and sent to an initial crushing stage if the concentrate is not ground to 95% - 35 mesh. All concentrates are then roasted (or calcined) at a temperature of about 1,300°F or more to reduce the dioxide to manganese monoxide or MnO. The roasted ore must be leached in sulfuric acid in very large tanks, such as an 8,000 gallon tank holding 1,500 tons of ore agitated by a turbine type propeller. After pumping through a thickener which cleans and neutralizes the solution, it is sent to the electrolytic cells in the same plant. For effective electrolysis, the leach solution must be cleaned of undesired trace metals such as copper, zinc, nickel and cobalt. This is accomplished by precipitating out these metals over several hours in the electrolytic cells before electrolysis begins. With the proper electrolytic treatment, pure manganese dioxide is plated out on the anodes. This is stripped by hand and crushed or sold.

#### 47. Metallurgical Grade Ore

According to a study done by Battelle Laboratories for the U.S. Bureau of Mines, metallurgical-grade manganese dioxide ore is produced either from open pit or underground mines. "Most all of the manganese ores mined today undergo some form of concentration, but in most cases it consists of a single crushing and washing operation."<sup>21</sup> A study done by the Bureau of Mines<sup>22</sup> on a small-scale manganese mine in Arizona producing ore specifically for stockpiling, reveals somewhat different information. Diesel shovels and a rotary drill were used to remove the overburden and load the ore onto trucks. The trucks brought the ore to the concentrating plant where the ore was first crushed in two stages, sampled, stored and sent to either the heavy media or concentrating sections. In the latter, a complex flotation circuit was used to remove silica, alumina, and other ore impurities. The pure solution was thickened, filtered, and sent to the sinter plant. The sintering process is fairly standard, using 5% coke or coal in the charge spread on moving metal pallets. Complete, detailed flowsheets for the operation are available in reference [46-50-145] but are not reproduced here.

#### 48. High-Carbon Ferromanganese

The previously mentioned report for the Bureau of Mines contains the following description of high-carbon ferromanganese production, beginning with metallurgical ore concentrates:<sup>23</sup>

"Standard high-carbon ferromanganese is produced by two different processes. In one the manganese ore is reduced by coke in a blast furnace which is located within an integrated steel plant, and the ferromanganese is used by the company. In 1973 only two blast furnaces were producing ferromanganese. Blast furnace production of ferromanganese has been in a declining trend for several years.

The second process is the usual ferroalloy method which uses a submerged-arc electric furnace. In this process there are two generally accepted practices. In one, known as the "high-manganese slag practice", the degree of manganese reduction to metal is limited and a slag is produced which usually contains more than 25 percent manganese. This slag is then used to produce silicomanganese in a separate operation. The second alternative, known as the "low-manganese slag practice", produces a slag containing 8 to 12 percent manganese which is discarded. The choice of practice depends upon several factors, including the relative costs of manganese ore and electrical energy and the ability to use a high-manganese slag."

#### 49, 50. Low- and Medium-Carbon Ferromanganese<sup>24</sup>

These products are made with only slight variations in the same basic method. The process begins with sintered nodules of metallurgical grade manganese dioxide -- see process description for material 47 above for details. This concentrate is mixed intact with metallurgical coke, limestone, and dolomite or iron ore turnings and charged into an electric arc furnace. After 12 or more hours of preheating, the "melt" assaying about 50% Mn is tapped off at prescribed intervals into a ladle containing molten silicomanganese. The final reaction forming low or medium carbon ferromanganese occurs in the ladle and depends on the amount of coke in the furnace charge and other measures. The molten metal is poured and cast.

#### 51. Silicomanganese<sup>25</sup>

Silicomanganese is produced either from medium- or high-carbon ferro-manganese slag, which is separated as a waste product in the ferromanganese smelting stage. This slag can either come in rough lumps from the waste heap of a ferromanganese producer or be tapped in molten form directly from

a concurrent ferromanganese smelt. The slag is mixed in a single phase furnace with some combination of coal, coke, limestone and silicomanganese or silica and heated to over 1,400°C. Over a twenty-hour period the alloy is tapped off the furnace bottom and poured directly into molds. The slag is cascaded to a waste heap to cool.

## 52. Electrolytic Manganese<sup>26</sup>

This is produced by the exact same process as synthetic manganese dioxide with the exception of the final electrolysis stage. In this the anolyte and catholyte solutions used are different. The cells operate at a current density of about 16 A/ft<sup>2</sup> and a pH of about 2. Pure metal is allowed to plate out on steel cathode plates for between 20 and 150 hours, at which time the coating is about 1/8" thick. Again, the cathodes are stripped by hand and are ready for sale or stockpile if packaged properly.

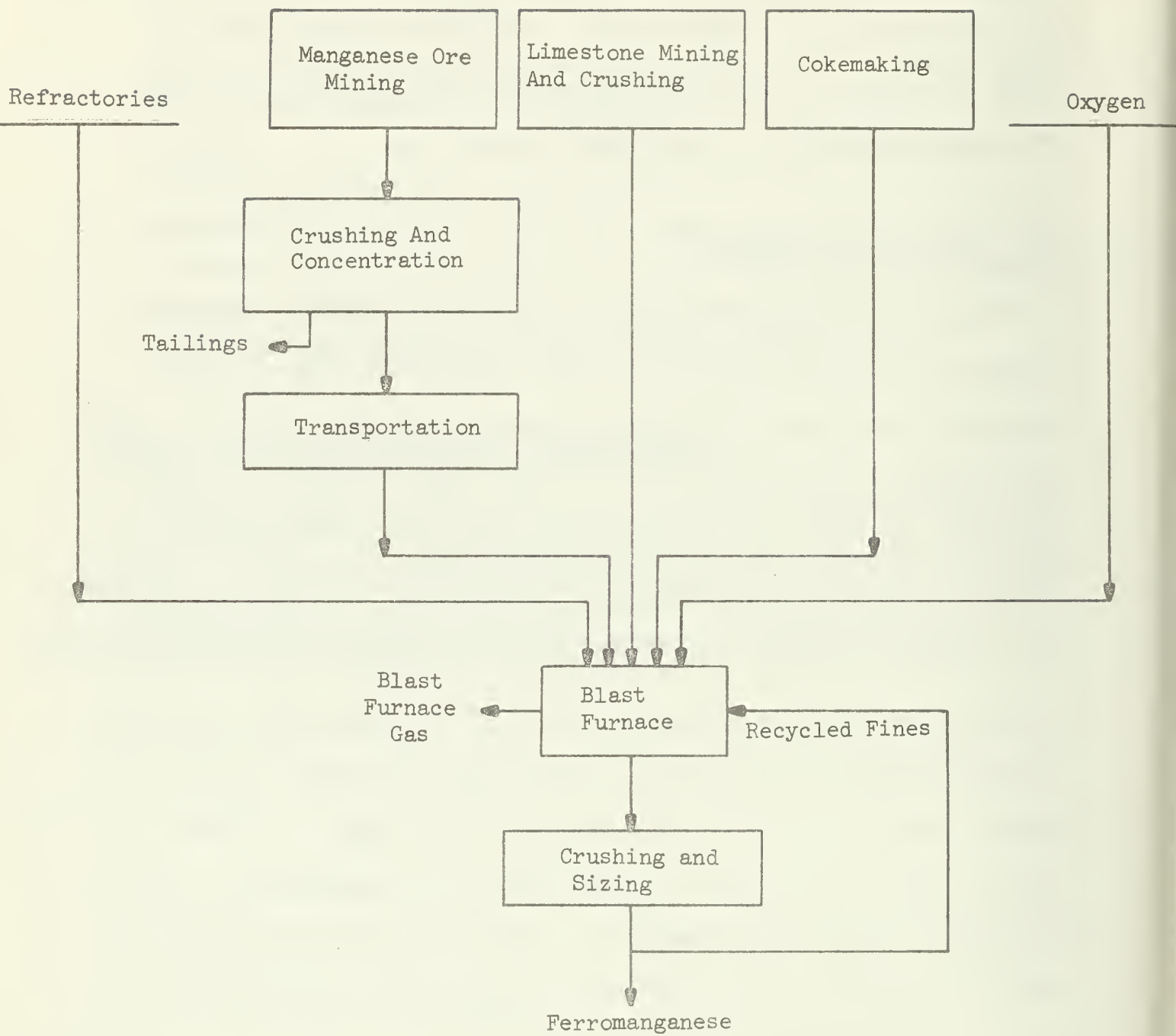


Figure 48a: Production of High-Carbon Ferromanganese  
( Blast Furnace)



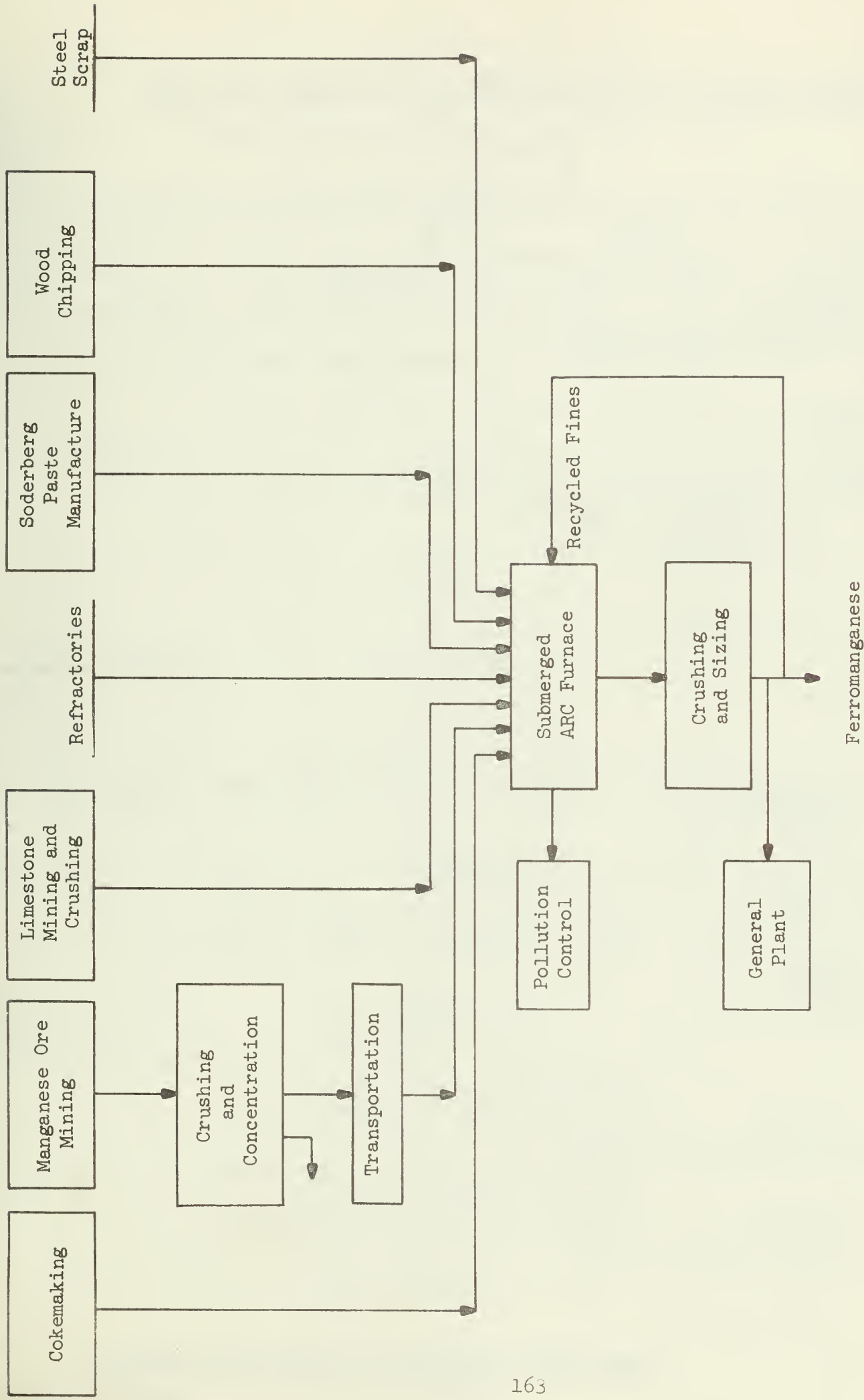


Figure 48aa: Production of High-Carbon Ferromanganese (Electric Arc)

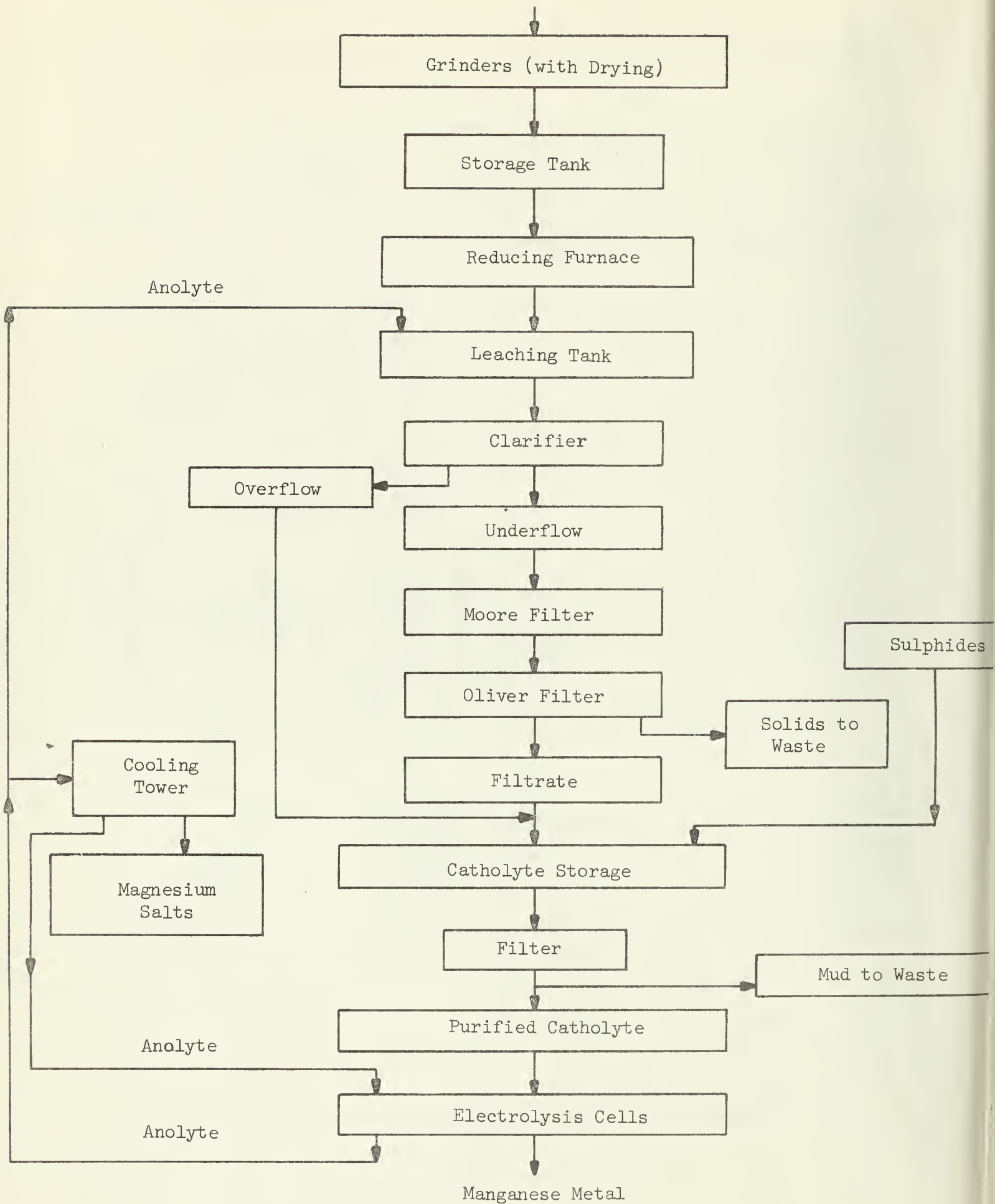


Figure 52a: Production of Electrolytic Manganese

Table 43. PRODUCTION OF NATURAL BATTERY GRADE MANGANESE DIOXIDE<sup>a</sup>

(Basis: One ton of washed, dried Grade B ore.<sup>b</sup>)

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	fuel oil <sup>c</sup>	22.64 gal.	<u>3,389</u>
<i>Subtotal</i>			<u>3,389</u>
2. Washing and Drying	electricity	37.5 kWh	492
	fuel oil <sup>c</sup>	21.13 gal.	<u>3,810</u>
<i>Subtotal</i>			<u>4,302</u>
<u>TOTAL</u>			<u>7,691</u>

NOTES TO Table 43

<sup>a</sup> Source: [43-300]

<sup>b</sup> Ore produced is 64% MnO<sub>2</sub> (dry basis) while federal specifications call for 68%.

<sup>c</sup> Caloric value assumed is 149,690 Btu/gal.

Table 44. PRODUCTION OF SYNTHETIC BATTERY-GRADE MANGANESE DIOXIDE<sup>a</sup>

(Basis: 1 ton of dioxide to federal specifications)<sup>b</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Initial Material	Metallurgical-Grade Manganese Concentrates	1.27 ton <sup>c</sup>	5,326 <sup>d</sup>
<i>Subtotal</i>			5,326
2. Kiln Reduction <sup>e</sup>	natural gas	15,240	17,333
<i>Subtotal</i>			17,333
<i>Cumulative Subtotal</i>			22,659
3. Acid Leaching	electric <sup>f</sup>	8.75 kWh	115
	materials <sup>g</sup>	-	675
<i>Subtotal</i>			790
<i>Cumulative Subtotal</i>			23,449
4. Electrolysis	electric	3,000 kWh	39,369
	materials <sup>h</sup>	-	3,502
<i>Subtotal</i>			42,871
<i>Cumulative Subtotal</i>			66,320
5. Cathode Stripping and Crushing <sup>i</sup>	electric <sup>i</sup>	4.0 kWh	52
<i>Subtotal</i>			52
<b>TOTAL</b>			<b>66,372</b>

NOTES TO TABLE 44

- a Source: [44,52-203] and [52-101] unless noted.
- b See [43/44-140]; actual dioxide produced by the process exceeds specifications.
- c Metallurgical grade manganese contains 48% manganese or about 75% manganese dioxide by weight ([43/44-140]). For one ton of 98%+ purity synthetic dioxide, 1.27 tons of concentrate are required.
- d See Table 47 for details.
- e Due to highly processed condition of metallurgical concentrates they may be calcined directly. Alternate processes use coal or No. 3 fuel oil.
- f Based on estimated use of four ten-horsepower motors per 8,000 gallon batch (1,500 lb. ore) for one hour. Miscellaneous pumping energy use neglected [50-101] p. 28.
- g .4 lb.  $H_2SO_4$ /lb. manganese (consumed) @ 415 Btu/lb ([0-325a] p. 108 and .2 lb (N H<sub>4</sub>) SO<sub>4</sub>/lb manganese @ 500 Btu/lb.\* (Ibid).
- h .004 lb  $H_2S$ /lb. manganese @ 500 Btu/lb.\* (ibid)  
and .068 lb N H<sub>3</sub>/lb. manganese @ 20,245 Btu/lb. [0-321] p. 94.  
Material use based on production of pure metal.  
\* Misc. inorganic reagents.
- i Stripped by hand but must be crushed to 98% -60 sieve. Estimated power consumption from [0-325b] p. 94.

Table 47. PRODUCTION OF METALLURGICAL-GRADE MANGANESE ORE<sup>a</sup>

(Basis: 1 ton of ore to federal specifications)<sup>b</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>c</sup>	diesel oil	2.13 gal. <sup>d</sup>	355
	gasoline oil	.026 gal. <sup>d</sup>	4
	materials <sup>e</sup>	-	51
	transportation <sup>f</sup>	-	215
<i>Subtotal</i>			625
2. Milling <sup>g</sup>	electric	145.44 kWh	1,909
	transportation <sup>h</sup>	-	9
<i>Subtotal</i>			1,918
<i>Cumulative Subtotal</i>			2,543
3. Sintering <sup>i</sup>	electric <sup>i</sup>	11.11 kWh	146
	petroleum coke	.05 ton	1,494
	transportation <sup>j</sup>	-	2
<i>Subtotal</i>			1,642
<b>TOTAL</b>			<b>4,185</b>

NOTES TO Table 47.

- <sup>a</sup> Applies to combined open-pit and underground mining of manganese ore prepared specifically for stockpiling (type III). Source: [46-50-145] unless noted.
- <sup>b</sup> See [47-140].
- <sup>c</sup> Average concentration of manganese in ore mined was 19.82%. Since a final concentrate of 48% manganese is required to meet [47-140], 2.42 tons of ore must be mined.

<sup>d</sup> Computed as follows:

The mine produced 300 tons of ore per eight-hour day or 37.5 tons per hour. Fuel consumption is estimated for the following equipment:\*

AMOUNT	TYPE	FUEL USE(gal/hr)	SOURCE
1	600 c.f.m. compressor	10 gal/hr.	[47-200]
2	315 c.f.m. compressor	4 gal/hr.	[47-200]
1	3 kW. generator	.4 gal/hr(gas)	[47-200]
1	rotary drill, 3-1/2" x 1000'	neglected	
1	40 h.p. tractor (Case 140)	2 gal/hr.	[47-201]
1	191 h.p. bulldozer (Caterpillar D-7)	4 gal/hr.	[47-201]
1	.75 cu. yd. power shovel	5 gal/hr.	[47-201]
1	1.5 cu.yd. power shovel	8 gal/hr.	[47-201]
TOTAL PER 37.5 TONS (1 hour):		33 gal. diesel	
		.4 gal. gasoline	
TOTAL PER 2.42 TONS:		2.13 gal. diesel	
		.026 gal. gasoline	

\* haulage trucks are neglected

- <sup>e</sup> 1.69 lb. explosives @ 30,000 Btu/lb. [0-325b] p. 94.
- <sup>f</sup> 116 ton-miles by truck @ 1,850 Btu/TM [0-208].
- <sup>g</sup> Includes crushing, fine grinding, flotation, heavy media, and tables.
- <sup>h</sup> 4.84 ton-miles by truck @ 1,850 Btu/TM [0-208].
- <sup>i</sup> For windrowing, pelletizing drum, crushing, sizing, and sintering. Electrical energy use estimated by E.R.G based on data in [46-50-145]. At that stage, ore is assumed fully concentrated, or one ton of sinter plant input produce 1 ton final output.
- <sup>j</sup> From windrowing to sintering bins - 1 ton-mile @ 1,850 Btu/TM.

Table 48. PRODUCTION OF HIGH CARBON FERROMANGANESE<sup>a</sup>

(Basis: 1 ton of ferromanganese to federal specifications)<sup>b</sup>

STAGE	ELECTRIC ARC FURNACE			BLAST FURNACE		
	TYPE	AMOUNT	10 <sup>3</sup> Btu	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>c</sup>	electric	12.0 kWh	157	electric	12.0 kWh	157
	unspecified	-	550	unspecified	-	550
	materials <sup>d</sup>	-	45	materials <sup>d</sup>	-	45
	transportation <sup>e</sup>	-	<u>1,032</u>	transportation <sup>e</sup>	-	<u>1,032</u>
<i>Subtotal</i>			<u>1,784</u>			<u>1,784</u>
2. Charge Preparation and Smelting	electric	2,765.88 kWh	36,297	electric	2500 kWh	8,808
	petroleum coke <sup>g</sup>	.5 ton	16,935	natural gas	325 ft <sup>3</sup>	
	materials <sup>f</sup>	-	4,410	petroleum coke	1.423 ton	49,258
	transportation <sup>h</sup>	-	189	coke oven gas	121 ft <sup>3</sup>	61
				Blast furnace gas	68,000 ft <sup>3</sup>	8,160
				Steam	1,200 lb.	1,200
			materials	-	1,478	
			transportation <sup>j</sup>	-	355	
			Energy credit for Blast Furnace Gas	114,000 ft <sup>3</sup>	-13,680	
<i>Subtotal</i>			<u>57,831</u>			<u>55,640</u>
<i>Cumulative Subtotal</i>			59,615			57,424
3. Crushing and Sizing	electric	1.0 kWh	13	electric	1.0 kWh	13
	<i>Subtotal</i>		<u>13</u>			<u>13</u>
TOTAL			59,628			57,437



NOTES TO Table 48.

<sup>a</sup> Source: [0-325b.] p. 92, 94.

<sup>b</sup> See [48-140].

<sup>c</sup> Mining figures used here are not the same as those used in Table 47.

<sup>d</sup> 1.5 lb. explosives @ 30,000 Btu/lb.

<sup>e</sup> 12,300 T.M. by water @ 250 Btu/TM and 1,540 TM @ 670 Btu/TM.

<sup>f</sup> Materials as follows:

<u>MATERIAL</u>	<u>AMOUNT</u>	<u>ENERGY INTENSITY</u>
limestone	.3 ton	104,000 Btu/ton
refractories	45 lb.	12,500 Btu/lb.
soderberg paste	.02 ton	37.92 Million Btu/ton
wood	.175 ton	7.28 Million Btu/ton

<sup>g</sup> Caloric values assumed: coke: 31.5 million Btu/ton;  
natural gas and steam: 1,000 Btu/ft<sup>3</sup>; blast furnace gas: 120 Btu/ft<sup>3</sup>

<sup>h</sup> 250 TM by rail @ 670 Btu/TM and 8.75 TM by truck @ 2400 Btu/TM.

<sup>i</sup> .5 ton limestone @ 104,000 Btu/ton; 5 lb. refractories @ 12,500 Btu/lb;  
and 7,450 ft<sup>3</sup> oxygen @ 183 Btu/ft<sup>3</sup>.

<sup>j</sup> 530 TM by rail @ 670 Btu/TM.

Table 50. PRODUCTION OF MEDIUM-CARBON FERROMANGANESE<sup>a</sup>

(Basis: 1 ton of medium-carbon ferromanganese)<sup>b</sup>

	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Initial Materials	metallurgical concentrates	1.93 ton <sup>f</sup>	8,077 <sup>c</sup>
<i>Subtotal</i>			<u>8,077</u>
2. Charge Preparation and Smelting <sup>d</sup>	electricity	1,050 kWh	13,779
	materials <sup>e</sup>	-	42,818
<i>Subtotal</i>			<u>56,597</u>
<i>Cumulative subtotal</i>			<u>64,674</u>
3. Crushing and Sizing <sup>g</sup>	electricity	1.0 kWh	13
<i>Subtotal</i>			<u>13</u>
<b>TOTAL</b>			<u>64,687</u>

NOTES TO Table 50

<sup>a</sup> Source: [50-200] and [50-300] unless noted. Production is by current processes.

<sup>b</sup> Product is equivalent to refined grades of Union Carbide ferromanganese. For federal specifications see [49/50-140].

<sup>c</sup> See tabular data for material 47.

<sup>d</sup> In tilt furnace.

<sup>e</sup> .73 tons silicomanganese @ 55.283 million Btu/ton (see tabular data for material 51) and .29 tons lime @ 8.487 million Btu/ton [0-325b] p. 46.

<sup>f</sup> 1.93 tons MnO<sub>2</sub> are required consumed in the sintering stage but of this only 1.76 tons<sub>2</sub> are actually sent to smelting.

<sup>g</sup> Assumed same as high-carbon ferromanganese. Source: [0-325b], p. 92.

Table 51. PRODUCTION OF SILICOMANGANESE<sup>a</sup>

(Basis: 1 ton of silicomanganese to federal specifications)<sup>b</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Initial materials	High- and Medium-Carbon Ferromanganese Slags	5,600 lb.	- <sup>c</sup>
2. Smelting <sup>e</sup>	electric	3,600 kWh	47,243
	coal	625 lb.	7,948
	materials <sup>d</sup>	-	102
<b>TOTAL</b>			<b>55,283</b>

NOTES TO Table 51.

<sup>a</sup> Source: [49, 50, 51-203] and [46-50-144] unless noted.

<sup>b</sup> See [51-140]

<sup>c</sup> We follow the practice used by Battelle Laboratories in [0-325b p. 94] by considering the slag to be an energy-free byproduct.

<sup>d</sup> .3 ton limestone @ 240,000 Btu/ton ([0-325a] p. 107)  
 .085 ton graphite electrode @ 160.72 Btu/ton ([0-325a] p. A-6)  
 .3 ton silica @ 100,000 Btu/ton.

<sup>e</sup> Smelted and tapped directly into molds.

Table 52. PRODUCTION OF ELECTROLYTIC MANGANESE METAL<sup>a</sup>

(Basis: 1 ton of manganese to federal specifications)<sup>b</sup>

STAGE	TYPE	amount	10 <sup>3</sup> Btu
1. Initial material	metallurgical grade manganese concentrates	2.08 tons <sup>c</sup>	8,710 <sup>d</sup>
<i>Subtotal</i>			<u>8,710</u>
2. Kiln Reduction <sup>d</sup>	natural gas		28,388
<i>Subtotal</i>			<u>28,388</u>
<i>Cumulative Subtotal</i>			<u>29,098</u>
3. Acid Leaching	electric <sup>d</sup>	14.33 kWh	188
	materials <sup>d</sup>		5,735
<i>Subtotal</i>			<u>5,923</u>
<i>Cumulative Subtotal</i>			<u>35,021</u>
4. Electrolysis	electric	11,000 kWh	144,354
	materials <sup>d</sup>		5,736
<i>Subtotal</i>			<u>150,090</u>
<b>TOTAL</b>			<u>185,111</u>

NOTES TO Table 52.

<sup>a</sup> Source: [44, 52-203] and [52-101] unless noted.

<sup>b</sup> See [52-140].

<sup>c</sup> Metallurgical grade concentrates are 48% (min.) manganese and final metal is 99.9% (min) manganese.

<sup>d</sup> See Table 47 for details.

## ENERGY-VERSATILITY CONSIDERATIONS FOR MANGANESE

The manganese group of metals form an intricate, interrelated system of materials. Such a large number of useful forms is indicative of a material chain having a complex versatility function. In fact, versatility considerations for these materials are probably more important than energy use or other parameters. It is therefore difficult to make simple judgements on the optimum forms for stockpiling. One certain result of a careful versatility study would be that some manganese should be kept in every current strategic and critical material form. The exact proportions stockpiled can be decided only when versatility factors such as industrial capacity, expected technological change, future demand, and other items from Table 0-3 are analyzed in detail. See figure 43/52b.

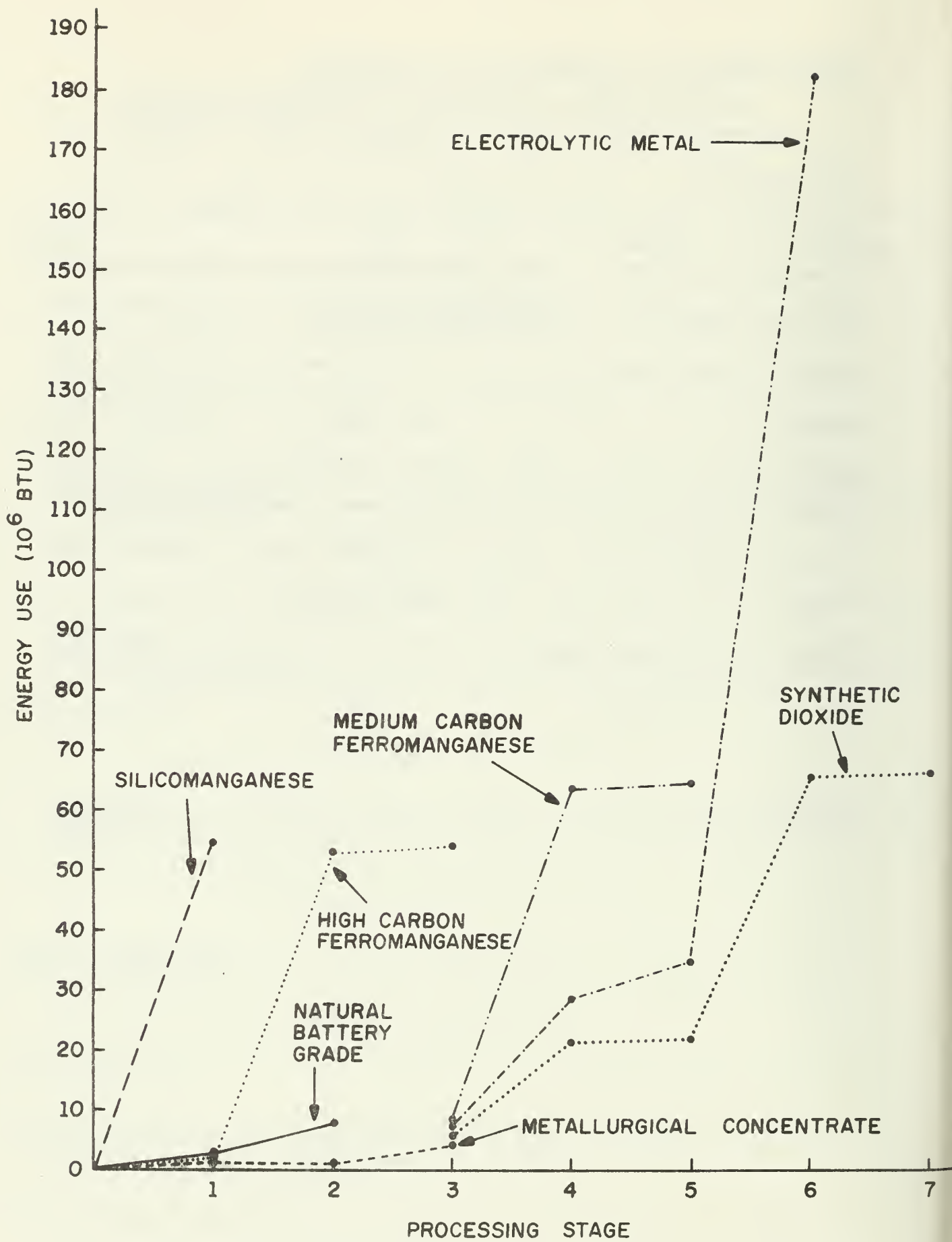


Figure 43-52b: Production of Manganese Materials

NOTES TO SECTION 43...52

- <sup>1</sup> [43-52-100] p. 255 and [0-149] p. 315, 316.
- <sup>2</sup> [0-149] p. 317.
- <sup>3</sup> Ibid, p. 318.
- <sup>4</sup> [0-140I] p. 752.
- <sup>5</sup> [0-149] p. 317.
- <sup>6</sup> See [43/44-140] to [52-140].
- <sup>7</sup> [0-140I] pp. 751-754.
- <sup>8</sup> [0-145] p. 48.
- <sup>9</sup> Ibid.
- <sup>10</sup> [0-149] p. 322, 323.
- <sup>11</sup> Ibid.
- <sup>12</sup> Ibid.
- <sup>13</sup> Ibid.
- <sup>14</sup> Ibid.
- <sup>15</sup> Ibid.
- <sup>16</sup> Ibid.
- <sup>17</sup> [0-122] p. 47.
- <sup>18</sup> [0-149] p. 323
- <sup>19</sup> Source: [43-200]
- <sup>20</sup> Source [44, 52-203] and [52-10.]

NOTES TO SECTION 43...52 continued)

<sup>21</sup> Source: [0-325b] p. 88.

<sup>22</sup> [46-50 - 145].

<sup>23</sup> Source: [0-325b] p. 88-89.

<sup>24</sup> Source: [46-50-144] and [49, 50, 51-203]

<sup>25</sup> Source [46-50-143], [46-50-144], and [49,50,51-203].

<sup>26</sup> Source: [52-101] and [44, 52-203].



## 53. MERCURY

### Overview

Mercury, atomic number 80, is a silvery white, lustrous liquid metal, often referred to as quicksilver. It is the only metal that is liquid at room temperature. Its essential properties give it an industrial and economic importance disproportionate to the small size of its producing industry. In addition to its fluidity, some other important properties include high density, uniform volume expansion, electrical conductivity, ability to alloy readily, high surface tension, chemical stability, and toxicity of its compounds.

The abundance of mercury in the earth's crust is 0.5 ppm, which is about five times that of silver. Mercury is found in rocks of all geologic ages and all classes. Although it has been identified in 25 minerals, it is recovered almost entirely from the red sulfide mineral, cinnabar (HgS -- 86.2 percent mercury and 13.8 percent sulfur); other sulfides, such as arsenic and antimony are often associated with it. Mercury is sometimes found naturally in small quantities in the liquid state.

Deposits usually occur at relatively shallow depths: from less than 1,000 feet to a maximum of 2,400 feet, and may be classified into two general types: 1) disseminated cinnabar ore, in which the cinnabar has impregnated a more or less finegrained or highly brecciated gangue; 2) cinnabar ores deposited in fissures and cracks of the country rock.<sup>1</sup>

Global reserves occur in Spain (35%), Italy (10%), People's Republic of China (9%), Yugoslavia (11%), U.S.S.R. (17%), Mexico (4%), Canada (4%), U.S.A. (3%), Japan, Philippines, Turkey (7%). Mercury resources of the United States are found in California, Nevada, Alaska, Idaho; less significant quantities in Oregon, Texas, Arizona, New York and Washington.<sup>2,3</sup>

Due to the small size of the domestic deposits, there are only six consistent producers of primary mercury; in 1973 there were almost 18 other operations each producing less than 100 flasks. Extraction is relatively straightforward: after mining and ore beneficiation, the concentrate is subjected to a multiple distillation process, leaving practically no co-products or by-products of any importance. One domestic goldmining operation produces co-product mercury, and one domestic mercury producer recovered and marketed stone from the furnace calcine. None of the domestic producers operate mines in foreign countries or is vertically integrated. Each sells virgin mercury through bookers or dealers, or directly to consumers.

The quantities of scrap or dirty mercury available for treatment are increasing, and in recent years have accounted for a significant part of the domestic supply. Secondary mercury is reclaimed and refined by the same companies that process virgin metal and is returned to consumers as metal or in mercury compounds.

The U.S. total primary production in 1973 was 2,171 flasks, a sharp and steady decline from 28,552 flasks in 1969, and less than 1% of the world's production. Over 46,000 flasks were imported, whereas secondary recovery amounted to 7,746 flasks.<sup>4</sup> Between 1969 and 1973 the ratio between secondary and primary production increased from 37% to 378%.<sup>5</sup> U.S. mercury reports were low, only .5% of a total supply of 74,284 flasks. With 19,659 flasks in industry stocks, actual demand involved 54,283 flasks and had the following distribution: electrical, 33%; caustic soda and chlorine, 24%; paints, 16%; instruments, 13%; dental supplies, 5%; other, 11%.

The wide range of uses includes application of mercury cells in the preparation of high purity chlorine and caustic soda as required in rayon manufacture; batteries, rectifiers, oscillators, power control switches, fluorescent and high-intensity arc discharge lamps; industrial control and laboratory instrumentation, thermometers, barometers; catalyst in the plastic and resin industry; phenyl mercurial compounds in antifouling and mildew proofing paints and for the preservation of textiles; agricultural chemicals, pharmaceutical preparation, dental supplies and equipment.

There are few satisfactory substitutes for those applications in electrical operations and industrial and control instruments that depend on mercury's specific properties.

Instead of mercury, the diaphragm cell is increasingly used as a cathode for the production of electrolytic chlorine and caustic soda. Some pharmaceuticals, antiseptics, fungicides, dyes and other chemical applications have suitable alternatives.

New developments in vinylchloride production are likely to reduce the need for mercury containing catalysts in acetylene-based plants. Ship bottoms can be protected with plastic or copper oxide paints.

## PROCESS DESCRIPTION

Conventional mining methods treat as much as 300 tons of ore per day at underground mines and 175 tons at open pits. Milling of the ore consists of crushing, sometimes followed by screening. The principal purpose of these operations is to reduce the material to a size required for furnacing. Concentration of mercury minerals by flotation is efficient and produces a high-grade concentrate.

Mercury is extracted from ore and concentrate by heating in retorts or furnaces under vacuum to liberate the metal as a vapor, followed by cooling of the vapor and collection of the condensed mercury. The same installation serves to process scrap or dirty mercury. Retorts can handle one quarter to five tons per day of high-grade sorted ore. For large operations, either rotary or multiple hearth furnaces with mechanical feeding and discharging devices are preferred.

Mercury can also be leached from its ores and concentrates and subsequently recovered by precipitation with aluminum or by electrolysis. This process has not been practiced extensively because of reagent consuming constituents in some ores and the high cost of fine grinding.

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NOTE: No optimization section is included for this material. Only one single step consumes significant energy, distilling. Since this does not significantly decrease versatility, mercury should be stockpiled in refined form.

Table 53. PRODUCTION OF MERCURY

(Basis: One ton of mercury to federal specification)<sup>a</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> BTU
1. Mining and Beneficiation <sup>b</sup>	Diesel Oil	98 gal.	16,294
2. Metal Production	Diesel Oil	42.6 gal.	7,083
	Electricity	3,921 kWh	51,455
	General Plant Energy <sup>c</sup>	-----	8,034
Total Energy for 1 Ton of Primary Mercury <sup>d,e</sup>			82,866

NOTES TO TABLE 53

- <sup>a</sup> See [53-140]
- <sup>b</sup> This entire table was obtained via [53-302]; it appears that about 400 tons of ore are required to produce 1 ton of Hg: [0-140 I] p. 759.
- <sup>c</sup> Thirty-four gal. of diesel oil/ton Hg @ 138,000 Btu/gal, and 15.8 gal/ton Hg of gasoline @ 125,070 Btu/gal.
- <sup>d</sup> This seems in accordance with an overall figure of 180 kWh/flask obtained via [53-202]. The primary energy equivalent of this would be  $62,162 \times 10^3$  Btu/ton Hg.
- <sup>e</sup> For secondary mercury, two considerably lower figures were derived: one source [53-200] reported 13,350 ft<sup>3</sup> of natural gas/ton Hg, which amounts to 15,183 Btu/ton of pure Hg. A second source, [53-301], reported 760 kWh/ton Hg, amounting to 9,973 Btu/ton of pure Hg.

FOOTNOTES TO SECTION 53

<sup>1</sup> [0-149] p. 641

<sup>2</sup> [0-140 I] p. 765

<sup>3</sup> See [53-142]

<sup>4</sup> [0-145] p. 49

<sup>5</sup> [0-140 I] p. 759

<sup>6</sup> [53-142] p. 33

## 59. MOLYBDENUM

### Overview

Molybdenum, atomic number 42, is a silver gray metallic element, nearly as heavy as lead, with a very high melting point: 4730°F, which is 2,000 degrees higher than steel's and 1,000 degrees higher than the temperature at which most of the earth's rocks would melt.<sup>1</sup> The melting points of only four other elements: tantalum, rhenium, tungsten and carbon, exceed that of molybdenum. Abundance in the earth's crust is estimated to lie between 5 and 15 ppm. about the same as lead. It occurs as primary ore in the mineral molybdenite,  $\text{MoS}_2$ , usually associated with granites, or pegmatites containing tin, tungsten and other sulfides; and also in the secondary mineral wulfenite,  $\text{PbMoO}_4$ .<sup>2</sup> However, about one-fourth of the current U.S. output is obtained either as a by-product or coproduct during the processing of copper, tungsten and uranium ores.<sup>3</sup>

Approximately 85% of the free world's molybdenum resources occur in one long mountain chain stretching from the Rockies of Canada through the U.S. to the Andes of South America. Five deposits that contain over 90% of the U.S. resources are located in Climax (Col.) Utah Copper (Utah), San Manuel (Arizona), Morenci (Arizona) and Orange Hill (Alaska).<sup>4</sup> In 1973, two mines in Colorado and one in New Mexico produced over 34,000 tons of molybdenum from primary ores having a molybdenite concentration from .1 to .5%. The world's largest producer, with over 29% of the total, is Climax Molybdenum, a division of AMAX, Inc.

By-products from molybdenum ores are iron pyrite, rare earths, sulfur, tin, and wolframite (tungsten). In Canada, the treatment of bismuth-molybdenum ores yields bismuth as a coproduct. Fourteen by-product plants,



processing copper porphyry, made some 24,000 tons of molybdenum with rhenium as by-product. Six companies, two primary producers and four by-product producers accounted for at least 96% of the United States output of molybdenum, or about 63% of the world's production in 1973.

Concentrated molybdenite is composed of at least 90% molybdenum disulfide, max. 0.45% copper, max. 0.15% lead, max. .15% tin-plus-arsenic. Roasting of the concentrate results in molybdic oxide ( $\text{MoO}_3$ ), containing a minimum of 60% Mo. In powder or granular form, it is white at ordinary temperatures. Molybdic oxide briquettes, made of technical grade molybdic oxide and carbon, are used to introduce molybdenum into steel. By the Thermit or by electric furnace process, molybdic oxide is converted into ferro molybdenum, a heavy dark gray metallic alloy of iron and molybdenum, containing 60% Mo. The oxide is also converted to calcium molybdate or other chemicals or metal powder for use in mill products for high temperature applications.

Molybdenum is used principally as an alloying element to impart hardenability, strength, toughness, and corrosion resistance to steel, cast iron and nonferrous metals. It is used either as the sole alloy material, or in combination with others such as chromium, manganese, nickel and tungsten. Molybdenum high speed tools contain from .5 to 9 percent molybdenum. It is extremely important in steel for hulls of submarines, military combat vehicles and aircraft carriers,<sup>6</sup> as well as in the manufacture of oil and gas transmission pipelines for service in geographical areas of sub-zero temperature. Molybdenum is further used in the manufacture of a variety of products ranging

from cutting and wear resistant materials such as piston rings, crankshafts, exhaust nozzle inserts in jet engines, to electronic semiconductor devices. Molybdenum compounds are used as chemical reagents, catalysts, and lubricants in paints and pigments, fertilizers, insecticides and ceramics.<sup>7</sup>

Virtually all of the 1973 consumption of 41,000 tons of molybdenum contained in concentrates was converted to molybdic oxide; a small fraction went into producing purified molybdenum disulfide. Steel production absorbed 70% of the reported consumption, cast iron 8%, superalloys 5%, alloys 3%, mill products (sheet, rod and wire) 5%, chemical industry 8%. An equivalent of 64% of the 1973 domestic output, namely over 28,000 ton of contained molybdenum was shipped to foreign markets.<sup>8</sup>

Scrap, mostly from electronic and catalyst industries is generally unsuitable for recycling, although it is an excellent feed material for the production of ferro molybdenum and metallurgical grade molybdic oxide. Currently, an estimated 1% of molybdenum metal scrap is reclaimed and used again.

A substitute for molybdenum as a coating for the piston rings of internal combustion engines could be chromium: stainless steel trim for automobiles can be replaced likewise. Hastelloy X, a 9 percent molybdenum nickel-base alloy for jet engine applications has possible substitutes in thoria-dispersion-strengthened nickel and nickel-chrome alloys. As a refractory structural material in electric furnaces, molybdenum generally can be replaced by graphite. At higher temperatures, tungsten and tantalum can be used but especially the first of these two implies higher cost, heavier weight and greater difficulty to fabricate. Boron,

chromium and manganese impart hardenability of steels in varying degrees; molybdate orange can be replaced by chrome orange, cadmium red, and other organic orange pigments.

## PROCESS DESCRIPTION

Molybdenum ore is mined by both open pit and underground methods. One method of underground mining is block caving, a low cost method in which the orebody is undercut to induce caving. Ore hauled from the mine is then dumped into hoppers which feed two types of crushers, jaw and gyratory. The rocks are first trimmed down to about nine inches in size and subsequently to three-eighths-inch pebbles, at which point the ore is ready for the milling process. Here separation of the highly disseminated desired minerals from gangue is accomplished by fine grinding and flotation, employing a reagent comprised of pine oils, hydrocarbon, and a synthetic wetting agent. Several steps of flotation raise the concentration of  $\text{MoS}_2$  (sized at 75 percent minimum passing a 325-mesh sieve) to about 90%.

"The concentrate is converted to molybdic oxide ( $\text{MoO}_3$ ) by roasting in a multiple hearth furnace. Temperatures of the various hearths are controlled within determined ranges with an average value of about  $1,100^\circ\text{F}$ . Significant quantities of the very fine concentrate are carried out of the roaster in the flue gas. Measurements of the dust effluent have indicated that between 10 to 15 percent of the concentrate charged into the furnace normally exists with the flue gas. Thus, long before the big drive for clean air became a major issue, it was economically necessary to recover as much as possible of the flue gas dust. After much development work, it was found that a dust collection efficiency of about 98.5% could be achieved with the use of two multiclones in series followed by an electrostatic precipitator. The recovered particulates are recycled to the roaster feed."<sup>9</sup>

Conversion into low carbon ferromolybdenum is done by the thermite reaction: technical molybdenum oxide, ferrosilicon, iron ore and aluminum are the reactants, while limestone and fluorospar are used as fluxes.

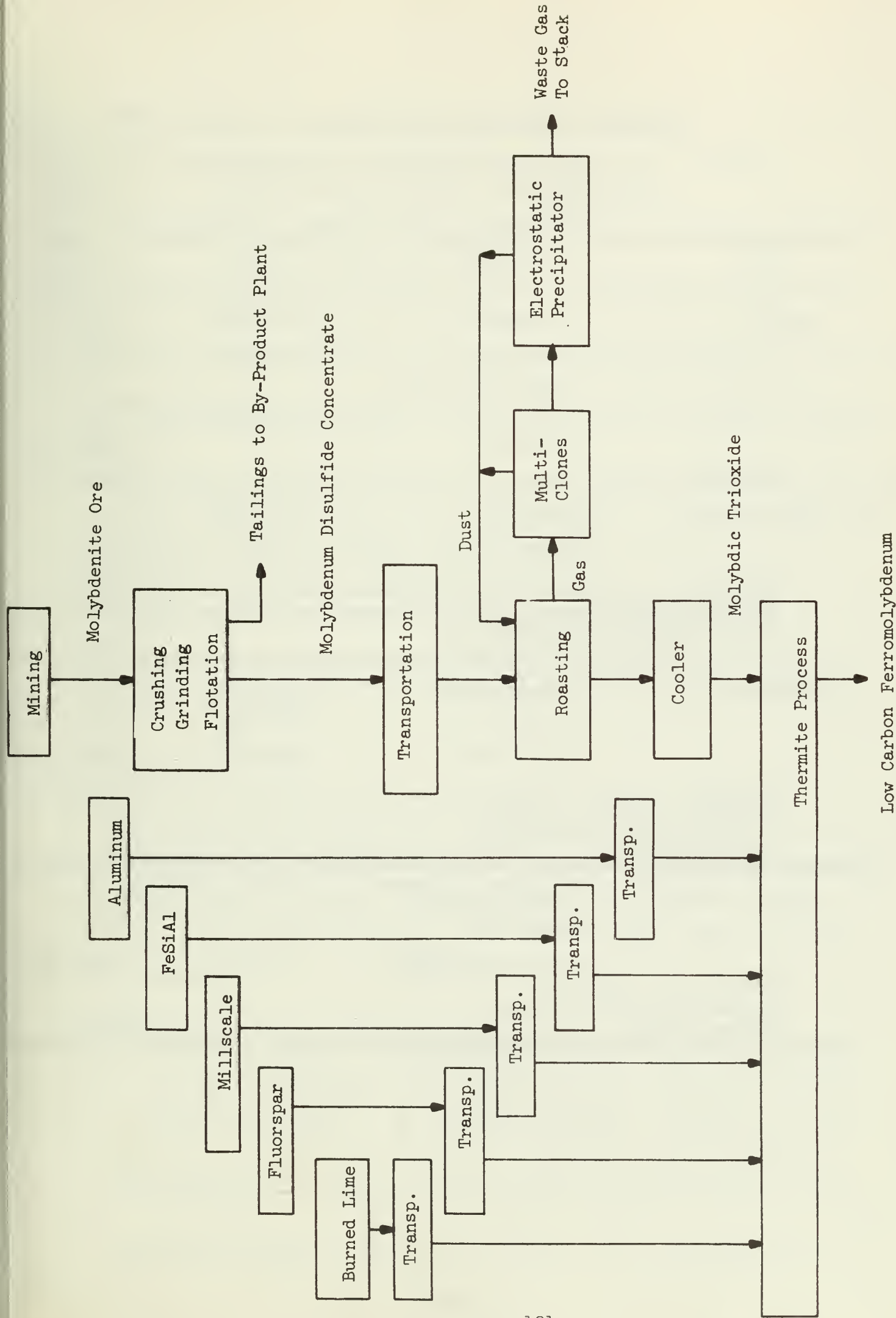


Fig. 59: Production of Molybdenum

TABLE 59. PRODUCTION OF MOLYBDENUM

(Basis: 1 ton of molybdenum disulphide, molybdc oxide, ferromolybdenum to federal specifications)<sup>a</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>b</sup>	electricity	1,765 kWh	23,162
	natural gas	21,100 ft <sup>3</sup>	23,862
	liquid hydrocarbon fuel <sup>c</sup>	52.7 gal.	8,572
	materials <sup>d</sup>	-	2,850
<i>Subtotal</i>			<u>58,446</u>
2. Concentration <sup>e</sup>	electricity	6,275 kWh	82,347
	materials <sup>f</sup>	-	16,185
<i>Subtotal</i>			<u>98,532</u>
<i>Cumulative Subtotal</i>			<u>156,978</u>
Energy required to produce 1 ton of molybdenum disulphide <sup>g</sup>			<u>108,943</u>
3. Roasting	transportation <sup>h</sup>	2,037 TM	1,365
	electricity <sup>i</sup>	875 kWh	11,489
	natural gas	2,500 ft <sup>3</sup>	2,841
<i>Subtotal</i>			<u>15,695</u>
<i>Cumulative Subtotal, energy required to produce 1 ton of molybdc oxide</i>			<u>172,673</u>
4. Thermite process	molybdc oxide <sup>j</sup>	1.1 ton	189,940
	materials <sup>k</sup>	-	125,355
	gen. plant energy <sup>l</sup>	750 kWh	9,842
<i>TOTAL energy required to produce 1 ton of low-carbon ferromolybdenum</i>			<u>325,137</u>

NOTES TO Table 59.

- a Source: [0-325b] p. 107, [59-141].
- b This analysis is based on the underground mining and beneficiation of a primary ore containing 0.34% molybdenite.
- c Battelle estimate of 135,000 Btu/gal.
- d Battelle estimate of about .25 lb/net ton of material blasted @ 30,000 Btu/lb.
- e About 380 tons of ore yield 1.44 ton of concentrate with 90% molybdenite content, or 60% molybdenum content.
- f Kellogg, H. H. "Energy Consumption in Flotation Beneficiation" (unpublished), Columbia University, New York, N.Y., July 1973.  
Grimes, G. R., and Witkamp, G., "Climax Conversion Practice II", Journal of Metals, February, 1971, pp. 17-24.  
1,210 lb. of inorganic reagents @ 5,000 Btu/lb.,  
176 lb. of organic reagents @ 20,000 Btu/lb.,  
378 lb. steel for grinding @ 17,500 Btu/lb.
- g Through a private communication with another major producer [59-301], a figure of 93,536 Btu for 1 ton of Molybdenum disulphide with 60% Mo content was derived.
- h 600 miles by rail.
- i For dust recovery system, see: Wheeler, E.S., "Climax Conversion Practice," AIME Technical Publication 1718, Metal Technology, 1944;  
"Hybrid Scrubber cuts costs," Chemical Engineering, April 28, 1975, p. 86.  
Breakdown of electrical energy for the roasting process:  
Grizzly mill and cooler: 15 kWh, multiclone: 22 kWh,  
Electrostatic precipitator: 27.5 kWh, General plant energy: 811 kWh.
- j [59-201].
- k [59-300]: Additives used in thermite process:
- |                      |                        |                     |
|----------------------|------------------------|---------------------|
| .96 ton of FeSiAl    | @ 120,000,000 Btu/ton; | 150 miles by truck. |
| .03 ton of Aluminum  | @ 285,000,000 Btu/ton; | 150 miles by truck  |
| .61 ton of Millscale | @ 160,000 Btu/ton;     | 300 miles by truck  |
| .03 ton Fluorspar    | @ 6,050,000 Btu/ton;   | 100 miles by truck. |
| .06 ton Burned Lime  | @ 8,500,000 Btu/ton;   | 100 miles by truck  |
- which amounts to  $124,539 \times 10^3$  Btu for materials and 340 miles by truck @ 2,400 Btu/TM.
- l Estimated by several producers to be between 2 and 4 percent of total production energy.

## ENERGY-VERSATILITY CONSIDERATIONS FOR MOLYBDENUM

Figure 59b shows clearly that the products of Stages 3 and 4 (molybdic oxide and ferromolybdenum) are preferred forms for stockpiling: both have comparable versatilities and should therefore be stockpiled in corresponding quantities.

Although energy use does not significantly rise between Stage 2 and 3, there is probably a noticeable versatility decrease. This suggests that a small amount has to be kept in the form of molybdenum disulphide, Stage 2.



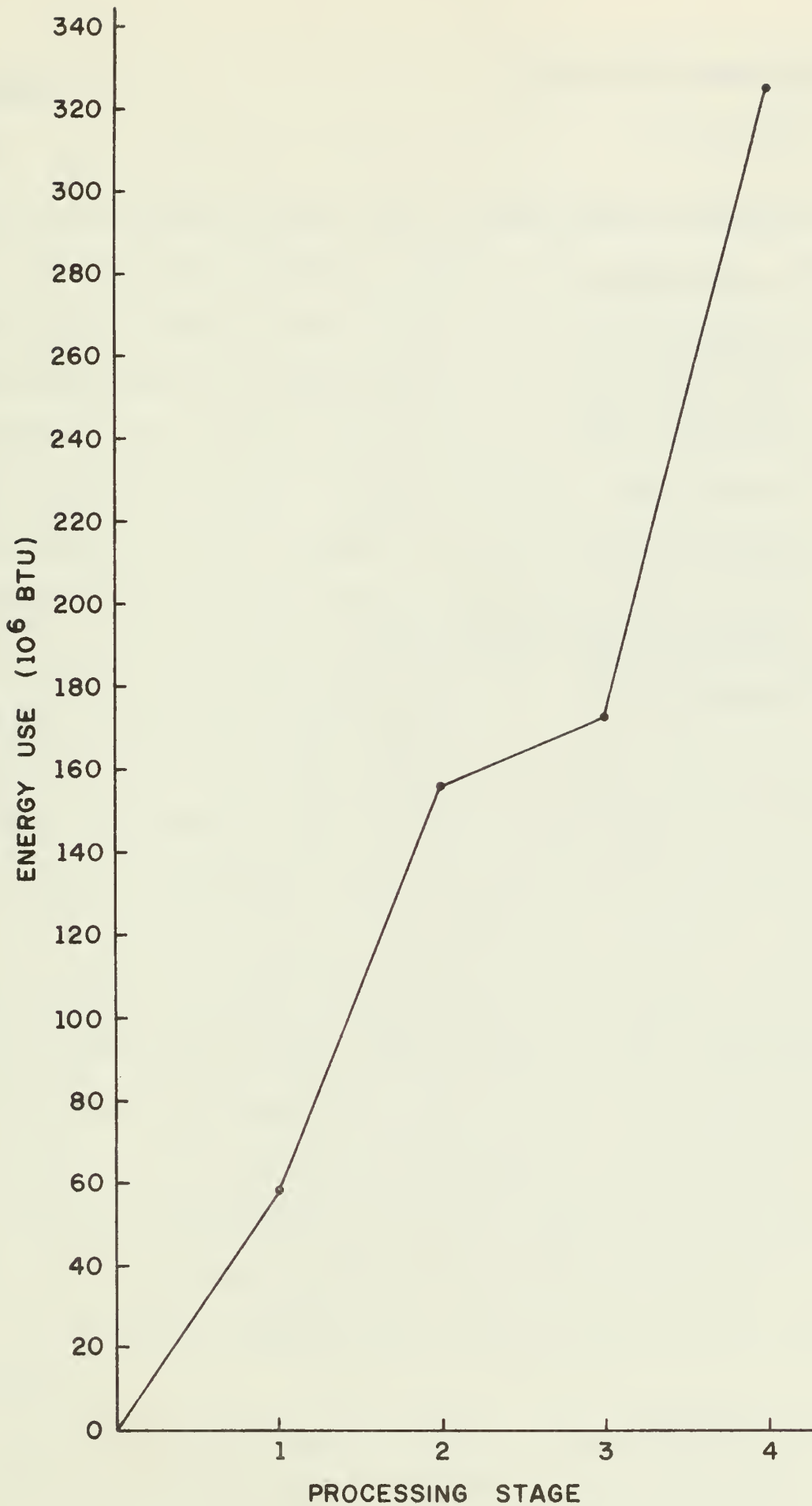


Figure 59b: Production of Molybdenum

FOOTNOTES TO SECTION 59

<sup>1</sup> [59-120] p. 2.

<sup>2</sup> [59-100] p. 271.

<sup>3</sup> [0-149] p. 333.

<sup>4</sup> [59-140] p. 6.

<sup>5</sup> [0-140 I] p. 781.

<sup>6</sup> [0-122] p. 53.

<sup>7</sup> [0-149] p. 338.

<sup>8</sup> [0-140I] p. 783, [0-145] p. 52.

<sup>9</sup> [0-325b] p. 104.

## 60. NICKEL

### Overview

After steel, aluminum copper, zinc, and manganese, the largest amount of elemental metal production is nickel, atomic number 28. Its concentration in the earth's crust is about .008 percent, chiefly in relatively rare deposits of either sulfide or oxide (laterite) ores.<sup>1</sup> Eighteen countries are currently exploiting commercial nickel deposits of one of these two mineral forms.<sup>2</sup> Canada, the largest mining country with 42% of world output, produces virtually all sulfide ores.<sup>3</sup> The two other major producers are New Caledonia (15% of world total) and the U.S.S.R. (21%).<sup>4</sup> There is only one mine in the U.S., and it produces ferronickel ores which are not processed to pure nickel.<sup>5</sup>

The worldwide nickel metal industry is strongly concentrated in the hands of a few producers which "operate internationally and have sales offices or agents strategically located to serve the free world's nickel markets."<sup>6</sup> The largest companies, the International Nickel Co., Falconbridge Nickel Mines, and Sherritt-Gordon Mines, all Canadian, produced 24% of all primary metal in 1973. Japan's Sulawesi Nickel Development Cooperative is the next largest free world producer with 12% followed by New Caledonia. In total, nineteen countries smelt primary nickel.<sup>7</sup>

The United States produced only about 13,895 tons of metal in 1973 with almost 1,000 as a by-product of processing other metals.<sup>8</sup> In order to meet a demand of 259,000 tons, a total of 191,100 tons of metal were imported.<sup>9</sup>

According to the U.S. Bureau of Mines, "over 90 percent of the nickel used [in the U.S.] is used in the form of metal, principally in alloys."

Nickel is used in many ferrous alloys, including stainless steel and super-alloys. These are used in transportation equipment, construction and construction hardware, a wide variety of industrial machines, ship-building, and in many electric and electronic components requiring resistive or high permeability elements. Nickel is also used extensively for electroplating and in nickel-cadmium batteries.<sup>10</sup>

Many significant substitutes exist for various uses of nickel, though most are not economically attractive. The nickel in stainless steel and other alloys can often be replaced by other metals. Plastics, paints and other coatings can be substituted where nickel is employed for protection against corrosion.<sup>11</sup>

As reported above, significant amounts of nickel are produced as by-products, chiefly from copper production. In other sulfide mines, iron, copper, gold, silver, cobalt, and several rare and precious metals are by-products. Most laterite mines produce valuable amounts of iron, cobalt and silver.<sup>12</sup>

Secondary recovery of nickel is an important domestic industry, producing 66,500 tons or 26% of total U.S. demand in 1973.<sup>13</sup> Most of this scrap is generated in factories making fabricated metal products from ferronickel alloys, and most nickel is recycled from this form into other ferrous alloys. In fact, even high nickel alloys cannot be economically converted to pure nickel due to the natural affinity of iron for nickel.<sup>14</sup>

## PROCESS DESCRIPTION

An extensive report done by Battelle Laboratories for the U.S. Bureau of Mines offers this description of the nickel-production process:<sup>15</sup>

"After mining, the ore is beneficiated to produce a nickel concentrate plus an iron concentrate and a copper concentrate. The nickel concentrate is roasted, in a limited supply of air, and the calcine smelted to produce a raw matte containing about 15 percent nickel plus copper and some iron, cobalt, and other base metals. The raw matte is blown in a converter to produce a primary matte that is crushed and separated into a nickel concentrate and a copper concentrate. The nickel concentrate is pelletized and roasted to nickel oxide and shipped to the refinery where it is reduced to impure metal and cast into anodes that are refined electrolytically. The electrolytic nickel cathodes are cleaned and sheared for shipment."

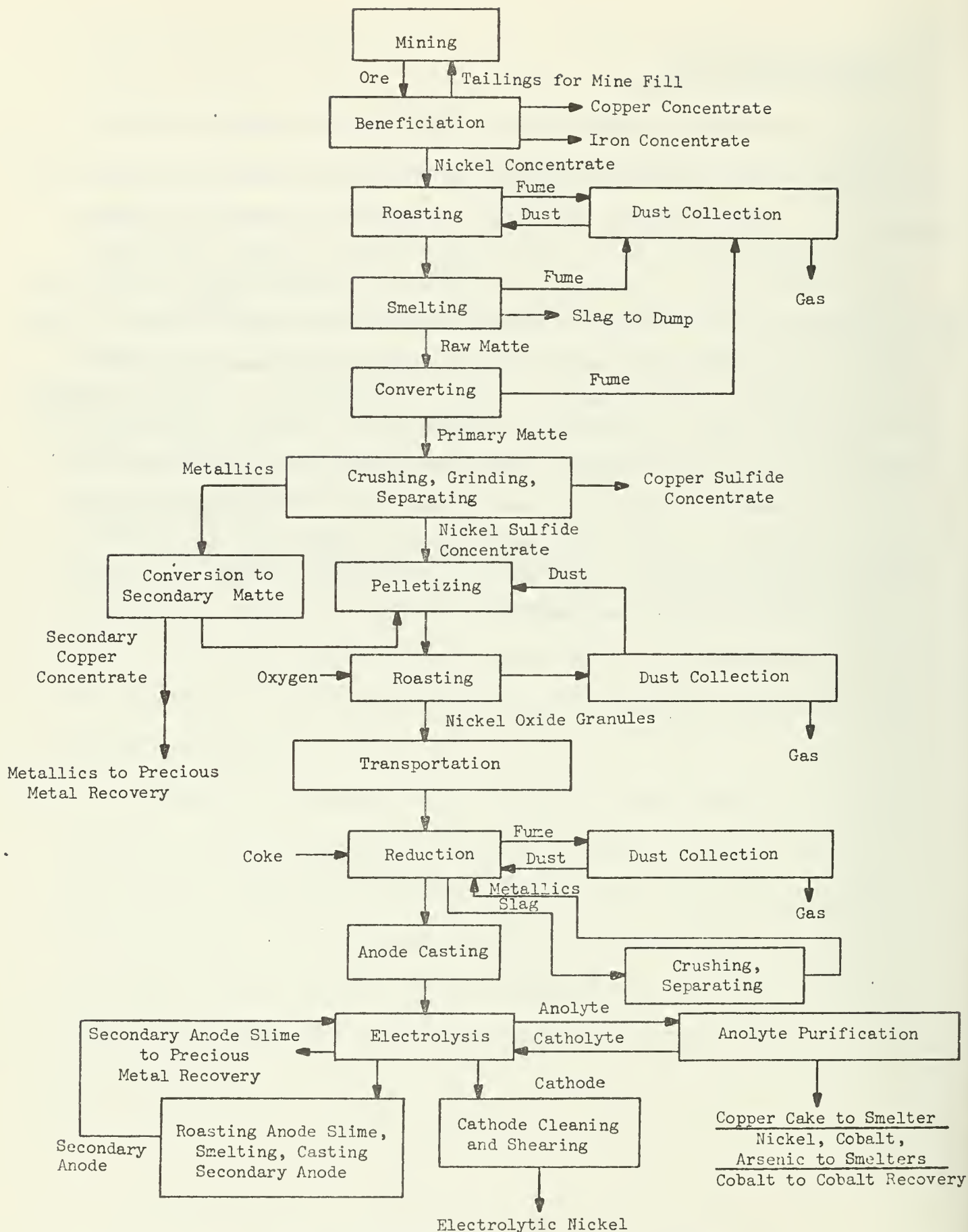


Fig. 60a. PRODUCTION OF ELECTROLYTIC NICKEL

Source: [O-325b]

Table 60. PRODUCTION OF NICKEL<sup>a</sup>  
(Basis: 1 ton electrolytic Nickel)<sup>b</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	electric	3,524. kWh	46,246
	distillate fuel oil <sup>d</sup>	53.5 gal.	8,964
	materials <sup>c</sup>	-	4,650
<i>Subtotal</i>			<u>59,860</u>
2. Beneficiation	electric	2,425 kWh	31,823
	materials <sup>e</sup>	-	11,110
<i>Subtotal</i>			<u>42,933</u>
<i>Cumulative Subtotal</i>			<u>102,793</u>
Energy allocated to nickel production <sup>f</sup>			65,893
3. Fluid Bed Roasting <sup>i</sup>	electric	261.1 kWh	3,426
	materials <sup>g</sup>	-	8,390
	transportation <sup>h</sup>	-	140
<i>Subtotal</i>			<u>11,956</u>
<i>Cumulative Subtotal</i>			<u>77,849</u>
4. Smelting <sup>i</sup>	electric	14.1 kWh	185
	natural gas	42,410 ft <sup>3</sup>	46,604
	materials <sup>j</sup>	-	
	energy credit for waste heat	-	- 13,900
<i>Subtotal</i>			<u>32,889</u>
<i>Cumulative Subtotal</i>			<u>110,738</u>
5. Converting <sup>i</sup>	electric	562.2 kWh	7,377
	materials <sup>k</sup>	-	4,760
	transportation <sup>k</sup>	-	80
<i>Subtotal</i>			<u>12,217</u>
<i>Cumulative Subtotal</i>			<u>122,955</u>
6. Matte Separation	electric	8.4 kWh	110
	materials <sup>l</sup>	-	260
<i>Subtotal</i>			<u>370</u>
<i>Cumulative Subtotal</i>			<u>123,325</u>

(continued)

Table 60. PRODUCTION OF NICKEL<sup>a</sup> (continued)  
 (Basis: 1 ton electrolytic Nickel)<sup>b</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
7. Secondary Matte	electric	301.5 kWh	3,957
	materials <sup>m</sup>	-	583
<i>Subtotal</i>			4,540
Cumulative Subtotal			127,865
8. Pelletizing and Roasting <sup>i</sup>	electric	38.95 kWh	511
	materials <sup>n</sup>	-	970
	transportation <sup>o</sup>	-	190
<i>Subtotal</i>			1,671
Cumulative Subtotal			129,536
9. Reverberatory Furnace	electric	1.29 kWh	17
	distillate fuel oil <sup>d</sup>	10.0 gal	1,675
	petroleum coke <sup>d</sup>	.13 ton	3
	transportation <sup>p</sup>		
<i>Subtotal</i>			1,695
Cumulative Subtotal			131,231
10. Electrolysis and assoc. Operations	electric	1613.23 kWh	21,171
	materials <sup>q</sup>		6,274
<i>Subtotal</i>			27,445
Cumulative Subtotal			158,676
11. Cathode cleaning and Shearing	electric	.1 kWh	1
<i>Subtotal</i>			1
TOTAL			158,677



NOTES TO Table 60

- a Source: [0-325b] p.112 unless noted.
- b There are specific federal specifications for electrolytic nickel; it is anticipated that the nickel represented here meets them. See [60-140].
- c 155 lb. explosives @ 30,000 Btu/lb.
- d Caloric value of oil assumed 139,000 Btu/gal; of gas 1,000 Btu/ft.<sup>3</sup>; of petroleum coke 30 million Btu/ton.
- e
- | MATERIAL            | AMOUNT    | ENERGY CONTENT       |
|---------------------|-----------|----------------------|
| Steel               | 273 lb.   | 17,500 Btu/ton       |
| Lime                | .492 ton  | 8.45 million Btu/ton |
| Organic chemicals   | 272.9 lb. | 2,000 Btu/lb.        |
| Inorganic chemicals | 236 lb.   | 500 Btu/lb.          |
- f Iron and copper are also present in the ore in valuable amounts. Allocation is made on the basis of contained metal weight in ore, or .44 unit iron and .12 unit copper per unit nickel. Thus nickel accounts for  $(1.56)^{-1} = .64$  total ore processing energy use.
- g 1.85 ton oxygen @ 4.4 million Btu/ton and 6.0 ton sand @ 42,000 Btu/ton.
- h 60 ton-miles by truck @ 2,400 Btu/ton.
- i Includes dust collection.
- j .89 ton oxygen @ 4.4 million Btu/ton.
- k 1.05 ton oxygen @ 4.4 million Btu/ton and 3.3 ton sand @ 42,000 Btu/ton; 33 ton by truck @ 2,400 Btu/ton.
- l .03 ton lime @ 8.5 million Btu/ton.
- m 7.2 lb. graphite electrodes @ 80,000 Btu/lb. and .08 ton sand @ 42,000 Btu/ton.
- n .22 ton oxygen @ 4.4 million Btu/ton.
- o 750 ton-miles by water @ 250 Btu/ton-mile.

p 13 ton-miles by water @ 250 Btu/ton -mile.

q .043 ton sponge nickel @ 129.5 Btu/ton; 58 lb. soda ash @ 9,000 Btu/ton; 13.0 lb. chlorine @ 9,000 Btu/lb.; .72 ton graphite electrode @ 80,000 Btu/ton and .016 ton sand @ 42,000 Btu/ton.

## SECONDARY NICKEL

### PROCESS DESCRIPTION and Energy Use

There are many possible ways to recycle metallic nickel. A large amount is recovered as home scrap within ferrous metal fabricators, steel mills, and related industries. Many foundries also buy old scrap back from large customers or on the open scrap market.

Significant quantities of nickel are used in high-nickel refractory alloys or super-alloys. These alloys, consisting of nickel, molybdenum, chromium, cobalt, and other rare metals, are used by specialized producers such as the aerospace industry. Once superalloys are made it is extremely difficult to separate the constituent metals; this separation is being performed commercially only in Japan and West Germany. However, the unique combinations of elements in superalloys make it economical to recycle them intact.<sup>17</sup>

The process begins with scrap collection from major industrial consumers, mainly aerospace manufacturers and other metal fabricators. If necessary, the scrap is vapor degreased, crushed, or briquetted, eventually being melted in an electric arc or induction furnace. The molten alloy is poured into ladles, analyzed spectrographically, and modified in some cases by the addition of pure metals. Addition of these metals, such as magnesium, titanium, or aluminum, also aids in deoxidizing the melt. When ready, the metal is cast into 56 lb. pigs.<sup>18</sup>

From private communication with the largest domestic superalloy recycling firm, which claims to be the largest metal recycling plant in the world, we estimate the energy cost of recycling one ton of superalloy to be about 11.6 million Btu/ton, excluding scrap transportation.<sup>19</sup>

## ENERGY-VERSATILITY CONSIDERATIONS FOR NICKEL

The largest incremental energy use in nickel processing is, surprising enough, mining and concentrating. This makes for a wide variety of choices for the stockpiled form. Either of the two mattes, for example, could conceivably be stored, possibly after pettelizing and roasting. However, considering the main uses of nickel, there is probably little advantage to leaving it in these forms. This needs to be examined more closely, but if it is true, the current physical specification is adequate.

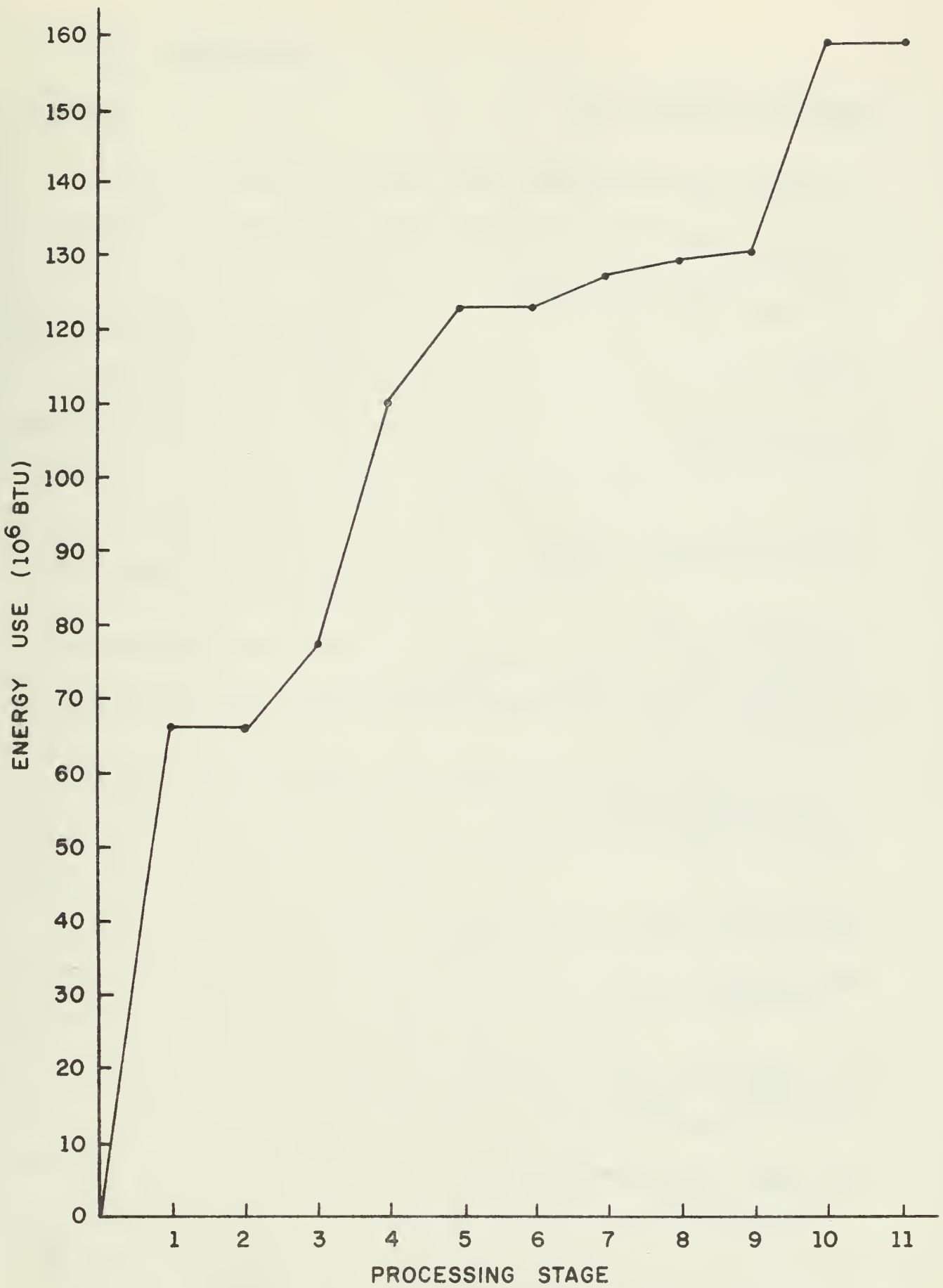


Figure 60b: Production of Nickel

FOOTNOTES TO SECTION 60

- <sup>1</sup> [0-149] p. 349 and p. 604.
- <sup>2</sup> [9-140I] p. 868.
- <sup>3</sup> Ibid and [60-100] pp. 27-55.
- <sup>4</sup> Ibid.
- <sup>5</sup> [0-149] p. 348.
- <sup>6</sup> Ibid.
- <sup>7</sup> Ibid and [0-140I] p. 869.
- <sup>8</sup> [0-140I] p. 869.
- <sup>9</sup> [0-145] p. 54.
- <sup>10</sup> [0-149] p. 354.
- <sup>11</sup> Ibid and [60-141].
- <sup>12</sup> Ibid, p. 353.
- <sup>13</sup> [0-145] p. 54.
- <sup>14</sup> [0-149] p. 353.
- <sup>15</sup> [0-325b] p. 109.
- <sup>16</sup> [0-149] p. 353.
- <sup>17</sup> Ibid, [60-200], and [60-201].
- <sup>18</sup> [60-201]
- <sup>19</sup> [60-201], [60-202] and [60-203].

## 62,63,64. PLATINUM GROUP

### Overview

Platinum, palladium, iridium, osmium, rhodium, and ruthenium comprise the platinum group metals. Their main characteristics are superior resistance to corrosion and oxidation, high melting points, and usefulness as catalysts.

Platinum, atomic number 78, is a silvery or grayish metal, extremely ductile and malleable. It does not tarnish even at elevated temperatures; it resists attack by all acids even under heat, but is soluble in aqua regia (a mixture of nitric and hydrochloric acids), and although resistant to alkalies, is attacked by fused alkalies.

Palladium, atomic number 46, resembles platinum, but is brighter. It is extremely ductile and malleable approximating gold in this respect.

Iridium, atomic number 77, is similar in color to platinum, but with a slight yellow cast. It is the most corrosion-resistant element known, even resistant to aqua regia.

The abundance in the earth's crust of these elements is at least a magnitude below that of silver; platinum has about 0.005 ppm, palladium 0.01 ppm, and iridium no more than 0.001 ppm.<sup>1</sup>

The platinum deposits occur in primary deposits of two types: the first is dunite rock often associated with chromate, which has native platinum, or iridosmine as the principal constituent. Known locations are in the Ural mountain region of the U.S.S.R. (palladium) and at Onverwacht in the Transvaal, Union of South Africa.

The second type of primary deposit includes nickel-copper sulfides, found in the Bushveld Igneous Complex in the Transvaal, in Southern

Rhodesia, in Ethiopia; further in Norway, in the Sudbury district of Ontario, and Thompson, Manitoba, Canada. The precious metals are obtained as by-products during the extraction of nickel and copper, as well as of iron, cobalt, silver and gold. Placer deposits of economic importance have been found in the Perm districts of the Ural Mountains, in Columbia, Australia, Tasmania, and in Abessynia.<sup>2</sup> U.S. reserves are almost entirely in copper ores with a very small quantity in placers at Goodnews Bay, Alaska. (Another possible area is the Stillwater District in southwest Montana). The copper ores are estimated to average about 1 ounce of platinum-group metals per 6,000 tons of ore. The aggregate reserve of by-product platinum-group metals in gold ores also is relatively small.

Indicated, recoverable reserves of platinum-group metals are approximately as follows: Republic of South Africa and U.S.S.R. both 47% of global estimate of 424 million troy ounces, Canada, 4%; Columbia, 1%; U.S., 7%. In the composition of most sources, platinum dominates, ranging from 40 to 70% (except in the U.S.S.R. where palladium takes its place), the occurrence of iridium and each of the other 3 group-elements is nearly everywhere significantly below 8%.<sup>3</sup>

Gold is recovered as a co-product or by-product with platinum metals from placer deposits. The bulk of the platinum-group metals output is associated with nickel-copper minerals and is separated from the base metals by ore milling, smelting and refining processes. In the Republic of South Africa, nearly all of the platinum metals are produced as the principal components of the ore, with nickel and copper recovered as co-products and gold and chromium as by-products.



The high value of platinum-group metals provides incentive for recovery from the residues from copper and nickel refining and from gold refining. Similarly, their high cost stimulates effort to minimize losses and to recover platinum group metals from all forms of scrap and used equipment, wherever economically feasible. With the exception of electrical contacts, applications of Pt-group metal are not dissipative and the quantity which is recycled each year in the U.S. normally is about two-thirds of that which is mined throughout the world. For this reason, the demand for platinum is not a demand for consumption of a certain amount during a certain period; rather it is demand for a given total stock at any point in time.

Total U.S. supply of platinum in 1973 was 1,586,000 ounces (excluding 754,000 ounces secondary refined for consumers' accounts, "Toll refining"), constituting 67% of the world production.

U.S. refinery production of platinum (palladium) amounted to 128 (53) thousand troy ounces in 1973; the bulk input was from Norway, other contributions came from South Africa and Columbia. Imported were 936 (1200) thousand troy ounces of metal, a little less than half (a quarter) of it from the United Kingdom, but also considerable quantities from Belgium-Luxembourg, U.S.S.R., Japan, South Africa and several other countries. Secondary refined petroleum was no more than 95 (150) thousand troy ounces.

Industry stocks of platinum (palladium) by the end of 1973 were 587 (536) thousand troy ounces, exported were 341 (261) thousand ounces.

The U.S. consumption of platinum, 658,000 ounces, was partitioned as follows: chemicals, 36%; petroleum and refining, 19%; electrical, 18% ;

ceramics and glass, 11%; dental supplies, 4%; jewelry and arts, 3%; other, 9%.

Consumption of 1,012,000 ounces of palladium was distributed over the following categories: electrical, 52%; chemicals, 26%; dental supplies, 13%; jewelry and arts, 2%; other 7%.<sup>4</sup>

The platinum-group elements are used almost entirely in the form of the metal and the alloys.

A 90% platinum-10% rhodium alloy is used in the form of gauze for the catalytic oxidation of ammonia to produce nitric acid, which is used in the production of fertilizers and explosives. This alloy also is used as bushings and for spinnerets in the production of glass fibers, and synthetic fibers such as acrylonitrile and rayon. An alloy containing 75% palladium-25 percent silver is used in refining hydrogen.

In petroleum refining, platinum and palladium are used as catalysts in the production of high-octane gasolines. These catalysts are also used in hydrogenation, dehalogenation, and other reactions in the production of pharmaceuticals, vitamins, and antibiotics.

The applications in electrical uses are equally diverse. Low power contacts in telephone equipment contain palladium. A 75% platinum-25% cobalt alloy is a magnet material with high coercive force which is used in traveling wave tubes for military applications and in electric watches. Platinum and palladium are used in powder form or as electro-deposits in components of electrical circuits.

Their use in jewelry and the decorative arts is well known. Addition of platinum and palladium to gold base alloys increase strength, hardness and wear resistance, raise the melting temperature, and enhance the age hardening of the alloys. These alloys are used extensively in fabricating

mechanical aids and devices for application in prosthodontics and orthodontics. Porcelain-overlay type of dental restoration uses palladium-rich alloys as supports, because palladium does not stain or discolor after it is fired.

Other miscellaneous uses include laboratory ware such as resistance thermometer, thermo-couples, electrodes, crucibles, resistance windings for furnaces which operate above 2000° F. Applications in which a high level of reliability is required, such as gas turbines, jet engines, and air frames use frequently alloys which contain palladium. For cathodic protection of ship hulls, platinum is used to control galvanic corrosion.

Finally, platinum and palladium catalysts may find widespread use in reducing the amount of air pollutants released in automotive exhaust gases.<sup>5</sup>

There are no substitutes for platinum metal where their particular properties are required. Some metal salts can be substituted for catalytic purposes, and other less satisfactory alloys can be used for electrical contact points.

## PROCESS DESCRIPTION

The methods by which platinum metals are obtained from their naturally occurring sources and from scrap precious metals should be discussed under various headings according to the source of the raw material. However, due to the extreme complexity of the procedures involved, a simplified outline will be given below.

The mining of crude platinum in placer deposits furnishes only a small part of total production. The mining and processing techniques for recovering crude platinum from placers are similar to those used for recovering gold.

The bulk of the world production of platinum-group metals is currently mined from lode deposits and is recovered both as principal products and as by-products of the milling, smelting, and refining of nickel and copper minerals.

In the Sudbury district of Canada, sulfide ore is processed by magnetic and flotation techniques to yield concentrates of copper and nickel sulfides. The nickel flotation concentrate is roasted with a flux and melted into a matte which is cast into anodes for electrolytic refining from which the precious metal concentrate is recovered.

The platinum, palladium, and gold in the concentrate are dissolved with aqua regia ( $\text{HNO}_3 + \text{HCl}$ ), leaving a residue containing iridium, osmium, rhodium, and ruthenium. After the gold has been removed from the solution with ferrous sulfate, platinum is precipitated with ammonium chloride. Palladium may be precipitated as a chloride by the addition of excess ammonia and hydrogen chloride. The chlorides of pla-

tinum and palladium are separately reduced to sponge metal which can be compacted and melted to massive metal.

Analogous procedures are used for the separation and reduction of iridium, osmium, rhodium, and ruthenium. Refining steps are needed for each metal to obtain a purity of generally more than 99.9%.

By-product platinum-group metals from gold or copper ores are sometimes refined by electrolysis and by chemical means. Metal recovery in refining is over 99 percent.

Secondary platinum-group metals are recovered by processing scrap material which includes discarded jewelry, used electronic components and spark plugs, sludges and sweeps. In addition, large quantities of worn out or contaminated platinum-metal-bearing materials are refined on toll. About 90% of toll refining operations represent used material, only 10% is metal recovered from virgin material. Recovery from scrap is very efficient, and only a small quantity of these metals is wasted or lost.<sup>6</sup>

NOTE: No optimization section is included for the platinum-group materials. Since the metal form is basic to nearly all applications, it is also the preferred form for stockpiling.

Table 62. PRODUCTION OF IRIIDIUM

(Basis: 1 ton of Ir to federal specification)<sup>a</sup>

Source Material <sup>b</sup>	High Grade Mixture		Upper Medium Grade Mixture	
	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu
1. Refining				
No. 6 oil	1,240 bbl.	7,377,707	1,051 bbl.	6,255,130
gas	563,607 ft <sup>3</sup>	641,025	507,246 ft <sup>3</sup>	576,922
electricity	170,966 kWh	2,243,587	188,061 kWh	2,467,945
chemicals <sup>c</sup>	-	4,031,023	-	4,031,023
TOTAL		14,293,342		13,331,020

Table 63. PRODUCTION OF PALLADIUM

(Basis: 1 ton of Pd to federal specification)<sup>d</sup>

Source Material <sup>b</sup>	High Grade Mixture		Upper Medium Grade Mixture		Lower Medium Grade Mixture		Lower Grade Mixture	
	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu
1. Refining								
No. 6 oil	767 bbl.	4,568,267	803 bbl.	4,779,102	1,093 bbl.	6,500,995	591 bbl.	3,514,051
gas	281,803 ft <sup>3</sup>	320,512	309,983 ft <sup>3</sup>	352,564	479,065 ft <sup>3</sup>	544,871	5,072,456 ft <sup>3</sup>	5,769,222
electricity	85,482 kWh	1,121,793	102,579 kWh	1,346,151	188,061 kWh	2,467,945	1,795,133 kWh	23,557,658
chemicals <sup>c</sup>	-	3,443,081	-	3,443,081	-	3,443,081	-	3,443,081
TOTAL		9,453,653		9,920,905		12,956,892		36,284,012

Table 64. PRODUCTION OF PLATINUM

(Basis: 1 ton of Pt to federal specification)<sup>e</sup>

Source material <sup>b</sup>	High Grade Mixture		Upper Medium Grade Mixture		Lower Medium Grade Mixture		Lower Grade Mixture	
	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu	Amount	10 <sup>3</sup> Btu
1. Refining								
No. 6 oil	767 bbl.	4,568,267	827 bbl.	4,919,672	1,122 bbl.	6,676,697	708 bbl.	4,216,861
gas	281,803 ft <sup>3</sup>	320,512	338,164 ft <sup>3</sup>	384,615	535,426 ft <sup>3</sup>	608,973	5,072,456 ft <sup>3</sup>	5,769,222
electricity	85,482 kWh	1,121,793	102,579 kWh	1,346,151	188,061 kWh	2,467,945	1,709,649 kWh	22,435,865
chemicals <sup>c</sup>	-	3,458,189	-	3,458,189	-	3,458,189	-	3,458,189
TOTAL		9,468,761		10,108,627		13,211,804		35,880,137

NOTES TO TABLES 62, 63, 64

a) See [62-140].

b) Due to the many types of inputs to the process, a low percentage of which is actually of mineral origin, four general categories of source materials are considered.

The complexity and interrelationship of various refining stages do not provide a simple breakdown in consecutive processing steps. Furthermore, transportation energy is negligible compared to the high energy-intensity of the comprehensive refining operation.

(Private communication with Dr. M. I. El Guindy. Engelhard Industries, February-May 1976.)

c) Average major chemicals requirements in pounds per ton product.

Chemical	Production Energy Btu/lb.	Requirement for Ir.		Requirement for Pd.		Requirement for Pt.	
		lb.	10 <sup>3</sup> Btu.	lb.	10 <sup>3</sup> Btu.	lb.	10 <sup>3</sup> Btu.
HCl	4,625	204,166	944,268	175,000	809,373	175,000	809,373
H <sub>2</sub> SO <sub>4</sub>	259	-	-	29,166	7,554	87,500	22,662
HNO <sub>3</sub>	9,047	29,166	263,873	14,583	131,932	14,583	131,932
NaOH	17,980	58,333	1,048,825	14,583	262,202	14,583	262,202
PbO	30,000	11,666	349,992	5,833	174,996	5,833	174,996
NH <sub>4</sub> Cl	25,000	14,583	364,575	14,583	364,575	14,583	364,575
NaClO <sub>3</sub>	3,000	2,916	8,750	2,916	8,750	2,916	8,750
Al-metal	143,242	5,833	835,559	8,750	1,253,338	8,750	1,253,338
Zn-metal	73,778	2,916	215,181	5,833	430,361	5,833	430,361
			<u>4,031,023</u>		<u>3,443,081</u>		<u>3,458,189</u>

d) See [63-140].

e) See [64-140].

FOOTNOTES TO SECTION 62,63,64

<sup>1</sup> [0-122] p. 58.

<sup>2</sup> [62...64-100].

<sup>3</sup> [0-149] p. 656.

<sup>4</sup> [0-145] p. 63,64.

<sup>5</sup> [0-149] p. 661, [62...64-103] p. 834.

<sup>6</sup> [0-149] p. 665-657.



Overview

Titanium, atomic number 22, is the ninth most common element in the earth's crust.<sup>1</sup> It is present in six types of mineral deposits in the earth each having a different titanium concentration: beach sands containing rutile (about 24% Ti O<sub>2</sub>), beach sands containing ilmenite (1.3% Ti O<sub>2</sub>), Ilmenite rock (10-20% Ti O<sub>2</sub>), ferruginous ilmenite rock (10-30% Ti O<sub>2</sub>), high alumina clays (about 5% Ti O<sub>2</sub>) and titanium-rich soil (.2-1.5% Ti O<sub>2</sub>).<sup>2</sup> At present, high-rutile beach sands and high quality ilmenite are the only economical sources for titanium. About 80% of the world's estimated rutile reserves are found in large sand deposits in Australia and Sierra Leone; about 6% is on beaches in Florida, South Carolina, Tennessee and Georgia, with other possible rock deposits in Virginia and Arkansas.<sup>3</sup> Large ilmenite deposits are found in many locations around the world, including 100,000 tons or 20% of estimated world reserves in the U.S.<sup>4</sup> Total free world titanium ore reserves were estimated at 2 billion tons in 1955.<sup>5</sup>

According to the U.S. Bureau of Mines, "The titanium industry is characterized by a moderately high degree of integration from raw materials to semi-finished products. (One producer, Titanium Metals Corp. of America, is fully integrated). Virtually all the world's rutile output was from about a dozen mines along the east coast of Australia, several in the U.S.S.R., and one in Sierra Leone."<sup>6</sup> Similarly, most of the ilmenite in the world comes from a handful of mines, mainly in Canada, Norway and Australia. Domestically, no rutile has been produced since 1968 and ilmenite is produced in only two mines.<sup>7</sup> Sixty two world companies produce titanium metal or "sponge," alloys, and chemical titanium dioxide, over half of them in the U.S.<sup>8</sup> The domestic titanium industry, producing about

half of total metal output and 35% of total titanium pigment output, is dominated by N.L. Industries (estimated \$500 million in titanium sales) and E.I. du Pont de Nemours and Co. (35% of world pigment capacity).<sup>9</sup>

Frequently, both rutile and ilmenite forms of titanium are found in the same ore body, and therefore must be considered as co-products, unless they are processed in exactly the same manner. Several heavy minerals have also been recovered while beneficiating titanium ores, chiefly zircon, vanadium, monazite, garnet and staurolite.<sup>10</sup> In some instances, titanium ores are produced as byproducts of other mining operations.<sup>11</sup>

There is no significant recovery of titanium metal old scrap, partly due to the fact that most metal has only been produced since 1958. About 2/3 of new scrap is reused, partly for deoxidizing steel.<sup>12</sup> Titanium dioxide, used as a chemical, is entirely dissipated.

In 1973, U.S. demand for titanium in chemical form was about 615,000 tons. About 52% of this is used as titanium pigments in paint, with the rest going to the plastics, paper, rubber, ceramics, and other industries.<sup>13</sup> U.S. metal consumption for that year, about 30,000 tons, went almost entirely (85%) to the aerospace industry, which values its properties of lightness, strength, and corrosion resistance.<sup>14</sup>

## PROCESS DESCRIPTION

Reference [0-325b] contains the following complete description of the production of titanium sponge from rutile:<sup>15</sup>

The ore used in the production of titanium sponge is mined by dredging the beach sands of Australia. After beneficiation, the rutile concentrate is shipped to TIMET at Henderson, Nevada, and to chemical manufacturers. The concentrate is chlorinated to produce raw titanium tetrachloride, which is purified and fed into a reactor with magnesium (Kroll process at TIMET) or with sodium (two stage reduction process at RMI, Ashtabula, Ohio, uses purchased titanium tetrachloride). The chloride is reduced in the reactors to titanium sponge. After draining off the liquid magnesium chloride (Kroll process) or sintering the spalt (mixture of titanium sponge and sodium chloride in the two-stage reduction process), the reactor is cooled. Then the massive titanium sponge is removed and reduced to minus 3/8-inch mesh by chipping or crushing. The product is acid-leached to remove the residual magnesium chloride and unreacted magnesium (Kroll process) or to remove the sodium chloride (two-stage, sodium-reduction process). The dried sponge is sealed in metal containers for storage.

Note that for imported titanium sponge, 87% is made by the Kroll process and 13% by sodium reduction; for domestic production the breakdown is 65% and 35%, respectively.<sup>16</sup>

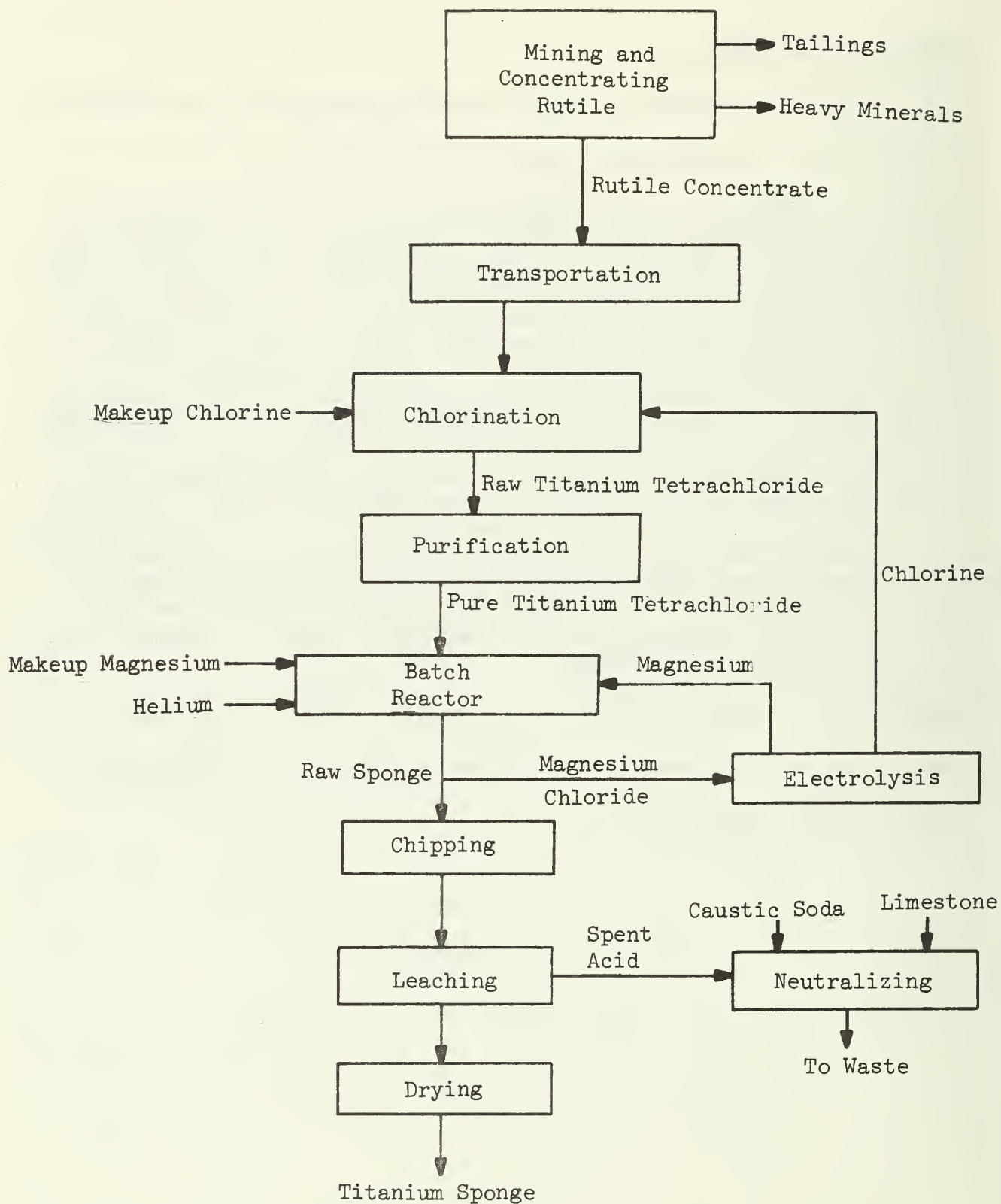


Figure 70,81a. PRODUCTION OF TITANIUM SPONGE

Source: [0-325b]

Table 70,81. PRODUCTION OF TITANIUM<sup>a</sup>

(Basis: 1 ton Titanium Sponge to federal specification)<sup>a</sup>

STAGE	KROLL PROCESS			SODIUM-REDUCTION PROCESS		
	Type	Amount	10 <sup>3</sup> Btu	Type	Amount	10 <sup>3</sup> Btu
1. Mining and Beneficiation of Rutile <sup>b</sup>	electric	292.22 kWh	3,835	electric	292.22 kWh	3,835
	residual fuel oil <sup>e</sup>	15.95 gal.	2,882	residual fuel oil	15.95 gal.	2,882
	transportation <sup>c</sup>	-	4,803	transportation <sup>c</sup>	-	4,803
	<i>Subtotal</i>		<u>11,520</u>			<u>11,520</u>
Total Energy required per ton Concentrated Rutile <sup>d</sup>			5,298	5,298		
2. Chlorination	electric	1,739.0 kWh	22,821	electric	1,720.0 kWh	22,570
	calcined petroleum coke <sup>e</sup>	.60 ton	19,450	calcined petroleum coke <sup>e</sup>	.64 ton	20,750
	materials <sup>f</sup>	-	20,740	materials <sup>l</sup>	-	20,948
	transportation <sup>g</sup>	-	360	transportation <sup>m</sup>	-	290
	<i>Subtotal</i>		<u>63,371</u>			<u>64,558</u>
Cumulative Subtotal			74,891	76,078		
3. Distillation	natural gas <sup>e</sup>	5,200 ft <sup>3</sup>	5,714	natural gas <sup>e</sup>	5,510 ft <sup>3</sup>	6,055
	<i>Subtotal</i>		<u>5,714</u>			<u>6,055</u>
Cumulative Subtotal			80,605	82,133		
4. Batch or Two-Stage Reactor	electric <sup>j</sup>	21,531.4 kWh	282,553	electric	31.0 kWh	407
	natural gas <sup>e</sup>	5,370 ft <sup>3</sup>	5,901	natural gas <sup>e</sup>	5,320.0 ft <sup>3</sup>	5,846
	materials <sup>h</sup>	-	111,350	materials <sup>n</sup>	-	37,740
	transportation <sup>i</sup>	-	343	transportation <sup>o</sup>	-	50
<i>Subtotal</i>		<u>400,147</u>			<u>44,043</u>	
Cumulative Subtotal			480,752	126,176		
5. Chipping and Crushing Sponge	electric	232.7 kWh	3,054	electric	232.7 kWh	3,054
	<i>Subtotal</i>		<u>3,054</u>			<u>3,054</u>
Cumulative Subtotal			483,806	129,230		
6. Leaching Titanium Chips <sup>p</sup>	electric	2.11 kWh	28	electric	23,383 kWh	306,857
	natural gas <sup>e</sup>	2,530 ft <sup>3</sup>	2,780	materials <sup>q</sup>	-	1,594
	materials <sup>k</sup>	-	390	transportation <sup>r</sup>	-	66
<i>Subtotal</i>		<u>3,198</u>			<u>308,517</u>	
Cumulative Subtotal			487,004	437,747		
7. Drying Sponge	natural gas <sup>e</sup>	240 ft <sup>3</sup>	264	electric <sup>s</sup>	6.0 kWh	79
				steam <sup>t</sup>	-	196
<i>Subtotal</i>		<u>264</u>			<u>275</u>	
TOTAL			487,268	438,022		

NOTES TO Table 70,81

- <sup>a</sup> Reference: [0-325b] pp. 175-181. See [70-140] and [81-140] for specifications.
- <sup>b</sup> Note that the production of rutile yields approximately .8 lb. valuable byproduct heavy minerals per pound of Rutile. Therefore, energy figures published represent  $(1.8)^{-1}$  or 55.5 % of total energy use in stage one.
- <sup>c</sup> 16,303 Ton-miles by water @ 250 Btu/TM and 1,086.0 TM by rail @ 670 Btu/TM. Fuel type unspecified.
- <sup>d</sup> About 2.174 tons rutile are required to produce 1 ton titanium sponge.
- <sup>e</sup> Caloric values assumed:   Coke: 32,420,000 Btu/ton.  
                                  Residual fuel oil: 150,000 Btu/gal.  
                                  Natural Gas:    1,000 Btu/ft.<sup>3</sup>
- <sup>f</sup> 196 ft<sup>3</sup> of argon pad @  $.2 \times 10^3$  Btu/ft<sup>3</sup> and 1.0 ton chlorine gas @ 20,700,000 Btu/ton
- <sup>g</sup> 101.0 ton-miles by truck @ 2,400 Btu/TM and 174.0 TM by rail @ 670 Btu/TM.
- <sup>h</sup> 484.0 ft<sup>3</sup> helium @ 640 Btu/ft<sup>3</sup>; 291 ft<sup>3</sup> argon @ 211 Btu/ft<sup>3</sup>;  
.31 ton Magnesium @ 358,000,000 Btu/ton.
- <sup>i</sup> 13.0 TM by truck @ 2400 Btu/TM; 465 TM by rail @ 670 Btu/TM
- <sup>j</sup> includes electric energy for electrolysis of MgCl.
- <sup>k</sup> 34.2 lbs nitric acid @ 7,100 Btu/lb., 9.8 lbs caustic soda @ 15,000 Btu/lb.,  
12.2 lbs limestone @ 52 Btu/lb.
- <sup>l</sup> 1.01 tons chlorine @ 20,700,000 Btu/ton and 194.0 ft<sup>3</sup> argon @ 211 Btu/ft<sup>3</sup>.
- <sup>m</sup> 92 TM by truck @ 2400 Btu/TM and 102 TM by rail @ 670 Btu/TM.
- <sup>n</sup> 102 ft<sup>3</sup> Argon @ 211 Btu/ft<sup>3</sup> and .41 ton sodium @ 92,000,000 Btu/ton.
- <sup>o</sup> 21 ton-miles @ 2400 Btu/TM.
- <sup>p</sup> Includes electricity for sodium and chlorine recovery, neutralizing limestone, and associated transportation.
- <sup>q</sup> .17 tons HCl @ 9,250,000 Btu/ton and .21 tons limestone @ 104,000 Btu/ton.
- <sup>r</sup> 27.5 TM by truck @ 2400 Btu/TM.
- <sup>s</sup> Both centrifugal and vacuum drying.
- <sup>t</sup> 140.0 lb. @ 1400 Btu/lb.

## ENERGY-VERSATILITY CONSIDERATIONS FOR RUTILE/TITANIUM

Figure 70 81b demonstrates several interesting aspects of titanium production. First, it is clear that producing concentrated rutile accounts for very little of the energy embodied in titanium metal. Also, both processes show a single energy-intensive step: batch reaction in the Kroll process and leaching in the sodium-reduction process. Because these steps alone require about 70% to 80% of total production energy, stockpile forms at these stages would provide the optimum energy storage and versatility. This major step occurs in the Kroll process at a much earlier point versatility-wise, so from this standpoint only Kroll-process titanium should be stockpiled. Certainly the titanium should not be kept at any form before chlorinated titanium, since at this point the material can be channeled either to metal or oxide production.

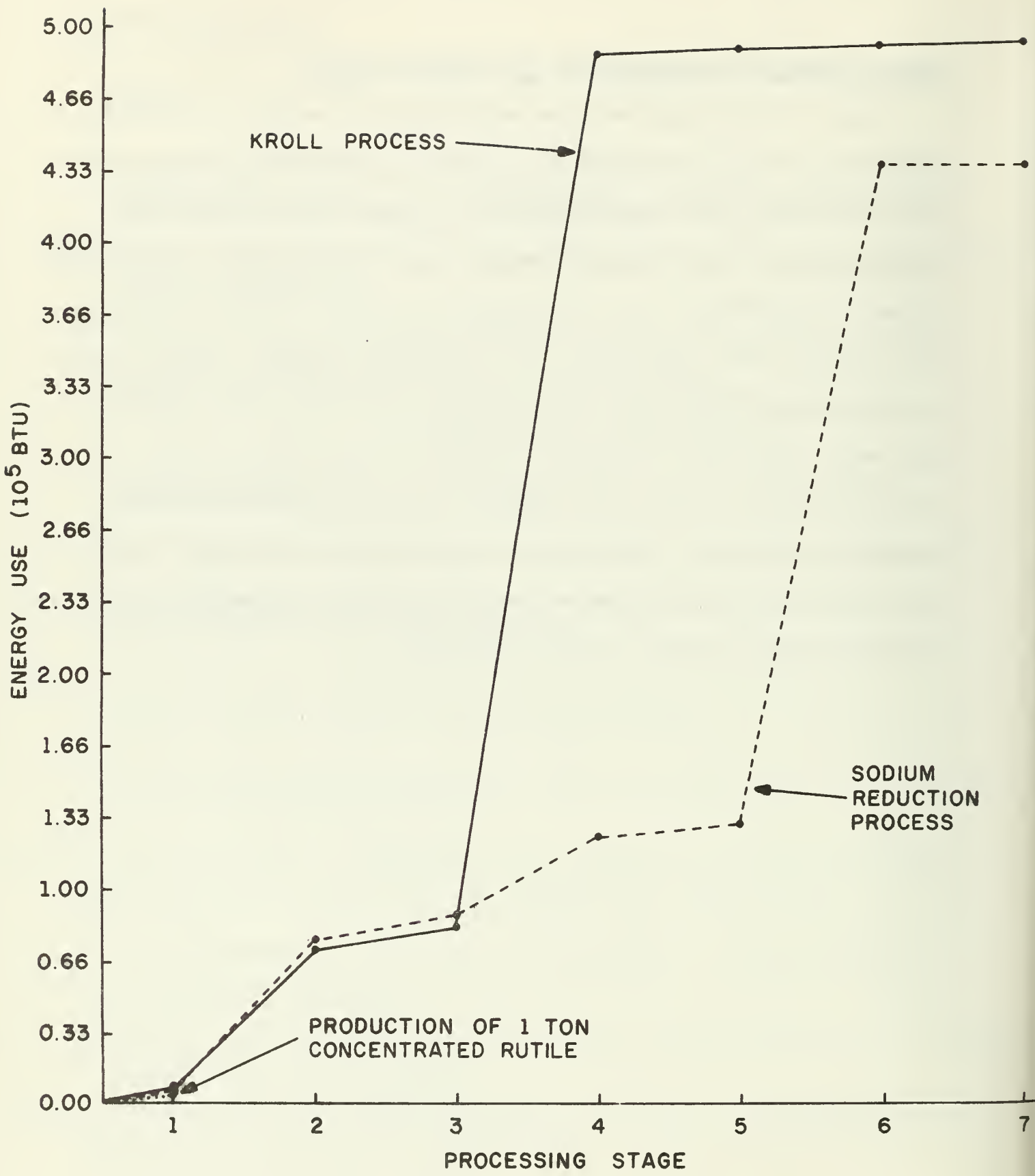


Figure 70,81: Production of Rutile & Titanium



FOOTNOTES TO SECTION 70,81

- <sup>1</sup> [0-300] p. 39.
- <sup>2</sup> Ibid, p. 40.
- <sup>3</sup> [0-149], p. 780.
- <sup>4</sup> Ibid.
- <sup>5</sup> Ibid.
- <sup>6</sup> Ibid, p. 774.
- <sup>7</sup> [0-107].
- <sup>8</sup> [0-149], p. 774.
- <sup>9</sup> Ibid, p. 782.
- <sup>10</sup> Ibid.
- <sup>11</sup> Ibid.
- <sup>12</sup> [0-145], p. 89 and [0-127], p. 78.
- <sup>13</sup> Ibid.
- <sup>14</sup> [0-325b], p. 172.
- <sup>15</sup> Ibid, p. 173.

#### 74. SILVER

Silver is a rare and valuable metal, not only for its uses in coinage, but for its unmatched thermal and electrical characteristics as well. It occurs naturally in very small concentrations in orebodies of copper, lead, zinc, gold and other metals.<sup>1</sup> Most commercial deposits of silver and associated metals in the U.S. are in the Coeur d'Alene district of Idaho, though a few other significant producers are scattered throughout the West. Fifty-five other countries produce significant amounts of silver ore, the major ones being Canada (16%), the U.S.S.R. and Peru (13% each), and Australia (7%).<sup>2</sup>

In the U.S., twenty-one nonferrous metal producers and four silver-only companies produced 84% of total output in 1973.<sup>3</sup> Many of these companies are financially interlocked, many control large amounts of mining in Canada and Australia and many smelt silver concentrates from abroad.<sup>4</sup> In 1973, U.S. mine production was 37.8 million troy ounces, refinery production was 151.275 million ounces, and demand stood at 196.86 million ounces.<sup>5</sup> Most imports (both bullion and concentrates) came from Mexico and Canada, which contains the world's largest silver mine at Kidd Creek Ontario.<sup>6</sup>

Aside from the relatively small use of silver in coins, industrial usage of silver metal continues to grow in both magnitude and diversity. In 1973 the major consuming industries were silverware (23% of demand), photographic chemicals (26%), a variety of electrical conducting parts (13%), electronic components and batteries (9%). Surprisingly large amounts of silver are also used in industrial refrigeration equipment (6%) and home appliances (7%).<sup>7</sup>

Byproducts and coproducts are extremely important to silver production. According to the Bureau of Mines, silver production produced as a byproduct

1.6% of all lead, .5% of all gold, .4% of zinc, and .3% of copper in 1968. For the same year, 29.2% of total silver output came from ores primarily mined for their copper, 17.0% from lead ore, 12.7% from zinc ore and 1.4% from tungsten ore.<sup>9</sup>

In the opinion of General Services Administration, "compared with total consumption, there is little potential for substitution in the use of silver."<sup>10</sup> Small changes can be made by using aluminum, rhodium, tantalum, other coinage metals, and various substitutes for photography not requiring photographic paper.<sup>11</sup>

## PROCESS DESCRIPTION<sup>12</sup>

Silver and its coproduct metals (in this case lead) are mined from deep underground veins described as "unpredictable in size and distribution."<sup>13</sup> After drilling and blasting, the ore is transported in small side-dump cars and hauled to the top of the mine shaft.

Some separation of many impurities and other metals is accomplished in the crushing, grinding and flotation beneficiation. Even so, a typical concentrate shipped to the smelter contains several percent of other metals and less than one percent silver.

At the smelter, the concentrate is unloaded from the rail car or truck carrier, sampled, sorted, proportioned and stored. It is then pelletized in a pugging drum and sintered to remove the sulfur and other impurities. The gas from sintering is used to make sulfuric acid while the "sinter cakes" are conveyed to charging buckets. When a bucket is filled with the correct amounts of sintered ore, coke and other materials, it is hoisted and dumped into the top of a blast furnace. The slag is drained off the furnace into a hydraulic system flowing into the slag stockpiling area and the useful furnace output, or bullion, is tapped with ladles to drossing kettles. It is in these kettles that all silver is removed from the remaining metals. The procedure for doing this, called the Parke process, consists of adding zinc to form a gold/copper/zinc crust and then, separately, a silver/zinc crust. The second crust is skimmed repeatedly into another kettle, cooled, and charged along with some coke into another small furnace heated to 920°C. This produces a low-grade silver-zinc alloy, or sinter, and high quality silver retort metal. The latter is oxidized until it reaches a purity over 99.4% and is then cast into 1,000 oz. bars or 250 oz. anodes.

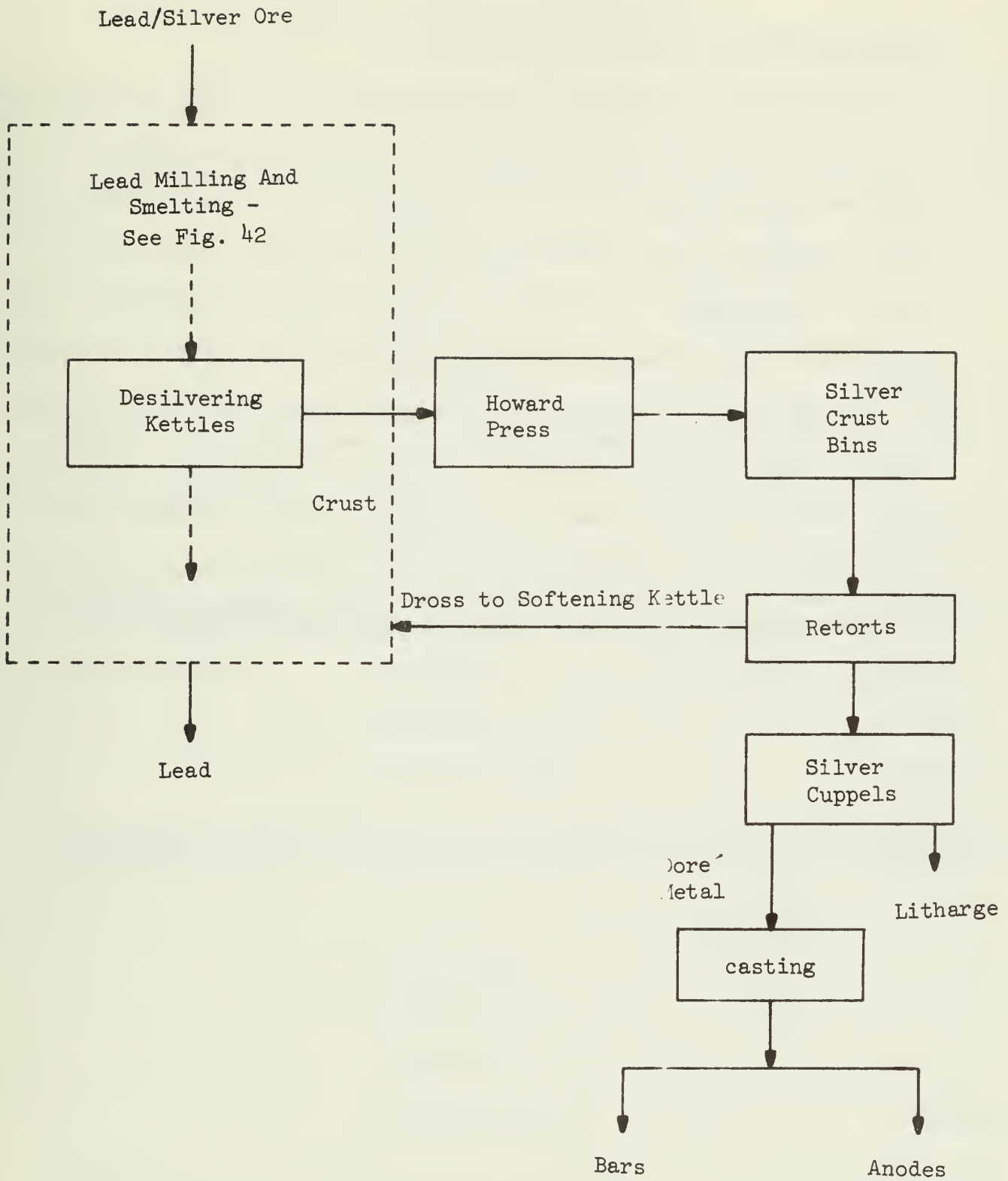


Figure 74a: Production of Silver

A NOTE ON ENERGY ALLOCATION TECHNIQUES<sup>14</sup>

In the case of silver, it is not uncommon to consider it entirely as a by-product, even though its economic value is extremely high. This is the case with several producers.<sup>15</sup> Researchers at Batelle/Columbus Labs. take a somewhat related approach by considering silver to be the major product (even though it is present in smaller quantities than the other metals) and considering all other joint products as negligible by-products.

Though the usual practice in this report has been to use an allocation scheme based on the partial values of joint product outputs, the form in which data are available makes this approach impossible in this case. Accordingly, we use a methodology identical to Batelle's and assume that the joint product (lead) is produced energy-free at the end of the delivery process.

Table 74. PRODUCTION OF SILVER<sup>a</sup>

(Basis: 1 ton refined silver to federal specifications)

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining	electric	145,198 kWh	1,905,447
	diesel oil	2,912 gal.	485,069
	gasoline	233 gal.	35,046
	materials <sup>c</sup>	-	<u>328,321</u>
<i>Subtotal</i>			<u>2,753,883</u>
2. Crushing, Grinding, Beneficiation	electric	144,352 kWh	1,894,349
	materials <sup>d</sup>	-	<u>216,819</u>
<i>Subtotal</i>			<u>2,111,168</u>
<i>Cumulative Subtotal</i>			<u>4,865,051</u>
3. Ore Beneficiation	electric	55,500 kWh	728,329
	materials <sup>e</sup>	-	39,986
	transportation <sup>f</sup>	-	<u>179,550</u>
<i>Subtotal</i>			<u>947,865</u>
<i>Cumulative Subtotal</i>			<u>5,812,916</u>
4. Sintering	electric	26,322 kWh	345,436
	natural gas	24,568 ft <sup>3</sup>	368,795
	metallurgical coke <sup>g</sup>	10 ton	240,964
	materials <sup>h</sup>	-	46,435
	transportation <sup>i</sup>	-	<u>6,552</u>
<i>Subtotal</i>			<u>1,008,182</u>
<i>Cumulative Subtotal</i>			<u>6,821,098</u>
5. Blast Furnace	electric	22,464 kWh	294,800
	natural gas	16,285 ft <sup>3</sup>	132,131
	petroleum coke <sup>g</sup>	121.57 ton	3,632,486
	transportation	60,786 TM	<u>40,726</u>
<i>Subtotal</i>			<u>4,100,143</u>
<i>Cumulative Subtotal</i>			<u>10,921,241</u>

Table 74. PRODUCTION OF SILVER<sup>a</sup> (continued)

(Basis: 1 ton refined silver to federal specifications)

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
6. Drossing	electric	58,106 kWh	762,526
	natural gas	1,051,426 ft <sup>3</sup>	194,697
	diesel oil	211.43 gal.	35,214
	metallurgical coke <sup>g</sup>	3.17 ton	76,420
	materials <sup>j</sup>	-	102,859
	energy credit <sup>k</sup>	-	320,261
	transportation	2,114 TM	1,417
<i>Subtotal</i>			1,852,872
<i>Cumulative Subtotal</i>			12,774,113
7. Softening	electric	1,374 kWh	18,035
	natural gas	398,542 ft <sup>3</sup>	452,849
<i>Subtotal</i>			470,884
<i>Cumulative Subtotal</i>			13,244,997
8. Desilvering and Dezincing	electric	11,100 kWh	145,666
	natural gas	475,713 ft <sup>3</sup>	540,535
	materials <sup>l</sup>	-	192,399
<i>Subtotal</i>			878,600
<i>Cumulative Subtotal</i>			14,123,597
9. Dezincing <sup>m</sup>	electricity	2,520 kWh	33,070
<i>Subtotal</i>			33,070
<i>Cumulative Subtotal</i>			14,156,667
10. Retort Metal Purification <sup>p</sup>	bunker c fuel oil <sup>n</sup>	489.6 gal.	95,914
	materials <sup>o</sup>	-	205,795
<i>Subtotal</i>			301,709
<i>TOTAL</i>			14,458,376



NOTES TO Table 74

<sup>a</sup> Based on lead production data from [0-325a] p. 107-108. Allocated to silver only (see note on allocation in text) based on the following [13-121] p. 7:

Avg. assay of concentrate:	lead	37%
	silver	.07%

(528.57 tons lead for every ton silver)

See note a, Table 42.

<sup>b</sup> See [74-140].

<sup>c</sup> 7,389 lb. steel @ 17,500 Btu/lb. and 6,634 lb. explosives @ 30,000 Btu/lb.

<sup>d</sup> 12,390 lb. steel @ 17,500 Btu/lb.

<sup>e</sup> 771.71 lb. organic chemicals @ 20,000 Btu/lb. and 4,910.42 lb. inorganic chemicals @ 5,000 Btu/lb.

<sup>f</sup> 267,985 ton-miles by rail @ 670 Btu/TM.

<sup>g</sup> Caloric value of metallurgical coke "breeze" assumed to be 20,000,000 Btu/ton and petroleum coke, 24,800,000 Btu/ton [0-206] Table B1, delivery efficiency is 83% [0-210] and [0-201].

<sup>h</sup> 63.42 ton limestone @ 240,000 Btu/ton; 37 ton iron ore @ 715,000 Btu/ton; 47.57 ton silica sand @ 100,000 Btu/ton.

<sup>i</sup> 9,779 ton-miles @ 670 Btu/TM.

<sup>j</sup> 1.05 ton sulfur @ 5,800,000 Btu/ton and 5.28 ton soda ash @ 18,300,000 Btu/ton.

<sup>k</sup> Energy credit for by-product sulfuric acid production of 385.86 ton @ 830,000 Btu/ton.

<sup>l</sup> 2.96 ton zinc spelter @ 65 million Btu/ton.

<sup>m</sup> Coke use neglected: Source [13/74-300].

<sup>n</sup> caloric value assumed to be 162,548 Btu/gal.

<sup>o</sup> Zinc used in retort dross bath: 3.42 ton @ 60.174 million Btu/ton [0-325a] p. 170.

<sup>p</sup> Source: [13/74-300].

## ENERGY-VERSATILITY CONSIDERATIONS FOR SILVER

The choice of an optimum form for stockpiling silver is made difficult by the by-product nature of silver smelting and refining. A very large portion of the energy expended to manufacture silver occurs in stages which are also treating at least one other metal and thus must be split according to some allocation technique. The stages pertaining only to silver metal use only about 8% of total allocated energy use so the choice among them is not critical. It may be based on versatility, though this is probably also insignificant, or on other parameters such as strategic importance, industry capacity, etc.

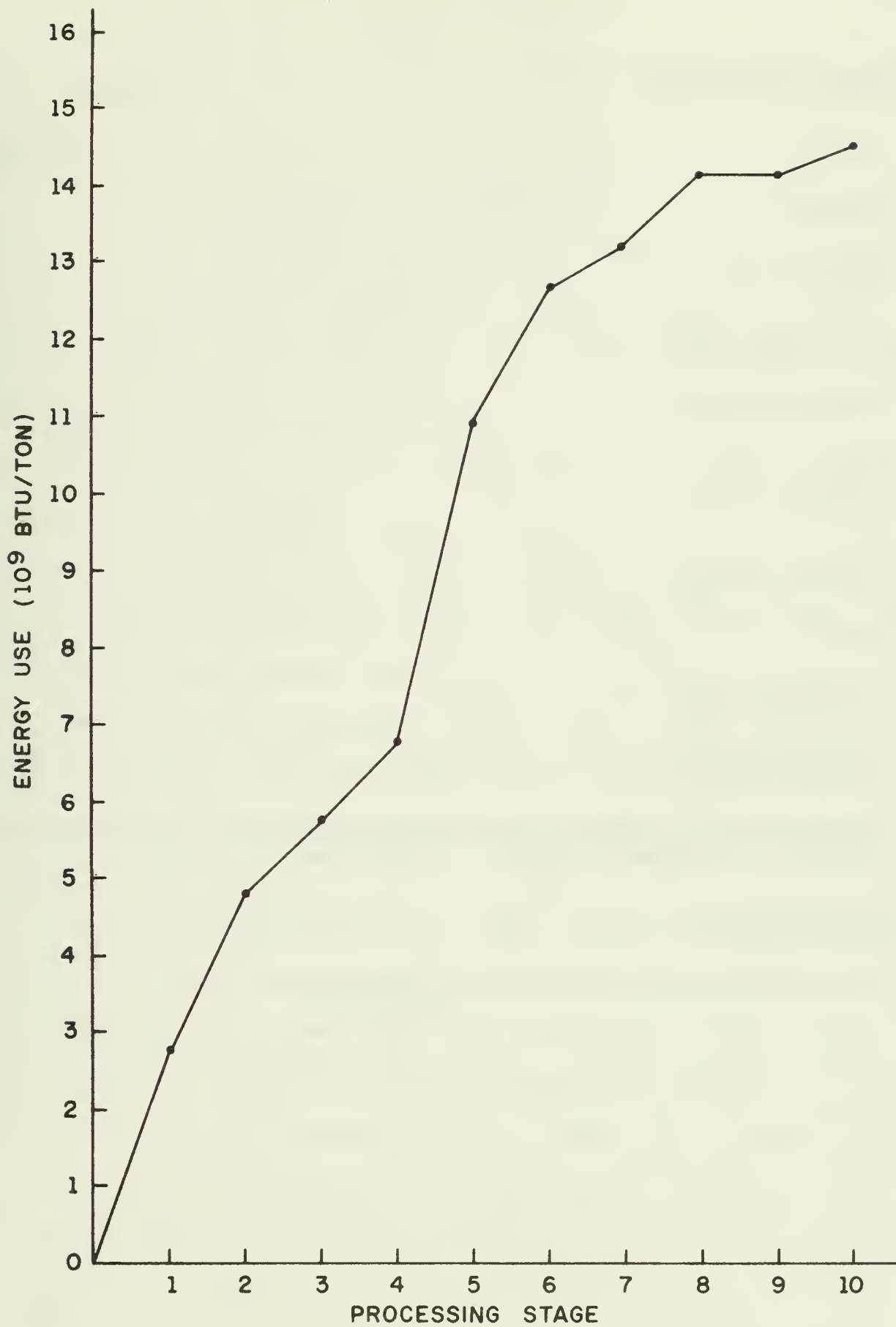


Figure 74b: Production of Silver

NOTES TO SECTION 74.

<sup>1</sup> [0-122] p. 69.

<sup>2</sup> [0-140I] p. 1138.

<sup>3</sup> Ibid, p. 1124.

<sup>4</sup> Ibid and [0-149] p. 724.

<sup>5</sup> Ibid and [0-145] p. 77.

<sup>6</sup> Ibid.

<sup>7</sup> [0-145] p. 77.

<sup>8</sup> [0-149] p. 728.

<sup>9</sup> Ibid.

<sup>10</sup> [0-122] p. 69.

<sup>11</sup> [0-149] p. 729

<sup>12</sup> Applies to Hecla Mining Co. Mines and Brunswick Mining and Smelting Division, Smelters and Refiners. Sources: [13-141] and [13/74-121].

<sup>13</sup> [13-121] p. 4.

<sup>14</sup> Also see process description for 4. Antimony.

## 79. THORIUM

### Overview

Thorium, atomic number 90, is a mildly radioactive silver to grayish material with a rather high melting point of 3300° F. It is widely distributed in nature and is usually associated with uranium or the rare earth elements. Its geochemical abundance is 12 ppm, comparable to that of lead and molybdenum and about three times that of uranium.

The only two true thorium minerals, thorianite and thorite are scarce, however. The major source of the oxide and metal is monazite, essentially a phosphate of cerium and lanthanum, containing from less than 1 percent to as much as 18 percent  $\text{ThO}_2$ . There exist at least 15 more thorium-bearing minerals with resource potential.

World deposits (measured and inferred) occur in India (Travancore, Ceylon), 31%; U.S., 34%; Canada (Blind River, Ontario), 13%; U.S.S.R., 11%; Central and South Africa, 6%; Brazil, Malaysia, Greenland, others, 5%.<sup>1</sup>

Important domestic deposits are found in Florida (Jacksonville Beach), and South Carolina, where monazite was recovered as a by-product of ilmenite; further in Idaho (Lemhi County) and Montana, where it occurs with euxenite. In California (Mountain Pass, San Bernardino), Colorado (Powderhorn district, Gunnison, and Custer County, Wet Mountains), Wyoming (Balá Mountain), Georgia, North Carolina (Henderson County), New Mexico (Gallinas Mountains) and several other states, minor quantities of varying composition and concentration have been identified and/or mined.<sup>2,3</sup>

Monazite is generally recovered from river and beach sands by placer mining methods. Conventional milling and gravity practice yield a

wet black sand concentrate from which other erosion-resistant, heavy minerals such as magnetite, ilmenite, rutile, zircon, garnet have to be removed. To separate thorium from a predominant percentage of rare earth elements and phosphate, a complex series of chemical processing methods is applied. The result is a very pure thorium nitrate, feed material for the production of thorium oxide and metal. The existence of only one plant, presently operating in the U.S. could be determined. As stated above, monazite, the principal source of thorium, is a by-product in the mining of titanium, tin and zirconium minerals. In thorite and thorianite ores, thorium and uranium are often co-products; many uranium ores contain thorium as a by-product.

In 1973, the world production was no more than 1000 tons. One hundred-and-fifty tons were imported whereas no figure for the U.S. production could be disclosed. In previous years, large quantities of monazite (up to two-thirds of the new additions to domestic supplies) were imported, mainly from Australia and Malaysia, because it is the cheapest source of several of the rare earth elements and yttrium.

The U.S. demand of 90 tons in 1973 was distributed over the following categories: nuclear reactors, 55%; lamps and lighting, 22%; aerospace, 5.5%; refractories, 5.5%; other 12%.

The largest use of a thorium compound is thorium nitrate, which is of importance in the manufacture of incandescent gas mantles. Mantles are made from cotton or synthetic fibers woven into cloth and impregnated with a 25 to 50% thorium nitrate solution containing 1 to 2% of cerium nitrate, dried and denitrated with ammonia, hydrofluoric acid or alkali fluoride solution. In kerosene, gasoline and LPG lamps, when the

cloth burns away, a skeleton of thoria ( $\text{ThO}_2$ ) remains, which, when heated, gives a brilliant white light.

Thorium oxide is used in the production of dispersion hardening of metal, such as stainless steel, nickel and tungsten and in specialized refractories, and catalysts for the petroleum and chemical industries.

Thorium metal is used in thorium-magnesium master alloy. Magnesium alloys (with a low percentage of thorium and doped with small amounts of zirconium) derived from it, are suitable for high speed aircraft and missiles, because of their light weight and high-temperature strength.

Thorium metal, dioxide, fluoride and carbide have a potential for the nuclear industry. The development of successful thorium thermal and breeder reactors would require large tonnages of thorium in future years.

For most non-energy uses of thorium and its compounds, especially in alloys and gas mantles, there are no suitable substitutes. As getters in electronic tubes, titanium and zirconium are superior to thorium. Beryllia and yttria can often replace thoria as a refractory above  $2000^\circ \text{C}$ . Uranium breeder reactors are potentially competitive with thorium breeder reactors.<sup>6</sup>

## PROCESS DESCRIPTION

The principal method used to recover thorium from monazite comprises decomposing finely ground concentrate with hot, concentrated sulfuric acid and converting the thorium and the rare-earth elements to sulfates. (Another monazite opening process developed recently employs caustic soda digestion; it is preferred if the monazite contains recoverable uranium and is relatively free of gangue minerals. The acid process makes the recovery of uranium more difficult). The mixture is cooled and minerals insoluble in concentrated sulfuric acid, such as quartz, rutile, and zircon, remain as a residue after the mass is treated with water. The filtered solution containing the thorium and rare-earth metals is neutralized, and the thorium is precipitated as a hydrate with ammonium hydroxide or magnesium hydroxide. The thorium precipitate is purified further by fractional precipitations or by nitric acid digestion followed by a solvent extraction process for the recovery of thorium.

In solvent extraction, an efficient method for separating thorium from the rare earth elements, the thorium-bearing aqueous solution is brought into contact with an organic solvent, such as kerosene, which is immiscible with water. The solvent contains an organic compound, like TBP (tributyl phosphate), which forms a complex compound with thorium. The thorium complex dissolves in the solvent phase leaving the impurities in the aqueous phase. After the two liquids are separated, the thorium is stripped from the solvent with a dilute nitric acid solution which is then passed countercurrently through the solvent, stripping the thorium into a new aqueous phase. The thorium nitrate product is either crystallized or precipitated as an oxalate for further



processing.<sup>5,6,7</sup> The oxalate, after filtering and drying, undergoes calcination, at which point thorium occurs in the form of an oxide.

Subsequent hydrofluorination yields anhydrous thorium tetrafluoride, which can be reduced to massive thorium metal with metallic calcium if a booster of zinc is used.

NOTE: No optimization section is included for this material. Only one single step consumes significant energy, thorium-separation. Thorium hydroxide would therefore be a good candidate for stockpiling. Since there is very little versatility decrease during the next two processing steps of purification and calcining, stockpiling of both thorium nitrate and thorium oxide should be considered.

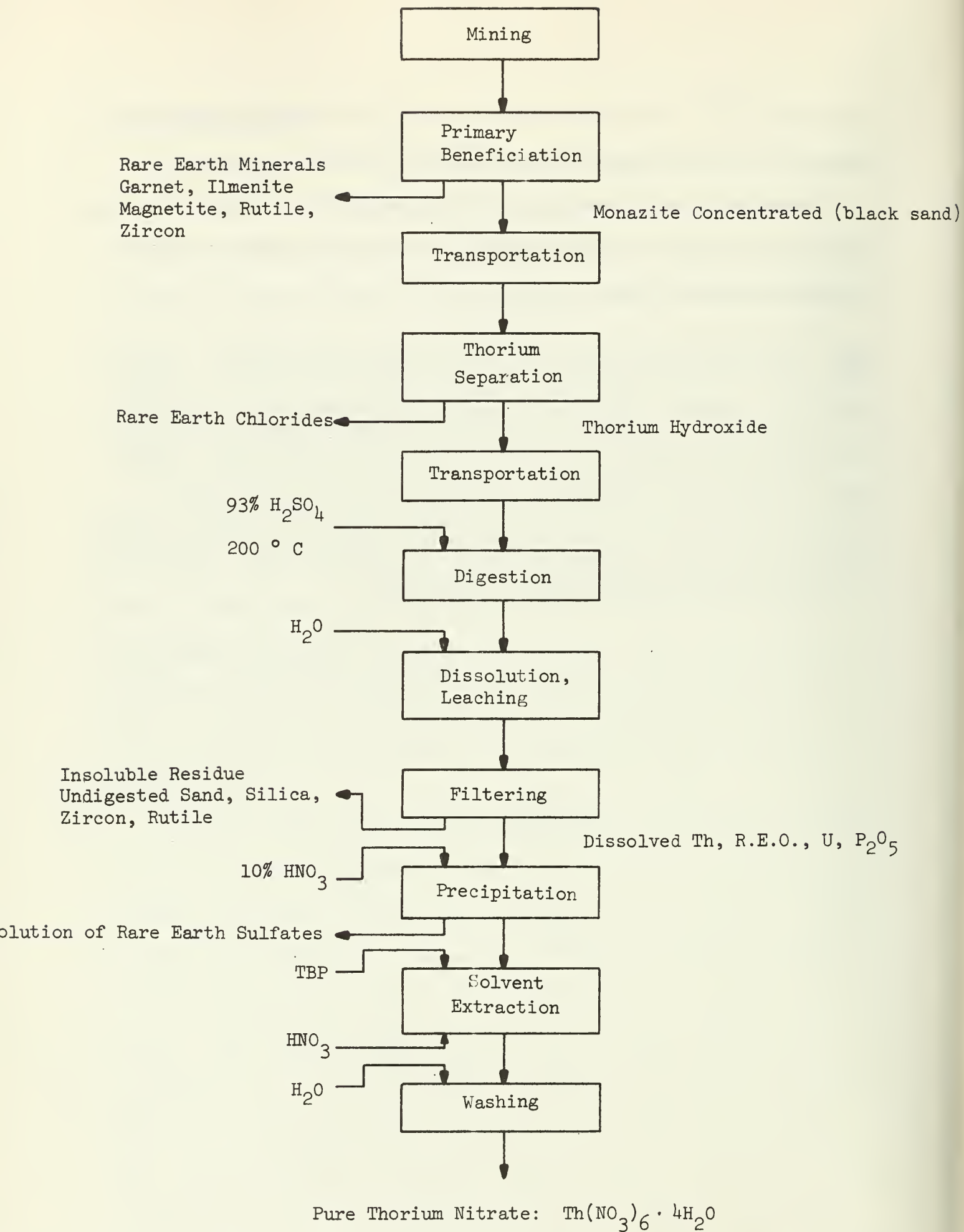


Figure 79: Production of Thorium Nitrate

TABLE 79. PRODUCTION OF THORIUM NITRATE

(Basis: One ton of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  to federal specification)<sup>a</sup>

STAGE	TYPE	AMOUNT	$10^3$ Btu
1. Mining and Beneficiation <sup>b</sup>	Monazite Sand Concentrate	100 net ton	146,440
	Transportation	---	230,375
	Subtotal		376,815
2. Thorium Separation <sup>d</sup>	Fuel Oil	1,660 gal	277,381
	Materials <sup>e</sup>	---	399,156
	Subtotal		676,537
Cumulative Subtotal			1,053,352
3. Thorium-Purification	Diesel Fuel No. 2	428 gal	71,517
	Electricity	285 kWh	3,740
	Materials <sup>f</sup>	---	44,574
	Transportation <sup>g</sup>	900 TM	603
Subtotal			120,434
Total			1,173,786

NOTES TO Table 79.

<sup>a</sup> See [79-140]

<sup>b</sup> According to one producer, raw ore is upgraded from 1% to 95% monazite. The concentrate contains 55% rare earth oxides and 5% thorium-oxide. Energy cost of mining and concentrating based on data for mining of similar materials (ilmenite from beach sands). See [0-300] p. 45.

$$\frac{1.4}{90} \times 95 \times 7551 = 11,159 \text{ kWh;}$$

<sup>c</sup> Seventy-five ton over 10,500 miles by ship @ 250 Btu/TM, and 75 + 25 ton over 500 miles by rail @ 670 Btu/TM.

<sup>d</sup> Data provided by two chemical companies in a central state. Thorium-hydroxide content of monazite sand: about 20%.

<sup>e</sup> 22.2 ton of 50% NaOH @ 35,960,000 Btu/ton.

<sup>f</sup> 7.675 ton of 93% sulfuric acid @ 518,000 Btu/ton,  
6.25 ton of 40% nitric acid @ 18,094,000 Btu/ton,  
.5 ton of TBP @ 36,520,000 Btu/ton.

<sup>g</sup> 180 miles @ 670 Btu/TM.

FOOTNOTES TO SECTION 79

<sup>1</sup> [0-149] p. 207.

<sup>2</sup> See [79-100].

<sup>3</sup> [79-141] p. 9.

<sup>4</sup> [0-122] p. 75.

<sup>5</sup> [79-141] p. 8.

<sup>6</sup> [79-142] p. 45.

<sup>7</sup> [79-104] p. 62, 146.

## 80. TIN

### Overview

Tin, atomic number 50, is one of the oldest metals used by man, as in for example the "Bronze Age" of ancient man. The only ore of any commercial significance is cassiterite or tin dioxide. This is found in two sorts of deposits: surface and underwater tin-placer mines and underground eluvial tin deposits.<sup>1</sup> Most of the world's tin is mined in placer deposits in Malaysia (32% of 1973 world mine output), Thailand, China and Indonesia (all 9%). Important underground deposits occur in the U.S.S.R. (12%) and Bolivia (13%).<sup>2</sup> No commercial tin is mined in the U.S., though experimental amounts are being produced from placer mines in Arizona.<sup>3</sup>

A variety of countries smelt tin, including several which do not produce any ore. The largest smelting country, producing 37% of the world metal supply, is Malaysia. It is followed by the U.S.S.R. (12%), England (10%) and Thailand and China (9% each). Bolivia and Indonesia, though very large producers, smelt only small amounts. The U.S. contains only one tin smelter in Texas City, Texas, which produced 2% of world tin in 1973.<sup>4</sup>

In contrast to its small production, the United States consumed 65,849 long tons of tin in 1973 or 28% of total metal production, of which 45,845 long tons or 70% was imported.<sup>5</sup> About 35% of this is used in producing tin-plate used for metal food cans, kitchen utensils, bottle caps, etc.<sup>6</sup> Another important use is in solder, which is used for car body production and plumbing and heating parts.<sup>7</sup> Much tin is alloyed into bronze, a 10:1 copper-tin alloy used in transportation equipment, industrial machinery, and some weaponry.<sup>8</sup>

Placer tin deposits usually contain insignificant amounts of valuable by-products. Lode deposits often contain other metals such as antimony, arsenic, bismuth, columbium, copper, iron, lead, silver, tantalum, tungsten or zinc. Occasionally, one or more of these is recovered.<sup>9</sup> Secondary production is extremely important to the domestic tin industry and is discussed later in this section.

## PROCESS DESCRIPTION<sup>10</sup>

Tin ore is mined in either open-pit placer mines, mainly in Asia, or in deep underground mines in South America. The underground mines are 3,000 - 4,000 ft. deep and employ crosscut mining techniques similar to those used in the Western United States. On the first day shift, about 6 feet of additional tunnel is drilled and blasted by a four-man team. After the air is allowed to clear for twelve hours, another shift moves in and loads the ore onto underground railways.

At the mine head, the ore is crushed, gravity concentrated, and beneficiated by flotation techniques. Losses in these processes amount to 50% of the total embodied tin. Concentrates of twenty to fifty percent tin are shipped directly to smelters in 50 kg. sacks.

At the smelter, the concentrates are crushed and roasted in Herreshoff furnaces if necessary. All are eventually sent to pressure digesters which use hydrochloric acid and steam to remove most of the iron, lead, silver, copper and bismuth from the ore.

After drying and sampling, ore is sent to a two-stage reverberatory furnace smelting operation. This complex operation combines coal, flue dust ore, limestone, and in some cases slag from previous stages to iteratively produce a rich hardhead alloy assaying about 80% tin and several discarded slags.

From smelting, the metal is cast into 400 lb. anodes and inserted by crane into electrolytic cells. With the proper temperature and electrolyte materials, extremely pure tin is deposited on 200 lb. cathodes. Every few days the cathodes are removed, remelted in a cathode hold kettle, and cast into 85 lb. pigs of Grade A tin.





Table 80. PRODUCTION OF TIN

(Basis: 1 ton of electrolytic tin pig to federal specifications)<sup>b</sup>

STAGE	TYPE	AMOUNT	10 <sup>3</sup> Btu
1. Mining <sup>c,d</sup>	electric	33,200 kWh	435,686
	materials <sup>o</sup>	-	6,804
<i>Subtotal</i>			442,490
2. Crushing and Grinding <sup>c,d</sup>	electricity <sup>p</sup>	1,204 kWh	15,800
	<i>Subtotal</i>		
<i>Cumulative Subtotal</i>			458,290
3. Flotation Beneficiation	electric <sup>q</sup>	27,790 kWh	364,695
	materials <sup>r</sup>	-	37,600
	transportation <sup>s</sup>	-	2,741
<i>Subtotal</i>			405,036
<i>Cumulative Subtotal</i>			863,326
4. Roasting	natural gas <sup>e</sup>	64,020 ft <sup>3</sup>	72,814
	<i>Subtotal</i>		
<i>Cumulative Subtotal</i>			936,140
5. Acid Leaching	electric <sup>f</sup>	31.2 kWh	409
	natural gas <sup>g</sup>	10,867 ft <sup>3</sup>	12,360
	materials <sup>i</sup>	-	12
<i>Subtotal</i>			12,781
<i>Cumulative Subtotal</i>			948,921
6. Two Stage Smelting	electric <sup>n</sup>	1,207.4 kWh	15,845
	natural gas <sup>n</sup>	22,914 ft <sup>3</sup>	26,062
	coal <sup>h</sup>	.7457 ton	18,492
	materials <sup>j</sup>	-	351
<i>Subtotal</i>			61,200
<i>Cumulative Subtotal</i>			1,010,121
7. Acid Leaching and Precipitation <sup>k</sup>	materials <sup>i</sup>	-	32,605
	<i>Subtotal</i>		
<i>Cumulative Subtotal</i>			1,042,726
8. Electrolysis	electric	194.17 kWh	2,548
	materials <sup>l</sup>	-	505
<i>Subtotal</i>			3,053
<i>Cumulative Subtotal</i>			1,045,779
9. Cathode Melting and Casting	natural gas <sup>m</sup>	10,867 ft <sup>3</sup>	12,360
	<i>Subtotal</i>		
<i>TOTAL</i>			1,058,139

NOTES TO Table 80.

<sup>a</sup> Source: [80-120] unless noted.

<sup>b</sup> See [80-140]; grades produced are approximately equivalent to grade AA pig tin.

<sup>c</sup> Figures given are for 200 tons ore. Bolivian tin mines produce ore containing about 1% tin. This is beneficiated to a concentration of 50% with a recovery rate of only 50%. Thus 200 tons of ore produce one ton tin [80-200].

<sup>d</sup> The electrolytic tin plant receives its ores from the large underground Bolivian mines owned by the Bolivian government (OMIBOL) ([80-120] and [80-200]). This mining is similar to other nonferrous metal mining ([0-149] p. 761 and [80-200]) and so figures for copper, silver, antimony underground mining and beneficiation are used. The copper, silver, antimony is present in the ore in concentrations of about 1% and is also processed to a concentrate assaying about 50% metal. Source of figures for this part of the table: Table 4 of this report.

<sup>e</sup> According to [80-120], 51,818.2 ft<sup>3</sup> of gas are required per ton of concentrate roasted. According to [80-200], about one-third of all concentrates require roasting. Since the concentrate averages 28.43% tin by weight and total plant recovery is 94.9% of input tin, one ton of tin requires:

$$(.333)(.2843)^{-1} (.949)^{-1} 51,818.2 \text{ cubic feet of gas.}$$

<sup>f</sup> This is consumed by a 15 h.p. motor running for 4 hours [80-120]. Such a motor consumes 32.5 A @ 240 V. continuously and this requires 31.2 kWh over four hours.

<sup>g</sup> For drying and steam production; estimated to be 10% of total plant gas use.

<sup>h</sup> Caloric value of coal: 24.8 million Btu/ton.

<sup>i</sup> In the leaching stage, approximately 1500 gal HCl are required per 20,000 lb concentrate or 3.13 tons recovered metal. This converts to a value of:

$$\begin{aligned} & 479.3 \text{ gal. HCl/ton tin produced} \times 1.18 \text{ g/cc ([0-100] p. 0-223)} \\ & \times 3,785.41 \text{ cc/gal ([0-100] p. F223)} \times (.0022 \text{ lb/g)} \\ & = 4,710 \text{ lb. HCl/ton tin} = 2.35 \text{ ton HCl/ton tin.} \end{aligned}$$

Since total plant use of HCl is 3.02 ton HCl/ton tin, by difference HCl use in this stage is .673 ton/ton @ 48.43 million Btu/ton. Also used in this stage is 1.36 lb. caustic soda/ton tin @ 18.3 million Btu/ton.

Energy cost of hydrochloric acid is neglected because it continues on with the leach residue to a scrap iron concentration process which (when chlorine and iron borings are added) produces several valuable by-products. Thus it is assumed here that the value of the by-products cancel the energy inputs.

<sup>j</sup> .443 tons limestone/ton tin @ 104,000 Btu/ton [0-325b] p. 180, 80.45 lb. sodium carbonate @ 43,090 Btu/lb. and .455 tons sulfur @ 3498 Btu/lb [0-321] p. 99. Energy required to manufacture furnace silica alumina bricks neglected.

<sup>k</sup> Energy use neglected for: solution pumping, cathode steel use, and steam heat exchanger.

<sup>l</sup> Material use is as follows for this stage:

<u>CHEMICAL</u>	<u>AMOUNT [80-120]</u>	<u>ENERGY INTENSITY [0-325b] p.107</u>
Cresylic acid*, #	6.54 lb/ton	20,000 Btu/lb.
Sulfuric acid <sup>†</sup>	.022 ton/ton	830,000 Btu/ton
Phenosulfonic acid <sup>†</sup>	.022 ton/ton	5,000 Btu/lb.
Alolin (animal glue)*	.003 ton/ton	20,000 Btu/lb.

\*organic    †inorganic    # converted to weight using values in note i.

Aluminum ingots used in alternative pyrolytic refining included here:

1.25 lb. Aluminum @ 142,321 Btu/lb. (see Section 1.)

<sup>m</sup> Includes reduction furnace gas use estimated to be 10% of total plant gas use.

<sup>n</sup> Allocated by difference from total plant use.

<sup>o</sup> 226.8 lb. dynamite @ 30,000 Btu/lb. [0-325b] p. 37.

<sup>p</sup> See note e, Table 4.

<sup>q</sup> See note f, Table 4.

<sup>r</sup> See note g, Table 4.

<sup>s</sup> Transportation from Bolivia is about 5,000 miles by ship (Rio de Janeiro-Houston), ([80-201]) @ 250 Btu/TM ([0-325a] Table A1) and 3 miles by truck [(80-120)] @ 2760 Btu/TM ([0-208]). Transportation inside Bolivia is estimated to be 200 miles by rail @ 560 Btu/TM ([0-208]). Two tons of 50% concentrate are transported.

## SECONDARY TIN

### Overview

Secondary tin accounted for a full 20,000 tons or 30% of U.S. demand in 1973.<sup>11</sup> Most of this came from recycling brass and bronze from alloy form to alloy. The majority of this recycling is done by eleven companies in the Chicago area. About 5,000 tons is recycled as solder and drosses and the rest is from reclaimed tinplate.<sup>12</sup> The latter operation is performed commercially by two U.S. companies who use either sorted municipal refuse or industrial tinplate wastes.<sup>13</sup> Oddly enough, advances in tin technology have made it possible to use less and less primary tin in most items -- thereby decreasing the amount of tin available for recycle from a third (of total output) to a fifth.<sup>14</sup>

When tinplate is recycled, both steel and tin are produced in usable forms.<sup>15</sup> The tin is purer than that produced at many primary tin smelters.<sup>16</sup> The steel is somewhat brittle, though it can be used for cast iron and certain other steel industry functions.<sup>17</sup> Proposals have been made to increase tin recycling both from tinplate and from junk automobiles.<sup>18</sup>

### PROCESS DESCRIPTION<sup>19</sup>

Scrap tinplate is collected either from large industrial producers such as can companies (new scrap) or from municipal reclamation systems such as the one operated by Hamilton Steel in Ontario, Canada. The scrap is transported to the recycler by truck or rail and unloaded by crane into storage or the first detinning stage. There are three major detinning processes, but the most common one is the alkali-electrolytic method. This consists of adding caustic soda and an oxidizing agent (a form of sodium nitrate) to a tank of scrap. The tin dissolves into sodium stannate

and is pumped into the electrolytic section while the remaining steel is crushed, baled, and ready for shipment. In the electrolytic section, the entire solution is subjected to electrolysis which plates out pure tin metal. The electrolytic plates are melted and cast into pure tin pigs or ingots.

Table 80b. SECONDARY TIN<sup>a</sup>

(Basis: 1 ton of tin metal to federal specifications)<sup>b</sup>

STAGE	TYPE	AMOUNT	Assumption 1 <sup>e</sup>	Assumption 2 <sup>e</sup>
			10 <sup>3</sup> Btu	10 <sup>3</sup> Btu
1. Scrap Col- lection & Transportation	See note d		406,437	406,437
<i>Subtotal</i>			<u>406,437</u>	<u>406,437</u>
2. Unloading & Initial Pro- cessing	electric	12,960 kWh	170,100	170,100
<i>Subtotal</i>			<u>170,100</u>	<u>170,100</u>
Cumulative Subtotal			576,537	576,537
3. Alkali De- tinning	natural gas	5,574.14 ft <sup>3</sup>	634,000	634,000
	materials <sup>c</sup>	-	22,226,925	22,226,925
Energy Credit for Steel Produced <sup>e</sup>			<u>-581,670</u>	<u>-9,805,140</u>
<i>Subtotal</i>			<u>22,279,255</u>	<u>13,055,785</u>
Cumulative Subtotal			23,152,080	13,632,322
4. Tin Electro- lysis	electric	6,400 kWh	83,988	83,988
<i>Subtotal</i>			<u>83,988</u>	<u>83,988</u>
Cumulative Subtotal			23,236,078	13,716,310
5. Ingot Pro- duction	natural gas	2,126 ft <sup>3</sup>	2,418	2,418
<i>Subtotal</i>			<u>2,418</u>	<u>1,418</u>
TOTAL			23,238,496	13,718,728

NOTES TO Table 80b

<sup>a</sup> Sources: [80-202] and [80-300] unless noted.

<sup>b</sup> Electrolytic tin produced is consistently grade AA, often grade AAA, and can be produced at a purity of 99.9999% tin [80-203].

<sup>c</sup> 411.5 lb. caustic soda @ 74.7 million Btu/lb. and 61.5 lb. sodium nitrite @ 42.25 million Btu/lb. [0-325] p. 109. Assumes that scrap input is municipal waste.

<sup>d</sup> Conforming to note c above, the following derives an estimated energy cost for collection of ton of old scrap tinplate:

- 1) 3-5% of solid total waste in U.S. is metal cans. [0-204] p. 148. 3% is assumed to be tinplate cans.
- 2) National average energy consumption for collection of one ton of solid waste is 255,900 Btu/ton [0-204] p. 144.
- 3) Because all solid waste must be collected whether valuable or not, energy use for tinplate scrap collection is considered to be energy required per ton garbage collected to the proportion of tinplate in the scrap. Therefore, energy use for collecting one ton of tinplate scrap is 255,900 Btu. However, this tinplate must be separated from the rest of the solid waste stream.
- 4) Based on data from can manufacturers, energy requirements to separate, process, transport ferrous scrap, including unloading, conditioning, cleaning, reloading, and intermediate transportation is 1,391,100 Btu/ton scrap. [0-204] p. 145.
- 5) Therefore total energy required to collect, process and transport one ton of old scrap to recycled is 1.647 million Btu/ton scrap.

Industrial new scrap can also be recycled in this process. The energy cost of new scrap is the sum of the energy costs of collection in-plant, rail-car loading, and and rail transportation. For one ton of new scrap the costs are:

in-plant collection.....	neglected
rail-car loading	
(assumed equal to unloading).....	30.09 kWh
rail transport	
(100 miles [0-208] @ 1980 Btu/°M [0-210]..	<u>19,800 Btu</u>
TOTAL (1 ton of new scrap) .....	414,670 Btu

A total of 426.67 short tons of scrap are required for one ton of tin, 90% new and 10% old. The weighted average energy cost of one ton of tin is therefore  $4.06437 \times 10^6$  Btu.



e 423 tons of steel are produced for every ton of tin produced. In the first case we assume the steel to have energy value equal only to similar tinplate steel collected and separated. This is a lower bound because detinned secondary steel is certainly more valuable to industry than tinplate, though both can sometimes be used in the same processes. Because the steel output is 98% of gross input, 98% of energy in note d, part 4, is deducted. In the second case it is assumed that the by-product steel can be used as a substitute for pig iron in certain applications. Source for energy value: [0-325a p. 98]. This is an upper bound on the value.

## ENERGY-VERSATILITY CONSIDERATIONS FOR TIN

This is a rather interesting case in that some 81.6% of all energy use for tin production is used in the earliest ore processing stages. These are stages the U.S. has little control over. After this, each stage adds significantly to total energy use with a (probably small) decrease in versatility (See Figure 80b). Few of these stages offer much possibility for increasing energy storage or keeping versatility high. Therefore we recommend by default that tin be stockpiled in its current form.

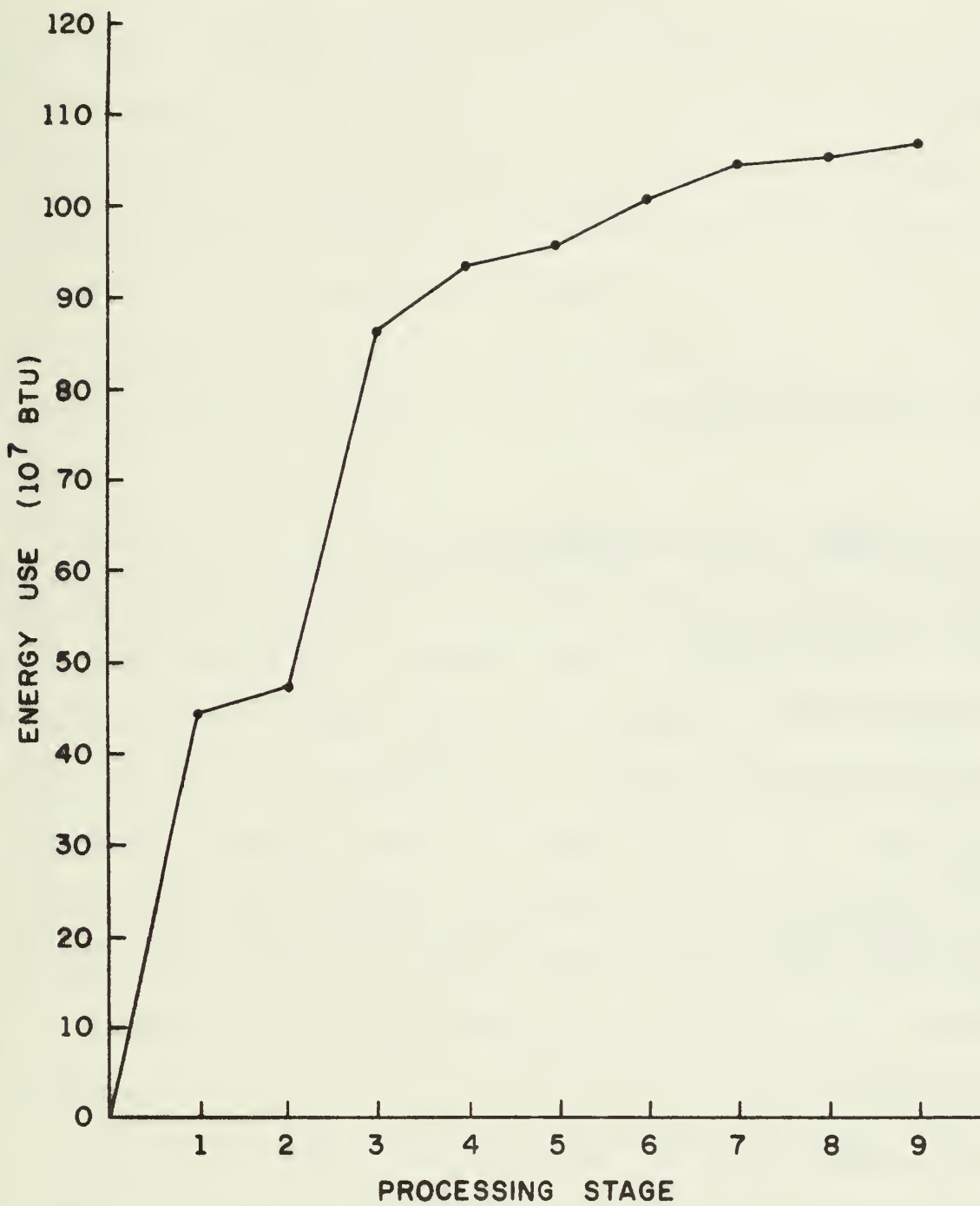


Figure 80b: Production of Tin

FOOTNOTES TO SECTION 80.

<sup>1</sup> [0-149] p. 760.

<sup>2</sup> [0-140I] p. 11 (of preprint)

<sup>3</sup> [80-200]

<sup>4</sup> [0-140I] p. 12.

<sup>5</sup> [0-145] p. 88.

<sup>6</sup> [0-149] p. 763.

<sup>7</sup> [80-203].

<sup>8</sup> [0-149] p. 763 and [0-122] p. 77.

<sup>9</sup> Ibid.

<sup>10</sup> Source: [80-200], [80-120] and [80-122].

<sup>11</sup> [0-145] p. 88 and [80-205].

<sup>12</sup> [80-204] and [80-205].

<sup>13</sup> [80-206] and [80-203].

<sup>14</sup> [80-206].

<sup>15</sup> [80-203] and [80-124].

<sup>16</sup> [80-203].

<sup>17</sup> [80-203] and [80-124].

<sup>18</sup> [80-123] and [80-124].

<sup>19</sup> Sources: [0-149] p. 762, [80-300], [80-206], and [80-204].

## 82...86. TUNGSTEN

### Overview

Tungsten (Wolfram), atomic number 74, has the highest melting point of all metals: 6,170° F; three times that of copper and twice that of martensitic stainless steel. It is one of the heaviest of all elements, with a specific gravity equal to that of gold: 19.3. At temperatures above 3,000° F, tungsten outranks all metals in tensile strength. It has good corrosion resistance, good electrical and thermal conductivity, and a low thermal expansion coefficient.<sup>1</sup>

Tungsten does not occur as native metal, abundance in the earth's crust is 70 ppm, which ranks it as the twenty-sixth most plentiful element.

Tungsten ores are widely distributed however: about three-quarters of the world's reserves occur in China, whereas the U.S., South America and Korea possess about 5 percent each.<sup>2</sup> In Europe, the most important deposits are in Portugal (1% of world resources). Small quantities also occur in Australia and Africa. The principal known tungsten resources in the U.S. occur at 15 sites and 11 general locations in California (36%), Colorado (21%), Nevada (17%), North Carolina (15%), Idaho (4%), Montana (4%), Arizona and New Mexico (3%), Alaska.<sup>3,4</sup>

Among 15 known types of ores, four are considered of commercial importance:

Scheelite,  $\text{CaWO}_4$ , feberite,  $\text{FeWO}_4$ , huebnerite,  $\text{MnWO}_4$ , and a mixed crystal of the latter two: wolframite  $(\text{Fe,M n})\text{WO}_4$ . Most deposits are of low grade: Chinese ores average 2%  $\text{WO}_3$ , Mawchi ores (Burma), 1.5%  $\text{WO}_3$  and 2% Sn, Bolivian ores 2.0 and even as high as 5%, U.S. scheelite ores carry .4 to 1%  $\text{WO}_3$ . "Synthetic" scheelite can be precipitated from

any tungsten ore or tungsten scrap to form  $\text{CaWO}_4$ .

Beneficiation methods, which vary greatly with the composition of the type of crude ore treated, will generally yield concentrates with over 70% contained  $\text{WO}_3$ . Besides usual common gangue minerals like quartz, feldspar, garnet, mica, sulfides, arsenides, there are often other valuable minerals such as molybdenite and bismithinite.<sup>5,6</sup>

Most tungsten concentrate is converted either to ferrotungsten, metal powder, or intermediate products before being consumed in end uses. Some scheelite, however, is used directly in steelmaking.

In manufacturing tungsten metal powder, tungsten mineral concentrate is treated chemically to produce intermediate tungsten compounds which are then reduced to metal with hydrogen or carbon. The processes vary depending on raw materials, product specifications, and plant design: methods used for treating wolframite are not satisfactory for treating scheelite, and vice-versa. Hydrogen reduced tungsten powder is the input to the production of tungsten carbide powder.

Tungsten recovery from scrap is considerable, often occurring within the generating company, as an alloy without the separation of the constituent elements. Although tungsten carbide is recovered from metal-shaping dies, throw-away inserts, cutting tools and rock bits, substantial quantities of this material in sludges from metal cutting operations are being discarded because of high chemical processing costs and low tungsten content. Molybdenum operations provide most of the tungsten produced in the U.S. as a co-product. On the other hand, tungsten mines produce minor quantities of copper, gold, silver as a co-product.<sup>7</sup> Tin smelters, processing cassiterite, could also become a source for tungsten recovery.<sup>8</sup>

About 60 percent of the U.S. requirements for tungsten ores and concentrates were produced domestically in 1973; 7.5 million pounds of contained tungsten, which corresponds to 9% of the world production. Imports of concentrates from Canada, Bolivia, Peru, Thailand, Korea, Brazil, Australia, West Germany, Portugal and other countries amounted to 10.5 million pounds of contained tungsten. Ferrotungsten imports containing 1.1 million pounds came from the United Kingdom, Austria, West Germany, Portugal, France and other countries. Further contributions to the U.S. supply in 1973 were .5 million pounds from secondary tungsten, 1.5 million pounds stockpile release and 4.2 million pounds industry stocks.

By the end of 1973 about 9.3 million pounds had gone to industrial stockpiles, whereas .750 million pounds had been exported: a little less than half of it as carbide powder, some 40 percent as chemicals and the rest as concentrate and alloys.<sup>9</sup>

U.S. demand, the remaining 15.4 million pounds, was partitioned into intermediate products as follows: tungsten carbide, 43%; tungsten metal powder, 35%; chemicals and ferrotungsten, 11% each. End use distribution: 56% for cutting and wear resistant materials, 15% for mill products, 11% for specialty tool steels, 7% for welding and hard-facing materials, 11% for miscellaneous applications such as chemicals and electronic components.<sup>10</sup>

Over 50 percent of tungsten metal powder is used to make tungsten carbide powder, the basis for cemented or sintered tungsten carbide which in turn is used for cutting edges, in dies, machine tools, rock bits, tire studs, ammunition shells and gas turbines.

Wire products are made from metal powder by compressing, sintering and heating to incipient fusion by passage of electrical currents, then swaging and drawing. Hydrostatic pressing of metal powder into slabs, bars and tubes produces mill shapes, strip sheet and foil. Tungsten alloys, with for instance 85% tungsten, 15 percent molybdenum are produced by consumable arc vacuum melting. Addition of rhenium and thorium results in ductile tungsten.

To obtain hardness at high temperatures, wear, abrasion and shock resistance, ferrotungsten is used in high speed tool steels, standard tool steels and alloy steels. The composition of these steels varies greatly: one class requires from 2 to 6 percent tungsten in addition to chromium, molybdenum, vanadium and cobalt. Another class may contain as much as 22 percent tungsten and lesser amounts of other elements. Among the applications are: furnace supports, jet engine and spacecraft components, teeth for bucket and wheel excavators, rock crusher jaws.

Other general applications of tungsten include: receiving, power or transmitter, x-ray and cathode ray tubes, lamp filaments, electrodes, contact points in relays and automotive electrical distributor points, heating elements, crucibles for nuclear fuel handling, counter weights and balances in stabilizers of aircraft.

Lead, zinc, sodium tungstate and other tungsten compounds find their way in pigments, paints, textile dyes, high temperature thermocouples, lubricants, lasers.

In metal shaping applications requiring retention of hardness at elevated temperatures, no completely satisfactory substitute for tungsten exists. Tantalum, titanium and chromium carbides, aluminum oxide ceramics



and industrial diamonds could occasionally take its place in cutting tools. Cutting materials containing 8 to 85% titanium with little or no tungsten in a matrix of molybdenum, nickel or cobalt are feasible.

In tool steels, molybdenum is substituted for tungsten at the cost of a lowered melting point, less hardness and a greater tendency to decarburize.

As counterweights for aircraft applications, depleted uranium is being substituted for tungsten.

## PROCESS DESCRIPTION

Tungsten ores are usually concentrated before shipment and each type of tungsten deposit presents its individual problems. The physical properties of the ore and its composition, both in respect to values other than tungsten and to the nature of the gangue require consideration.

The  $WO_3$  content in ores is rarely greater than 2 percent: the objective is the preparation of a concentrate having at least 76 percent  $WO_3$ .<sup>11</sup> The operations used in beneficiation are crushing, grinding, leaching, and others that may be of value in specific instances.<sup>12</sup> Synthetic scheelite can be precipitated from chemically processed slimes, or any tungsten ore or scrap to form  $CaWO_4$ . Tin-wolfram concentrates can be separated by magnetic methods. Recovery of tungsten from tin smelter wastes can be effected by a pyrometallurgical sulfide-volatilization process. During volatilization of the tin from the slag, nearly all the tungsten and a large percentage of the iron is reduced to an Fe-W-Si-C alloy. The tungsten can be removed from this alloy with an oxidizing-roast alkaline-leach treatment.<sup>13</sup>

Some scheelite is used directly in steel making. Most tungsten concentrate, however, is converted either to ferrotungsten, metal, powder or intermediate chemical products.

Because of its high melting temperature, ordinary smelting and refining practices are not suitable; the metallurgy of tungsten, therefore, must employ methods of chemical decomposition and purification rather than pyro-metallurgy. The art is presently largely empirical and based upon patents. Patents, being keys to the technology of tungsten, provide most of the source material of this subject.<sup>14</sup>

The chemistry of the decomposition process used is based on the solubilities of the various tungstates ( $R_2O \cdot WO_3 \cdot H_2O$ ), and of tungstic acid ( $H_2WO_4$  or the hydrated oxide  $WO_3 \cdot H_2O$ ).

The alkalitungstates are soluble; alkaline earth and heavy metal tungstates and tungstic acid are insoluble. A specific property is the insolubility of APT, ammonium paratungstate  $x(NH_4)_2O \cdot yWO_3 \cdot zH_2O$ . A few processes that have been proposed employ the volatility of tungsten halides.

Wolframite ores may be treated by an alkali carbonate fusion or digestion with aqueous caustic to form soluble tungstates and insoluble iron and manganese oxides or hydroxides. Variations of these processes employ digestion under pressure.

Scheelite ores are usually treated with hydrochloric acid, a process that yields insoluble tungstic acid and water soluble salts of the metals to be removed. Decomposition with sodium carbonate is another possibility for scheelite.

The purification of a tungstate before final conversion into tungstic acid may be accomplished by several methods: recrystallization, or calcium treatment to precipitate calcium tungstate which upon reaction with hydrochloric acid yields tungstic acid.

A more recent method which has gained general acceptance, is the liquid-ion-exchange process.

For the preparation of tungsten of the purity required for ductile, workable metal, hydrogen reduction of the APT or tungstic oxide is universally employed. The use of other reducing agents has been studied but traces of the agent remain in the metal powder, although carbon-reduced

tungsten finds a limited use as an alloying agent, because of its lower cost.

A common type of reduction furnace consists of 6 to 12 tubes of heat-resistant alloy 12 or more feet long, and 1 and-a-half or 2 inches in diameter, enclosed in a refractory-lined frame. The tubes are heated by gas with automatic temperature controls. The APT or oxide is spread in a thin layer in heat-resistant nickel alloy boats 12 to 18 inches long, and these are introduced into the furnace at regular intervals. Hydrogen is introduced into the system at the cooler unloading end so that no water vapor, formed in the reduction, comes into contact with the reduced metal.

The product is a gray powder in the form of loosely caked friable lumps. These are broken up and the powder is screened and stored in tight containers to avoid absorption of atmospheric moisture and subsequent surface oxidation. It is general practice to blend the metal made from one or more oxide lots. The particle size of tungsten powder required for subsequent operations ranges from 0.5 to 5 microns and is affected by temperature, as well as the rate of flow of hydrogen.<sup>15</sup>

In producing ferrotungsten, tungsten concentrate is reduced in electric furnaces with carbon, aluminum, or silicon. A batch-type operation is necessary because the high melting point of ferrotungsten precludes tapping. Any tungsten mineral, or combination of minerals, can be used as starting material provided the Fe-W ratio permits formation of an alloy containing 72% or more of tungsten. Alumino-thermic or metallo-thermic methods are also suitable. Some high purity ferrotungsten is produced by compacting tungsten metal powder and iron powder.

For the purpose of charging tungsten to steel, Fe-W is usually crushed to a size of half an inch or less.

Cemented (sintered) tungsten carbides are usually made from hydrogen-reduced tungsten metal powder. The powder is carburized, compacted with a cobalt binder into the desired shape, and then sintered. Mixed carbide powders containing titanium, tantalum or intermetallic compounds such as  $WTiC_2$  are also used.<sup>16</sup>

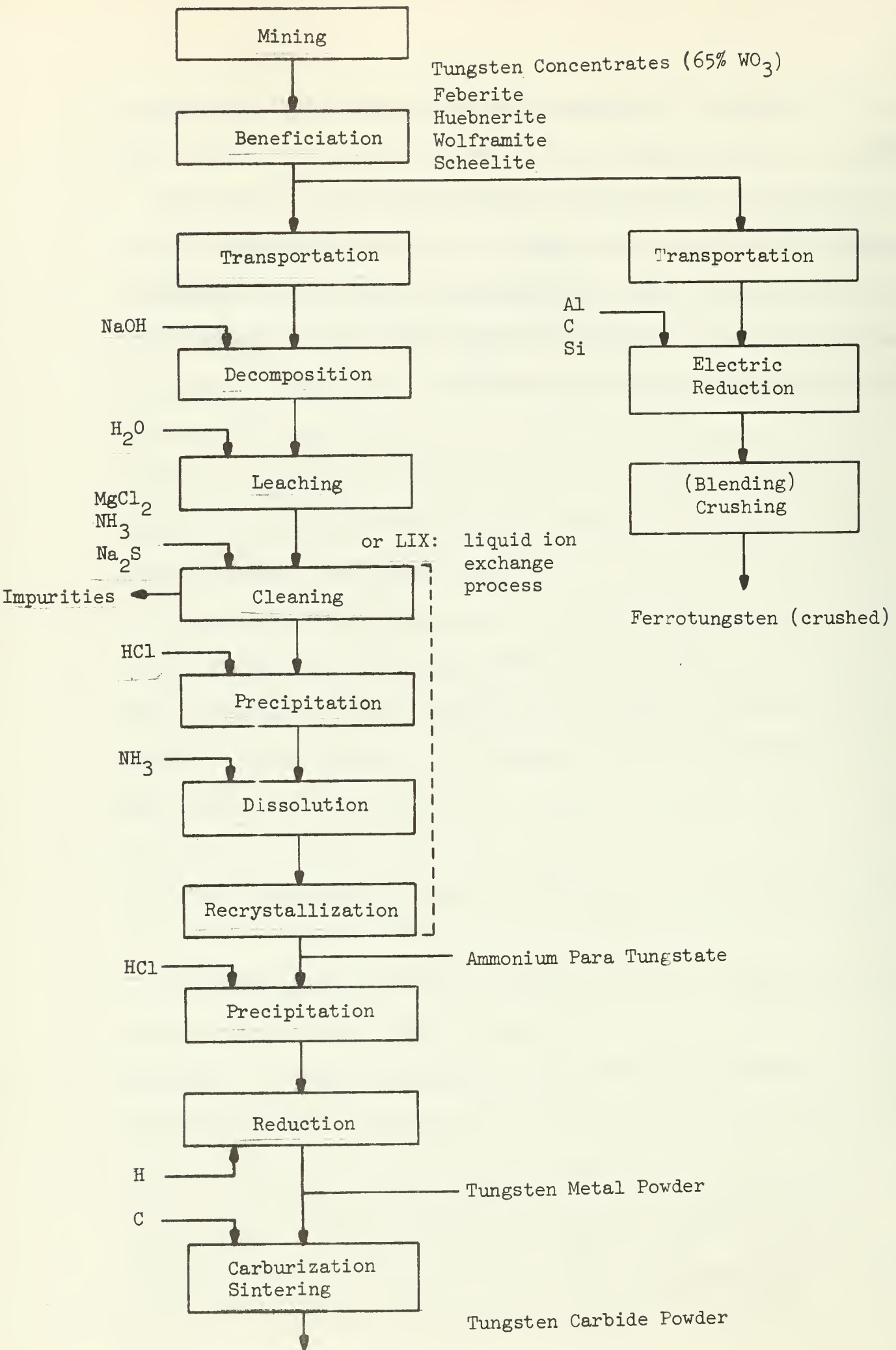


Figure 82...86: Production of Tungsten

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Table 82...86: Production of Tungsten.

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Notes to Table 82....86.

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Energy/Versatility Considerations for Tungsten

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FOOTNOTES TO SECTION 82...86

- <sup>1</sup> [0-149] p. 401.
- <sup>2</sup> [82...86-100] p. 4; [0-122] p. 81 gives: 55% of the world's reserves in the People's Republic of China, U.S.S.R.-12%. South Korea - 7%, U.S.A.-6%.
- <sup>3</sup> [82...86-141] p. 7-9.
- <sup>4</sup> [82...86-142] p. 4,5.
- <sup>5</sup> [82...86-103] p. 114.
- <sup>6</sup> [82...86-102] p. 13.
- <sup>7</sup> [0-149] p. 405.
- <sup>8</sup> See [82...86-143].
- <sup>9</sup> [0-145] p. 90.
- <sup>10</sup> [0-140 I] p. 1247.
- <sup>11</sup> [82...86-101] p. 484.
- <sup>12</sup> See [82...86-103], [82...86-141], and [82...86-142] for very detailed descriptions.
- <sup>13</sup> See [82...86-143].
- <sup>14</sup> [82...86-103] p. 166.
- <sup>15</sup> [82...86-101] p. 485.
- <sup>16</sup> [0-149] p. 402.

## 87. VANADIUM.

### Overview

Vanadium, atomic number 23, is a grayish, malleable, ductile metal with a silver luster; its melting point is 3450° F. With an abundance in the earth's crust of 150 ppm, it ranks above copper, lead and zinc. It is widely distributed throughout a great variety of rocks and ores including sulfides, oxides, silicates, and vanadates. Recovery is therefore principally as a co-product of other metals; mining for the vanadium content alone is rare and occurs only in a few places: a deposit of vanadiferous titaniferous magnetite of the Bushveld Complex in the Republic of South Africa and the recently developed vanadium mine at Wilson Springs, Arkansas. The famous Mina Ragra deposit discovered over half a century ago in the Peruvian Andes is now inactive.<sup>1</sup> At least 65 types of vanadium mineral have been identified. The vanadium pentoxide content is seldom higher than 1%, a value around 0.2% being more common. Four groups of commercially important ores, which in concentrate form may contain from 10-24 percent vanadium are:<sup>2</sup>

- Patronite, a vanadium sulfate, sulfide or oxide found in Peru;
- Roscoelite, a vanadium-bearing mica found as a vein mineral in a number of rich gold-bearing veins; in important quantity as a secondary mineral in the sandstone of Colorado and Utah, Mexico and Turkestan;
- Carnotite, an uranyl potassium vanadate found in Colorado, Utah, Mexico and Turkestan;
- Metallic Vanadates, such as descloizite, mottramite, vanadinite, occurring in South Africa, Argentine, Mexico, Arizona, Nevada and Turkestan.

Other sources of vanadium concentrates include;<sup>3</sup>

- Titaniferous magnetites in New York, Wyoming, Minnesota, Alaska, Finland, South Africa;
- Ash from burned asphaltite (Peru, Argentina);
- By-products from the treating of the phosphate rock of Idaho, Wyoming, Montana;
- Ash residue from combusted oils deriving from Venezuela and the Netherlands West Indies;
- By-products from processing vanadium-rich blast-furnace slags.

An estimated 80% of the world's reserves is assumed to be in the U.S.S.R., 18% in the Republic of South Africa, 12% in the U.S.A., furthermore small quantities in Finland, Norway, Sweden, Canada, India, Australia.

Recovery of vanadium from ores, residues and slag is usually accomplished by saltpreheating and leaching sometimes modified by solvent extraction or ion exchange to obtain vanadium pentoxide. In the U.S. this is done by three companies at four plants, two of which also recover uranium; another produces the oxide from ferrophosphorus; and the remaining plant is operated solely for vanadium.

One company produces a vanadium ferroalloy principally from imported slag. The principal producer of vanadium oxide is also the principal oxide consumer, but is not a large end use consumer.

There are five domestic producers of ferrovanadium, including Carvan and Ferrovan, one of which is a subsidiary of a German metal firm. Of the five, one is the principal producer of vanadium oxide and four are processors of purchased raw material.<sup>4</sup>

In the rest of the world, vanadium is a co-product mainly from iron, followed by lead, titanium and bauxite. Since the application of vanadium-base alloys and high purity vanadium metal is a recent development,

secondary recovery is of low volume; should the fabrication of nuclear reactor components increase, the necessity for recycling in order to reduce costs will certainly become an important issue. Although it cannot be considered as a secondary source of supply, because separation of the vanadium from other alloying constituents is not being undertaken, returns of vanadium-bearing iron and steel scrap have some significance to the general pattern.

In 1973, some 4,864 short tons of contained vanadium were produced by the U.S.; this is 21% of the world production of that year. Imports of residues and slag from South Africa, Venezuela and other countries amounted to 2,637 short tons; imported ferrovanadium from Austria and West Germany was no more than 197 short tons.<sup>5</sup>

From a total U.S. supply of 13,600 short tons, 900 tons were exported and 4100 tons constituted industry stocks; the industrial demand of 8600 tons contained vanadium was composed of 88% ferrovanadium, 3% oxide and 9% other intermediate products, principally vanadium-aluminum alloys. A breakdown of end use consumption shows 86% for steels, about seven tenths of which went to full alloy and high strength, low alloy (HSLA) types, 1% for cast irons and superalloys, 9% for cutting and wear resistant materials, welding rods, nonferrous alloys; the remaining 4% for chemical purposes, mainly catalysts, and miscellaneous applications.<sup>5</sup> Vanadium content of most alloys is rather low, ranging from 0.03% to 2.5%.

In the construction industry, to lower weight and increase durability, HSLA steels are frequently used for structural members of buildings and bridges, oil and gas pipelines and pressure storage tanks. Architectural trim on buildings may contain small quantities of vanadium.

Many kinds of construction equipment that require resistance to

shock and wear, serving the construction, mining, agricultural, and chemical industries use vanadium steels and iron castings. The use for vanadium in this application is expected to rise because of the increasing replacement of carbon steel by specialty steels.

The manufacture of automotive vehicles, ship structures and railroad transportation equipment takes advantage of the excellent wear-resisting properties of HSLA stainless steels.

Titanium base alloys, containing up to 6% vanadium, possess the high-temperature strength needed for the structural and rotating parts of aircraft turbine engines, airframes, and other components of aerospace technology.

Well known is the usage of vanadium in tool steels and metal-forming equipment requiring hard wear-resisting surfaces.

Vanadium compounds have applications as oxidation catalysts in chemical processes, such as contact sulfuric acid plants. As a fuel cladding and structural material in nuclear reactors, especially of the liquid-metal-cooled, fast-breeder type, vanadium is gaining importance.

Substitutes for vanadium steels are manganese-titanium steels, and molybdenum or molybdenum-silicon steels with a grain-refining addition of aluminum. For many of its alloying purposes, vanadium is interchangeable to some degree with other alloying elements, such as tungsten and columbium.

## PROCESS DESCRIPTION

Many technologies exist for the production of vanadium, their differences depending on mineralogy or origin of the source material. Most of them are proprietary and patented. However, main procedures for the production of commercial-grade and ultimately of reagent-grade  $V_2O_5$  are very much alike for patronite, titaniferous magnetites, vanadates, sandstones containing carnotite or roscoelite, phosphate rock, oil residues and slags. The ores crushed to -10 to -14 mesh are mixed with 6...10% sodium chloride and roasted, usually in multiple hearth furnaces at about  $850^\circ C$ , this temperature being rather critical. The vanadium oxides are converted to a water soluble sodium metavanadate ( $NaVO_3$ ). The addition of sulfuric acid to the wash liquor causes the precipitation of the salt, sodium hexavanadate ( $Na_2H_2V_6O_{17}$ ). When dried, this precipitate is marketed as commercial-grade vanadium pentoxide; it contains 85...94%  $V_2O_5$  with 6...11%  $Na_2O$  and 2-3% of other impurities (Fe, Si, Mo, water).

This acid process is efficient for the recovery of both uranium and vanadium. A major limitation is imposed by the lime content of the feed material which must be restricted to less than 2.5%.

A second leaching method, especially applicable to carnotite is the carbonate process. For ores containing more than 1% vanadium, the hot calcines are quenched with a sodium carbonate solution and agitated if necessary; for ores containing less than 1% vanadium, the raw ore is leached directly with a hot sodium carbonate solution.

The carbonate process requires more careful plant control than the acid process.

A reagent grade of  $V_2O_5$  can be produced via the formation of ammonium metavanadate ( $NH_4VO_3$ ). Commercial-grade  $V_2O_5$  is fused with sodium carbonate, or redissolved in NaOH. Upon dissolution of the resultant mass in water, Fe, Si, and Al can be precipitated. After filtering,  $NH_4VO_3$  is precipitated by the addition of  $NH_4Cl$ . When  $NH_4VO_3$  is calcined, a very pure  $V_2O_5$  residue is left.<sup>7</sup>

Ferrovandium is usually made by reducing vanadium pentoxide and iron by the Thermit process or in the electric furnace with silicon, ferrosilicon, or carbon. Although aluminum is generally a more expensive reducing agent, the process is exothermic and the product relatively pure. The 50% grades of ferrovandium are generally produced in a standard, open top electric furnace lined with magnesia. The charge consists of  $V_2O_5$ , aluminum, iron scrap, and fluxes such as calcium fluoride. The electric furnace is required only to kindle the reaction by generating a threshold temperature of 1730° F and at later stages to superheat the slag to improve the yield.

The 70 to 80 percent grades of ferrovandium are produced in magnesite-lined pots ignited by a charge containing barium dioxide and aluminum to develop the kindling temperature of 1730° F.

NOTE: No optimization section is included for this material. Only one single step consumes significant energy, oxide production. Since this does not significantly decrease availability, vanadium should be stockpiled in oxide form.



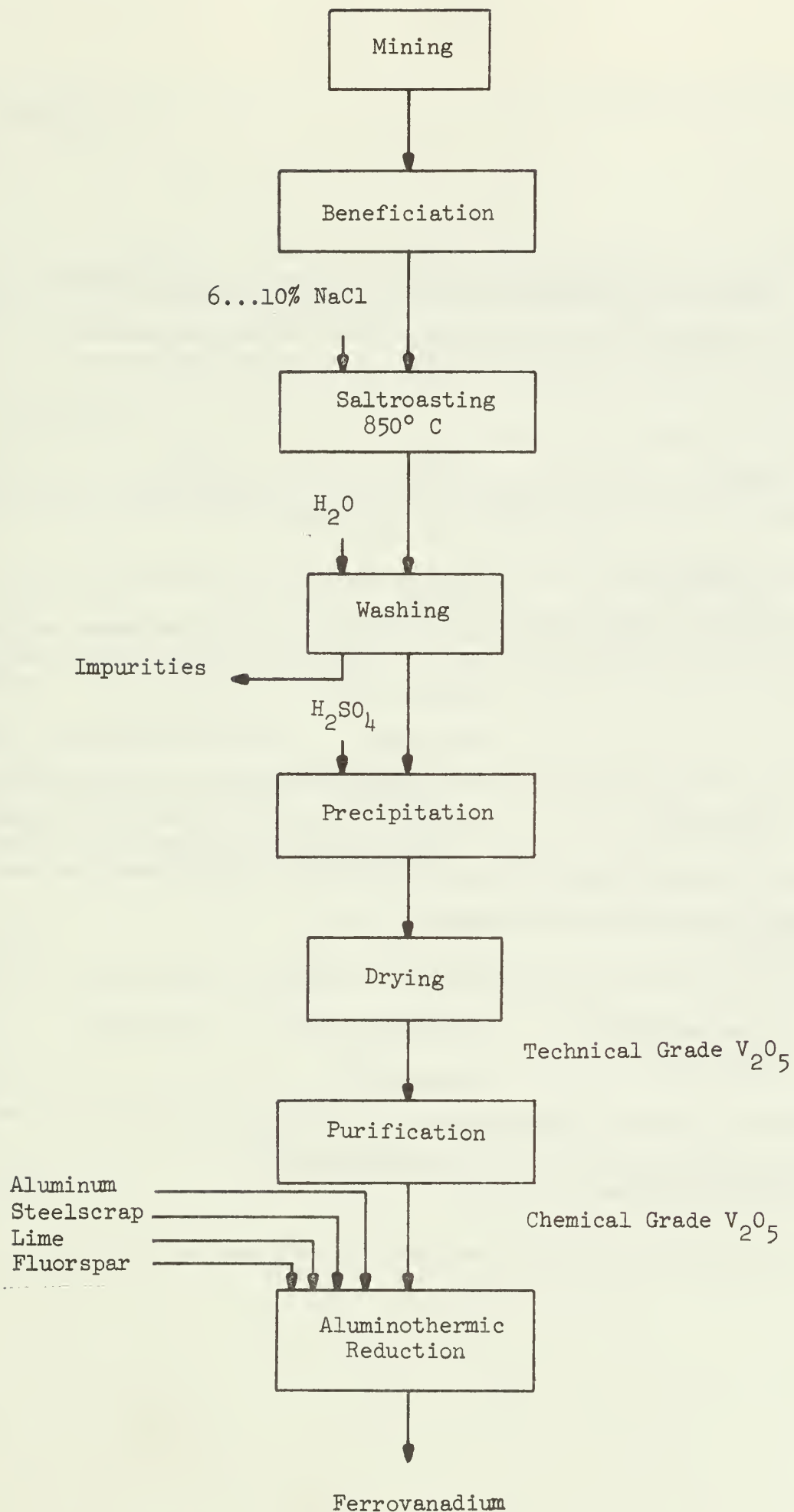


Figure 87: Production of Vanadium Pentoxide and Ferrovanadium

Table 87. PRODUCTION OF VANADIUM PENTOXIDE AND FERROVANADIUM

(Basis: One ton of  $V_2O_5$ , FeV to federal specification)<sup>a</sup>

STAGE	TYPE	AMOUNT	$10^3$ Btu
1. Mining and Beneficiation <sup>b</sup>	Ferrophosphorus <sup>c</sup>	14.28 ton	2,291,940
2. Oxide Production <sup>d</sup>	Electricity	9,400 kWh	123,357
	Natural Gas	200,000 Ft. <sup>3</sup>	227,472
	Fuel Oil	120 Gal.	19,518
Subtotal <sup>e</sup>			2,662,287
Energy Required for the Production of 1 Ton $V_2O_5$			1,331,143
3. Aluminothermic Reduction	Transportation <sup>f</sup>	4,800 TM	3,216
	Materials <sup>g</sup>	--	526,595
Total Energy Required for the Production of 1 Ton Ferrovandium			3,192,098

NOTES TO Table 87

- <sup>a</sup> See [87a-140], [87b-140]
- <sup>b</sup> A note on allocation: raw materials for the production of vanadium are of different origin and have different composition. Approximately 40% comes from a mine in Arkansas, and the remaining 20% consists of boiler residues from refineries on the East Coast and in the Caribbean, various other imports, by-products of uranium and of elemental phosphorus production. The following calculation is based on phosphorus production.
- <sup>c</sup> From [0-325a] p. 128, a value of  $160,500 \times 10^3$  Btu/ton of ferrophosphorus is derived. The embodied energy of the chemicals used for the production of the oxide is considered to be negligible.
- <sup>d</sup> One ton of ferrophosphorus contains 280 pounds of pure  $V_2O_5$ . [87-203].
- <sup>e</sup> Vanadium pentoxide obtained from imported preprocessed ores has considerably lower embodied energy: a first approximation gives  $320,000 \times 10^3$  Btu/ton.
- <sup>f</sup> 2,400 miles @ 670 Btu/TM.
- <sup>g</sup> 2 ton of aluminum @  $244 \times 10^6$  Btu/ton.  
1 ton of iron powder @  $34 \times 10^6$  Btu/ton.  
.2 ton of fluorspar @  $6 \times 10^6$  Btu/ton.  
.4 ton of lime @  $8.487 \times 10^6$  Btu/ton.

FOOTNOTES TO SECTION 87

<sup>1</sup> [0-149] p. 418

<sup>2</sup> [87-104] p. 575

<sup>3</sup> [87-102] p. 3

<sup>4</sup> [87-143] p. 1

<sup>5</sup> [0-145] p. 92

<sup>6</sup> [0-140 I] p. 1291

<sup>7</sup> [87-102]

### III. SUMMARY AND CONCLUSION

In the coming years, world supplies of materials will dwindle to dangerously low levels. As this happens the pressure for careful international monitoring and control of natural resources will greatly increase. Materials will be as important to economic and social structures as they now are to the defense establishment. Materials data collection, analysis, and policymaking will be necessary for many more industries than is now the case. Appropriately, this report is submitted to those involved with current materials stockpiling practices. It is hoped that this research begins the work of bringing together versatility considerations, materials processing information, and energy data. Only the combination of these three elements can allow for policy decisions which accurately reflect global environmental constraints.

With regard to general governmental policy on materials, we recommend that several long term goals be adopted. First, to eliminate basic data collection problems, large consumers of materials should be required to disclose physical data on flows of these materials through their plants. Similarly, laws concerning energy consumption have already been proposed. The large amount of data resulting from such a program makes a standardized system of accounting techniques a necessity. The system should be implemented in consultation with producers, trade associations, and government experts. Finally, the specific subject area of this report would benefit greatly from further studies of material flows in the economy and of industrial capacity as a function of time.

Table 0-4 summarizes the findings reported for each material in part II. Several definite trends can be observed. For most non-metals, energy use and versatility changes are not large, leaving few forms possible for

stockpiling. For most metals, there are many processing steps, each requiring significant amounts of energy. This usually results in a choice of several stages for optimizing energy and versatility up to and including the pure elemental metal. Our results indicate that there are very few cases which call for stockpiling highly upgraded forms of materials. Thus any decision to stockpile these should be made on the basis of strategic need, industrial capacity, or other overriding factors.

TABLE O-4

SUMMARY OF ENERGY-VERSATILITY RECOMMENDATIONS

	<u>Material Group</u>	<u>Recommendations</u>
1,7,8	Aluminum and Metallurgical Grade Bauxite	Stockpile as ore, anodes, or possibly upgraded forms.
2,3,73	Abrasives	Stockpile in current forms except abrasive grade aluminum oxide.
4.	Antimony	Stockpile unrefined after electrolysis.
6.	Asbestos	Stockpile in current form.
9.	Refractory Bauxite	Stockpile in current form.
13.	Bismuth	Stockpile in current form.
14,91	Zinc, Cadmium	Stockpile after electrolysis; stockpile decision must be made on basis of strategic and versatility considerations.
16...22	Chromium	Stockpile some material in all current forms; detailed versatility studies required to find exact proportions.
28.	Copper	Stockpile decision must be made on the basis of strategic and versatility considerations.
35,36	Fluorospars	Stockpile in current form.
42.	Lead	Stockpile in some form after smelting; detailed versatility study required.
43...52	Manganese	Stockpile some material in all current forms; detailed versatility study required to find exact proportions.
53.	Mercury	Stockpile in current form.
59.	Molybdenum	Stockpile in current forms, and possibly a small amount of molybdenum disulphide.

<u>Material Group</u>	<u>Recommendations</u>
60. Nickel	Stockpile in current form and possibly in mattes.
62,63,64 Platinum Group Metals	Stockpile in current forms.
70,81 Titanium, Rutile	Stockpile as ore or chlorinated form for maximum versatility; stockpile metal after either batch reactor or leaching, such as in current specification.
74. Silver	Energy use insignificant. Stockpile on basis of strategic and versatility considerations.
79. Thorium	Stockpile in hydroxide or later form. Current specification is adequate.
80. Tin	Stockpile in current form
87. Vanadium	Stockpile some material in oxide form for maximum versatility.



## BIBLIOGRAPHY

(Note: the following listing consists of two parts. Immediately below, publications of general importance to this study, having reference numbers preceded by a "0". The second part lists books, monographs, brochures, phone reports and letters pertaining to specific materials their reference numbers are preceded by identification numbers adopted from FPA usage.)

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### 0-100 - 0-199 - MATERIALS

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