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PHD DEGREE

Earth and Environmental Science and Technologies
Cycle XXXIII°

TREATMENT OF MINERAL-METALLURGICAL RESIDUES FOR THE RECOVERY OF USEFUL SPECIES AND THE REUSE OF PROCESS WASTE

Scientific Disciplinary Sectors: ING-IND/28 and ING-IND/29

PhD Student:	*Carla Mercante*
Supervisor:	*Prof. Ing. Pier Paolo Manca*
Co-Tutor:	*Prof. Ing. Giorgio Massacci*

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Abstract

Millions of tons of mining waste now represent a huge ecological challenge, perhaps also an economic opportunity.

This paper illustrates and discusses an innovative approach in the reclamation of old mining areas, which is inspired by the principle of circular economy and considers the waste from old mining and mineral processing activities as potential secondary raw materials.The research proposes to apply the technique of flotation to extract from solid mining residues fractions of useful but polluting species, obtaining the double result of downgrading the material below the CSC (Contamination Threshold Concentration) and extracting a concentrate with commercial characteristics. The materials of potential interest are those of which the dumps from the cultivation and processing of the ores of Pb and Zn are composed.

The establishment of the Centre of Excellence for Environmental Sustainability (CESA) has enabled an experimental activity based on the treatment of various mining residues in the Sulcis Iglesiente Guspinese area. The results obtained appear to be important in terms of both technological feasibility and costs compared to those of a Permanent Safety Deposit [1] [2].

The project has been developed, with reference to a pilot basin; the studies carried out so far have concerned samples taken from the Montevecchio Levante mud basin on which batch flotation tests were carried out for the reconstruction of a two-section plant flowsheet, one for the recovery of Zn sulphide and the second for the separation of the oxidized fraction from the final waste. Starting from feed concentrations around 2% Zinc, three products were obtained: a commercial Zn sulphide concentrate with 50% content; a final waste with heavy metal concentrations (Zn and Pb) lower than the CSC for industrial sites; and an intermediate concentrate (not marketable) whose residual Pb and Zn content requires inerting or disposal in a collection site.

The collaboration with the Geological Survey of Finland (GTK), Europe's leading competence center for the evaluation and sustainable use of geological resources, has allowed the realization of a project aimed at the implementation of high quality data that have highlighted important characteristics of mineralogical composition of the treated material.

The thesis was produced during the PhD course in Earth and Environmental Sciences and Technologies at the University of Cagliari, a.y. 2019/2020 - XXXIII cycle, with the support of a scholarship funded with the resources of the CESA Project, funded by the Autonomous Region of Sardinia, which aims to develop and enhance the technical and scientific skills in the field of reclamation of mining sites, in agreement with the University of Cagliari and the Company IGEA S.p.A . The topic of the project is one of those proposed and coordinated by the Scientific Technical Committee of CESA.

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Chapters overview

Chapter 1 outlines the problem associated with mining areas and the consequent pollution of resources, related to the dispersion of toxic metals. Critical aspects related to pollutants and their economic value are introduced and the need to develop a remediation system that fits into the circular economy is explained. Consequently, the approach and solution proposed in this paper are introduced by explaining the purpose, novelty and goals.

Chapter 2 specifically describes the situation of mineral dumps in the Sardinian context, the mineralisation and associated alterations, and finally a focus on the study area.

Chapter 3 introduces both the sample materials on which the experiments were based and the established methods for the extraction of heavy metals. The chapter is divided into five parts: the first part describes the "Froth Flotation technique" and all the parameters influencing the procedure. The second part describes the sampling technique and the samples for study. The third part describes the material characterisation techniques and the strategies adopted for the analysis of toxic metals. The fourth part describes chemical characterisation analyses and analytical detection techniques. The fifth and final part describes methods of statistical analysis and data reconstruction.

Chapter 4 reports the study published at the 18th International Symposium on Environmental issues and Waste management in Energy and Mineral production, held in Santiago, Chile, as a result of the experiments carried out in the first year of the study on a sample representing the Montevecchio Ponente area.

Chapter 5 reports the study published at the VI Symposium on Mining in the Mediterranean Basin, held in Iglesias, Sardinia. The paper summarises the procedures and results obtained on a sample of tailings representing the Montevecchio Levante area and it introduces new strategies and methods of investigation.

Chapter 6 summarises the study carried out at the Geological Institute of Finland GTK (Geologian tutkimuskeskus), in which 4 months of investigations were carried out on the same sample from the Montevecchio Levante area. The results are compared with those obtained in Italy in order to verify the data obtained.

Chapter 7 concludes the thesis by summarising the main findings.

Chapter 1: Introduction

1.1 Contaminated sites and pollution

The issue of contaminated sites is of great topicality and importance. After the final closure of mining activities (1990s), the need to search for recovery and mitigation strategies has become evident.

The global economy absorbs 92.8 billion tons of minerals, fossil fuels, metals and biomass each year. Only nine percent of this goes back into circulation, threatening climate, resource adequacy and opportunities for sustainable growth. Mining has made a significant contribution to global wealth, but mineral extraction disfigures the landscape and is among the industrial activities most likely to damage, pollute and alter land, because it involves the creation of unstable morphologies prone to landslides and collapse [3]. Exposure to the exogenous environment of large amounts of material rich in potentially toxic metals causes changes in environmental chemistry, (Cu, Pb, Zn, Cd, As, Cr and Ni). These elements are released through a variety of modes:

- mechanical tools (gravitational slip, runoff, wind transport);
- chemical tools (solution transport).

The latter may represent the least obvious risk, but in the long run it is the most dangerous and limiting to human activities, as well as the most difficult to be removed [4] and [5].

Tailings that have not been properly deposited or rehabilitated can produce acid drainage for hundreds of years or more after the termination of mining. Once started, the acid generation process is extremely difficult to stop and can kill most living organisms in an entire water system for years, turning it into a biological challenge and a huge economic burden. Measures to monitor chemical reactions and treatment and drainage control must be site-specific and appropriate for the source and type of contaminant.

The metalliferous veins from which metals of interest are extracted in non-coal mines are mostly sulfide minerals, such as galena (PbS, lead sulfide), sphalerite (ZnS, zinc sulfide), pyrite ($FeS2$, iron sulfide), and chalcopyrite ($CuFeS2$, copper iron sulfide).

Precious metals were commonly separated using grinding, leaching, and electrolysis. Waste materials from precious metal mining, referred to as "gangue," were deposited in waste rock dumps or abandoned in riverbeds. These materials are still very rich in potentially toxic metals, which are mobilized into the environment; they also have varying grain size, which determines the potential for dispersion of the toxic elements. The smaller the grain size (e.g., fine tailings), the greater the surface area exposed to weathering. A predominant role is played by flotation muds, originally deposited in ponds where high concentrations of toxic metals are found and their leaching by weathering causes significant pollution in mining areas. In any case, the surface water circuit represents the preferred route for the dispersion of these toxic elements, even at considerable distance from the source. The importance of implementing interventions aimed at reducing the polluting potential is unquestionable, especially if it is considered the number of settling basins and the dumping of tailings whose materials are dispersed in the surrounding areas with extreme ease, as happened in the case of the marine area of Piscinas, which is located in the mining complex of Montevecchio-Ingurtosu (Sulcis-Iglesiente, South-West Sardinia), in Figure 1.1 it is shown a dumping of residues of Laveria Pireddu not far from the beach of Piscinas. Figure 1.2 shows a case of contamination of the Rio Piscinas in 2009.

Figure 1.1 Mining residues of Laveria Pireddu, mining complex of Montevecchio-Ingurtosu (Sulcis-Iglesiente), in the background the dunes of Piscinas beach.

Figure 1.2 Contamination of Rio Piscinas (south-western coast of Sardinia), caused by the transport of mining residues [6].

The following images show two examples of mining areas characterized by the presence of mining waste dumped on vast portions of land and which are subject to territorial requalification actions. One of these, the mining complex of Montevecchio, in the municipalities of Guspini and Arbus, is disused and it has been the subject of study in this work, with the ultimate aim of creating a pilot plant for the management of industrial waste. Montevecchio is part of the historical and environmental geo-mineral park of Sardinia, included in the GEO-PARKS network of UNESCO. Given its long history of mining activity, several monuments of industrial mining archaeology are housed within its premises.

Figure 1.3 Montevecchio mine, SW Sardinia.

During my training period at the Finnish Geological Survey GTK, I was able to visit the Pyhäjärvi mine. It is an active plant that has introduced an efficient system for reprocessing industrial waste in the context of a circular economy. The purpose of the visit have been to observe a mining waste reprocessing plant already in operation and to hypothesise a possible related future case in Sardinia. Both the process and the materials are similar and the aim is to address the issues within a circular economy.

The Pyhäsalmi volcanic deposit hosting the copper-zinc-silver-gold-pyrite deposit is located 4 km southeast of the town of Pyhäjärvi on Lake Pyhäjärvi, Finland, ~400 km north of NNE Helsinki (location: 63° 39' 34 "N, 26° 2' 31 "E).

Pyhäsalmi is one of the oldest and deepest underground mines in Europe. It is also one of the most efficient underground mines in the world. It was developed by the Outokumpu Oyj company in 1962 following the accidental discovery of the deposit by a farmer. From here it began operating as an open pit mine based on a resource estimate of 33.4 Mt.

Figure 1.4 Pyhäsalmi mine, Finland

The mine went underground in 1967 and mining ceased in the open pit in 1979. In the 1990s, a 1450-meter deep automated lift shaft was constructed to exploit the deeper ore. In 1996, additional ore was discovered at depth. The operation was sold to Inmet Mining in 2002 and it was acquired by First Quantum Minerals in 2013 through the purchase of Inmet. Mining operations are expected to end in 2021. It has produced approximately 60 million tons of ore in its history, production guidance for the year 2020 is 3000 t of copper, 1000 t of zinc, 0.06 t of gold and 0.45 Mt of pyrite.

1.2 Heavy Metals

The EU's metallic minerals sector offers a wide range of minerals that produce metals or metallic substances. The EU is a major producer of chromium, copper, lead, silver, and zinc. Sphalerite is the world's main source of zinc supply, considering the economic value and increasing demand for zinc metal, tailings can be used as an appropriate source of zinc.

However, most of the metal ores that supply the European metallurgical industry are imported. Only a few EU countries have active mines. These include Austria, Finland, Greece, Ireland, Poland, Portugal, and Sweden. In these countries, metal mining contributes more than 1% to the overall production of a particular metal ore. The Geological Survey of Finland (GTK) is searching for gold in Finland. Many gold deposits in Finland, including some gold mines, have been discovered based on mining geochemistry and heavy mineral evaluations. Fine native gold grains and other heavy minerals can be mapped to define the physical dispersion of minerals in the deposit. Such dispersion mapping and study of the grain morphology, surface structures or mineral chemistry of these deposits will provide information on rock source and distance that could lead to the discovery of important gold and other base metal mining operations [7].

Heavy metals are elements at the base of the composition of the earth's crust and of many living organisms, therefore commonly present in our lives. The problem arises when the amount that penetrates into our body exceeds the tolerability reaching toxic levels.

The danger of a metal is related to its mobility, ie migration to deeper layers (contamination of groundwater) and its bioavailability, ie the availability for absorption by living organisms, animals and plants with the risk of entering the food chain [8]. Several heavy metals are defined as essential micronutrients as they are required in the physiological and biochemical cycles of living organisms and they are also capable of associating with various enzymes. The functioning of many proteins depends on the presence of a cofactor (HM) within the organic molecule.

Unlike the atmosphere and water whose decontamination processes can be carried out in a relatively short time if deprived of the sources of pollution, for soil and sediments contamination can persist for much longer periods, and HMs are very persistent.

They are characterized as having the same characteristics:

- Density higher than 5 g/cm3.
- In nature, concentrations of less than 0.1% are achieved.
- Concentrate in sulfides (calcophilic elements).
- They form complex chemical bonds.
- They possess different oxidation states depending on pH and Eh conditions.

- They behave as cations, i.e. as positively charged ions when they enter an electromagnetic field.
- They have a low solubility of their hydrates.

Heavy metals are [9]; [10]:

Table 1.1 Heavy metals

Heavy metals					
silver	Ag	barium	Ba	cadmium	Cd
cobalt	Co	chromium	Cr	manganese	Mn
mercury	Hg	molybdenum	Mo	nickel	Ni
lead	Pb	copper	Cu	tin	Sn
zinc	Zn	arsenic	As	antimony	Sb
bismuth	Bi	selenium	Se	vanadium	V

From the environmental point of view, the most significant ones, at the eco-toxicological level, are: As, Hg, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, Zn, and Se [11].

1.3 Critical Raw Materials

In recent years the issue of raw material supply has become of primary importance in Europe and worldwide. Raw Materials are the basis of industrial processes, they are fundamental for the European economy as they can be used for many purposes in everyday life. CRMs (Critical Raw Materials) are updated indicative lists that the European Commission has created to address this challenge. CRMs combine raw materials of great importance to the EU economy and the high risk associated with their supply [12]. Many studies carried out by, among others, the World Health Organization (WHO), the European Centre for Environment and Health and, in Italy, the Istituto Superiore di Sanità, show that the number of industrial sites where excessive levels of contaminants in the soil may represent a risk for human health has increased [13] [14].

Globally, the scale of the contaminated sites problem is evident; according to a U.S. inventory of abandoned mines (US BLM, 2010) as of January 5, 2017, the inventory contained 52,381 sites, of which approximately 20% have been remediated or do not require further action.

At the European level, a systematic review of former mining districts is being conducted. There are approximately two million potentially contaminated sites in Europe. Mining in Europe began thousands of years ago. There are many regions in Europe where there are large mining districts that should be considered economically depleted. In fact, a theme that has emerged in the last 10 years is the one of raw material availability for the EU. This issue has reopened the discourse of geo-resources on a continental level.

Since 2010, Critical Raw Materials (CRM) have been defined by the European Commission as a list of materials of great importance for the economy and industry of the EU, for which there are concerns about supply risks due to both geological and geopolitical factors: import restrictions for some politically risky countries such as Russia and China, or difficulties in the availability of raw materials from risky countries such as Africa. The list of CRMs is updated regularly (most recently in 2017) and now it includes 27 CRMs, including large groups such as HREE (heavy rare earths), LREE (light rare earths), and PGM (platinum group minerals).

The European Commission has proposed a series of recommendations regarding member state policies on raw materials. Among these, priority is given to policies for the systematic recycling and re-evaluation of domestic mineral resources. As a result, new activities have started in several districts (old mining areas of Europe). Where old deposits have been exploited for several centuries and are now considered exhausted, new activities have started to evaluate their residual potential in terms of CRM resources. Sardinia is part of this context as it represents the most important mining district in Italy both in terms of territorial extension and duration of activities over time.

The trade-in Rare Earths and the intricate economic discourse surrounding their production is an increasingly discussed topic. China continues to dominate the global supply of rare piles of earth. Currently, the world's REO production comes mainly from bastnasite, monazite, xenotime and Chinese ion adsorption minerals. As the world's demand for REE is increasing, other REE minerals or resources could become new REO sources in the future, [15]. According to China's Ministry of Industry and Information

Technology, the mining and separation production quotas for 2019 were 132,000 tonnes and 127,000 tonnes. Global mined production is estimated to have increased to 210,000 tonnes of rare earth oxide, up 11% from 2018. In the US, domestic production of mineral concentrates, all of which were exported, increased to 26,000 tonnes, 44% higher than in 2018 [16]. However, the extraction of these elements is very complex, and most companies are trying to dispense with rare earth and recycle those already present in technological products. Research has been conducted into the possibility of using mining waste as a raw material for REE recovery [17], [18], [19], [20].

1.4 Minerals trading market

Considering the economic value and growing demand for zinc metal, tailings can be used as an adequate source of zinc. Having defined the tractability of the material, the design of the mineralurgical plant must consider the market in which the commercial concentrate would be sold.

Among the external parameters that affect the resolution of the economic problem, which underlies choices in the domain of Mineral Preparation, fundamental is the mineral market. For example, for Pb, Zn and metal ores in general, in the Western world reference is normally made to metal quotations on the London Metal Exchange (LME). Mineral prices are linked to these quotations with formulas that have universally adopted structures and parameters, except for the corrections inherent to subsidies and penalties for accessory elements, transport and commercial expenses in general, customs and other duties, and also the particular condition of the user.

In the U.S.A., which represents for many metals a relatively closed market, reference is made to the quotations of the country's stock exchanges (New York, Saint Louis, etc.), quotations that to a certain extent may differ from those of London, and generally differ in a more stable character compared to the quotations of L.M.E. because of the customs policy adopted by that country.

The formulas for the purchase and sale of metalliferous minerals have an international value structure. One of these is described below.

- American type formula: $\mathbf{V = (P - R)(T - q) - S}$

where V is the value of 1 tonne of merchant ore returned to the metal workshop, P is the metal quotation on the reference price list, T is the mineral content, q is the deduction corresponding to processing losses, R is the refining charge per tonne of metal, S is the smelting charge and it also includes all the other foundry expenses and fees that refer to the tonne of ore entered.

The formula, perfectly rational, highlights the two basic items of expenditure of the smelter: one S refers precisely to the ton of ore and therefore its incidence on the metal increases with the decrease of the content T, the other R that instead relates directly to the metal.

1.5 Reclamation Technologies

The methods of remediation and making safe of mining areas are many, the application of a method rather than another depends on various factors such as the type of pollution, the peculiarities of the site affected by pollution, the availability of necessary equipment and specialized personnel, the time needed to reduce / eliminate the contamination in place and finally the cost of the remediation operation also in relation to the benefit brought to human health and the environment in the short and long term. Tables 1.2, 1.3 and 1.4 show a list of the most used remediation and safety treatments, including flotation, which is of interest for this thesis work.

The main method used to recover metals is flotation, while on material that cannot be valorized, i.e., whose metal concentration is too low to be marketable but exceeds the contamination threshold concentrations (CSC), inerting is performed.

Table 1.2 Remediation and/or safety methods, with description in relation to the degree of protection of human health and the environment, short- and long-term effectiveness, technical feasibility and costs. Source [21].

Renovation technology	Barriers/containment systems	Solidification/ stabilisation (in situ or ex situ)	Vetrification (in situ or ex situ)	Chemical treatment (oxidation, reduction, neutralisation)
Protection of human health and the environment	They can significantly reduce the rate of release, but are not a permanent remedy. They are often used in combination with a treatment technology.	Reduces the potential for release of the contaminant into water or air. However, the contaminant is not removed.	Long-term effective permanent system. It can simultaneously treat organic and inorganic contaminants.	Potentially protective because metals are transformed into less mobile forms.
Long-term effectiveness	They protect against on-site exposure and control the migration of contaminants. They are not considered to be a permanent solution. Monitoring of aquifers is required to verify that there is no percolation of the contaminant.	Data on long-term effectiveness are limited. The contaminant is not removed from the waste.	Low leachability. Products can be reused.	Immobilisation of metals and/or reduction of toxicity are subject to the external environment. Changes in the external environment may lead to remobilisation.
Reduction in toxicity, mobility or volume	Does not reduce the toxicity or volume of the contaminated site. It reduces downward and lateral mobility and offsite migration caused by wind erosion, surface runoff and percolation.	Volumes increase (approximately 10 to 100%). It can reduce the mobility of many metals in the soil.	Metals are immobilised in a glassy solid. Volume reduction.	It can reduce the mobility of many metals. The most common example is Cr(VI) converted to Cr(III).
Short-term effectiveness	Excavation dust. Use of DPI for worker protection and there must be a dust control system.	Excavation dust. Use of DPI for worker protection and there must be a dust control system.	Excavation dust. Use of DPI for worker protection and there must be a dust control system.	Excavation dust. Use of DPI for worker protection and there must be a dust control system.
Feasibility	Rapidly implementable, except for horizontal barriers. Technologies for implementation are readily available.	Widely used. The presence of organic components can inhibit the solidification process. It is difficult to formulate the right binding agent when several types of contaminants are present.	Pilot plant testing required. Highly qualified personnel, sophisticated instrumentation required. Limited commercial availability.	It can be done easily with simple instrumentation. However, sites that have contamination by many metals create complications.
Cost	They are generally less expensive than most forms of treatment	\$50-\$150/ton.	High costs and energy use, typically > \$500/ton.	Variable, depends on the specific technology used. From \$25/ton.

Table 1.3 (Continued) Remediation and/or safety methods, with description in relation to the degree of protection of human health and the environment, short- and long-term effectiveness, technical feasibility and costs. Source: [21]

Renovation technology	**Bioremediation in phytoremediation plants**	**Physical separation (screening, gravity separation, flotation)**	**Metallurgical treatment**
Protection of human health and the environment	Usually used when other more effective technologies are not feasible. Does not allow for complete remediation.	if high removal efficiencies are achieved, these treatments are very useful in protecting human health.	Recovery of metals for other uses.
Long-term effectiveness	ffectiveness depends very much on the process. Removal of contaminants can occur if the chemical conditions change.	Excellent if high removal efficiencies are achieved	High if high efficiencies are achieved. Enriched products can be reused or recycled.
Reduction in toxicity, mobility or volume	It does not lead to volume reduction but can transform metals into less mobile and/or less toxic forms.	It permanently reduces soil toxicity and concentrates metals in a much smaller volume.	Permanent removal of most metals and immobilisation of traces in mud and waste.
Short-term effectiveness	It is a very slow process.	Excavation dust. Use of DPI for worker protection and there must be a dust control system.	Excavation dust. Air emissions to atmosphere requiring treatment.
Feasibility	It is only applicable to a limited group of metals. It takes several years to complete the process.	Required pilot plant tests. Specialised (but not expensive) equipment required.	Most smelting plants do not have permits to treat hazardous waste. Requires specialised facilities and personnel. Need for air treatment.
Cost	Large areas can be treated with relatively low costs.	The cost varies greatly, from $10 to a few hundred, depending on the complexity of the process.	Variable as a function of metal concentration, the metal market and the form of metal in the waste.

Table 1.4 (Continued) Remediation and/or safety methods, with description in relation to the degree of protection of human health and the environment, short- and long-term effectiveness, technical feasibility and costs. Source: [21]

Renovation technology	**Hydro-metallurgical extraction (chemical or aqueous leaching)**	**Electrokinesis**	**Offsite excavation and blasting**	**No action**
Protection of human health and the environment	If high efficiencies are achieved, this treatment provides excellent protection. It requires treatment of the washing fluid.	The contaminant can be permanently removed from the waste.	Moving waste from one site to another. A controlled landfill is considered one of the safest sites to dispose of waste.	Remediation not performed.
Long-term effectiveness	Excellent if high removal efficiencies are achieved.	Permanent, metals are recovered and recycled.	The long-term effectiveness on site is excellent because the material is removed from the site. However, the contaminant is not treated or removed from the waste.	Contaminants would continue to migrate offsite and into the aquifer. The aquifer must be monitored.
Reduction in toxicity, mobility or volume	Concentrates contaminants in a much smaller volume. Reduces soil toxicity by removing metals.	It permanently reduces soil toxicity by removing metals and concentrating them.	It does not reduce the toxicity or volume of contaminants in the soil. Mobility is reduced by placing the contaminants in a controlled dump.	Toxicity, mobility and volume of contaminated soil are not reduced.
Short-term effectiveness	Excavation dust. Use of DPI for worker protection and requires dust control.	Air emission can be a problem. It can release gas to the electrodes.	Excavation dust. Use of DPI for worker protection and requires dust control.	No remediation action involved. Minimal protection of public health from exposure to soil surface.
Feasibility	Subject to many incompatibilities. Pilot plant testing required. High removal efficiencies difficult to achieve with simple processes. Requires simple equipment.	Pilot plant test needed. Difficulty in achieving high removal efficiencies. Requires specialised instrumentation. Presence of many different metals creates complications. Applicable to clayey soils.	The necessary technologies are well established and readily available. Restrictions on landfills could be applied. There is no interference with other future remediation actions on site.	No consideration of feasibility.
Cost	Hundreds of dollars per tonne. The value of the recovered metal can partially cover the cost of treatment.	Relatively expensive. Limited data at industrial scale.	Between $300 and $500/ton.	There are no capital costs. There would be associated costs for sampling and analysis.

1.6 Purpose of this study

The subject of this research is the inertisation treatment of mineralurgical tailings in the Montevecchio mining area. This research is part of the above-mentioned themes and, although it deals with very specific cases, it constitutes a representative model of the specific problems linked to disused mining areas. The methods used in this work aim to achieve two general objectives. On the one hand, waste management is applied by recovering Pb and Zn sulfides and sulfates present within mineral wastes with a commercial value through the flotation technique, and on the other hand, a polluted site is reclaimed. These two goals, however, must be considered as a single goal to be achieved through the application of a circular economy. The intention pursued wants to be supported in its validity through the comparison of the management of the problem implemented with a Finnish geological research service, GTK (Geological Survey of Finland), for this purpose the training period at the foreign company mentioned above was organized.

1.6.1 Flotation and the circular economy

Over the past 15 years, the mining industry has integrated the concepts of sustainable development and sustainable mining practice into every area of mining operations. In January 2018, the European Commission published a report [22] which highlights the importance of sustainable use of CRM in our economy. The report describes relevant EU policies, it references key initiatives, presents and provides data sources, identifies best practices, and it identifies possible further actions.

In May 2019, another report was published [23] in which existing practices for recovering CRM and other raw materials from mining and landfill wastes are shown. The report outlines technological processes for recovering various materials from mining tailings and industrial waste, as well as best practices for improving the knowledge base on the availability of secondary materials. It also provides estimates of the recovery potential of certain materials and outlines prerequisites for recovery practices on a larger scale than today.

In Sardinia, mining has played a key role in economic development, reaching one of the most important outputs in Western Europe. For this reason, the amount of mining waste is higher than in the rest of Italy. The recovery of these residues as secondary raw materials could bring many advantages, improvements and benefits both from an environmental and an economic point of view.

There are many methods of remediation and safety, the application of one method rather than another depends on various factors, such as the type of pollution, the peculiarities of the site affected by the pollution, the availability or not of the necessary equipment and specialized personnel, the time required to reduce/eliminate the contamination in place and lastly the cost of the remediation operation also in relation to the short and long term benefit to human health and the environment.

The application of the circular economy approach to waste originated from Pb and Zn sulfide-based mining residues has been discussed by several authors [24].

Waste management becomes a problem for mining companies as they have to incur costs to dispose, stabilize or contain the inert material, (busisness cost). In addition, there is a lack of consensus among these companies: There is a gap in uniformity of view by policy, companies and international institutions.

The guiding principles for proper disposal in relation to the lack of international consensus proposed in the literature are [25] :

- Mining wastes must be managed so that they remain physically, geographically, chemically, and radiologically stable.
- Waste that interacts with the environment must be inert
- If they are not inert, they must be isolated
- They must be stored (geographically, physically, chemically).
- Must be managed based on the environmental and social conditions of the site
- Minimize post-closure impacts
- Opportunities for their reuse must be pursued when feasible.

Due to the increased demand for metals by society, the required content of minerals has decreased.

For each ton of metal, it is estimated 2 to 12 tons of waste [26].

Chile→ 1.6 million tons of tailings per day

South-Africa→ 17.7 million tons of tailings per day

European Union→ 1.2 million tons of tailings per day

Valuing tailings means recovering residual metals and reusing the matrix. The waste hazard can be turned into a valuable secondary metal resource by combining metal recovery with environmental management.

There are currently about 75 major tailings reclamation projects globally [27].

The circular economy aims to minimise the amount of waste and reuse existing waste. this is done by making the best use of resources and redesigning and optimising products for reuse. The circular economy represents a systemic change that builds sustainable economic development and provides environmental and social benefits.

The circular economy concept follows the 3Rs principle, "Reduce, Reuse, and Recycle" (fig. 1.5), which promotes the reduction of waste generation, reuse of material, and recycling or even transformation of the same material into a usable form [28] [29].

Figure 1.5 Circular economy graphic.

The second figure aims to introduce, as applicable also in the mining context, a new concept: the reuse and therefore the redevelopment, recovery and recycling of material to transform it into secondary raw material.

Waste reduction can be achieved by implementing mining efficiency through the use of modern technologies, thus reducing mineral losses and emissions of various pollutants, including mine wastewater. Reuse can consist of the recovery of components used as waste or the production of new substances using the waste materials as raw material. Recycling reduces pressure on mineral resources, energy consumption, and the environment.

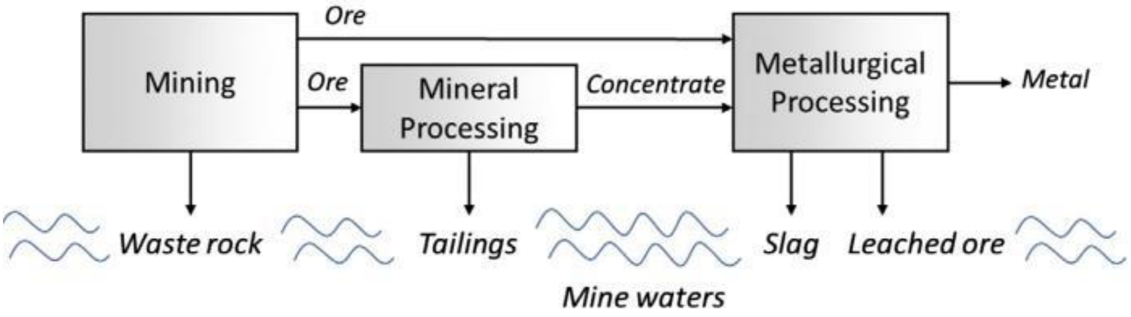


Figure 1.6 Simplified scheme of a process of mining activity [30] .

A general outline of the main processes and residues produced by mining is shown in Figure 1.6. Three types of solid residues are produced: waste rock (the barren rock), mining waste (tailings) from mineral processing, and waste from metallurgical treatments. The primary method used for metal recovery is froth flotation. The process separates minerals from gangue by exploiting differences in their hydrophobicity. The differences in hydrophobicity between the valuable minerals and the waste gangue are increased by the use of surfactants and wetting agents. Selective separation of minerals makes it economically feasible to process complex (i.e., mixed) minerals.

1.6.2 Aim

This PhD project simultaneously addresses the fundamental challenges of waste disposal and environmental remediation. The work aims to show the technical feasibility and economic viability to the reprocessing by flotation of Tailings of Pb and Zn sulfides. The innovative aspect of this work was based on the reuse of the materials in the following production cycles, thus cancelling the waste and closing the economic cycle of the materials. To achieve this goal, the main purpose was to provide a valid method for the reprocessing of mining residues through the application of ad hoc process schemes, adapted to the composition characteristics of each sample. The construction of these schemes requires analyses aimed at understanding the multiple aspects of their ultimate purpose:

- The transformation of the residue into a non-polluting material that can be reused.
- The production of marketable concentrates with characteristics corresponding to the requirements of metallurgy.

The scope of the internship period in Geological Survey of Finland (GTK) office in Kuopio (laboratory work in Outokumpu) was to reprocess the test material through mineralogical analysis and flotation testing, using advanced techniques (MLA) and comparing similar techniques (flotation testing) to result in a high validity study in the field of mining tailings reprocessing.

1.6.3 Research Objectives

In the context of the above-mentioned issues, the specific objectives that characterised this research were.

- Checking the floatability of the materials: from a technical point of view, the floatability depends on the mineralogical characteristics of the useful species and of the gangue, as well as on the degree of liberation of the minerals to be treated and the size of the grains (characteristics to be assessed on a case-by-case basis); it also depends on the efficiency of metal recovery in the concentrate.
- Chemical analysis and data processing aimed at understanding system trends with the aim of reducing concentrations below the contamination concentration threshold in industrial areas (CZn/Pb ≤ CSCZn/Pb industrial sites)
- Statistical processing based on the application of physical and chemical strategies evaluated on a case-by-case basis in order to verify the possibility of obtaining

commercial concentrates with characteristics corresponding to the metallurgical requirements, CZn/Pb ≈ 50% for the sulphide concentrate and CZn/Pb≈2.5% for the oxide concentrate.

- Reconstruction of the implemented process schemes and observation of the best strategies to be applied at each point of the waste treatment process, in order to elaborate a proposal for an optimal plant flowsheet.
- Treatment of the same material in the laboratories of the Finnish service. Various chemical reagents were tested and innovative techniques were applied that were comparable to the methods used at UNICA's university laboratories. The objective thus became to verify the applicability of the various methods for the characterisation of sediments consisting of mine tailings.

1.7 Cases history

Cases of reprocessing of tailings and low-grade minerals can be found in the literature. These concern various authors, Güven et al., 2010 (Zn% 3.23) [31], Zhou et al., 2014(Zn% 0,74) [32], Soltani et al., 2014 (Zn%3.5) [33], Evdokimov, 2014 (Zn% 5.22) [34], Lv et al., 2015 (Zn% 0.33) [35], Zhang et al., 2019 (Zn%2.73) [36], Bagheri et al., 2020 (Zn% 12.7) [37]. The following are two examples of tailings treatment with experimentation of new phases in the circuits. In recent years, there has also been an increase in the number of projects that investigate the phases and distribution of rare earths during ore processing, with the aim of assessing their possible recovery. Some examples are: X. Yang et al. 2019 [38], [39], [40], [41], 2015 [42].

1.7.1 Recovering zinc and lead from tailings through flotation [31] :

Report of some lead-zinc ore tailings containing 3.12% Zn, 3.43%Pb, 0.71 g/t Au and 74 g/t Ag. The objective is to recover zinc and lead from the Tailings. The Pb and Zn ores were heavily oxidised. The methods used are, sulphide flotation, to obtain a sulphide concentrate and oxide flotation, for an oxide concentrate. The Tailings come from Balikesir in Turkey. Sulphides are used for the recovery of zinc and oxidates for the recovery of lead. First the Pb sulphide is floated, then the Zn sulphide, then the Pb oxidates and finally the Zn oxidates.

The tailings of Pb and Zn through flotation are evaluated.

It is noted that increasing the number of roughing stages, followed by cleaning stages, increases the metal content in the concentrate. They had accumulated 1 tonne of gravimetric and flotation tailings in the mine, containing a considerable amount of Pb and Zn.

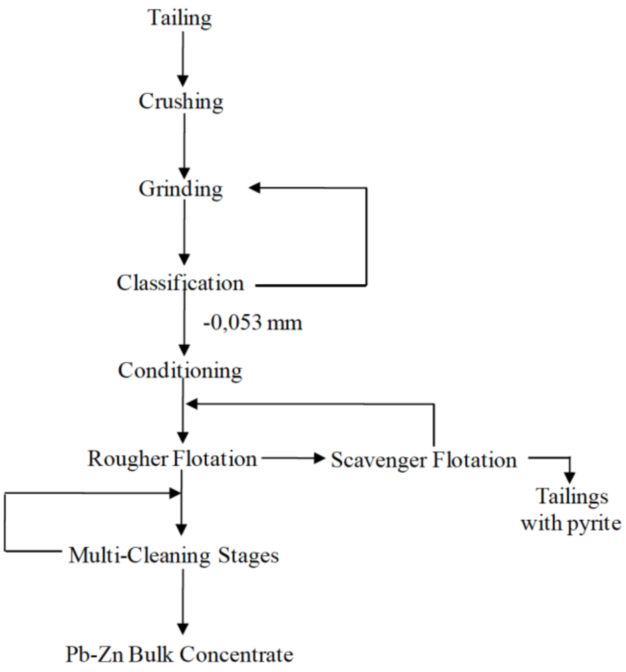


Figure 1.7 The proposed flowsheet for evaluation of Pb-Zn tailings.

Sodium sulphide or sodium hydrosulphide in combination with isopropyl or amyl xanthate are the collectors of choice for flotation of Pb ores.

For the test they use ERO(dtp), potassium amyl xanthate, AERO(DTP) as collectors, sodium metabisulphite ($Na2S2O5$) as a pyrite depressant, $CuSO4$ as a sphalerite activator, sodium sulphide ($Na2S$) as an activator and oxidised minerals and MIBC as a foamer.

Different procedures were tested: In a first trial in order to test the collectors, they float Pb and Zn together.

By increasing the stages of roughing and cleaning, they notice that the recovery of Pb and Zn increases.

During the tests, 5 roughings and 13 cleaning were carried out for Pb-Zn sulphides; 4 roughings and 4 cleaning for lead oxides. Grinding was carried out at 53 µm.

Flotation of sulphides was effective to obtain concentrates with high zinc content. Flotation of oxidates was effective for concentrates with high lead content. After flotation of the sulphides, a lead-zinc concentrate with 43.02% Zn and 12.23% Pb was produced: the highest lead content obtainable from the oxide flotation was 22.7%.

1.7.2 Two steps for the conversion of sulphides into marketable selective concentrates [34]:

This article reports on the analysis of tailings processing technology from the Unalsky tailings pond. It studies the conversion of sulphides into marketable selective concentrates in two stages: the sulphide product is first extracted from the tailings using a channel hydroseparator and then processed, either together with the current ore material, using accepted technology, or separately, by jet flotation.

Thus, in the first case, the product is obtained from the tailings with a polymetallic content similar to the content of lead-zinc ore from the Dzhimidon deposit processed at the Mizurskaya Processing Plant (MPP); in the second case, the product obtained and the current ore were processed together.

The analysis of the curves shows that the recovery of all metals increases with the increase in the yield of the deposit fraction (the lowest result is obtained for gold wear). The recovery of iron, copper and lead sulphides increases gradually within the range of the yield of the deposit fraction. However, gold recovery reaches its limit already at the deposit fraction yield of 20-25%, and lead recovery does not increase after the deposit fraction yield exceeds 30%. From the point of view of recoverable value, it is reasonable to maintain that level of yield in the deposit fraction.

Recovery in the deposit fraction reached 56.57% Pb, 60.30% Zn, 28.15% Au.

Marketable concentrates of lead (content 65% Pb at recovery 84.01% Pb) and zinc (content 50% Zn at recovery 86.06% Zn) were produced by separation of the deposit fraction by gravity flotation, together with ore searches by MPP (direct selective flotation and Sheridan-Grissvold mode).

1.7.3 Mineral liberation analyses for rare earth detection [38]:

This paper describes how to determine the presence of Rare Earths (REEs) using MLA, mineral liberation analysis and EPMA, electron probe microanalysis. The carrier phases and their distribution on Rare Earth Oxides (REOs) during the treatment of a phosphate ore are observed. The process involves the enrichment of Apatite by flotation and treatment of the concentrate with sulphuric acid. Most (85%) of the REEs resulting from phosphate rock processing end up in waste (clay waste, flotation tailings and phosphogypsum) [43]. The association of MLA and EPMA analysis provides accurate analyses: for this case study the MLA identifies less than 20% of the REOs in the gypsum-containing phase. More than 80% of the REOs existing in the gypsum phase cannot be recognised by this method. The EPMA is able to acquire more precise and quantitative elemental analyses of all REEs phases, so that the distributions of REEs in the products of the ore enrichment process and the wet concentration process can be determined and the values of these products on REE recovery can be quantitatively assessed.

Compared to ICP-MS analysis, the MLA-EPMA method can quantify the chemical compositions of the mineralogical phases by measuring solid materials on a micrometre scale.

In this study, it appears that most REEs are concentrated in the waste and PG (Phosphogessum), which contain 26% and 62% of the total REEs in the rock, respectively. Apatite, allanite, monazite and pyrochlore are identified as REE minerals in the enrichment process. Flotation could be used to concentrate apatite and monazite using fatty acids or hydroxamates as collectors. In PG, REEs are mainly found in the gypsum and monazite phases. Physical methods such as screening, flotation and magnetic separation could be applied to concentrate monazite, although only 26% of REEs are transported by monazite in the sample studied. Most (73% REO) of the REEs transported by gypsum cannot be enriched by physical methods.

In addition, the highest contents of REEs are distributed in very fine size fractions, (-45 µm).

Chapter 2 State-of-the-art

Sardinia is the richest region in Italy in terms of mineral deposits, and as evidence of this are the many mines and related landfills distributed throughout the territory, which give an idea of how much this land has provided in terms of mining and then mineralogical. In Sardinia, there is the most important lead-zinciferous basin in Italy and among the first in Europe, but the secular and continuous exploitation has brought to the almost total scavenger of the deposits.

Geologically, the region is of very ancient formation: granite rocks dominate, which came into contact with pre-existing rocks, determining the formation of metalliferous concentrations. Remarkable are the cupriferous deposits (Sulcis, Iglesiente, Nuorese) from which specimens of great mineralogical and scientific interest originate. Unique crystallizations of Phosgenite, Barite, Anglesite, Amethyst Quartz and Silver have been found in Sardinia and are exhibited in the most prestigious museums and the most important collections in the world. XRD analysis showed the presence of oxidised zinc minerals on which the literature demonstrates the effectiveness of cationic collectors (amines) as the most effective recovery technique preceded by activation with sodium sulphide.

2.1 Mining activities in Sardinia: geological availability of resources

The most ancient testimonies show that already from the sixth millennium b.C. in Sardinia the mining production through the extraction and processing of obsidian was active; later the Sardinian mining production was enriched, thanks to new mining technologies and metallurgical techniques, with the extraction in particular of sulphides of lead, silver and copper. Thanks also to its strategic position, Sardinia became a main pole of the Mediterranean markets.

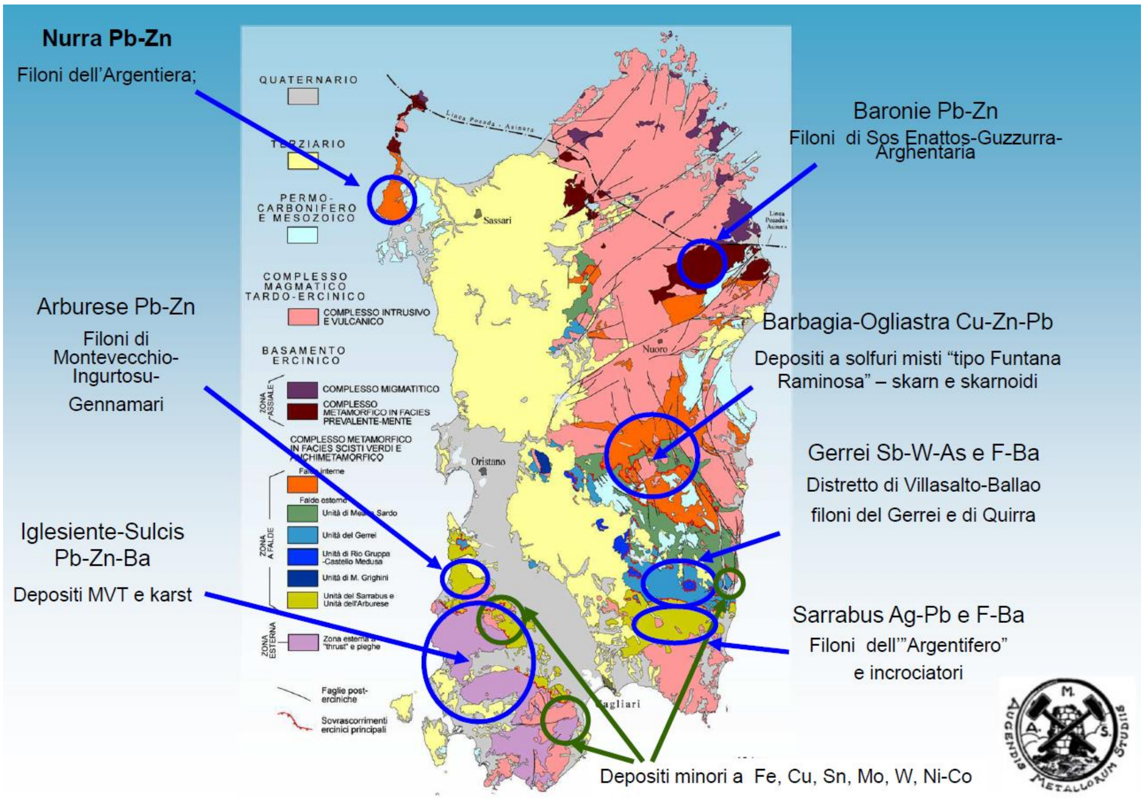


Figure 2.1 Mining activities in Sardinia.

When referring to mining activities in Sardinia, it is talked about districts that have more than 2000 years of mining activity:

- The historical productions of the Iglesiente and Arburese districts, about 6.0 Mt of Pb+Zn concentrates
- Historical productions of fluorspar concentrates: >3Mt
- Historical production of Barite concentrates: >3.5 Mt
- Historical production of Coal (sulcis coal)>28 Mt
- Current production of IM&R (industrial minerals) >2 Mt/year

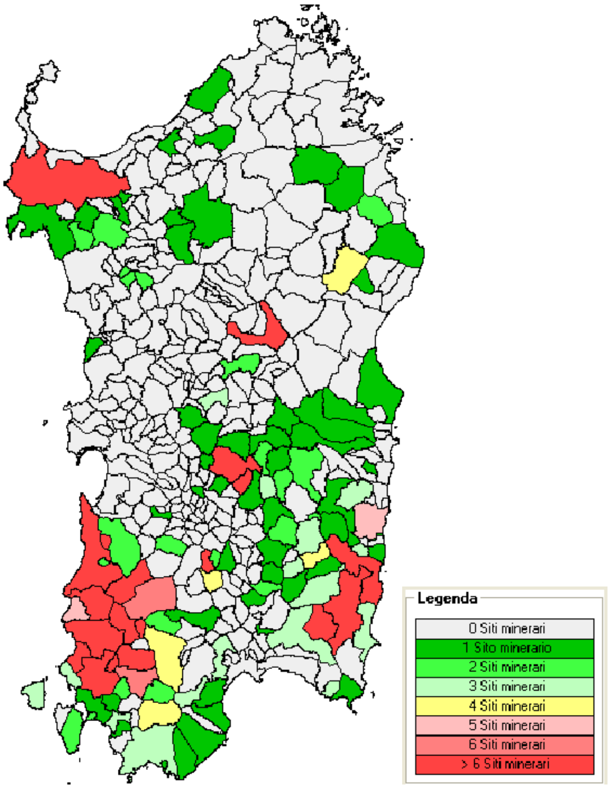


Figure 2.2 Map of Sardinian mining districts divided by mining sites within them.

What is highlighted are the enormous volumes of waste from past mining activity >70 Mm³ in 169 disused mining sites, of which over 80% are in Sulcis-Iglesiente-Guspinese. These volumes lead to the definition of a polluted site of national interest, directly linked to past mining activity (AREA SIN identified by Ministerial Decree 468/01 as a reclamation site of national interest, by Decree of the Ministry of the Environment of 12 March 2003 and subsequent amendments, most recently in 2011).

An element that marks these past districts is the need for priority interventions on these materials through the securing/remediation/restoration of abandoned mining sites. Operations for which costs of over 630 million euros are estimated (regional plan 2003).

In this framework, falling within the perspective of the circular economy, a residual economic potential (metallogenic) is investigated for this district.

As in all the European districts, 3 main lines are highlighted in the evaluation of the residual potential of the Sardinian districts:

- Waste and residues from previous mining and related metallurgical activities. A top priority is the economic revaluation of these materials, mapping operations of sites of potential economic interest are currently underway (National Environment Agency, ISPRA).

- Hitherto unexploited marginal deposits, in which raw materials other than the current ones were extracted (CRM) considered exhausted or close to exhaustion; these are the deposits of Pb and Zn that could have other resources either as by-products or as marginal parts of the districts never used.
- New discoveries such as hitherto unexplored, unassessed or unidentified deposits.

From the late 1990s to the present time, since the end of mining in the main Sardinian districts, there has been a significant advancement in the geology of Sardinia. Historical mining data and past scientific studies indicate in the mineralizations of the Sardinian districts the presence of a large set of CRMs:

- Fluorite + Barite
- Sb, W
- In, Ga, Ge (very high value, one of the most requested elements at the moment)
- REE
- Co
- Te

Other resources:

- Base and ferrous metals: Zn, Pb, Cu, Sn, Mo, Ni, Cd, Bi
- Precious metals Au, Ag

2.2 Sardinian mining waste

The Autonomous Region of Sardinia has prepared the Reclamation Plan for the Mining Areas of Sulcis - Iglesiente - Guspinese (the latest version of the Department of

Environmental Protection of the Region of Sardinia submitted for SEA and approved by the Regional Council in February 2019). The Plan contains the Guidelines to be followed for the design and execution of remediation and safety interventions for contaminated areas. In the previous versions (2003 and 2008), the Regional Plan highlighted the technical and economic difficulties of a proper reclamation of mining areas and indicated that the most feasible intervention was permanent safety measures to be carried out by means of "capping" operations (waterproofing of mining deposits) and/or by grouping the hazard centres into one or more special "collection sites" to be located, if possible, in areas already degraded by mining activities [44]. In this latest version, the Plan provides for "promoting, where technically feasible and sustainable, the recovery of materials derived from mining waste in synergy with the implementation of safety measures..." [45]. This is in line with the opinion of the European Economic and Social Committee on 'The processing and exploitation, for economic and environmental purposes, of industrial and mining waste in the European Union' [46].

Each type of mining activity corresponds to a different type of product, with a different environmental impact. In particular, the generic activity phases and related products are:

- - open-pit mining research and cultivation or through the construction of trenches and tunnels for inspection and cultivation. Outside this area, inert material was accumulated;

- - the mineral-siderurgical treatment of mines. Accumulations of mineralised material, enriched material and mining treatment residues can be found in this area;

- - the metallurgical treatment, which may take place in situ or ex situ, and it involves the processing of the material enriched in the previous stage with the accumulation of the residual material resulting from the treatment.

The products that have the greatest impact on environmental matrices are residues with a grain size between sand and silt, resulting from the enrichment of raw mineral by using processes such as hydrogravimetry and flotation. Waste management used to be a marginal and improvised aspect, and the ponds in which the material accumulated were not suitable for ensuring that the contaminants (heavy metals) found within the minerals did not bleach out, resulting in contamination of various environmental matrices (soil, surface, transitional and groundwater).

The spread of pollutants was even accelerated by the geotechnical instability of heaps sometimes built on steep, built with short-term embankments. In addition, the loading of enriched minerals took place in small jetties and sometimes on beaches, with an impact on the coastline.

As the problems are multiple and the nature of the deposits, the location, the management policy and the use of treatment plants differ, in order to characterise the disused mines in the Mining Areas Reclamation Plan (2008), it was decided to divide the territory into six macro-areas subdivided in such a way as to group together areas with similar environmental problems.

The six macro-areas are listed below:

- Montevecchio Ponente, which groups together the mines of Montevecchio, Ingurtosu and Gennamari;
- Montevecchio Levante;
- Barraxiutta macro-area, which includes six main mines (Barraxiutta, Perda Niedda, Reigraxius, Sa Duchessa, Sarmentus, Su Corovau), divided into numerous sites;
- Masua macro-area;
- Macro area of Malfidano, which groups together the mine of the same name and the PlanuSartu mining centre;
- Macro-area of the Rio San Giorgio - Iglesias, hosting numerous mines (Domus Nieddas, Monte Onixeddu, Monte Uda, San Giovanneddu, Cabitza, Campera, Campo Pisano, Genna Rutta, Genna Maiori, Monte Agruxau, Monte Scorra, Monteponi, San Giorgio, San Giovanni, SeddasModdizzis, Stagno di Sa Masa).

Data on the volumes and levels of lead and zinc in each of the listed mine sites can be found in Table 2.1. Data are not available for some sites (Domus Nieddas, Laveria Malfidano Buggerru, Palude Sa Masa, San Giorgio, Asta Fluviale Rio San Giorgio). The data come from the IGEA SpA PdCs according to the Legislative Decree 152/2006, validated by ARPAS (Regional Agency for Environmental Protection of Sardinia) and approved by the Industry Department of RAS (Autonomous Region of Sardinia), and made available to the CESA Project.

Table 2.1 Mining sites, relative volumes and Pb and Zn contents.

Site	**Volum (m^3)**	**Pb %**	**Zn %**
Cabitza	2100	0,58	1,28
Campera	424000	0,06	0,34
Campo Pisano	9340000	0,34	1,33
Genna Maiore	18000	0,22	3,47
Genna Rutta	21000	0,32	8,53
Masua basins	3800000	0,23	0,98
Masua industrial area	660000	0,5	2
Monte Agruxau	320000	0,58	2,5
Monte Onixeddu	90000	4,18	0,98
Monte Scorra	231000	0,9	4,5
Monte Uda	26300	2,71	0,87
Monteponi Cungiaus	600000	1,64	4,4
Monteponi S. Marco	170000	0,76	2,63
Monteponi Gravimetrica	260000	1	4,8
Monteponi Fanghi Rossi	620000	1,2	6,4
Montevecchio Levante dumps	60000	1,12	0,73
Montevecchio Levante industrial area	700000	2,06	2
Montevecchio Levante basin	5000000	0,28	0,67
Montevecchio Levante tailings	6900000	0,31	0,25
Montevecchio Ponente Ingurtosu dump	2200000	0,81	0,75
Montevecchio Ponente Ingurtosu fine dumps	670000	0,62	1,19
Nebida	215000	1,57	3,15
San Giovanneddu	2320000	0,83	2,02
San Giovanni	270000	2,33	2,34
SeddasModdizzis	350000	1,72	5,03

2.3 Mineralization and metallogenic potential of mining dumps

In the metallogenic map of Sardinia, the distribution of mineralisation on the island can be seen, and it is immediately apparent that most of the deposits are concentrated in the south of Sardinia in two large geostructural units:

- Palaeozoic basement (Cambrian and Varisian metallogenesis) therefore the whole of eastern Sardinia and especially the SW of Sardinia, therefore, the Iglesiente area.
- <<Sardinian Trench>> (tertiary metallogenesis) affecting everything on the edge of the Campidano and further north.

The Palaeozoic basement can be related to two main tectonic units: an autochthonous one, referable to the Silurian, and an allochthonous one, known as the 'Arburese Unit' [47], consisted of a low-grade metamorphic complex that is part of the outer stratum zone of the Cambrian-Ordovician Hercynian chain of Sardinia. In the Montevecchio area, this unit emerges with metamorphoses of predominantly sedimentary origin (metargylites, metasiltites, metarenaries, metacomposites) and secondarily volcanic origin (metavolcanites of acidic origin). After the tectonic-deformative phases derived from the Hercynian orogeny, there was intense magmatic activity of a prevalently intrusive nature, well represented in the Arbus area by the so-called Arburese batolite, characterised by an approximately concentric structure, consisting of granodiorites (dominant in the border area) and leucogranites (in the core) [48]. The location of this pluton has created a metamorphic aureole, extending up to about 1 km within the metasediments, in which minerals typical of contact metamorphism are found: biotite, chlorite, sericite, quartz and cordierite.

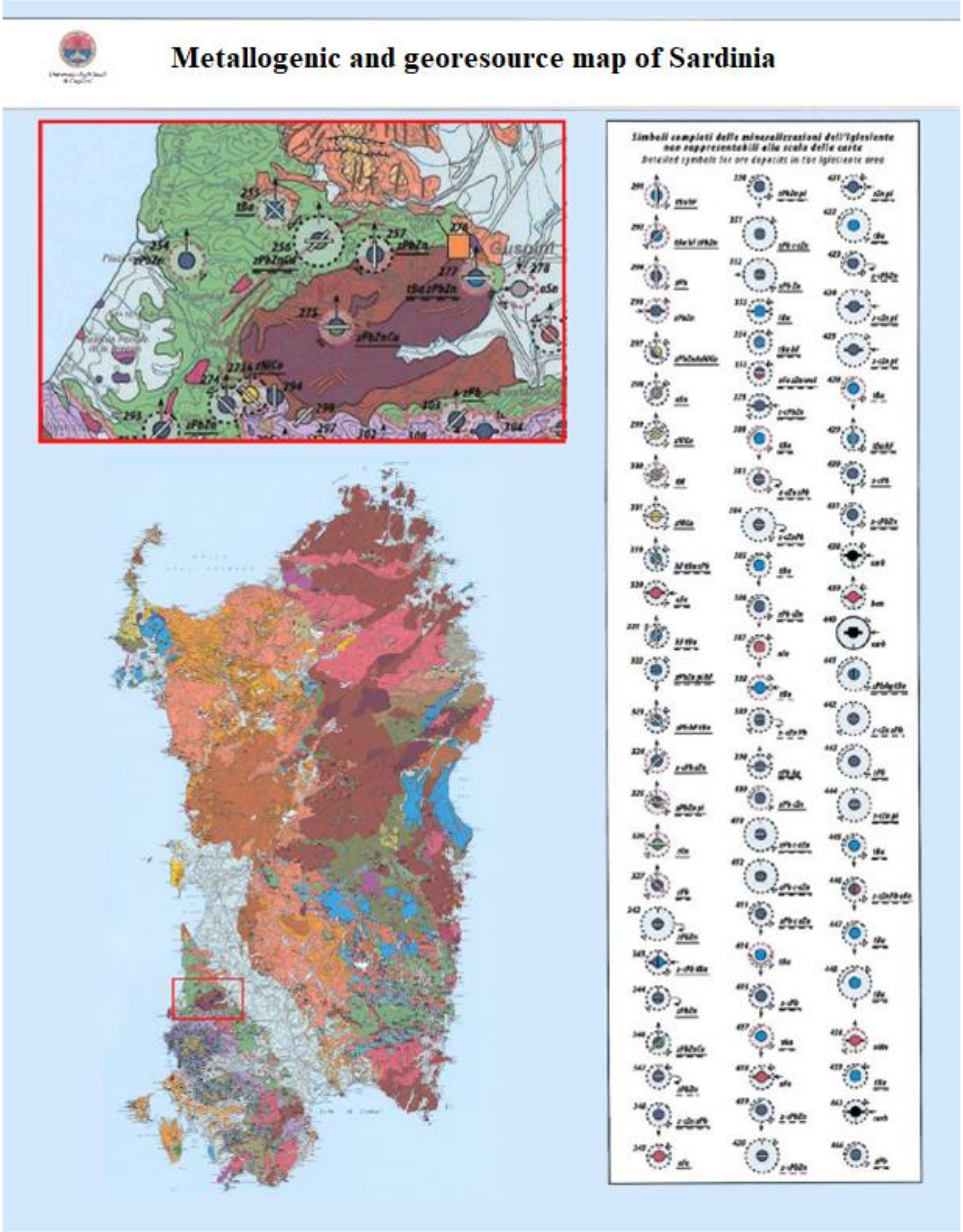


Figure 2.3 Metallogenic map of Sardinia with overview of the study area.

The ore deposit, developed over a length of more than 10 km, consists of hydrothermal veins that fill a fracture field occurring both in the lithic-quartzitic arenaceous-sediments of the post-Gotlandian series and in the Hercynian granitic batoliths [49].

The mineralogical composition of the strands that make up the Arburese phylonic field shows great variations from one strand to another and even within the same strand; moreover, the mineralogical paragenesis can also vary in the same strand, differing both in direction and depth.

The useful minerals grown are galena and blende, while pyrite, found in non-cultivable quantities, and chalcopyrite, present in much smaller quantities than pyrite but detectable macroscopically, remain far subordinate to lead and zinc sulphides. The size of these deposits, assessed by some authors as a whole [50] (in 50-60 million tonnes of ore (galena + blende) with an average content of 10-11% lead + zinc (5-6 million tonnes of Pb + Zn metal), places them among the largest in Europe.

- Galena from more recent mining operations (1960s-1970s) contains silver in the order of 650 g/tonne and antimony in the order of 4200 g/tonne; these elements, together with small amounts of gold, have been recovered in metallurgical processes, contributing to the economic value of the ore.

- The blende shows recoverable cadmium contents of the order of 10,000 g/t. Gangue minerals are represented by quartz, carbonates (siderite, dolomite carboniferous, calcite), barite, rare in the Ingurtosu area and relatively abundant in the S. Antonio vein at Montevecchio. The phyllonian field originates with the placement along the useful fractures of a large quantity of quartz that we find in the ganglia of the mineralised filaments and also as the sole component of numerous sterile radial filaments.

- Quartz often appears impure (grey quartz) due to unassimilated or incompletely assimilated schist residues (brass filament), while in other cases it is white, compact and crystallised.

In the upper parts of the mineralised strands there is often a band of surface alteration of varying strength, sometimes several tens of metres, which is manifested by the presence of the characteristic burn consisting of oxidised iron associated with minerals characteristic of the supergene environment, formed at the expense of the oxidation of the original minerals of the strand.

In this way, the alteration of galena, the silvery and antimoniferous minerals it contains, blende, pyrite and chalcopyrite, forms minerals characteristic of an oxidising environment that only in the case of cerussite, lead carbonate, have been mined. Other minerals such as monhelmite, phosgenite and anglesite, which are present in Montevecchio in crystals of a very rare light green colour, although not of mining interest, are of enormous mineralogical value and are also sought after by international collectors. In the oxidised parts of the Arburese veins there are other minerals that are very interesting from a scientific and collecting point of view.

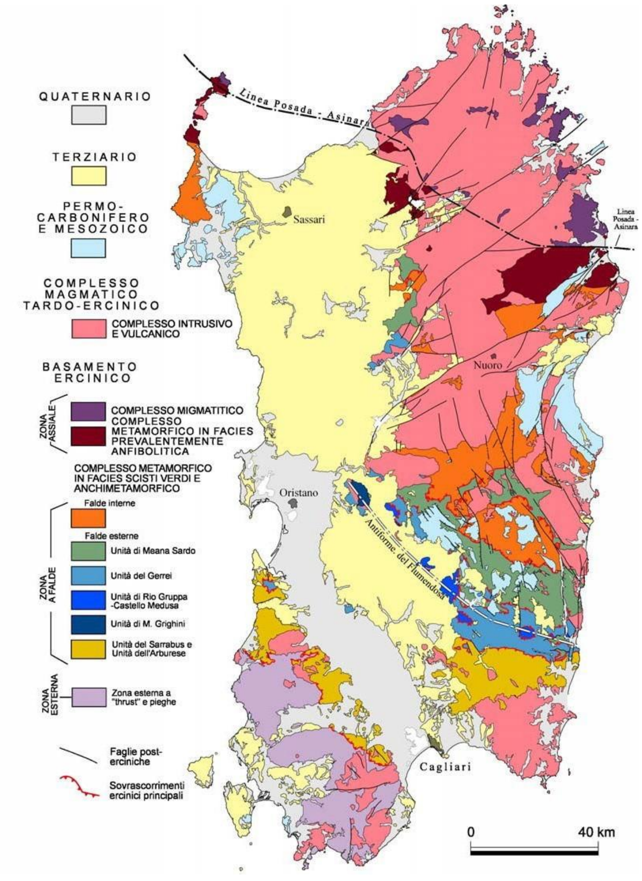


Figure 2.4 ISPRA geological map, Sardinian Varisian basement

From the point of view of Sardinia's geological history, all the above is associated with three major phases of formation of metallogenic deposits or metallogenic 'peaks':

- Cambrian peak ca. 515-510 Ma. preceding the Sardinian Phase and recorded mainly in the Iglesiente, south Sardinia.

- Varisian Peak ca. 305-280 Ma. upper Cambrian-Permian.
- Cenozoic Peak ca. 32-15 Ma. made up of digo-miocene magmatism.

2.4 Main minerals of the Montevecchio fields

The primary sulphide mineral association consists mainly of sphalerite and galena, with a wide variety of subordinate minerals: the most abundant are chalcopyrite, fahlore, arsenopyrite, pyrite and argentite. Ni-Co accessory phases (gersdorffite and ullmannite) are common throughout the mining district; in addition, Ni-Co arsenides (rammelsbergite, skutterudite) have been reported in veins in the southern sector (Nieddoris). Gangue minerals include quartz with abundant siderite, ankerite, barite, dolomite and calcite. Galena was also found in massive quantities; it prevailed in the veins of Sant'Antonio (Montevecchio pole) and Ingurtosu, where large masses have been described. Sphalerite was abundant in the Sanna vein (Montevecchio pole), and in many others of Casargiu, Ingurtosu and Gennamari, and it is also found in quartz and siderite intrusions. Generally, during mining exploitation, sphalerite, as well as pyrite, chalcopyrite and fahlore, were reported to be more abundant at increasing depths (Rolandi, 1940; Cavinato and Zuffardi, 1948; Zuffardi, 1962). The main minerals associated with the lead and zinc veins of the Montevecchio Ingurtosu Genna-mari deposits are listed in the following tables.

Table 2.2 Minerals grown in the Montevecchio mines

Blenda (sphalerite)	$(Zn.Fe)\ S$	+ Cd 10 kg/t	+Ge +Ga +In + Fe
Cerussite	$PbCO_3$	XX acidulars	Oxidation zone
Galena	PbS	+Ag 500-1000 g/t	+Sb 4000 g/t + As +Bi

Table 2.3 Main gangue minerals

ankerite	$Ca\ (Fe^{+2},\ Mg,\ Mn)$	(feral dolomite)	
barite	$BaSO_4$	XX tabulari transp.	S.Antonio-Sanna
calcite	$CaCO_3$	massive	Telle - Casargiu
dolomite	$CaMg(CO_3)_2$	massive	Telle - Casargiu
quartz	SiO_2		
siderite	$FeCO_3$		

Table 2.4 Table 1.4 Other sulphides associated with primary mineralization

argentite	Ag_2S - *cubic*	various outcrops	Ingurtosu
arsenopyrite	$FeAsS$ -	Strand Brassey liv. -	Ingurtosu
bornite	Cu_5FeS_4 - *cubic*		Montevecchio
bournonite	$PbCuSbS_3$ -		Montevecchio
calcopyrite	$CuFeS$ -	galenose areas	S. Antonio
covellite	CuS - *hexagonal*		Gennamari
enargite	$CuAsS_4$ - *rhombic*		Montevecchio
galenobismutinite	$PbBi_2S_4$ -		Montevecchio
gersdorffite	$PbBi_2S_4$ - *cubic*		strand Brassey
greenokite	CdS - *hexagonal*	green patinas on gal.	blenda zones
linnaeite	$Co^{2+}Co_2^{3+}S_4$ -		southern strands
marcasite	FeS_2 - *rhombic*	associated with	Montevecchio
millerite	NiS - *trigonale*		southern strands
nichelite	$NiAs$ - *hexagonal*		southern strands
pyrargyrite	Ag_3SbS_3 - *cubic*		Montevecchio
pyrite	FeS_2 - *cubic*		Montevecchio
pyrrhotite	FeS - *hexagonal*	associated with	Montevecchio
polybasite	$(AgCu)_{16}Sb_2S_{11}$-		Montevecchio
proustite	Ag_3AsS_3 -		southern strands
rammelsbergite	$NiAs_2$ - *rhombic*		southern strands
skutterudite	$CoAs_{2-3}$ - *cubic*		southern strands
tetrahedrite	$(Cu,Ag,Fe,Zn)_{12}$	Associated with	S. Antonio

The alteration of primary minerals and the consequent release of contaminants into the environment depend on various factors including their absolute concentration at source and the chemical and physical properties of the phases in which the metals are found. Sulphide minerals contained in rocks are released through crushing and grinding. Exposure to atmospheric agents produces oxidation and acidification reactions of sulphides that bring heavy metals into solution.

In order to contemplate the mineralogical situation of Montevecchio - Ingurtosu - Gennamari, the processes of sulphide alteration and the formation of secondary minerals will be indicated.

2.5 Alteration of sulphides

When it comes to chemical stability, the first and foremost environmental problem facing the mining industry today is acid mine drainage (AMD) or acid rock drainage (ARD). AMD is associated with base metal, gold and uranium mining operations, as well as coal and lignite mining. AMD is produced by the oxidation of sulphide minerals, mainly pyrite and pyrrhotite, in the presence of air, water and bacteria, resulting in the formation of acidic solutions with increased concentrations of sulphate anions and dissolved metals. The overall process of pyrite oxidation can be described by the following equation:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

In most deposits, potentially toxic elements are mainly contained in sulphides such as galena, sphalerite, chalcopyrite and arsenopyrite, which are often accompanied by iron sulphides such as pyrite, marcasite or pyrrotine. All these sulphides have formed in reducing environments and at high temperatures and pressures compared to those existing on the Earth's surface. When these minerals are found in exogenous conditions, they become thermodynamically unstable and therefore tend to rebalance with the new environmental conditions. However, reactions that should lead to thermodynamically more stable balances and therefore to mineralogical associations different from those formed in the endogenous environment are often hampered by various chemical, physical and biological factors. Sulphides have a natural tendency to persist beyond the expected alteration conditions (pH-Eh). This resistance to alteration of a mineral depends on several factors, including:

- the compactness of the crystalline structure and the type of bonds that are present in it.
- the different degree of stabilization of ions in the electric field of crystalline polyhedra.

However, most sulfides oxidize and disappear in areas of the earth's surface where there is a large availability of water and free oxygen. [4]. It should also be borne in mind that the stability of sulphides varies considerably depending on the composition of the sulphide itself, the mineralogical association in which it is found and the conditions under which the alteration processes take place [5] .

The main geochemical process responsible for the dispersion of heavy metals is the oxidation (and hydrolysis) of sulphides leading to the solubilization of potentially toxic elements. Monometallic Fe sulphides play an important role in solubilization, in fact their alteration produces a typically acidic environment, with formation, depending on pH and Eh conditions, of a wide range of oxides-hydroxides and/or Fe sulphates.

The oxidation mechanism of pyrite has been widely studied, and according to an accepted scheme (Blowes et al., 2003), the first products of the reaction would be ferrous iron and sulphate in solution with H+ release:

$$FeS_2(S) + \frac{7}{2}O_2(aq) + H_2O(l) \rightarrow Fe^{2+}(aq) + 2SO_4^{2-} + 2H^+(aq)$$

The Fe^{2+} (aq) released by the oxidation of sulphide can be further oxidised and hydrolysed, precipitating as amorphous or crystalline Fe^{2+}(aq) according to a reaction of the type:

$$Fe^{2+}(aq) + \frac{1}{4}O_2(g) + \frac{5}{2}H_2O(l) \rightarrow Fe(OH)_3(s) + 2H^+(aq)$$

Alternatively it may precipitate a hydroxysulphic iron phase to which corresponds a different amount of H^+ (aq) released. At pH<3, however, Fe^{3+} may remain in solution, so the oxidation reaction of Fe^{2+} is as follows:

$$Fe^{2+}(aq) + \frac{1}{4}O_2(g) + H^+(aq) \rightarrow Fe^{3+}(aq) + \frac{1}{2}H_2O(l)$$

Under these conditions the Fe^{3+}becomes an important oxidizing agent:

$$FeS_2(S) + 8H_2O(l) + 14Fe^{3+}(aq) \rightarrow 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq)$$

This last reaction, very fast, plays an important role in the oxidative processes of metal sulphides and Fe^{3+} is the main oxidizer of pyrite even at pH close to neutrality, but the reaction cannot take place in the absence of dissolved oxygen. Iron has an oxidizing action not only against pyrite, but also against most sulfides.

Whatever the dissolution mechanism, pyrite oxidation always produces a large amount of H^+ (aq), acidifying the runoff water (AMD = Acid Mine Drainage). The same phenomenon occurs during the oxidation of most sulfides.

Sphalerite and galena are among the most widespread and important minerals for the extraction of heavy metals. As far as sphalerite is concerned, it often contains quantities of Cd that are potentially harmful to the environment, while Zn is a toxic element only at high concentrations. Galena instead represents the main source of Pb contamination in mining areas.

The oxidation of sphalerite in an aqueous environment determines the formation of a solution rich in dissolved Zn, Cd and sulphate ion; while for galena there is generally the formation of a secondary product (anglesite - $PbSO_4$) in equilibrium with Pb^{2+} and SO_4^{2-} in solution:

$$ZnS + 2O_2 \rightarrow Zn^{2+}(aq) + SO_4^{2-}(aq)$$

$$PbS + 2O_2 \rightarrow PbSO_4(s) \leftrightarrow Pb^{2+}(aq) + SO_4^{2-}(aq)$$

Although the reactions described above do not lead, in the presence of oxygen, to the formation of H^+, if oxidation occurs by ferric iron, these sulphides can also generate acidity.

2.5.1 Secondary minerals formation complex Pb-Zn sulfide ores

Some of the elements that are released during the alteration of primary minerals can re-precipitate into a wide variety of secondary minerals, of which the most common and important are usually sulphates, oxides and hydroxides. The sulphate ion is the stable end product of sulphide alteration, and it is therefore often present in large quantities in groundwater and surface water that has interacted with the mineralisation and materials present in the landfill. Crystallisation of secondary sulphates (e.g. epsomite) is frequent and occurs easily: evaporation of the leaching water is sufficient for the various sulphates to reach their solubility product and precipitate in different forms. Since both anions and cations are distributed in a complex manner in natural waters, not only simple sulphates but also double or multiple salts containing numerous cationic and anionic groups, sometimes even rare, are formed in the supergeneric alteration zones of mining areas. The formation of these sulphates, or other insoluble and stable secondary minerals in a supergeneic environment, leads to a withdrawal of metals from the system, and thus, a reduction in their availability. On the other hand, soluble sulphates, which are formed in semi-arid conditions, can mitigate acidity and retain metals during dry periods, but they themselves become a source of acidity during rainy periods. This leads to a drastic seasonal variation in the concentration of metals with various consequences for the environment and this must be taken into account when monitoring these areas. Among the soluble sulphates, the most common are the iron sulphates. The geochemistry of iron in a supergene environment is complicated by the fact that iron is found in two oxidation states: Fe^{2+} and Fe^{3+}, and so depending on the environmental conditions we will have sulphates of Fe^{2+} and/or Fe^{3+}. The processes linked to the formation of Fe and Al oxyhydroxides also deserve some attention; several studies have demonstrated the role of ochres in attenuating the dispersion of Fe and other metals in water from mining sites following co-precipitation and/or adsorption reactions [5].

2.6 The Iglesias Valley

Large volumes of dumps from metallurgical mining activities are present in the area. The original size of the deposits that were mined in this area exceeded 100 Mt of Pb-Zn sulphides (120-150 Mt). Mining activities ceased in 1999. There are few or marginal opportunities for mineralisation extraction as there have been major crops that have fully exploited resources. Different studies [24] [51] [52] [53], have shown that the primary minerals in these landfills are altered and as heavy and toxic elements, present in significant concentrations, are released into the environment.

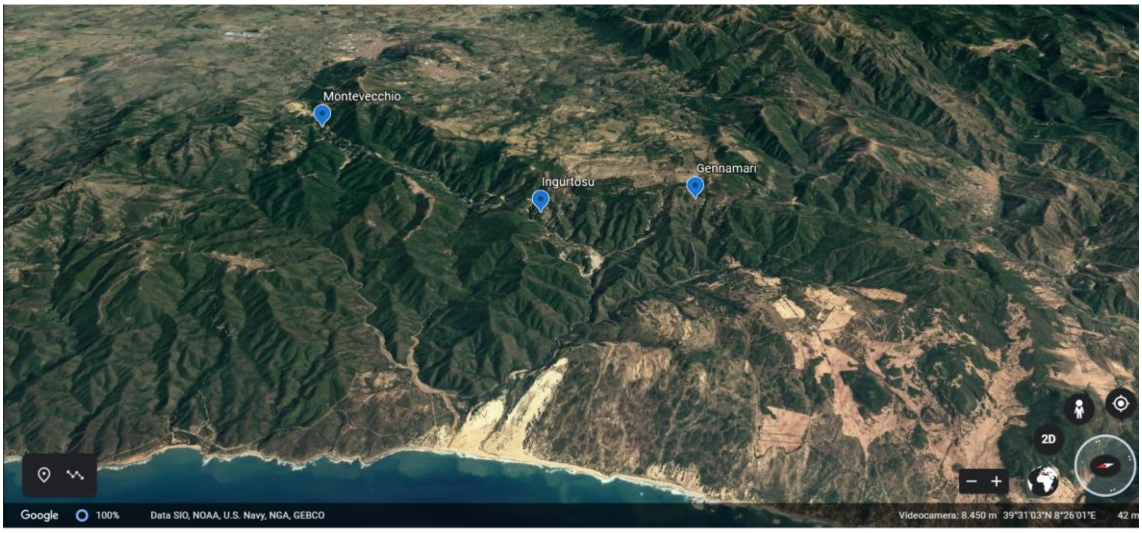


Figure 2.5 Mining area of Montevecchio-Ingurtosu-Gennamari in the Iglesias valley, google earth.

The main metalliferous minerals are sphalerite and galena, with pyrite, chalcopyrite, covellite, arsenopyrite and tetrahedrite subordinate. The gangue is mainly quartz, siderite, ankerite and sporadic barite and calcite. Mining in the 20th century intensified to a steady production in the 1950s and 1960s, with the introduction of sink and float facilities, of about 500,000 tonnes/year of ore. In the 1970s the activity began to decline and was finally closed in 1992. Total production of Pb and Zn was over 3 million tonnes.

The Montevecchio area was divided into three sectors:

- Levante (East), comprising the mines of Sciria, Piccalinna and S. Antonio;
- Ponente (West), comprising the mines of Sanna, Telle and Casargiu;
- Ingurtosu, comprising the mines of Ingurtosu Gennamari, S'Acqua Bona and Perda S'Oliu.

The richest parts of the complex were the N60°E vein belt (Piccalinna, Sanna, Telle, Brassey) and the S. Antonio vein (with a 2 km long and approximately 8 m thick outcrop). In both cases the exploitation was 600 m deep.

In the Montevecchio district, the two landfills on the west and east have conspicuous volumes, particularly Levante. In Montevecchio there has been a large historical production of minerals: 1,700,000 t of Pb and >1,200,000 t of Zn metal; but the most characteristic thing about the material in this district is that during the metallurgical process the mineralisations reveal a high quantity and variety of accessory metals.

Figure 2.6 Montevecchio Ponente, laveria Sanna

Many of these elements were actually recovered in the metallurgical cycle, for example Ag, Bi, Sb, Cu, Cd, Ge, Ga.

Mine data from exploratory campaigns by the Montevecchio company, indicate up to 220 ppm Ga and 290 ppm Ge, 140 ppm.

What is brought to light is that these discharges involve several Mm^3 consisting of large deposits of hydro and tailings in the two main laveries: > 9,000,000 m^3. This original content of supporting elements to mineralisation makes it very interesting to define the potential and the treatment techniques necessary to assess its feasibility, i.e. whether the material is recoverable.

Figure 2.7 Montevecchio Levante, mud basin

Chapter 3 Research methodologies

The procedures carried out for this research project were performed at the laboratories of the DICAAR department (department of civil environmental engineering and architecture) of the University of Cagliari. In particular, the old mining engineering laboratories were used to carry out the flotation tests, where the instruments and machinery used for the studies on the materials coming from the mines were used.

Part of the analysis of this work was carried out in the laboratories of the Geological Survey of Finland (GTK). This is an internationally oriented geoscientific research organization operating under the Ministry of Economic Affairs and Employment. It is a leading European centre of expertise in the assessment and sustainable use of geological resources. It offers a variety of specialist and research services, continuously developing digital services and a wide range of laboratory services; working to solve the challenges of creating a circular economy, to detect the potential of geo-energy and to survey battery mineral resources. To carry out the flotation tests, GTK has made available the laboratories at its Outokumpu site. The Outokumpu pilot plant and its laboratories provide comprehensive services on process mineralogy and mineral processing. Mineralogical analysis has become an essential tool for the development of new mining methods, among other things. Modern equipment such as the Mineral Liberation Analyser (MLA), in particular, has introduced new opportunities to characterise mineral products and environmental samples in mineral exploration, mining and extraction technology. In the following paragraphs, the main technique and technologies used in this project will be examined.

3.1 Froth flotation

3.1.1 Principles of Froth Flotation

As a metal separation technique, flotation owes its importance to the possibility that this technique offers of extracting complex, low-grade mineral clusters and re-evaluating their economic value. Indeed, today, many plants process tailings with much lower concentrations of heavy metals than previous practices. This has led to the increased use of the flotation technique in various application areas. To vouch for its history, one historian of technology has described flotation as "perhaps the greatest single metallurgical improvement of the modern era" [54].

Flotation is a process in which a finely ground mineral is concentrated into an intermediate phase based on its surface physicochemical properties. The size of the solids on which this process operates range from a few mm to 10^{-4}mm. Flotation of fines is difficult, so it is best to limit their formation.

Flotation processes are based on the different surface wettability properties of materials [55]. In froth flotation, a solid species pass into the foams, i.e. the flotation concentrate, and a solid species remains in the underlying aqueous phase, i.e. the non-flotation concentrate or waste. The two species are separated by the introduction of air bubbles into the slurry (added with appropriate reagents), resulting in the flotation of the solid particles on the surface. The hydrophilic particles, on the other hand, do not adhere to the air bubbles and remain in the slurry.

The phenomena occurring during the flotation process are due to specific physical or chemical interactions of all the elements and compounds forming the solid, liquid and gaseous flotation phases. These interactions, located at the interfaces, are governed by the actions of interatomic or molecular forces, which are a direct consequence of the bonds existing within each phase and the electronic structure of the atoms involved. The different types of bonds, their relative strength and the effects they produce are important aspects in the interpretation of the surface phenomena involved in flotation.

The use of hydrogen sulphide, which is a sulphur-based agent widely used in flotation, leads both to adsorption of this reagent on the solid surface and its solution in the aqueous phase with a consequent alteration of the hydrogen ion concentration in the latter phase. Similar results may also occur when carbon dioxide is used as a gaseous flotation phase.

In flotation systems, the liquid phase is usually represented by water, both because it is the most readily available and economical medium and because some of its properties are important in flotation, in particular, its high dielectric constant, its high solvent power and its equally high ionising power.

Water molecules are found in the liquid either free (H_2O) or associated ((H_2O)n; in the latter case, the molecules are called polymerised or simply polymers. One of the reasons why molecules associate is the existence of the hydrogen bond.

In addition to being in the form of associated molecules, water has the additional characteristic of containing dissociated molecules according to the two classical dissociation schemes:

$$H_2O \rightarrow H^+ + OH^- \qquad \text{and} \qquad H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

in which the H_3O^+ ion is called the hydroxonium ion.

However, these ions are not free, but hydrate due to the structure of the water. This means that there is an interaction between the dipoles of the water molecules and the ionic charges in the water, with the formation of a highly condensed atmosphere of water dipoles around the ion, the inner layer of which is oriented and stable, while the outer layers become increasingly disordered due to thermal agitation. Thus, the H+ and OH- ions hydrate to give rise to $(H^+)(mH_2O)$ and (OH^-) $(m'H_2O)$.

The process of ion hydration shows that the energy of the bond between the ion and the water dipoles is greater than the mutual attraction of the dipoles themselves. The hydration energy of ions increases as their valence increases and, for the same valence, increases as the ionic radius decreases. In general, the hydration energy of an ion is given by:

$$H = \frac{e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right)$$

where **e** is the charge of the ion, **r** the ionic radius and **ε** the dielectric constant of the medium. The hydration process is exothermic: a considerable amount of heat is developed during the formation of the inner layers, which gradually decreases as the subsequent layers are formed. If the temperature is increased, hydration decreases, and this decrease is so significant that an increase in the temperature of the flotation slurry leads to an increase in the flotation ability of the minerals. Of course, other factors, such as the solubility of the solids, their interaction with the flotation reagents and the specific surface area, all of which vary with temperature, help to influence flotation.

3.1.2 Mineral classification

In flotation, due to contact with the minerals by dissolution, the water contains various impurities. These can be classified into:

- dissolved gases,
- major ions,
- biological substances,
- organic substances.

There is a chemical bond between two atoms or groups of atoms whenever the interacting forces are such that an aggregate of sufficient stability is formed that, from a chemical point of view, it can be considered an independent molecular species.

There are three types of chemical bond: the ionic bond, the covalent bond and the metallic bond. This classification is not strict because, although each of these bonds has well-defined properties, the transition from one type to another can be gradual, allowing the existence of intermediate bonds. These include the resonance bond, the hydrogen bond and the electrostatic Van der Waals forces.

The flotation gas phase is generally air, although any other gas can be used. The gas does not usually interact with the flotation of the minerals unless there are reactions between the gas molecules and the solid surfaces or reagents dissolved in the slurry or the water itself. While the use of oxygen proves advantageous in some cases (flotation of metal sulphides with xanthate collectors), it turns out to be unfavourable in others, due to the surface oxidation of the solid phase that it causes and the consequent anomalous behaviour during flotation. Similar problems may also arise with the gaseous phase air.

The hardness of the water due to dissolved salts causes a change in the interaction between the minerals and the flotation reagents, forming insoluble compounds. The pH of the water is also important as it influences the solubility of the minerals. As far as the solid phase is concerned, the properties of natural solids depend on their composition and structure. The structure of crystals is determined by the spatial arrangement of atoms, ions or molecules in the crystals themselves, as well as by the type of bond that determines their aggregation and their polarisability. Given the difficulties encountered in classifying crystals from the point of view of their flotation properties concerning the bonds between atoms or groups of atoms, it seems more appropriate to classify minerals according to their general flotation characteristics. From this point of view, minerals can be classified into the following groups:

Table 3.1Minerals classification.

Minerals	Description
Native metals and sulphides of heavy metals.	Minerals of Cu, Pb, Zn, Hg, Sb and others, characterised by poor surface wettability if they have not been subjected to oxidation processes during mining and preparation procedures. The most effective collectors for the flotation of such minerals are xanthates.
Non-polar, non-metallic minerals.	Minerals which possess weak wettability in water, such as graphite, sulphur, coal and talc. Extremely weak collectors and sometimes only frothers are used for the flotation of these minerals.
Oxidised minerals of non-ferrous metals.	Carbonates and sulphates of Cu, Pb, Zn and other salts derived from oxygenated acids (cerussite, anglesite, malachite, azurite, wulfenite, etc.). These minerals can be floated with xanthate collectors after sulphuration, or with fatty acids directly without sulphuration.
Polar salt minerals containing Ca, Mg, Ba and Sr cations	These minerals react actively with anionic collectors such as fatty acids. The predominant ionic character of their bonds in the crystal lattice means that there is an active interaction between the cations on their surface and the anions in the collector; the use of activators with these minerals is in most cases unnecessary or at least insignificant. Apatite, fluorite, calcite, barite, magnesite, dolomite, phosphorite, etc. belong to this group.
Oxides, silicates and aluminosilicates	To this group belong silica, corundum, gibbsite, boehmite, diaspore, zircon, rutile, hematite, magnetite, cassiterite, ilmenite, pyrolusite, andalusite, kyanite,

	feldspar, spodumene, mica, sericite, kaolinite, tourmaline, asbestos, beryl. In general, most of these minerals can be floated with either anionic or cationic collectors. Also, a particular feature of many of them is that the flotation efficiency depends largely on the conditions under which they were formed. For example, flotation with anionic collectors can vary greatly depending on the presence and concentration of activating cations adsorbed on the solid surface.
Soluble salts of alkalis or alkaline earth metals	They can be divided into two groups. To the first group belong the salts having high solubility in water such as halite, sylvite, to the solid phase a condition of dynamic equilibrium. To the second group belong minerals with a lower solubility in water, such as gypsum, hydroboracite and others, whose flotation can instead be achieved in unsaturated solution. For both groups, kainite, carnallite, etc., the flotation of which must be carried out in saturated solution to prevent the use of either anionic reagents of the fatty acid type or cationic reagents.

This classification is very general as it can be seen that even minerals which are identical in composition and structure may respond completely differently to flotation. This can be due to a variety of causes such as the possible presence of impurities. These may be macroscopic, so they are mechanically incorporated into the crystal during its growth, or they may be very finely dispersed; in this case, they may be due to the presence of solid solutions, isomorphism, or adsorption processes.

The formation of a solid solution is caused by the similarity of the lattices of the dissolved substance and the solvent. Isomorphism is a special case of a solid solution in which the solute and solvent have similar structures, so that substitution at common lattice points can result. Finally, the presence of oxidation veils on the surfaces of metal sulphides can have a decisive influence on the flotation result.

The flotation characteristics of the blende are also closely dependent on the nature of the deposit from which the ore comes: blends containing Fe, or Cu, or Cd, behave differently from those without them. The floatibility of pyrite with xanthate collectors, whether modulated with lime or not, is different depending on whether the ore comes from metalliferous or carboniferous deposits. Finally, the floatability of galena with xanthates is closely linked to the degree of oxidation of its surface.

For this reason, the flotation characteristics of a certain mineral can only be achieved through careful laboratory analysis.

Interactions, at the interfaces, are governed by interatomic or molecular forces, which are electrical in nature and determine the properties of the minerals, water, flotation reagents and their interactions.

3.1.3 Flotation Chemistry

3.1.3.1 Electric double layer

The mechanism of flotation is strongly influenced by certain electrical phenomena at the interphase. Let's take a solid with an ionic crystalline lattice immersed in chemically pure water: since, in general, the ions characterising the lattice do not have the same hydration energy, i.e. the same capacity to interact with the water dipoles, the ions of a certain sign tend to pass into the aqueous phase more than the ions of the opposite sign, and this until the force that solicits them is balanced by the Coulombic force that holds them back. This preferential transfer of a certain type of ion causes an alteration in the electrical balance of the surface of the solid, which then becomes electrically charged, thus establishing a potential difference.

Helmholtz schematised it as an electrical double layer, in which the layer of charges on the surface of the solid and the layer of charges in solution are comparable to the plates of a capacitor [56].

According to Gouy, however, the ions in the double layer cannot be concentrated at a defined distance from the solid surface because there must be an equilibrium between the electrical forces responsible for the existence of the double layer and the osmotic forces that tend to maintain homogeneity.

Consequently, there cannot be an abrupt change in the concentration of any type of ion in the vicinity of the double layer, but a gradual increase in the concentration of ions of a certain sign and decrease in ions of the opposite sign. The electric charge density in the ion atmosphere decreases according to an exponential law and not linearly as postulated by Helmholtz. Finally, Stern suggested an electrical double layer model which is a combination of Helmoltz's fixed layer model and Gouy's diffuse layer model. This model seems to better describe the actual distribution of potentials when, as in fact is expected in flotation, specific adsorption of counter-ions takes place, i.e. counter-ions having a particular affinity towards the solid surface.

According to Stern, it is possible to distinguish:

- a layer of potential-determining ions, due to the charged solid surface, forming part of the crystalline lattice of the solid;
- a layer of solvated ions, specific counter ions (Stern's layer), closely linked to the solid by electrostatic and Van der Waals forces;
- a diffuse layer (Gouy's layer), which extends for a certain depth in the liquid phase, gradually decreasing in concentration.

3.1.3.2 Zeta potenzial

The development of the potential varies with distance from the Stern layer, as can be seen in Figure 3.3, and is usually denoted by $\psi 0$ in the proximity of the solid and $\psi\delta$ the Stern potential. Although the surface charge cannot be measured, it is possible to determine the potential difference between the mineral surface and the undisturbed solution by determining the surface potential itself.

The zeta-potential ζ or electrokinetic potential can be measured; it varies as a function of pH. It takes on positive values for acidic pH and negative values for basic pH [57] .

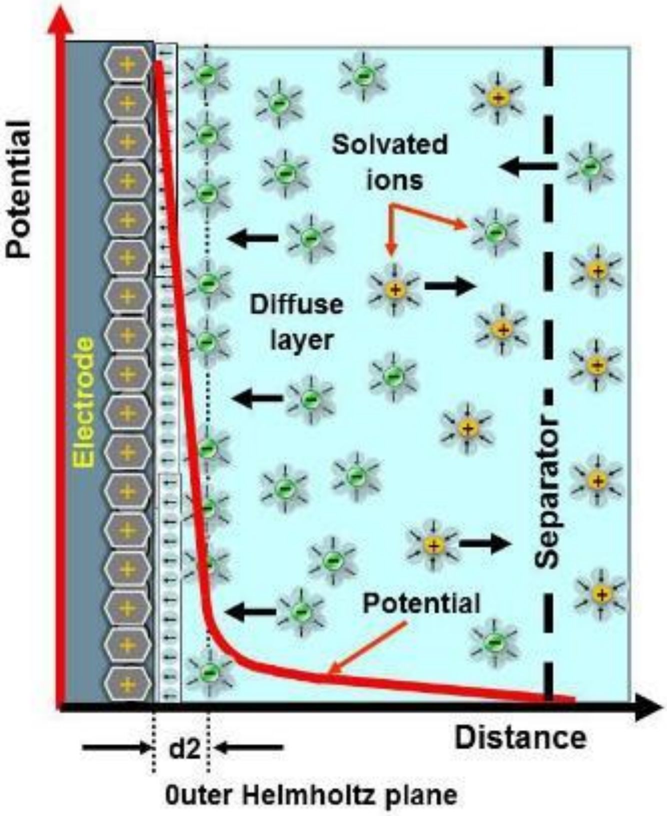


Figure 3.1 Stern's model.

3.1.3.3 Potential of hydrogen (pH)

The pH is responsible for what happens to the solid in water. When pH is lower than 6.7, OH^- is removed from the site with Fe, reacting with H^+ and forming water, leaving a net positive charge. The opposite is true at pH> 6.7 [54].

This interpretation applies to many minerals to explain the effect of pH on the zeta-potential, and OH^- and H^+ are referred to as potential-determining ions. The isoelectric point is called the point of zero charge (PZC). The potential increases at pH<6.7 and decreases at pH>6.7. Based on the potential, a decision is made whether to use an anionic or cationic collector. The PZC differs from mineral to mineral, so if you have several minerals within a pH range, they may have opposite charges and attract each other, resulting in coagulation and hetero coagulation. One form of hetero coagulation is slime coating. Isoelectric point differences can be used as a guide to pH-collector conditions for selective flotation.

As the potential increases, the anodic current increases and the cathodic current decreases.

Galena flotation is generally done at a pH of between 9 and 11. Lime is used to change the pH, (but may depress the pyrite itself), or sodium carbonate is used (preferably if the pyrite content is low).

Cyanide (up to 0.15 kg/t) and $ZnSO_4$ (up to 0.20 kg/t) are used as depressants, in an alkaline environment, alone or in combination.

Ethylxanthate is used as a collector and MIBC as a foamer. Isopropyl can be used if the galena is opaque.

Once the galena is floated, zinc is floated with copper sulphate (0.2 to 1.6g Cu per kg Zn), lime (0.5 - 2kg/t) to depress pyrite to pH 10-12, using sodium isopropyl xanthate. The conditioning time of the activator should be about 10-15 minutes [58].

3.1.4 Flotation reagents/surfactants

The measurement of surface tension γ also provides useful indications as to whether or not interaction (adsorption in the electrical double layer) is taking place between the solid surfaces and the reagents introduced into the slurry.

This is because, in the flotation of solids, the control of the properties of the interfaces (solid-water-air) is achieved by the use of reagents (organic and inorganic agents) which have the property of modifying the surface tension. Reagents that tend to concentrate at interphase, lowering the surface tension, are called surfactants. The concentration of a surfactant on the solid surface has the effect of making it hydrophobic and therefore suitable for adhering to air bubbles intentionally generated in the slurry.

Surfactants consist of heteropolar molecules, one part of which is actively attracted to the water molecules (hydrophilic group) while the other (hydrophobic group) is only weakly attracted. The dissolution process in the water of a surfactant agent can be considered as a process of immersion in water of the hydrophilic group of the molecule and resistance to the immersion of the hydrophobic group.

Surfactants can be classified according to the electrical charge marking the polar group (anionic, cationic and non-ionic), or according to the structure of the hydrocarbon chain (alkyl, aryl, alkyl-aryl, cyclohexyl, etc.) or, according to the specific polar group (monopolar surfactants) or the specific polar groups (multipolar surfactants).

From the point of view of flotation, it seems convenient to distinguish surfactants into:

- monopolar, when a single polar group is bound to a hydrocarbon chain;
- multipolar, when more than one polar group is bound to separate carbon atoms of the same hydrocarbon chain.

Each of the two preceding categories may then be distinguished according to the electrical charge associated with the polar group, or polar groups, in:

- anionic surfactants, in which the active radicals have an anionic character;
- cationic surfactants, in which the active radicals have a cationic character;
- non-ionic surfactants, in which the polar group consists of one or more alcohol radicals;
- the aldehyde or ketone surfactants.

A special class of multipolar surfactants is the amphoteric surfactants, also known as ampholytic surfactants, which possess both anionic and cationic groups. A further classification of each of the previous categories examines the different types of polar group. From this point of view, the polar groups of most interests in flotation include $-OH$ (alcoholic), $-COOH$ (carboxylic), $-OCS_2^-$ (xanthic), $-NH_2$(amine), $-SO^-$(sulphate), $-SO^-$(sulphonate), etc.

In the mineral flotation technique, the function required of surfactants consists of:

- in making the surface of a hydrophilic solid (collectors) hydrophobic by adsorption at the solid-liquid interphase; the collector molecules, by adsorbing on the solid surfaces with the hydrophilic group, in limiting the propensity of the surfaces to interact with the surrounding liquid phase thanks to the shielding effect determined by the hydrophobic chain which is oriented towards the liquid phase;
- in controlling the adsorption of the collectors (modifying agents); the previous adsorption of the surfactant influences the subsequent adsorption of the collector;
- Controlling the size of the bubbles and stabilising the flotation frothers. The surfactant molecules, by adsorbing to the liquid-air interphase, reduce the

coalescence speed of the bubbles and also influence the kinetics of bubble adhesion to the solid particles.

In general, ionisable surfactants perform both functions of a collector and a foamer at the same time, whereas non-ionic surfactants are currently used as foamers or depressants.

Reagents added to the slurry may be::

- collectors, which adsorb on the solid surfaces to make them hydrophobic, i.e. floatable;
- frothers, which are necessary for foam formation;
- modifying agents, which control the selectivity of the process, favouring or hindering the adsorption of the collectors on the solid surfaces (activating and depressing respectively);
- modifying agents, which act as regulators of the ionic composition (pH) of the liquid phase of the slurry.

3.1.4.1 Collectors

The reagents most frequently used as collectors in industrial flotation practice are either anionic surfactants (anionic collectors) or cationic surfactants (cationic collectors). The collectors must have the property of being selective: the functions mentioned above (adsorption, surface hydrophobisation, etc.) must be manifested towards certain solid species in preference to others. Depending on the characteristics of use in flotation, anionic collectors can be divided into two classes:

- hydroxyl anionic collectors;
- sulphydryl anionic collectors.

These differ, respectively, by the presence in their molecule of the functional groups -OH and -SH. The connecting element between the solid surface and the hydrocarbon chain of a hydroxyl moiety is an oxygen atom, whereas the similar element in a sulphydryl moiety is a sulphur atom. The specific activity of the collector, i.e. its ability to make one or more species floatable, depends on the characteristics of the polar group, while the collector power depends on the type of hydrocarbon radical and its length.

The most important cationic collectors are amines. Amines are organic compounds derived from ammonia (NH_3), in which the hydrogen atoms are replaced by hydrocarbon radicals of the aliphatic, aromatic or heterocyclic series. Amines can be present as primary when one hydrocarbon radical replaces one hydrogen atom, secondary when two radicals replace two hydrogen atoms, and tertiary when three hydrogen atoms are replaced by three radicals.

Collectors are rarely used alone. Generally, it is necessary to modulate their action with the preventive use of reagents which act as modifiers, activators and depressants.

Thiols (sulphide collectors) are known to form insoluble precipitates with base metals and not with elements such as Si, Ca, Mg and thus give selectivity against non-sulphide gangue. It is chemical adsorption through a mechanism of accepting and donating electrons. If the mineral is not a conductor or semiconductor, it cannot sustain the electron exchange process.

3.1.4.2 Activators and depressant

The function of the modifiers (HCl and $NaOH$) is essential to regulate the pH of the flotation slurry. In general, the effectiveness of a collector varies according to the pH of the slurry. Activators and depressants help or hinder the adhesion of a collector to a certain solid surface, the most commonly used of which are cyanides and sodium silicate, as will be seen below. The densification of solute molecules at the interphase is called adsorption and can be obtained through the W.Gibbs equation by measuring surface tension γ and reagent concentration ci. Solutes that reduce surface tension ($d\gamma/dci < 0$) tend to concentrate on the surface layer ($\Gamma > 0$) and vice versa.

$$\Gamma\mathrm{i} = -\frac{\mathrm{Ci}}{\mathrm{RT}} \mathrm{X} \frac{\mathrm{d}\gamma}{\mathrm{dc}}$$

Γi is the excess of solute at the surface, or adsorption, expressed in [mole/cm2], **γ** is the surface tension expressed in [mN/m], **R** is the gas constant expressed in [J/gmole*K], **T** is the absolute temperature in [K] and **c_i** is the solute concentration.

Ion adsorption or exchange appears to be the most appropriate to explain the mechanism of action of ionisable collectors. The collectors dissolved in the slurry are adsorbed on the solid surface with an exchange mechanism that depends on the nature of the solid, the type and concentration of the ions belonging to the collector, and the nature and concentration of the other ions present in the slurry.

When the collector coating has occupied a sufficient portion of the surface, the action of the hydrophobic film will prevail over that of the remaining hydrophilic portion and the particle will be able to float. It is believed that the action of the collector encompasses all degrees of adsorption, from purely physical or molecular adsorption to ionic adsorption, to chemisorption, to the chemical combination of stoichiometrically defined compounds.

3.1.4.2.1 Hydrogen sulphide

The use of hydrogen sulphide, which is a sulphur-based agent widely used in flotation, leads both to adsorption of this reagent on the solid surface and its solution in the aqueous phase with a consequent alteration of the hydrogen ion concentration in the latter phase. Similar results may also occur when carbon dioxide is used as a gaseous flotation phase. The sulphide oxidation process may be of considerable importance in flotation with sulphidization because of two reasons.

- Since the excess HS^- ions present in a solution act as a depressor, not only for sulphide minerals but also for sulphidized ones, the oxidation process may be a way of converting excess HS^- ions into other species with a smaller depressing activity

  In flotation conditions where air is bubled through and the pulp is stirred, the oxidation of excess sulphide ions should take place at higher rates.

3.1.4.3 Frothers

One of the prerequisites for foam flotation is the production of air bubbles in the slurry, which adhere to the hydrophobic particles in the slurry and drag them to the surface to form a mineralised foam layer of varying thickness.

A foam is a particular emulsion in which the dispersed phase is gaseous. When the liquid phase is a pure liquid, whether polar or non-polar, the foam is unstable and very short-lived: the bubbles generated in the liquid phase tend to gather spontaneously to form larger bubbles, in a process known as coalescence, which quickly rises to the surface without creating a foamy layer. However, when the liquid phase contains active surface impurities, the coalescence of the bubbles is greatly retarded and conditions for the formation of a foam layer are created.

Frothers agents are heteropolar organic substances. In general, homologous surface-active substances, i.e. having the same general structure and the same polar group, provide a foaming power which increases with increasing hydrocarbon chain length up to a certain limit, beyond which it decreases. An example of this is provided by the aliphatic alcohols series, whose foaming power increases up to 7-8 C atoms of the hydrocarbon chain and decreases drastically for longer lengths.

The quality of a frother depends above all on the polar group. In this respect, it should be noted that in two-phase systems the best frothers are ionic or at most mixed ionic-non-ionic surfactants, whereas in three-phase systems the commonly used frothers are characterised by non-ionic polar groups. Of course, frothers with polar ionic groups may also be conveniently used as frothers in three-phase systems, but only in situations where the solid particles and air bubbles have opposite electrical charges.

The polar groups can be hydroxyl (-OH), carboxyl (-COOH), carbon (CO), amine (-NH_2), sulphate (-SO_4), sulphonate (-SO_3) and phosphate (-PO_4). However, what has been said above underlines that surfactants with carboxyl, amine, sulphate, sulphonate or phosphate polar groups, although characterised by good foaming properties, are never used in flotation as pure foaming agents due to their collector characteristics.

In fact, hydroxyl surfactants, and among these some products with many C atoms between 5 and 20, which possess high foaming power without manifesting a collecting effect, are universally used foaming agents.

These reagents, like all surfactants, lower the surface tension of the liquid in which they are dissolved in accordance with the Gibbs equation. In other words, the foaming molecules adsorb to the air-water interphase with the hydrocarbon chain (hydrophobic) facing the air and the polar group (hydrophilic) facing the water. The existence of a surface film of foamer around the bubble gives it a certain resistance to coalescence and in general to any stress that tends to cause it to break: the bubbles possess a certain elasticity to resist tension or compression. If the surface of the bubble is extended by an instantaneous effort, the surface concentration of the adsorbed frothers decreases (water takes the place of part of the frothers), the surface tension increases and the film breakage is hindered. This mechanism is a function of the concentration of the foamer: activity is zero for pure water, weak at low concentration (gaseous molecular layer), maximum at a certain concentration (expanded monomolecular layer), beyond which it progressively decreases until it almost disappears at saturation concentration (compact monomolecular layer). Ultimately, the essential requirements for a good foaming reagent are as follows:

- be capable of producing a foam of sufficient volume and stability to enable the separation of floated and non-floated particles, but whose persistence is not such as to impede subsequent handling;
- have a low ionisation constant and low collector power;
- be insensitive to variations in pH and ionic strength of the liquid phase;
- have a solubility which is neither too high nor too low (0,5 to 10 g/l);
- limited cost and easy availability on the market.

The most common foamers in industrial practice are:

- pine oils;
- aliphatic alcohols with between 5 and 8 C atoms;
- polypropylene glycols and their ethers with at least 9 C atoms. To this class of foamers belong the series of Dowfroth reagents distinguished according to their corresponding molecular weights (200, 250, 450 and 1014).

Different classes of frothers naturally provide foams of different appearance and characteristics. The frothers also exerts an important action from the point of view of the collection, as it is shown by the fact that the addition of a suitable frothers to the system can allow even appreciable increases in flotation efficiency. The favourable influence of the frother-collector interaction is explained by the theory of mixed film formation, in which the molecules of the frother interpenetrate the layer of molecules of the collector, or vice versa, at the air-water and solid-water interfaces. The interpenetration, which results in an increase in the density of the adsorption film at the solid-liquid interphase, is determined by the weak intermolecular bonds that are established between the hydrocarbon chains of the two surfactants. Several factors must be present for flotation to occur, including:

- the collision between solid and bubble;
- destruction of the hydrated films surrounding both the bubble and the particle.

The probability of the formation of a bubble-particle aggregate is therefore equal to the product of the probability of collision and the probability of rupture of the surface hydration films. The probability of collision is a function of the motion of the bubble and the particle, as well as their size and shape. Theoretically, the probability of collision is zero if bubbles and particles are spherical and the motion is viscous, while it becomes appreciable (e.g. of the order of 6-7%) when:

- the motion is turbulent and with high-velocity gradients;
- the bubbles are not too small and non-deformable;
- the particles are sufficiently large in mass and angular in shape.

Once the collision has occurred, the layers of hydration separating the bubble and particle must be thinned and then removed for adhesion to occur. The degree of hydration is very important. Naturally, the final quantity of floated solid will depend, in addition to the formation of the aggregate, on the probability that the aggregate will resist the stimuli that tend to separate the particles from the bubble. These stresses are mainly due:

- to the force of gravity acting on the particle during the ascending phase of the aggregate and, if the ascending motion is accelerated, by the force of inertia of the particle;
- the weight of the particle and the centrifugal force due to the motion of the particle on the curved surface of the bubble;
- the impact of solid particles against the mineralised surface of the bubble;
- the impact of the mineralised bubble against an obstacle (cell walls, impeller, etc.).

Since all these forces are proportional to the mass of the particle, they increase with the cube of the size, and since the probability of adhesion increases with the square of the size, it follows that the flotation is maximum for intermediate particle sizes.

The bubble-particle aggregates form a column of ascending bubbles that collect as a layer of mineralised foam at the surface of the cell. The type of foam formed is a function of the degree of mineralisation of the bubbles. This coefficient is defined, with reference to the bubbles reaching the base of the foam layer, as the ratio between the surface of the solid-covered bubble and its total surface. It can be quantified with the expression:

$$f = K \times \frac{mhw}{R}$$

The degree of mineralisation f is directly proportional to a particle shape coefficient (w), which is greater the more angular the particles are, to the height of the slurry (h) and to the volumetric percentage of floatable particles (m) in relation to the volume of the slurry, while it is inversely proportional to the radius (R) of the bubbles. The degree of mineralisation does not depend on the particle size distribution of the floatable solid. On the basis of the degree of mineralisation, three different types of foam can be distinguished:

- if R is relatively small and f very large, the bubbles are completely, or almost completely, mineralised and even though they come into contact with each other they remain spherical; the corresponding foam is called 'superflocculated';
- if R is relatively larger and f moderately smaller than in the previous case, the almost completely mineralised bubbles take on a polyhedral form (polyhedral foam) and in the foam, the solid is distributed in the septa;
- finally, if R is relatively large and f is small, the foam is very aerated with large, deformable, poorly mineralised and short-lived bubbles due to rapid coalescence with free air; a surface fizzing effect is observed in this case *(fizzy foams)*.

In flotation, the frother is dosed in such a way that decaying foams are easily removed from the flotation apparatus. Methods for the removal of persistent foams during the process can be mechanical or chemical-physical. The most commonly used method consists of directing intense, well-directed jets of water into the foam, which is then broken down by mechanical action. Alternative methods of foam breaking down are by means of paddles or centrifugation. Chemical-physical methods essentially consist of changing the pH of the foam with bases or strong acids such as ammonia or sulphuric acid. The most drastic methods include the use of ultrasonic waves generated by special projectors: the vibrations reach the foams and penetrate deep into them, causing the baffles to break [57].

3.1.4.4 Sulfides and oxidized minerals circuit

The scheme of a flotation circuit consists of three stages:

- Roughing has the function of recovery, i.e. to extract the useful species in the foams. The cell bottom will be able to float further in the scavenging phase.
- The purpose of scavenging is to flotate the particles of useful species that were not collected during roughing. This objective is pursued even at the cost of significant pollution of the flotation concentrate by the presence of gangue particles. The fraction of useful species that is not recovered in this phase will, in fact, be lost; the bottom of the scavenger cell (treatment waste) leaves the treatment circuit.
- The purpose of cleaning is to "make tenor", ensuring that the concentrate reaches the quality requirements for that type of product. The cell bottom may float again in the roughing stage. Often more than one re-wash is necessary.

The flotation of oxidised zinc ores is normally a problem in its industrial application. The difficulty lies in the type of reagent used, its quantity and the type of ore to be treated. The success of enrichment by flotation in the oxide circuit therefore lies in a good compromise between different conditions which, if not respected, can lead to the opposite of the desired effect.

The most common flotation technique used commercially for the treatment of zinc oxide ores is sulphidation with $Na2S$, followed by treatment with amines [59].

To make the surface of oxidised zinc mineral particles hydrophobic, large quantities of reagents will be used. The possibility of obtaining a marketable oxidised zinc concentrate depends on obtaining a good proportion of each reagent in the system.

The most important methods used for flotation of oxidised zinc ores are reported by Ejtemaei et al. [60] :

- Sulphidation with sodium sulphide, and flotation with cationic manifold such as amines.
- Use of fatty acids.
- Sulphidation and activation with metal ions and flotation with an anionic manifold such as xanthate.
- Flotation with mercaptans.
- Chelating agents.
- Mixing of anionic/cationic collectors.

Excess of sodium sulphide acts as a depressant for the oxidised lead and zinc ores because the adsorption of bivalent sulphide ions on the surface of the lead oxide ores increases the negative charge, which prevents the adsorption of the collectors.

The presence of the fines fraction, i.e. gangue particles smaller than 20ηm, can be detrimental to the success of the process, which is why, if necessary, de-sliming is carried out before proceeding. Ferruginous materials are known to be more difficult to treat than silicate and carbonate materials.

As for all calamines [61], i.e. oxidised zinc ores, the mining waste covered by this study was treated with:

- Sodium silicate (Na_2SiO_3) as a mud dispersant and peptizer
- Sodium sulphide (Na_2S) as an activator of the oxidised zinc minerals and determinant of the required alkalinity;
- Amine as a collector;
- Dowfroth 1015 as a foam regulator.

3.2 Flotation technology

3.2.1 Mechanical and pneumatic cells

The flotation machines (cells) are designed to:

- ensure the most complete aeration possible of the slurry;
- ensure homogeneous dispersion of the solids in the slurry.

Modern flotation plants use two types of machines alternatively:

- mechanically stirred cells: the mechanical machine is clearly the most common type of flotation machine in industrial use today, cage rotor machines (Fagergren system), turbine machines (Denver system), turbine machines (Agitair system).

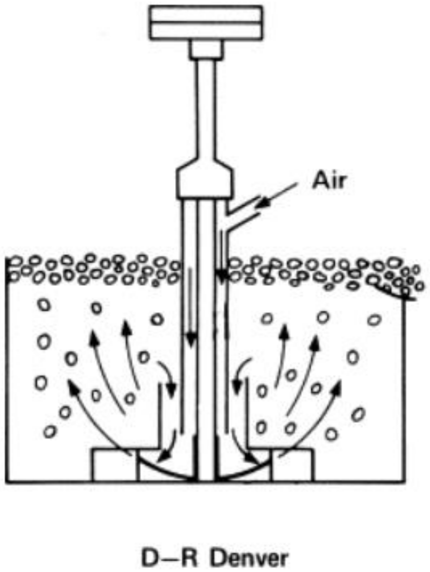


Figure 3.2 Illustration of an air delivery system in common mechanical flotation cells (D-R Denver) [105].

- pneumatic cells [62] : machines in which the air used to generate a mineralised froth is blown into the cell, either through a porous septum at or near the bottom, or through tubes that bring low-pressure air into that region. In the pneumatic flotation machine, the pulp must be pumped at high pressure (2.5 to 3.0 bar) to promote the suction of air (self-aerated air) and the collision between mineral particles and bubbles under high energy.

For all tests carried out in the DICAAR laboratories, a 1.5 dm3 Denver flotation cell with 500 g of sample was used to maintain the 1:3 ratio.

The Denver cell type used in this experiment is the "Denver free-flow" cell (Figure 3.5). This unit is characterised by a single compartment so that the slurry is free to flow through the machine without interference. The slurry level is controlled by a weir. The air is usually supplied under pressure.

Figure 3.3 Denver flotation machine

Figure 3.4 "GTK" Flotation machine (Outokumpu type)

The 2.5 dm3 "GTK" flotation machine ("Outokumpu type" flotation machine) was used in the Outokumpu laboratories. The feed quantity for each trial was 500 g. The rotation speed is 1500 rpm.

3.2.2 Laminar decantation: Slime separation

For the separation of the fine fraction during the flotation procedures, wet screening was used to remove the particle size fraction <20μn. For smaller particle sizes, hydrocyclones from the DICAAR department fig. 3.7 and the Outokumpu laboratory fig. 3.8 The hydraulic cyclone is an essential tool in mineral plants. It consists of a conical body into which the slurry is introduced tangentially through a feed nozzle under a pressure that can vary from 0.1 to 3-4 bar. Inside the cyclone, the slurry assumes a rapid rotational movement and the accelerations that can be achieved reach values of up to 1000 g. The largest and highest specific mass grains are centrifuged and exit through the orifice in the tip of the cone (underflow), the diameter of the tip used in the DICAAR department's hydrocyclone is 3 mm; the smallest and lightest particles and most of the water exit through the diaphragm (overflow).

In the Outokumpu laboratories, the hydrocyclone used is a 3 L sedimentation cell into which water is pumped at a rate of 0.126 L/min. The finer grains of slurry matter, due to the rotational movement, rise and overflow from the container sliding down the diaphragm. The settling speed of the particles is calculated according to Stoke's law:

$$v = (Ro - Ro') \times g \times \frac{d^2}{18 \times \mu}$$

where,

- (Ro) is the actual density of the material [2.80 t/m³].
- (Ro') is the average density of pure water [1.00 t/m³].
- (g) is the acceleration of the Earth's gravity [9.81 m/s²].
- (d) maximum particle size [15.0 µm]
- (myy) dynamic viscosity of pure water [0.01 g/(cm*s)]

The sedimentation velocity (v) derived from the above formula is 0.0002 m/s.

Figure 3.5 Hydrocyclone DICAAR

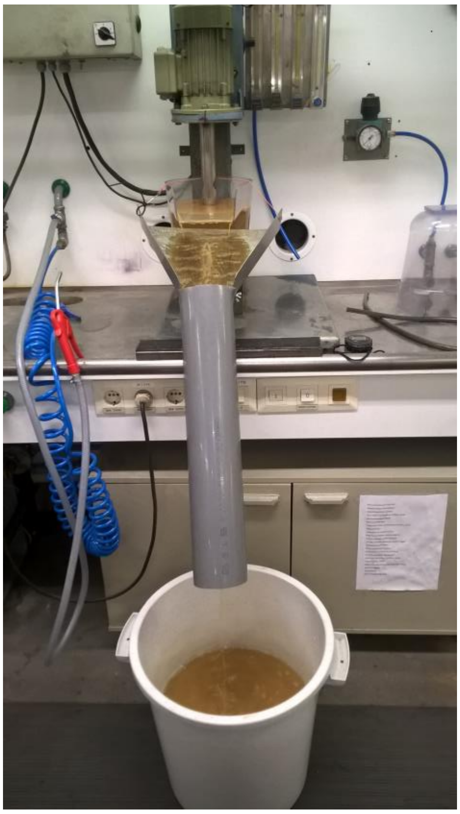


Figure 3.6 Hydrocyclone GTK

3.2.3 Flowsheet

The flotation process for metal recovery is focused on the separation of concentrates which are then used in copper, zinc and lead refineries. The flowsheet shows the steps of a process or activity from beginning to end using different forms connected by lines.

The great complexity of the materials under study has led to a subjective and progressive evolution of flowsheets. Depending on the sample under study, the flowsheets resulting from the best solutions in terms of both environmental and economic safeguards may be very simple or very complex.

Its structure varies according to several factors including the preliminary grain size cut, the grinding size, the slimness in the oxidised circuit (presence and regulation).

Experiments have led to the development of a process scheme consisting of three stages: roughing and sulphide scavenging; de-sliming; oxidised flotation. This type of process can be applied to the material Tal Quale or after a granulometric cut and/or grinding with different spill sizes (in a closed circuit).

Depending on the mineralogical composition of the feed to the flotation procedure, different reagent combinations and different flotation steps are used, which include re-milling steps in order to improve the degree of gangue ore liberation.

The flowsheet indicates the number of flotation steps in the sulphide circuit, the number of flotation steps in the oxide circuit, the number of waste scavenging steps in the oxide circuit, the type and dosages of reagents in the oxide circuit, the method of recirculation of the output intermediate products.

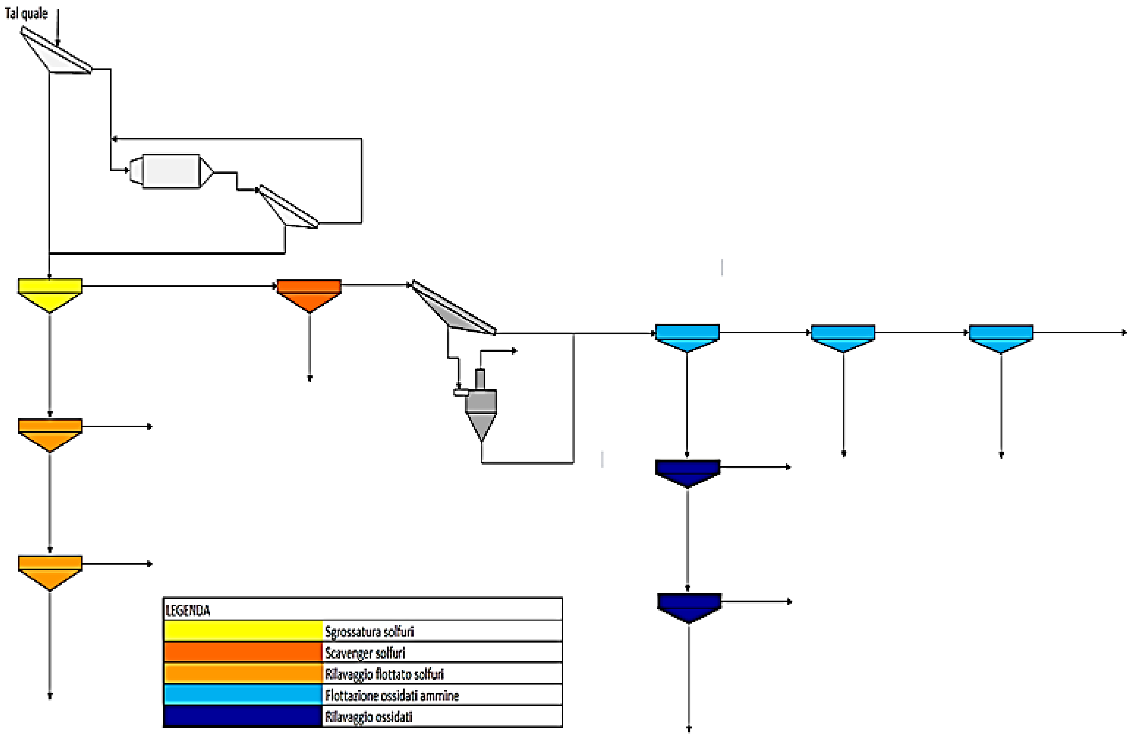


Figure 3.7 Flow sheet of Flotation procedures

3.3 Materials: Choice of sampling points

Appendix 1 of this document shows the volumes and contents of areas affected by the presence of industrial waste. The histograms in the appendix show the estimated volumes and average contents of Pb% and Zn%. From these data I was able to extract the following information: The sites of greatest interest (by volumes and residual contents); The variability of residual concentrations; The spatial distribution of residues. Based on the results of the Characterization Plan (PdC), prepared by IGEA SpA, in accordance with Legislative Decree 152/2006, on data validated by ARPAS and approved by the Assessorato Industria della RAS, and made available to the CESA Project, the sampling points with the highest Pb and Zn content and sampling depth were chosen.

Table 3.2 Sampling points.

SAMPLING POINT	LOCATION	DATE	NORTH COORDINATE	EAST COORDINATE	DEPTH
DM-051	*Montevecchio Ponente*	05/09/2017			
DM-091					
AF- 005					
SDBF-7	*Montevecchio Levante*	16/02/2018	4378979.00	464616.00	1.70m
SDAI-44			4378930.00	464629.00	surface
AF-51-5-A	*Montevecchio Ponente*	07/08/2018	4378051.54	1461279.03	1m
AF-51-5-B			4378019.36	1461300.52	
AF-51-5-C			4377999.57	1461305.66	
AF-51-5-D			4377990.99	1461291.87	
DM-119-14-A	*Ingurtosu Pireddu*		4374322.96	1456554.42	1.70m
DM-119-14-B			4374248.55	1456544.46	surface

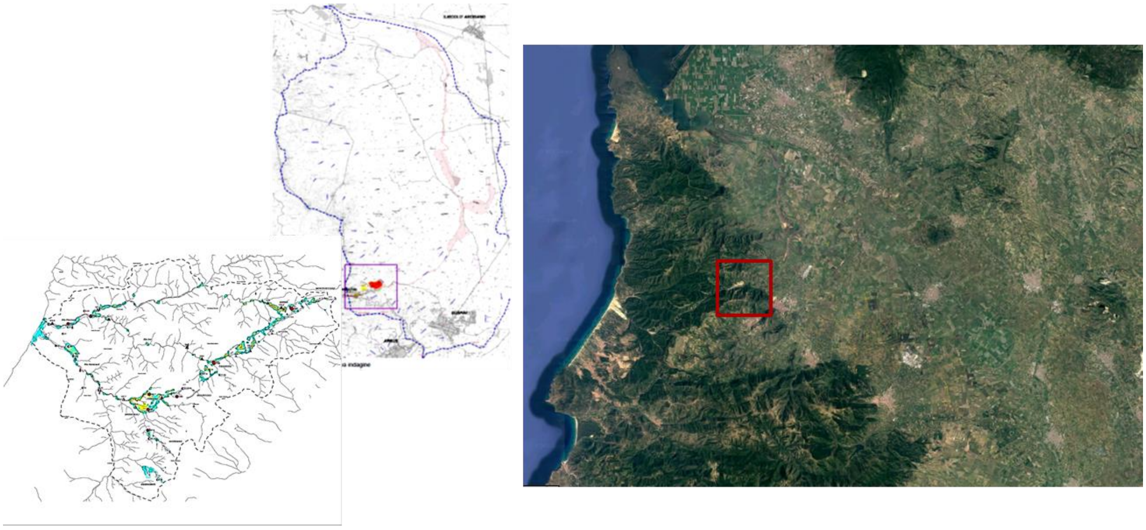


Figure 3.8 Geological survey of the area

3.4 Sample characterization

Particle size analyses, which aim to measure the "grain size" of such a collection, are carried out in the laboratory on representative samples. Particle size" is the set of properties characterising the size, proportions and shape of the particles making up a set of dispersed solids. The possible techniques are different depending on the size of the particles to be analysed.

To prepare the samples for the subsequent procedures of flotation and acid digestion, the following have been carried out: quartering, which aims to have the most representative portions possible; grinding, which frees the surfaces that have not deteriorated and are less exposed to weathering of the oxidised minerals and therefore to surfaces that are ideal for the correct execution of the flotation procedure; and screening, using vibrating screens, which is a direct classification method consisting of calibrated openings through which one tries to pass as quickly and completely as possible the solids that are smaller than a predetermined value. The fraction of smaller size constitutes the "passed" or "through", those of larger size constitute the "retained".

3.4.1 Sub-sampling

Sub-sampling is a procedure whereby a small representative sample is taken from a larger sample.

The Retsch DR100 sample divider, Figure 3.9 was used in the Outokumpu laboratory in Finland.

The Jones divider, Figure 3.10 was used in the laboratories of the DICAAR department.

Figure 3.9 Retsch Divider DR100

Figure 3.10 Quartering with Jones divider.

Rotary dividers ensure the representativeness of a sample and thus the repeatability of the analysis. The DR100 sample divider divides the sample in such a way that the composition of each sample fraction exactly matches that of the original overall sample. This applies to both fine and coarse powdered materials. The material feed and splitting processes take place automatically, without interruption and loss of material.

The dividing process is automatic and tamper-proof. The speed-controlled dividing head rotates at a constant speed of 110 rpm, independent of load and mains frequency. This means that when using a dividing head with ten outlets, the feed stream is divided into 1100 individual samples per minute, providing optimum division accuracy. The dividing heads distribute the material evenly between sample bottles.

3.4.2 Grinding

The milling process is carried out through a rod cylinder and lasts long enough to produce a few fine particles that are an obstacle to the subsequent flotation process.

Figure 3.11 Rod mill Barrotti

The bar cylinder, also known as a rod mill, is a cylindrical drum rotating around its horizontal axis, about half-filled with the solid to be ground and the grinding media, i.e. the steel bars. Due to the rotation of the drum, the grinding media dragged by the casing fall on the solid, grinding it. The rod mills are internally coated with an impact and liner. Grinding was performed on a representative fraction in order to characterise the material, and a screening operation was carried out on the samples so that the distribution of zinc in the different particle size classes could be determined. The same analyses performed on the Tal Quale sample were then repeated on the different slices. For the purpose of the flotation procedure, grinding was carried out on material with a particle size greater than 250 µm.

Figure 3.12 Mild steel laboratory rod mill

The rod mill used at the Outokumpu laboratory is the "Mild steel laboratory rod mill" ("GTK" Ø 200 mm x 225 mm) fig. 3.12.

3.4.3 Particle size distribution, sieving

Particle size distribution (PSD) was evaluated by granulometric analysis that was performed on around 0.1 Kg of samples. The method was according to UNI technical standards.

The machines used for screening have a unique two-dimensional operation: a horizontal, circular and a vertical typing movement. This special action allows the material particles to stratify and "search" for critical openings in the test media. These machines make it possible to perform the most accurate and consistent particle size distribution analysis tests. For sieving was used a mechanical vibrating sieve, the Ro-Tap Stein et Roubaix fig. 3.13. This type of sieve is characterized by a high vibration frequency (from 700 to 3500 per minute) with a relatively small amplitude (from 3 to 12 mm).

Figure 3.14 Ro-Tap Stein et Roubaix

Figure 3.13 Ro-Tap sieve shaker, model RX-29

In the GTK laboratories, a battery of sieves with mesh sizes that decrease downwards (usually ½ φ) was used. The sieves are stacked on a mechanical sieve that by vibration and tilting, favours the passage of the granules. In the end, each aliquot is weighed, together with any fraction present in the collection container. The vibrating sieve used in Outokumpu laboratories is the Ro-Tap sieve shaker, model RX-29 fig. 3.14.

The granulometric curve resulting from the analysis represents the percentage, referred to the sample total, of the finest sediment relative to each dimetric class. On the cumulative frequency curve, the diameters associated with a certain percentage of passerby are called percentile diameters and are indicated as D80 where the number indicates the percentage considered.

The fractions obtained from the particle size analysis were characterised from a mineralogical point of view by XRD analysis (X-ray powder diffraction) and chemically by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry).

3.4.4 Strategies for metal analysis

3.4.4.1 Mineralogic XRD analysis

The mineralogical XRD analysis was performed on dried mine residue samples reduced manually in agate jars and then subjected to XRD analysis using a Rigaku ULTIMA 4 diffractometer, in the LABMASTER-DICAAR Laboratory at the University of Cagliari. The operating conditions were geometry θ-θ, Cu tube (Cu radiation $K\alpha$; $\lambda = 1.54060$ Å), potential 30kV and current intensity 30mA. The diffraction spectra were analyzed with the Rigaku PDXL software and the International Center for Diffraction Data Database PDF-2.

X-ray diffraction (XRD) analysis allows the identification of minerals, but the mineral abundance is below 1 % w/w and requires a fine sample; the method does not provide information on particle and mineral grain sizes, particle compositions, mineral intergrowths and liberation.

3.4.4.2 The Mineral Liberation Analyzer (MLA)

Modern digital mine planning, plant design and mineral processing operations require detailed characterisation of ore and plant feed. Textural parameters, such as ore release size and ore association, combine with modal mineralogy data to strongly influence ore processing and recovery conditions. Normally, optical microscopes and semi-automatic SEM electron microscopes are used for the determination of these parameters. However, these methods are time-consuming, expensive and necessarily produce semi-quantitative results from data sets that are too small to be statistically valid. Over the past 10 years, modern SEM-based quantitative mineralogy tools have advanced rapidly with increasing computer power, improved SEM hardware and the development of sophisticated image analysis methods [63].

The Mineral Liberation Analyzer (MLA) is an automated Mineral Analysis System that operates on polished sections of cores or ground material identifying minerals and quantifying a wide range of mineral characteristics such as mineral abundance, grain size and liberation. The advantages of MLA over traditional light microscopy in the mineralogical analysis include [64]: High resolution; fine-grained or complexly intergrown minerals at the scale of micrometres can be distinguished Speed; the replacement of tedious manual analysis by systematic, computer-automated analysis Accuracy; increased throughput and the number of mineral grains examined provides a more statistically representative analysis of a sample, reducing also the potential for operator bias and human error.

The MLA combines a Quanta 600 automated scanning electron microscope (SEM) equipped with a spacious sample cell, plus energy-dispersive X-ray detectors with state-of-the-art automated quantitative mineralogical software. The software controls the SEM hardware to quantitatively analyse mineral and material samples [64]. Polished sections were prepared for testing. MLA measurements are based on backscattered electron (BSE) imaging of the polished section, analysis of grain shapes and positions for X-ray spectral acquisition, and classification of X-ray spectra characteristic of mineral species against a library of reference spectra. In practice, in order to determine mineral abundances, after measuring thousands of points, the surface area and weight percentages of the different minerals will be counted per mineral and, based on the results, the surface area and weight percentages of the different minerals will be calculated [65] [64]. The method is applicable e.g. for the determination of:

- Mineral abundances
- Grain size
- Degree of the liberation of specific minerals from gangue
- Microstructures in mine tailings

The mineral content was measured using the XMOD_std method. The XMOD mode is the one which provides the modal mineralogy data. It is essentially a modern version of the classic point-counting analyses. The entire sample is divided into a grid of points and an EDS spectrum is gathered from each point, The XBSE method was used to measure the liberation and particle size of sphalerite. The XBSE mode is an extended liberation analysis method in which each BSE image is collected and segmented to delineate mineral grain boundaries in each particle, then each segment of particles (mineral grain) is analysed with one x-ray analysis. The off-line processing generates particle mineral maps from particle segmentation data and x-ray spectra.

Each of the collected spectra (both modes) is being compared with the standard library spectra and a mineral name is assigned to each of them according to best match procedure. Finally, the numbers of each mineral's spectra are converted into percentage proportions by taking mineral densities into account.

3.5 Chemical characterization

3.5.1 Loss of Ignition (LOI)

A chemical-physical characterization of residues was carried out to assess their elemental composition, Loss of Ignition (LOI) and leaching test. The procedure consists in measuring the weight loss by calcination resulting from the loss of volatile or thermolabile constituents (crystallising water, organic matter, CO_2 from carbonates). The content of major elements was assessed by alkaline digestion of 0.2 g of fine dried residue with 2.5 g of lithium metaborate at 1000±25 °C for 2 hours; the resulting molten residue was dissolved in HNO_3 solution by a stirrer for an overnight. The solution was diluted to 200 ml with distillate water (2.5 % HNO_3). The weight is then measured using an analytical balance, repeated in duplicate to obtain an estimate of the error. The LOI is expressed as a percentage loss of the initial weight. LOI at 950°C was performed to evaluate the total carbon, reducing the mass of 1.0 g of dried sample (at 105 °C) in the oven at 950°, for 1 hour.

3.5.2 Microwave digestion: Mineralization with acid attack

The content of minor elements was evaluated by microwave-assisted acid digestion (Start D, Milestone) adding at 0.5 g of fine residue strong acid (3 ml of HCl, 9 ml of HNO_3 and

2 ml of HF), according to 3052 EPA method. After digestion, sample solutions were evaporated, filtered to 2-5 μm and diluted to 50 ml with HNO_3 (1 % v/v).

3.5.3 Sequential extraction

The partitioning of Zn from Pb in the mine residues was investigated by performing the 5 steps of the sequential extraction (SE) procedure proposed by Tessier. The method was carried out on 1.0 g of dry sample. An additional 6 step with the strong acid attack was performed for the mass balances calculation. SE was performed also on GSD 9 matrix standard. The principle of the method is based on the fractional of the metals contended into the matrix in different fractions which can be destroyed by using specific reagents. Metals bound to each fraction destroyed are then released in solution. The solid phase is separated by the solution phase and metals concentration in the solution phase is analyzed by ICP-OES. The fraction studied generally are:

- water-soluble;
- exchangeable (metals are extracted by a solution containing electrolytes or slightly acid);
- carbonate fraction (metals bound to carbonate, soluble in acid solution);
- iron and manganese oxides (metals bound to soluble in a reducing solution, followed by an acid treatment which allows precipitating metal-bound);
- natural organic matter (metals bound to organic compounds or sulphides, soluble in oxidizing conditions);
- the residual fraction (silicates and other minerals) which retain elements in the crystalline structure, and it can be destroyed by acid digestion.

In the first step, 1.0 g of dried pulverized mine residue was introduced in 50 ml polyethylene tubes and was added an amount of 20 ml of distillate water, then the suspension was stirred for 3 h. The obtained solution was separated from solid residue by centrifugation at 3000 rpm, for 10 min. The residue was washed with a 10 ml of distillate water, centrifugated and all separated solution were collected in a flask and diluted to 50 ml (1% HNO_3). In the second step, 20 g of $MgCl_2$ solution (1 mol/l, pH~6) were added to the residue of step 1 for second step extraction. The experiment was carried out at ambient temperature. In the third s*tep,* 10 ml of 0.1N CH_3COONa/CH_3COOH was added to the residue from step b in the centrifuge tube and extracted by shaking for 3 h at ambient temperature. Extraction and solid-liquid separations, as well as extract storage, were carried out as described above. In the fourth step, 10 ml of 0.1 N $NH_2OH \cdot HCl$ was added to the residue from step c in the centrifuge tube and extracted by shaking for 3 h at 60 ◦C. During this step, the reducible forms associated with oxides and hydroxides of Al, Mn and Fe. In the fifth step, 5 ml of H_2O_2, 8.8 M (pH 2–3, adjusted with HNO_3) solution was slowly added in small amounts to the residue from step 4. Extraction (digestion) was carried out in a covered vessel at room temperature for 1 h. It was continued with the cover being removed for 1 h at 85 ◦C to reduce the volume to a few ml. Aliquot of 5 ml of 8.8 M H_2O_2 solution was added into the cooled down solution and it was heated at 85 ◦C for another 1 h until the volume was reduced to a few ml. Then 25 ml of 1 M CH_3COONH_4 (pH 2, adjusted with HNO_3) was added to the cooled residue for 16 h extraction at ambient temperature. The solid residue was separated from the extract by centrifugation, the residue was awash in distillate water and solution was diluted into a 50 ml volumetric flask. In the end, the residual forms associated with oxides of Al, Na and Si was treated as described above by 3052 EPA method. The amounts of elements liberated by each sequential extraction were summed and compared with the certified total values as well as with the total digested data to examine the applicability and accuracy of the proposed method. The method was applied to 5 samples of each mine residue and on two GSD 9 samples matrix standard.

3.5.4 Laboratory-based analytical detection techniques

The trace element composition of samples gives us the metal content of the sample. The methods used in this work for the determination of heavy metals are highly sensitive and selective, although they require sample preparation, skilled personnel, expensive disposable equipment and gas to perform the experiments. The ICP-OES and ICP-MS techniques use plasma as the source of atomisation and excitation. Plasma is an electrically neutral gas with a certain percentage of ionisation (~5 %). The energy that maintains an analytical plasma comes from an electric or magnetic field. Most analytical plasmas operate with argon or helium, which makes combustion impossible.

A prepared pulp sample (0.2 g) is digested with a mixture of concentrated acids (hydrofluoric acid, perchloric acid, hydrochloric acid and nitric acid) in a Teflon tube by heating on a heating block. The solution is evaporated to dryness and the solid residue is dissolved in nitric acid. The final solution is diluted with water before instrumental measurements using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Perkin Elmer Optima DV 7000) and/or Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3.5.4.1 ICP-OES

Inductively coupled plasma source optical emission spectroscopy or ICP-OES is a technique discovered in the mid-1960s. The principle on which it is based is the interaction of plasma and electromagnetic radiation. The sample drawn from the container is vaporised in a chamber where it is ionised with argon and passes through a torch which reaches temperatures of 10,000° C. At high temperatures, the mixed gas emits photons that are captured by a lens. The photodetector converts the excited wavelengths into an electrical signal that is processed by a computer [66]. The ICP-OES is capable of analysing up to 70 elements simultaneously, but its "shortcoming" is that it cannot detect concentrations in the ppm range, and it also has interference in the response spectra. It is also used to calculate the fixed residue of water as it has a higher tolerance of dissolved solids than ICP-MS.

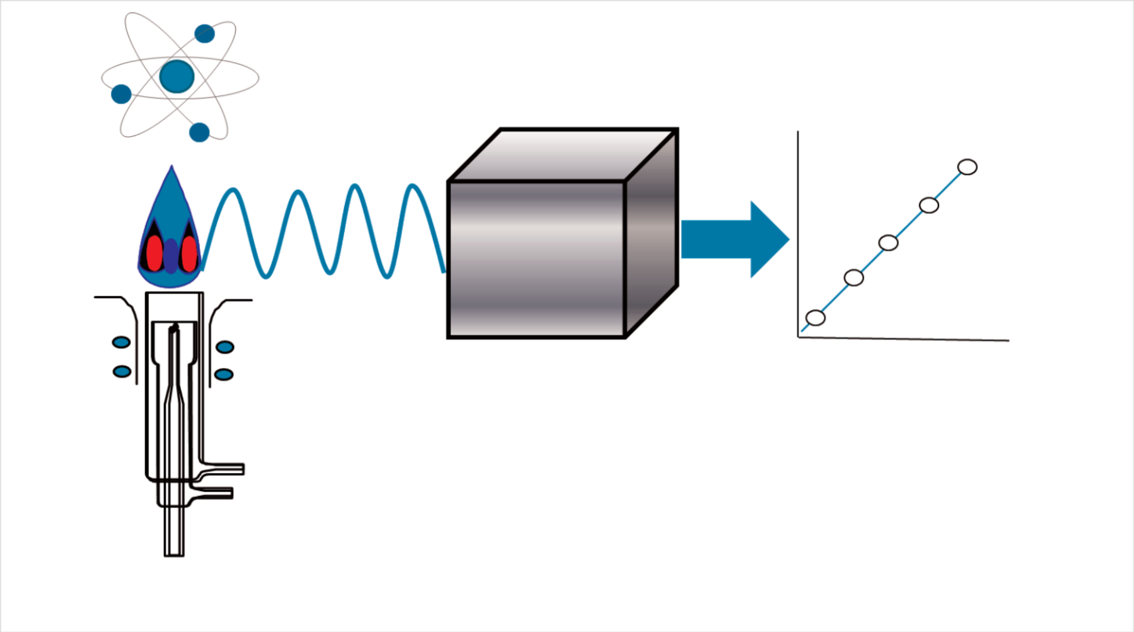


Figure 3.15 ICP-OES spectrometer operating diagram [67].

Figure 3.16 ICP-OES Perkin Elmer Optima DV 7000 from the DICAAR department of Cagliari University.

3.5.4.2 ICP-MS

Atomic mass spectrometry with an inductively coupled plasma source, or ICP-MS, was used at the GTK laboratories in Kuopio. In the late 1970s and early 1980s, the possibilities offered by this new technique were demonstrated. The methodology used combines plasma coupling technology with mass spectrometry, allowing the determination of elements in the ppt range with a wider dynamic range than ICP-OES. In addition, it is able to measure elemental isotopic concentrations in liquids. It can detect more elements (82) simultaneously than ICP-OES and requires a smaller sample volume (depending on the programme, how many elements and repetitions). The maintenance cost is 2 to 3 times higher than an ICP-OES. This instrument has been very useful in analysing samples with traces of elements belonging to the Rare Earth group. For this type of research, a fairly expensive internal standard was required.

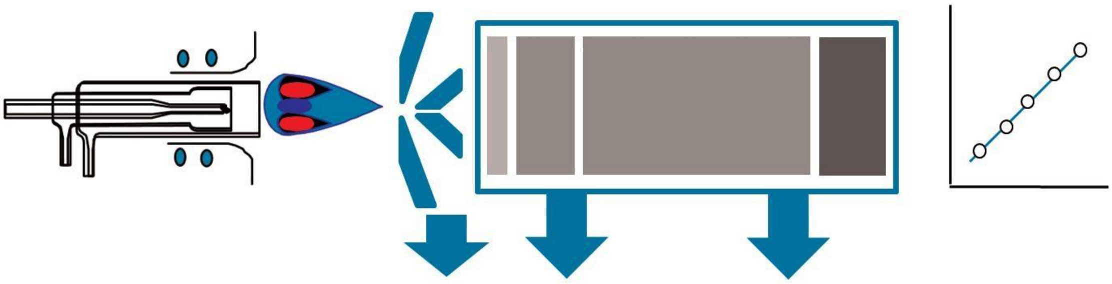


Figure 3.17 Schematic diagram of the components of an ICP_MS. [67]

Figure 3.18 ICP-MS from the GTK laboratory in Kuopio, Finland.

3.5.4.3 Advantages and disadvantages of the two gold standard methods

In summary, these gold standard methods for toxic metal analysis have several advantages, including high sensitivity, high accuracy, low detection limit (DL) (lower for ICP-MS) and the opportunity to detect many trace metals simultaneously. Their performance is compared in the Table. However, they have several disadvantages: they are expensive, require a constant supply of chemicals, reference (standard) materials are needed to ensure the quality of the results obtained, and require well-trained personnel to carry out the multi-step sample preparation and analytical procedures. The major disadvantage is the inability to be used in situ and in real-time at remote sites and to detect the immediate effects of accidental or unexpected contamination events.

Table 3.3 Summary of the performance of the two "gold standard methods" for metal analysis

	ICP-OES	**ICP-MS**
Sample separation	Plasma excites atoms, which emit photons	Plasma generates cations
Ion detection	emission wavelength	mass-to-charge ratio
DL in the	ppb range	ppt range
Multi-metal analysis	YES	YES
Sample preparation	YES	YES
N of elements detected	10	54
Extra	High tolerance on fixed residue	Isotopic analysis

3.6 Data analysis

3.6.1 Statistical analysis

Data processing and analysis aimed at achieving the proposed objectives concern the final stages of the research project. The data processing concerns the treatment of the acquired data and therefore any procedure, even non-statistical. In this regard, the following data were acquired:

- concentration in the final waste
- concentration in the final float sulphides
- Inefficiency index: $\eta Zn = W_{Tail\ scavenger} / W_{Feed\ rougher}$ (providing information on the effect of grain size and grinding size)

Besides, data were acquired on the effects of de-sliming before oxidised flotation:

- Weight percentage $\%_W = (100 \cdot W_{slim}/W_A)$
- Yield $\rho Zn = W_{froth}/W_{feed}$
- The proportion of metal units $UM = W_{over}/W_{feed}$.

Data analysis refers to decisions made after careful consideration of the results of the data processing. Based on the concentration data (of the final waste and the sulphide flotation concentrate) and weight, it was decided, for example, what is the optimal particle size cut-off and grinding size of the feed to the flotation procedure; the reiteration of analyses on the yield and distribution of the metal units made it possible to assess what is the best particle size regarding the removal of fines from the feed before the oxide circuit.

Chapter 4 Environmental management and metal recovery: re- processing of mining waste at Montevecchio site (SWSardinia) [68] [1]

4.1 Introduction

The affordability of mineral raw materials is crucial for the sustainable development. In the EU, however, mining activities can take place under very strict environmental regulations and constraints. Old mining and processing activities waste represent, in fact, a major environmental risk, so that the action of combining environmental management with metal recovery from processing waste is becoming more and more attractive [69]. Tailings or dumps re-processing should have two main objectives: obtaining a final tail with residual concentrations of heavy metals lower than the legal limit values, the first; producing a final froth that meets the metallurgy constraints, and can be considered a marketable concentrate, the second. These two objectives make the application of the process very different from the usual industrial beneficiation processes, for which the scavenger section is aimed at obtaining the maximum recovery in the final float while the tails grades are simply a result. The present study case is aimed at obtaining a residual concentration that should be below the environmental threshold, while the scavenger froth grade is a consequent result. Moreover, industrial plants have the scavenger float re-circulated back into the process (to maximize recovery), while, in this case, it is a final product non-marketable and in need of an inertization process.

This paper discusses the case of the waste disposed in the Montevecchio-Ingurtosu mining district (SW Sardinia) where the main minerals extracted were sphalerite and galena in siliceous gangue. The re-treatment of these tailings raises some difficulties, depending on: (i) the fine particle size and the low-content of the already floating material; (ii) the alteration processes due to the geochemical environment, through the high specific surface and time elapsed after deposition (between 50 and 80 years); (iii) the lead and zinc oxidized forms. These aspects will be discussed below along with the experimental results of batch laboratory tests.

4.2 Froth flotation applicability

Froth flotation is a highly versatile method for separating physically particles, based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in a mineral/water slurry [70]. The flotation system includes many interrelated components as shown in Fig. 4.1.

Collectors generally employed in flotation are surfactants that form, for instance, electrostatic bonds with the solids [71]. Difficulty arises when Pb or Zn minerals are separated from an ore having a low grade or a complex composition (complex sulfide ores) or when the mineral surface properties (oxidized Pb and Zn ores) make the response to flotation extremely poor. The design of a flotation plant therefore requires bench scale batch and locked cycle tests, followed by pilot plant trials [72].

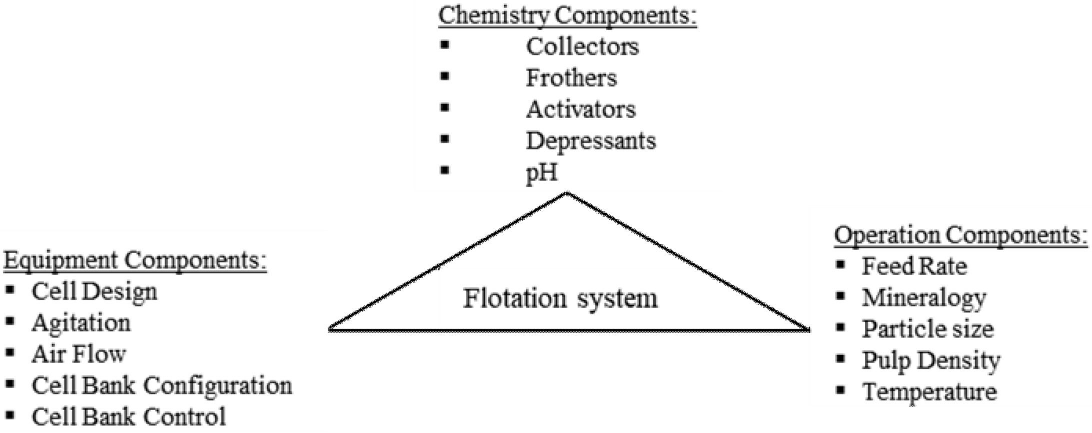


Figure 4.1 Interrelated components of a flotation system (Klimpel, 1995 cited in [70]).

4.3 Effect of surface liberation and particle size

The extraction of ore minerals from fine-grained flotation tailings is a commercially interesting but technologically challenging endeavor which needs to be supported by a full technical and economic feasibility study.

Jameson [73] discussed how recovery of mineral particles by flotation is strongly a function of the particle size. As the size of floatable particles increases, the recovery increases too, until it reaches a maximum, before de-creasing monotonically.

Büttner et al. [74] discussed the case study of a historic tailing storage facility containing on average 0.2 wt% of Sn as cassiterite. The viability of the flotation process was attributed to three material parameters, namely grade, liberation, and particle size of the mineral. These parameters were quantified for a set of ten exploration drill cores by chemical assay and mineral liberation analysis. Results illustrated the importance of combining chemical grade data with quantitative mineralogical and microfabric information to be able to assess objectively the residual value contained in the industrial tailings or any other residue to be re-processed.

4.4 Complex Pb-Zn sulfide ores

Complex sulfide ores are generally defined as those ores for which it is difficult to recover one or more selective products of acceptable quality and economic value having minimal losses and at reasonable costs. Complex sulfide ores are fine-grained, intimate associations of chalcopyrite, sphalerite and galena, disseminated in dominant pyrite, and containing valuable amounts of minor elements [75].

A great number of studies have been carried out on complex Pb and Zn sulfide ores. It is worth citing, as a recent example, the article of Kursun and Ulusoy [71] illustrating the case of a selective flotation circuit that is treating (−74 μm) Pb–Zn–Cu complex ore. The ore feed to the plant consists of sulfide minerals, namely galena (5.2%), sphalerite (5.1%), chalcopyrite (0.9%), and pyrite (7.8%). The main gangue mineral is quartz. Using three stages of cleaning and three stages of scavenging, a zinc concentrate having 58.81% Zn was produced with a recovery of 74.21%. The integration of the column flotation circuit to current conventional flotation circuits of the plant will lead to an improvement in final zinc concentrate grade by a minimum of 6% and 13% points of recovery and reduction of three cleaning stages at the same time.

4.5 Oxidized Zn and Pb minerals

There is a difference between sulfurized and oxidized minerals flotation. It is quite easy to recover Zn from sphalerite and Pb from galena even using xanthate collectors, while it is more difficult to recover Zn from smithsonite, and Pb from cerussite. This topic has been discussed extensively in the relevant literature.

The flotation of Zn and Pb oxidized minerals is difficult because there are no known direct-acting collectors capable of producing single metal concentrates. In the case of oxidized lead and zinc minerals their surface is not easily rendered hydrophobic by the collectors generally used, to achieve efficient flotation. Furthermore, the solubility of these oxide minerals is high. Consequently, the collector also interacts with the metal cations in the solution, increasing the quantity of reagent required for flotation. It is therefore common practice to sulfurize such minerals before flotation to prepare their surface to receive xanthates, which are the collectors generally used for concentrating sulfides [76]. Normally, the collectors used react when the ore underwent preliminary sulfurization surface. This is an extremely delicate and critical phase. In fact, sulfurization requires a careful dosage otherwise the mineral surface becomes inert.

Mehdilo et al. [77] investigated the flotation of smithsonite from a tailing derived from the cerussite flotation circuit using Armac C and Armac T collectors. The results indicated that the dosage of sodium sulfide, collector type, and de-sliming are the main affecting factors on the Zn grade and recovery of smithsonite flotation concentrate. Without consumption of any gangue depressants, an optimal concentrate was obtained with 94.4% recovery and 42.3% Zn grade. In such a condition, the collectors' consumption is decreased significantly. Thus, de-sliming before flotation is essential for a successful recovery of smithsonite.

Ejtemaei et al. [60] reviewed an interesting analysis of zinc oxide mineral beneficiation using flotation method. Dosages of sulfidizing agent and collector, de-sliming before flotation, and the use of sodium hydroxide instead of sodium carbonate to act as pH regulator are essential to the effective recovery of smithsonite in cationic flotation. Despite the use of sodium silicate and SH as depressants in oleic acid flotation, flotation was not selective. Flotation using mixed collectors (Armac C + Potassium Amyl xanthate) showed promising results. The ratio of the mixed collectors and the sequence of addition of mixed collectors were important criteria in obtaining true mixed collector flotation.

4.6 Montevecchio Ponente_Ingurtosu : DM091 DM051 site features and choice of points

The materials studied come from the Montevecchio-Ingurtosu mining area in south-western Sardinia, which was one of the largest mining districts in Sardinia for the cultivation of Pb and Zn. [78] .

Figure 4.2 Overview of the Montevecchio Ponente-Ingurtosu area

Figure 4.3 Mining dump classification, DM_051

The first aspect to be verified was the flotation of poor materials and the possibility of obtaining from these the high zinc content (up to 50% required by metallurgy) in the concentrate and the low content (below the CSC or Natural Fund) in the final sterile. In the mineralisation, in addition to the base metals, the presence of a wide set of elements such as In, Ge, Ga, Ag, etc. was ascertained [79]

Sampling carried out on 5/09/2017 resulted in the collection of representative samples from the mining dumps DM_051 and DM_091

Figure 4.4 Variable size elements in the mining dump DM_051

Figure 4.5 Ponente-Ingurtosu, DM_091

Figure 4.6 Sample from the Montevecchio Ponente-Ingurtosu landfill, DM_091

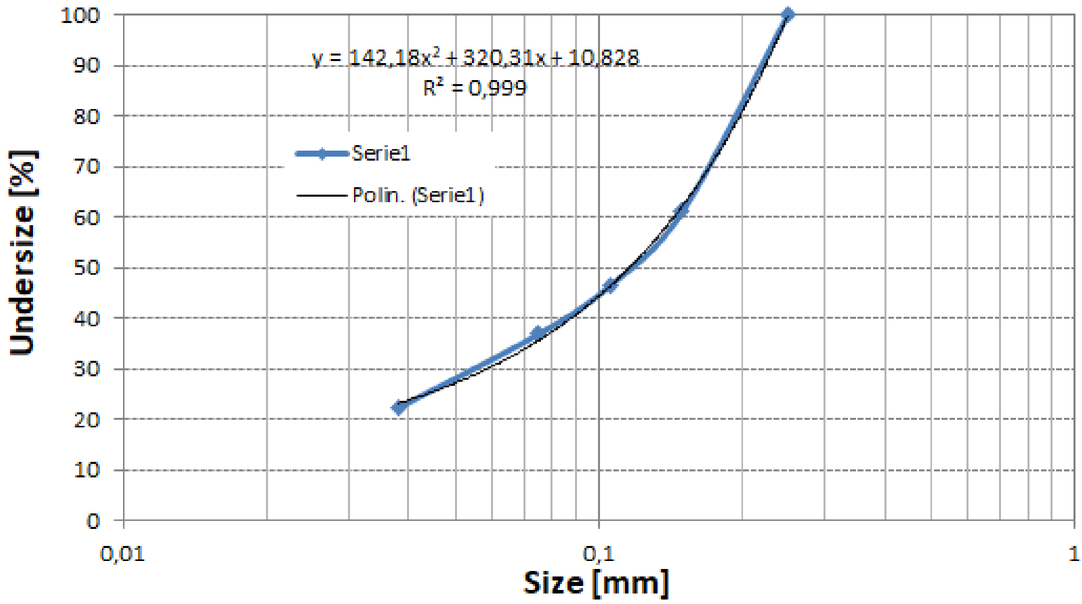
As can be seen from the images, the material consists of elements of varying sizes that differ between very poor and whole pieces of useful ore. In particular, in DM_091 samples were taken consisting of a few very large pieces which were then crushed.

4.7 Samples characterization

The samples characterisation phase therefore began with the decrease in sample size for the subsequent constitution of representative feeds for the flotation procedure. One ~30kg sack of DM_051 and 3 sacks of respectively 1265.1g. 996.5g. and 2191g. of DM_091 respectively were crushed through a jaw crusher and subsequently quartered. One eighth of the crushed material from each landfill was taken for subsequent characterisation steps. The material was then ground through a rod mill and screened at 0.250mm.

Table 4.1Particle size analysis of sample Tal Quale

PARTICLE SIZE CLASS		Retained	Retained	Retained Cumulative	Cumulative Passing
[mm]		[g]	[%]	[%]	[%]
	0,25	0	0	0	100
0,25	0,15	74,2	38,9	38,9	61,1
0,15	0,106	27,5	14,4	53,4	46,6
0,106	0,075	18,4	9,7	63,0	37,0
0,075	0,038	27,79	14,6	77,6	22,4
0,038	0,02	12,43	6,5	84,1	15,9
0,02		30,2	15,9	100	0
TOTAL		190,52			



The particle size composition results in a D80 of 0.198mm.

The determination of the minor elements of the T.Q. samples gives us the content of metals present in the sample. From the material from DM_051 it was possible to obtain a representative fraction useful for chemical analysis, Table ; for the material from DM_091 the contents of three characteristic samples were determined and kept separate to observe the differences in content.

Table 4.2 Minor analysis of the samples Tal Quale expressed in mg/kg and as a percentage.

Average concentration							
ID_sample	**kg**	**Ag**	**As**	**Cd**	**Cr**	**Pb**	**Zn**
		mg/kg					
DM_051	6,230	<DL	85,88	24,19	55,16	1844,58	4765,52
DM_091	1,265	<DL	132,90	1182,98	54,37	542,97	165875,69
	0,996		489,77	1235,48	28,46	1416,31	142137,80
	2,191		46,92	976,24	33,58	408,83	167418,42
CSC		-	**50**	**15**	**800**	**1000**	**1500**
	%						
DM_051	6,230	<DL	0,01	0,00	0,01	0,18	0,48
DM_091	1,265	<DL	0,01	0,12	0,01	0,05	16,59
	0,996		0,05	0,12	0,00	0,14	14,21
	2,191		0,00	0,10	0,00	0,04	16,74
CSC		-	**0,005**	**0,0015**	**0,08**	**0,1**	**0,15**

The tailings mineralogical XRD analysis indicates that muscovite, quartz and sphalerite were present. Five mixtures were considered, having a different Pb and Zn grade (from very poor tailings to a sample of sphalerite collected from the same dumps). These mixtures were obtained by adding 1 kg of mixed DM_051+DM_091 to 2 kg of sterile DM_051, which was found to be poorer in Zn, with the intention of increasing the content of the feed entering the flotation process. The two samples, sterile plus mixture, were mixed and then quartered and divided into feeds of ~700 g each. The multi-element chemical analysis results of the feed tailings in the flotation tests are shown in table 9. The reagents used in the flotation tests are shown in Table 3.

Table 4.3 Multi-element chemical analysis of the feed tailings in the flotation tests (metal grades in mg/kg).

ID_Test	**As**	**Cd**	**Cr**	**Pb**	**Zn**	**Cu**
	mg/kg					
Flot_01	158	240	50	1,796	29,207	206
Flot_02	164	259	50	1,762	31,364	209
Flot_03	123	135	53	1,806	17,339	190
Flot_04	120	126	53	1,809	16,290	189
Flot_05	104	78	54	1,826	10,837	181
CSC	**50**	**15**	**800**	**1000**	**1500**	**600**

4.8 Flotation procedure

The flotation tests were performed in a 2.5 dm3 Denver cell using 700 g of solid feed. The flotation flowsheet consisted of three parts Fig.4.6: Rougher, Cleaner and Scavenger. Three final products were obtained: Final Froth (the commercial concentrate), Final Tails (the reusable waste), and Scavenger Froth (the non- commercial concentrate). The third product should be taken into consideration too: in fact, it is not appropriate to recycle the Scavenger float since it would increase the grade of the Tail, while the goal is the opposite. Indeed, in the scavenger section the higher the Zn grade of the Froth, the lower the Zn grade of the Tails.

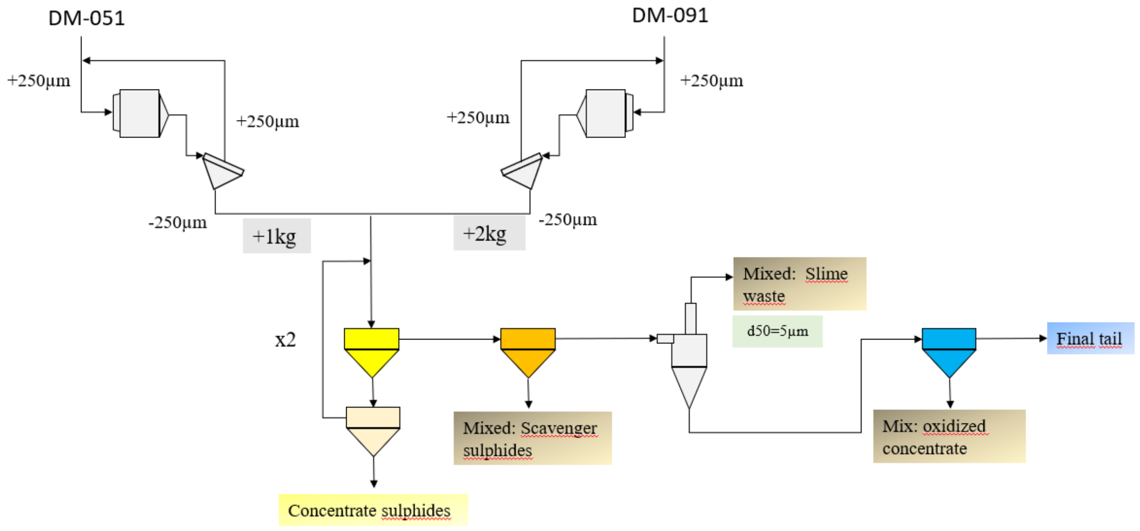


Figure 4.7 Flotation test flowsheet

Samples were ground and then sieved to collect the -250 +5µm fraction for a series of five groups of flotation tests carried out according to the flowsheet in Fig. 4.7. In the Rougher section, $CuSO_4$ was added and the pulp was conditioned for 5 min at pH equal to 6.5. The slurry was conditioned with collectors (conditioning time 10 min). Finally, Dowfroth was used as a frother (100 g/t). The froth collection was carried out for 10 min. The Final Froth, Final Tails, and Scavenger Froth were dried, weighed, and analyzed using a spectrometer ICP/OES (PerkinElmer 7000 Optima).

Table 4.4 Reagents used in the flotation tests.

Reagents	Concentration	Plant section	Role
Na Isopropyl xanthate	100g/t	**Sulphides Rougher and Cleaner**	Sulphide collector
CuSO4	400g/t		Sphalerite activator
Dowfroth 1015	100g/t		Frothers
Na2CO3	400g/t	**Scavenger**	pH regulator
Na Oleate	300-400g/t		Oxide collector

CuSO4 was added to the roughing section and the slurry was conditioned for 5 min at pH 6.5. The slurry was conditioned with collectors (conditioning time 10 min). Dowfroth (dosage 100 g/t) was used as a foaming agent. Foam collection was continued for 10 min. The final float was obtained after two finishing steps. Before scavenger, the material was de-slimed using a high-pressure hydrocyclone (0.5 MPa and d50 = 5µm). The content of each of the two products had to meet the following conditions: the final float had to have a Zn content > 40-50% (to meet metallurgical requirements); the final waste Zn < 1500 mg/kg (in accordance with Italian environmental regulations for industrial sites). The scavenger float was considered as a waste to be inerted at minimum cost.

The Final Float, the Final Waste and the Scavenger Float were dried, weighed and analysed with an ICP/OES spectrometer (PerkinElmer 7000 Optima).

4.9 Results and discussion

The flotation results of the 5 test groups are shown in Table 4.5 and in the histograms in Fig. 4.8, 4.9 and 4.10. The metal recovery in the Final Froth has always been between 95% and 70%, according with the modality of execution of the Cleaner Flotation, but not for the grade of Zn in the feed. The same happened for the weight distribution. Therefore, the best flotation groups were the first and last ones, for which a multi-stage cleaner was used. As far as the Final Tail product is concerned, compliance with the legal limits is highlighted in the histograms in Fig. 4.10, showing the values of the ratios between the measured concentrations and the corresponding thresholds (as required by the Italian Regulations) of the six elements analyzed. Since the values are all less than 1, the threshold value is always respected.

Table 4.5 Final Froth and Final Tails: multi-element chemical analysis results.

ID_Test	**Concentrate mg/kg**					
	As	**Cd**	**Cr**	**Pb**	**Zn**	**Cu**
Flot_01	366	3,164	27	5,208	502,003	2,535
Flot_02	312	2,425	56	4,894	552,273	2,521
Flot_03	894	99	43	11,109	506,512	88
Flot_04	711	3,675	33	8,900	477,833	3,967
Flot_05	673	454	42	6,449	446,623	466
	Final Tail mg/kg					
Flot_01	30	7	44	586	1,019	72
Flot_02	28	5	31	834	1,227	52
Flot_03	19	4	30	554	915	63
Flot_04	40	7	34	581	1,028	68
Flot_05	40	8	35	660	1,009	70
CSC	**50**	**15**		**1000**	**1500**	**600**

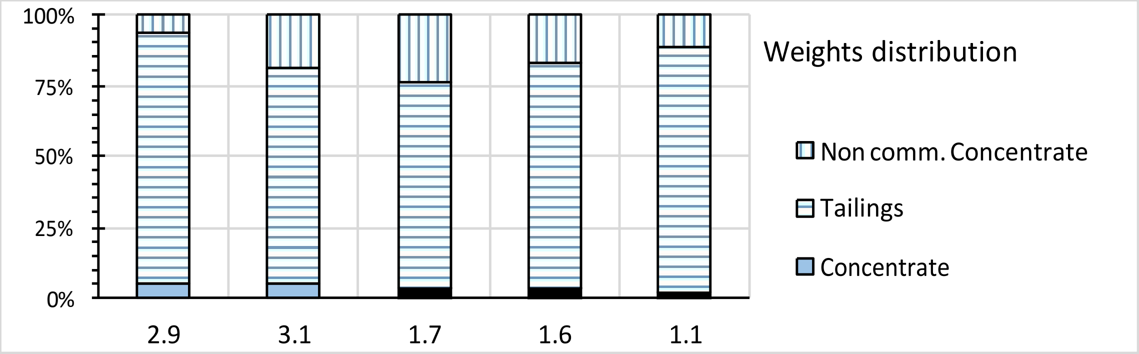


Figure 4.8 Flotation results: metal recovery vs feed grade.

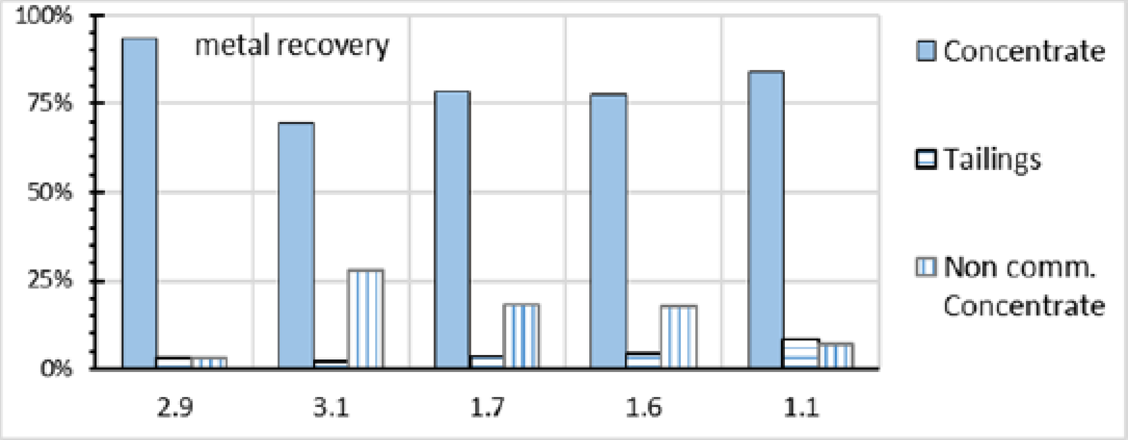


Figure 4.9 Flotation results: metal recovery vs feed grade.

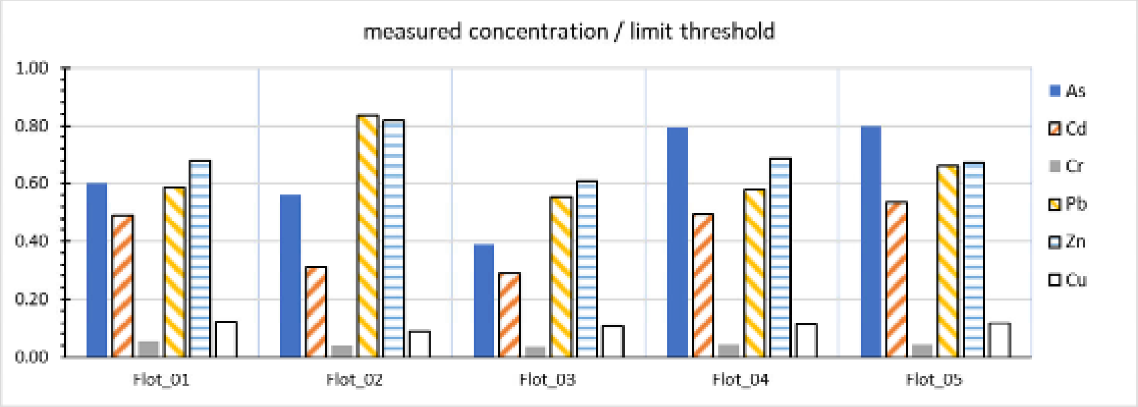


Figure 4.10 Flotation results: concentration/limit threshold.

The mining wastes in the Montevecchio area show a considerable variability in terms of particles size, time elapsed from the deposition and residual concentrations of lead and zinc minerals. In some dumps untreated materials are present as they were not thought of any interest from an economic point of view sixty years ago.

The results obtained on the mixed materials are particularly encouraging in terms of both environmental management (low grade of heavy metals in the Final Tail), and metal recovery (market value of the concentrate). Concentrates with a grade of zinc respecting the requirements of metallurgy were obtained: they can be considered as marketable products with a commercial value [80]. The Final Tail material can be used for other purposes, such as for filling and landscape modeling: as an example, in the Western part of Montevecchio (Ponente) surface excavations of about 1.5 mm^3 that could be filled in with the re-processing Tail are present.

However, the samples considered do not represent the totality of the Montevecchio wastes for both the relative high value of the Pb and Zn concentrations considered (between 1% and 3%), and the high recoveries obtained in the flotation tests (between 70% and 95%). On the contrary, tailing dam materials have grade lower than 1% (for both Pb and Zn) and a relevant component of oxidized minerals, difficult to be floated. The assessment of the whole waste on the site will require further investigation. In the future it is expected that it will be possible to distinguish between waste that can be re- processed and those which should be placed in a storage landfill.

Chapter 5 Flotation treatment of Montevecchio Levante mining tailings: summary of results [81]

5.1 Montevecchio Levante: site features and choice of points

The study was carried out on a sample of 25 kg of material taken from the tailings pond produced by the Principe Tommaso mineral processing plant (Montevecchio Levante). The volumetric and geochemical characteristics of the basin are described in the CESA document on the census of the contamination status of mining areas in Sardinia.

The sampling point and depth were chosen considering the results of the Characterisation Plan (PdC), drawn up by IGEA SpA, pursuant to Legislative Decree 152/2006. Examination of the data shows that the area around the IGEA SDBS_07 survey at a depth of between 1 and 9m from ground level can be assumed to be representative of the Zn and Pb concentrations present in the basin. The survey (maximum depth=20.80m, water table at 13m from pc) is located in the southern part of the lower esplanade and has WGS84 coordinates 39.557.963N, 8.586.827E. Sampling took place on 16 February 2018 at a depth of 1.70m (above the water table) and was carried out by excavator by IGEA staff. Location and sampling phases are illustrated in Figure 5.1.

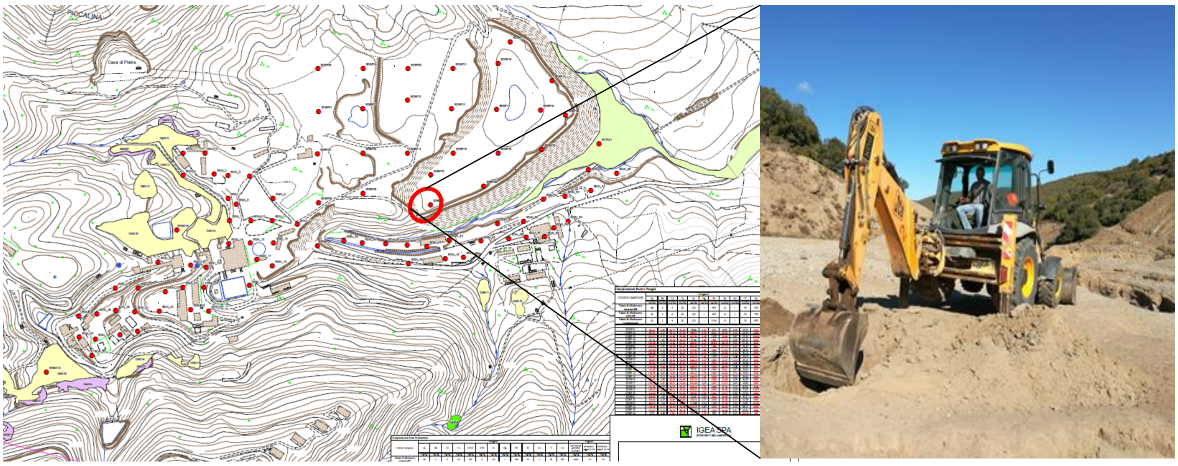


Figure 5.1 Location and sampling phases SDBF_07 from the Montevecchio Levante basin.

5.1.1 Features of the Sludge Basin and the SDBF_07 Survey

The so-called Mud Basin was investigated for the Characterisation Plan, for the solids component, with the execution of 26 drillings and the collection of 128 soil samples, on which chemical analyses were carried out for the determination of 18 inorganic analytes and 56 organic compounds of Table 1, Part IV, Annex 5, Legislative Decree 152/06. The following were also determined: pH, total and organic carbon, Al, Mn, total sulphur, sulphates, sulphides and total iron.

Inorganic CSCs (industrial sites) were exceeded throughout the basin only for the elements Sb, As, Cd, Pb and Zn. With reference to these analytes, the results of the IGEA chemical analyses on the samples taken from the SDBF_07 survey witnesses are reported in the histograms in the Figure 5.2 according to the depth from the PC (the values are not equispaced but follow the sampling criteria of 152/06).

In particular, the histogram on the left shows the value of the ratio between the measured concentration and the corresponding CSC. Values below unity indicate concentrations below the SCCs, while values above unity indicate that they have been exceeded, mainly for Zn and Cd and, to a lesser extent, Sb and As. The Zn concentration is highest for the samples taken at elevations 3 and 9m. The water table was measured at a depth of 13m from pc.

The histogram on the right in the figure indicates the numerical value in mg/kg of the highest concentrations (in absolute) detected, which are those concerning the three analytes Total Iron, Zinc and Lead.

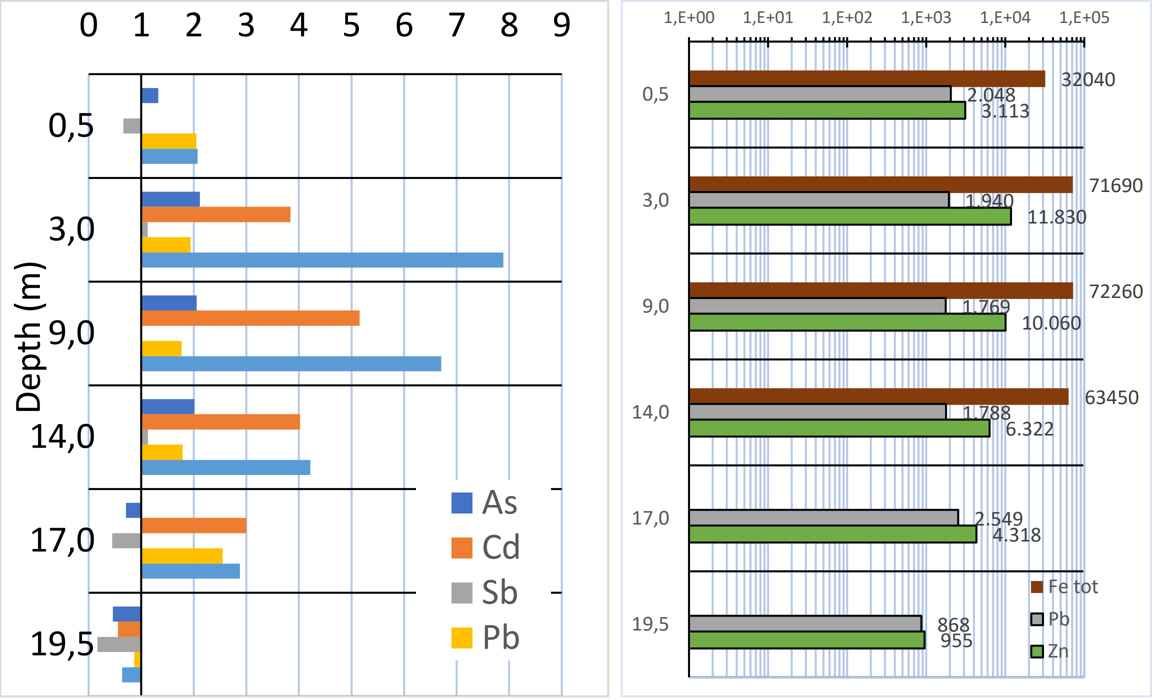


Figure 5.2 Geochemical data from survey SDBF_07; CSC exceedances and Fe tot, Zn and Pb values in mg/kg.

5.2 Samples characterization

25 kg of sample SDBF_07 were taken and quartered twice in order to obtain a representative sample until a sample of 6.7 kg was obtained. On the sample taken (with ID from the same survey), defined as Tal Quale, the following characterisation analyses were preliminarily carried out.

Table 5.1 Weight of the relevant particle size fractions of SDBF_7 mine residues.

GRAIN SIZE CLASS		RETAINED			PASSING
(mm)		(g)	(%)	accumulated (%)	accumulated (%)
	0.700	0.00	0	0	100.00
0.700	0.500	368.77	9.95	9.95	90.05
0.500	0.420	255.00	6.88	16.83	83.17
0.420	0.355	359.27	9.69	26.52	73.48
0.355	0.300	369.27	9.96	36.48	63.52
0.300	0.250	478.90	12.92	49.40	50.60
0.250	0.150	915.41	24.70	74.10	25.90
0.150	0.075	611.92	16.51	90.61	9.39
		348.09	9.39	100	0.00
TOT		3706.63			

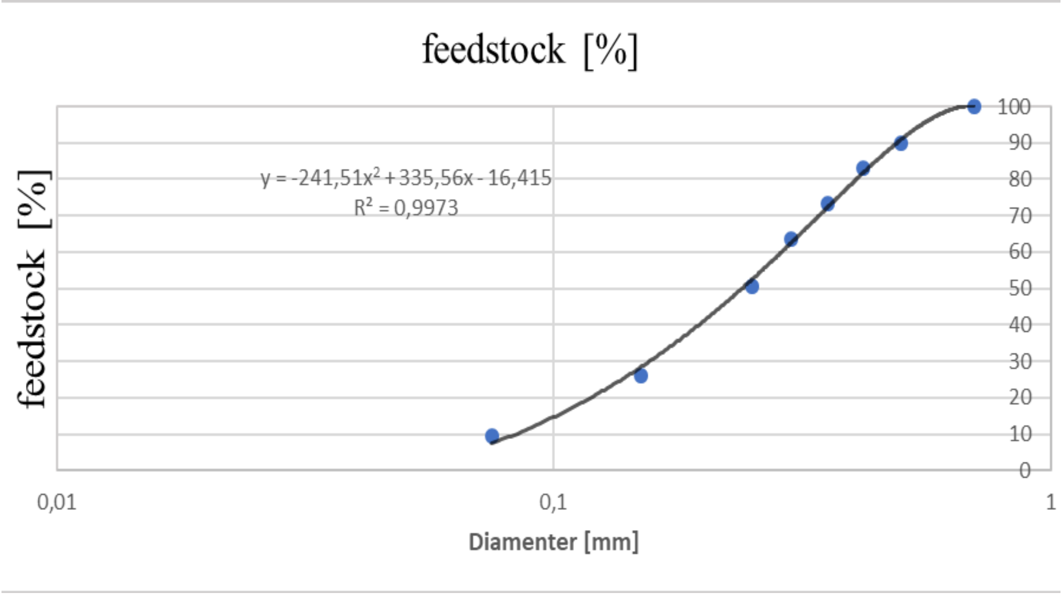


Figure 5.3 Particle size distribution curve of SDBF_07.

The particle size composition is reported in the table 5.1; the concentration of the major compounds is reported in the table 5.2; the concentration of the minor compounds distinguished by particle size class is reported in the table 5.3 and separate diffractograms for the four-particle size classes +250μm; -250μm +150μm; -150μm -+75μm and -75μm (see figure 5.4). The histogram in Figure 5.5 shows the distribution of the metallic units of Zn (equal to 69.76g) and Pb (equal to 3.63g) calculated on a sample of 3706g and distinguished for the eight particle size classes considered.

The following considerations can be made on the data reported:

- The particle size class with the highest weight (24.70%) is the one between 250μm and 150 μm; fines below 75μm represent approximately 10% of the total.

Table 5.2 Analysis of the main

Major	W%	Major	W%
Al_2O_3	5.47	K_2O	1.38
Fe_2O_3	10.72	Na_2O	0.14
MnO	0.50	TiO_2	0.24
MgO	0.56	P_2O_5	0.07
CaO	0.72	SiO_2	74.15
		LOI	5.03
TOTAL			98.97

Table 5.3 – Analysis of minors (mg/kg) by particle size class.

Class µm		**Sb**	**As**	**Ag**	**Cd**	**Fe**	**Pb**	**Cu**	**Zn**	**Weight (g)**
> 500		<10	51	1,3	78	33,551	767	70	9,674	369
500-420		<10	65	1,3	63	27,381	450	67	7,781	255
420-355		<10	57	1,6	78	35,701	556	71	9,652	359
355-300		<10	63	2,6	96	44,575	701	65	12,601	369
300-250		<10	57	3,4	155	66,809	823	171	18,549	479
250-150		<10	72	5,0	140	92,242	1010	116	25,821	915
150-75		<10	148	7,4	155	109,807	1245	195	24,767	612
< 75		<10	235	7,0	177	102,397	1981	208	24,190	348
Total weights (g)										3,707
Tal Quale		<10	93	4,1	126	72,279	978	127	18,822	3,706
CSC	**Column A**	10	20		2		100	120	150	
	Column B	30	50		15		1000	600	1500	

PN: values in red indicate that the reference CSC has been exceeded.

- The D80 of Tal Quale is 0.41 mm.
- CSC exceedances were recorded for the analytes Zn, Cd and As, on all particle size classes, for Pb on the classes below 250 µm.
- The highest concentrations in terms of metal units for Pb and Zn were recorded in the -250 µm - +150 µm class.
- The weighted average concentrations on the Tal Quale sample were: 1.88% in Zn and 0.07% in Pb (corresponding CSCs: 0.15% for Zn and 0.10% for Pb).
- The diffractograms show the presence of Quartz, Siderite, Muscovite, Gypsum, Goethite and Sphalerite in different proportions in the four particle size fractions into which the Tal Quale sample was divided (see Figures 5.4 and 5.5). In particular, the presence of sphalerite is highest in the >250µm class and progressively decreases; Goethite (Fe hydroxide with small amounts of Mn, $Fe + 3O(OH)$) is present in the <75µm class (in agreement with the data in Table 5.3). The distribution of sphalerite shown by the XRD analysis, in apparent contrast to that shown by the analysis of Zn (see Table 5.3), is justified by the fact that in the fractions >250µm Zn is present as sulphide (sphalerite), in the fractions <250µm as oxides and carbonates. This observation was taken into account in the

development of the Experimental Plan (assuming differentiated treatment of the two fractions).

- The results of the mineralogical analysis are in agreement with literature data [78] on the mineralisation present in the Montevecchio seams, among which Zn sulphide prevails over Pb sulphide and there are smaller proportions of oxidised forms of Zn and Pb (calamine or hemimorphite, $Zn_4[(OH)_2Si_2O_7]...H_2O$; PbO) and carbonate (smithsonite, $ZnCO_3$; Cerussite $PbCO_3$). Secondary oxidation forms (galena oxidation is faster than blende oxidation) are also present among the Mudstone Basin components, but they have not yet been highlighted in the study.

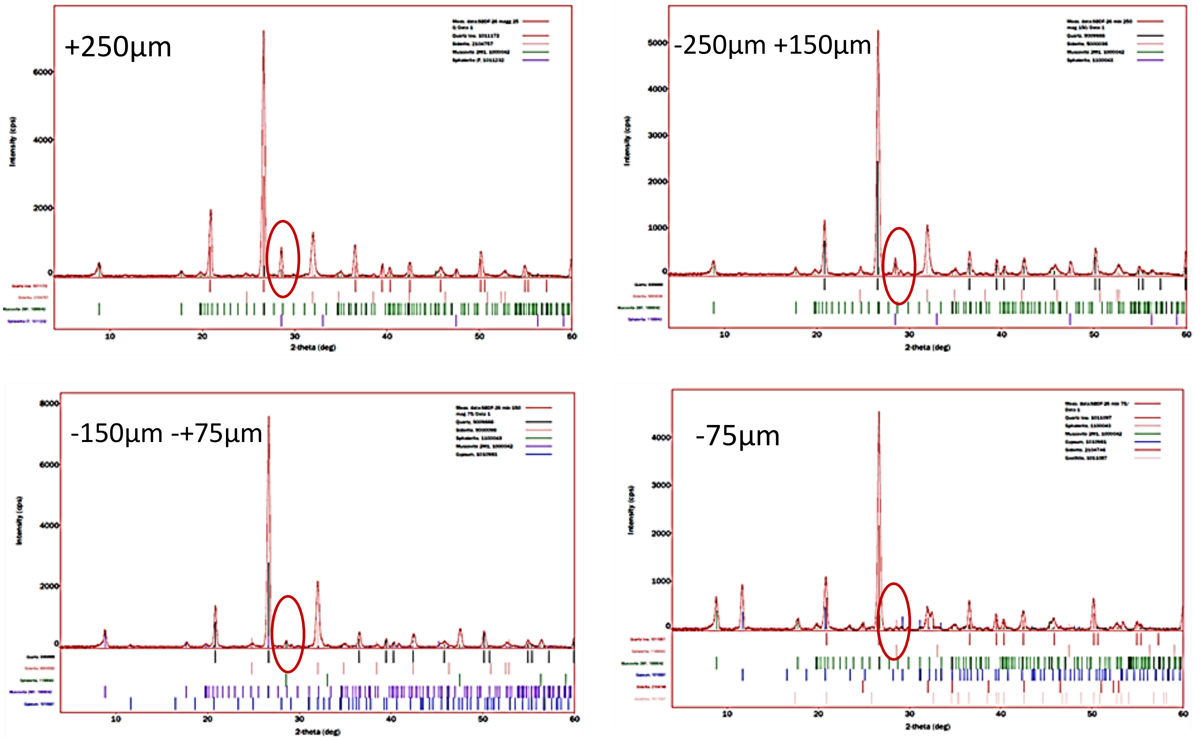


Figure 5.4 Sphalerite peaks in XRDs of the 4 particle size classes

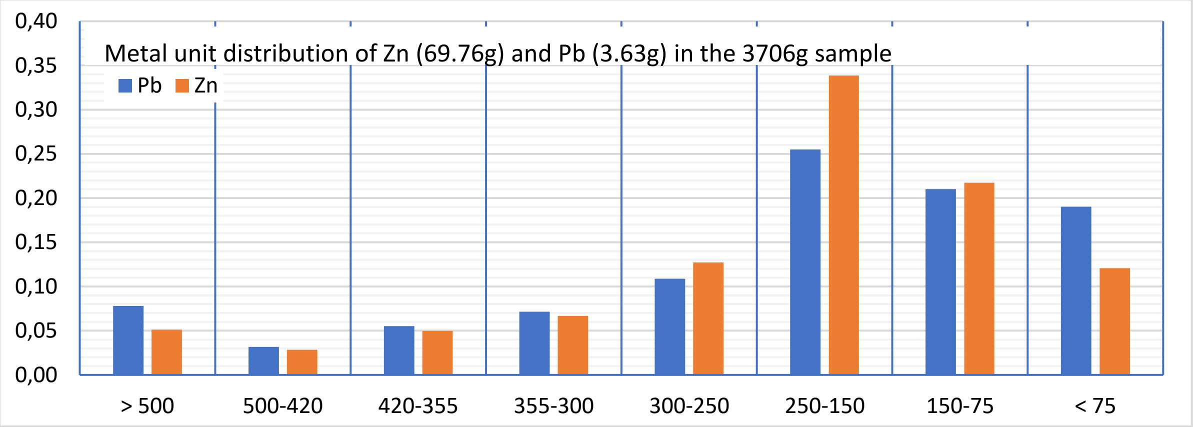


Figure 5.5 Distribution of Metal Units in different particle size classes

5.3 Flotation procedure

5.3.1 Equipment

The material undergoes a preliminary grinding stage using a rod mill, in order to increase the degree of liberation by exposing ore surfaces that have not been altered by oxidation processes. The mill is fed with a high circulating charge, for a grinding time of only 2 minutes, in order to reduce the production of very fine particles that constitute an obstacle in the oxide flotation. The comminution is followed by a screening operation through a mechanical vibrating screen Rotap Stein et Roubaix, characterised by a high vibration frequency (700 to 3500 rpm).

Air is supplied under pressure and the level of slurry is controlled by a weir. Sphalerite (ZnS) flotation is carried out using anionic collectors, in particular xanthate collectors, preceded by activation by Cu^{++} ions [82] [83]. The combination of the results obtained from the mineralogical and chemical analyses carried out on the individual granulometric slices suggests the presence of oxidised zinc minerals, for which the literature indicates flotation using amines as the most effective recovery method [84], preceded by activation using sodium sulphide [85]. The roughing and scavenging phases of the various tests were carried out for 4 minutes each, both in the sulphide ore treatment circuit and in the oxide ore circuit.

All flotation products were subjected to an acid digestion process using a microwave mineraliser. The digestion method was chosen from those proposed by the Environmental

Protection Agency (US-EPA 3052), so as to bring the metals into solution and allow the concentrations in the liquid phase to be read off using ICP/OES (PerkinElmer 7000 Optima).

5.3.2 Reagents employed

The following table lists the reagents used, distinguishing between products, concentrations, a section of plant, the function performed and identification code of the tests performed.

Table 5.4 Overview of reagents used

Products	**Concentration**	**Plant Sections**	**Roles**	**Test ID**	
$CuSO_4$	400 g/t	Sulphides Rougher, Scavenger and Cleaner	Sphalerite Activator	All	-
Na Isopropil xanthate	100 g/t		Sphalerite Collector	All	-
Dowfroth 1015	100 g/t		Frother	All	-
Na_2SiO_3	2000 g/t	Oxides Rougher (primary and secondary), and Cleaner	Gangue Depressant	All	-
Na_2S	4000 g/t		Oxides Zn Activator and pH controller	All	-
Amine MFA-15	100 – 200 g/t		Oxides Zn Collector	-	All except A – D – B2
Na Isopropil xanthate	20 - 45 g/t		Oxides Zn Collector	-	E – F – G – H1 – H2 – H3 – H4 - α
Flotigam SA	100 – 300 g/t		Oxides Zn Collector	-	A – D - B2
Oleina	20 – 250 g/t	Oxides Scavenger	Oxides Collector	-	7 – H3 – H4 - α
Flotinor SM15	20 - 200 g/t			-	7 – C – F – G – H3 – H4 - αβ

In all the tests carried out, the roughing, cleaning and scavenger phases of the sulphide circuit were performed using the same reagents; differences were introduced in the oxide circuit, particularly in the repeated scavenging phases (Re-scavenger).

5.4 Experimental plan

The study involved more than 150 flotation tests and the reconstruction of approximately 25 plant flowsheets. The concentrations of 10 analytes were determined on each sample taken. I personally performed all the tests with the help of the flotation laboratory team. The tests were conducted at the DICAAR (Faculty of Engineering of Cagliari) laboratories, and are part of the research programmes funded through the CESA Project (Sulcis Plan).

The experimental plan is summarised in Tables 5.5, 5.6 and 5.7, the rows of which group together the operations comprising each flowsheet reconstructed from the laboratory batch tests. A total of 36 groups of tests were carried out, divided into two series, of which the first (Table 5.5) comprises 22 the second 10 (see Table 5.6) and the third 4. The two series differ because the first refer to flowsheets that do not include product recirculation; on the other hand, those in Table 5.7 include in the oxidised circuit the recirculation (according to different possibilities) of the float obtained after roughing. See the schematic example of recirculation in Figure 5.6.

The two tables are structured identically and show the 5 possible treatment process steps: (i) size differentiation (or grain size cut); (ii) grinding; (iii) sulphide flotation; (iv) de-sliming; (v) oxide flotation. In detail: the particle size cuts (if any) and grinding were referred to the 250µm, 150µm and 75µm sizes. The two flotation sections contain the classic stages of roughing (*Rougher*), depletion (*Scavenger*) and cleaning (*Cleaner*), each consisting of a variable number of flotations.

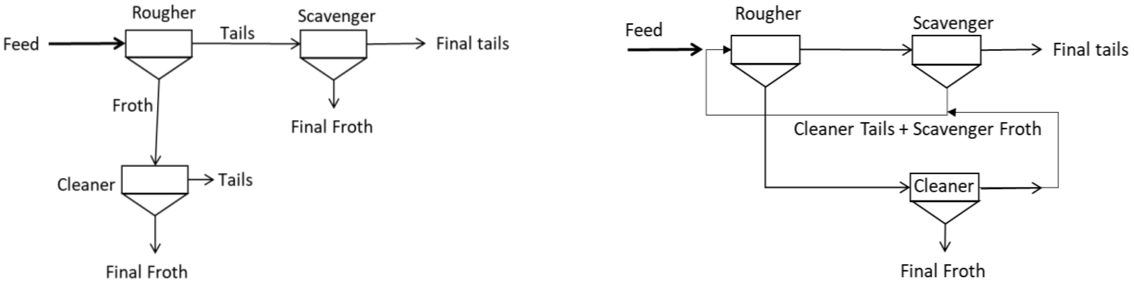


Figure 5.6 Flotation schemes without (left) and with recirculation (right)

Table 5.5 Experimental plan for batch tests without recirculation floating

ID_TEST	Grain size cutting						Grinding			Sulphide flotation						De-sliming		Oxidised flotation									
	Tal Quale	Tal Quale >75µm	250µm		150µm		250µm	150µm	75µm	Roughing	Scavenger	Floating Cleaner				Sieving 20µm	Cyclone d50=3µm	Roughing			Recirculation concentrate	Scavenger of refusal			Floating Relief		
			>250µm	<250µm	>150µm	>150µm						1	2	3	4			1	2	3		1	2	3	1	2	3
1	▨						▨			▨	▨																
2	▨						▨			▨	▨					▨		▨									
B2	▨						▨			▨	▨					▨	▨	▨				▨					
3			▨					▨		▨	▨					▨		▨									
4				▨				▨		▨	▨					▨		▨									
5a					▨				▨	▨	▨					▨		▨									
6a						▨			▨	▨	▨					▨		▨									
5b					▨				▨	▨	▨					▨	▨	▨				▨					
6b						▨			▨	▨	▨					▨	▨	▨				▨					
7			▨					▨		▨	▨					▨	▨	▨				▨	▨				
4				▨				▨		▨	▨					▨		▨									
A	▨							▨		▨	▨	▨	▨	▨		▨	▨	▨				▨					
B	▨							▨		▨	▨	▨	▨	▨		▨	▨	▨				▨					
C	▨							▨		▨	▨	▨	▨	▨		▨	▨	▨				▨			▨		
D	▨							▨		▨	▨	▨	▨	▨		▨	▨	▨				▨	▨	▨			
E1	▨							▨		▨	▨	▨	▨	▨		▨	▨	▨				▨	▨	▨	▨	▨	
E2	▨							▨		▨	▨	▨	▨	▨		▨	▨	▨				▨	▨	▨	▨	▨	
F					▨			▨		▨	▨					▨	▨	▨	▨			▨	▨				
G						▨			▨	▨	▨					▨	▨	▨	▨			▨					
H1		▨						▨		▨	▨	▨	▨			▨	▨	▨	▨			▨	▨		▨	▨	▨
H2		▨						▨		▨	▨	▨	▨			▨	▨	▨	▨			▨	▨		▨	▨	▨
H3		▨						▨		▨	▨	▨	▨			▨	▨	▨				▨			▨	▨	▨
H4		▨						▨		▨	▨	▨	▨			▨	▨	▨				▨			▨	▨	▨

De-sliming is provided in two parts: for sieving at 20µm and cycloning with d50=3µm. The column Recirculation concentrate, present in both Tables, has been filled in Table 5.6 only. In all cases where a particle size cut has occurred (at 250µm or 150µm) the Tables include (in succession) the cycle undergone by the two fractions; see the cases of tests ID=3 and 4, ID=5a and 6a; ID=5b and 6b, ID=F and G.

Table 5.6 Experimental plan of tests carried out with recirculation in the Oxidised Section

ID_TEST	Granulometric cut						Grinding			Sulphide flotation						De-sliming		Oxidised flotation									
	Tal Quale	Tal Quale >75µm	250µm		150µm		250µm	150µm	75µm	Roughing	Scavenger	Floating Cleaner				Screening 20µm	Cyclone d50=3µm	roughing			Recirculation concentrate	Rejection scavenger			Floating Relief		
			>250µm	<250µm	>150µm	>150µm						1	2	3	4			1	2	3		1	2	3	1	2	3
α_1	▨							▨		▨	▨	▨	▨	▨	▨	▨	▨										
α_2	▨							▨		▨	▨	▨	▨	▨	▨	▨	▨										
α_3	▨							▨		▨	▨	▨	▨	▨	▨	▨	▨										
α_4	▨							▨		▨	▨	▨	▨	▨		▨	▨										
α_5	▨							▨		▨	▨	▨	▨	▨		▨	▨										
β_1																		▨	▨	▨							
β_2																		▨	▨	▨	▨	▨					
β_3																		▨	▨	▨	▨	▨					
β_4																		▨	▨	▨	▨	▨					
β_5																		▨	▨	▨	▨	▨			▨	▨	▨

Table 5.7 Experimental plan of tests carried out with several Scavenger tests in the Oxidised Section.

ID_TEST	Grain size cutting						Grinding			Sulphide flotation						De-sliming		Oxidised flotation								
	Tal Quale	Tal Quale >75µm	250µm		150µm		250µm	150µm	75µm	Roughing	Scavenger	Floating Cleaner				Screening 20µm	Cyclone d50=3µm	roughing			Rejection scavenger					
			>250µm	<250µm	>150µm	>150µm						1	2	3	4			1	2	3	1	2	3	4	5	6
γ	▨							▨		▨	▨					▨	▨	▨			▨	▨	▨	▨	▨	▨
δ	▨							▨		▨	▨					▨	▨	▨			▨	▨	▨	▨	▨	▨
Ω	▨							▨		▨	▨					▨	▨	▨			▨	▨				
Ω_1	▨							▨		▨	▨					▨	▨	▨			▨	▨	▨	▨		

In all cases where cleaner was carried out, whether sulphide or oxide, the products obtained from the 2 or 4 previous depletions were joined to obtain a sufficient mass of solid (see groups A, B, C, D; or H1, H2, H3, H4). The union of 2 or 4 products can be read in the table because the corresponding boxes are vertically joined.

5.5 Research objectives

Given the composition of the sample under study, the possible routes to the Final Waste may vary for countless reasons, such as the application of a preliminary particle size cut (none or according to 3 sizes), a grinding (with 3 possible output sizes), a de-sliming (with 2 output settings); the application of several roughing, scavenging and cleaning stages applicable in the sulphide and oxide circuits, within which to evaluate the use of different reagents in terms of type and dosage. To cover such a vast experimental plan, it was decided to isolate individual problems by proposing partial flowsheets and transferring the individual results to a hypothesis of a complete synthesis process.

In summary, the research aimed to answer the following questions:

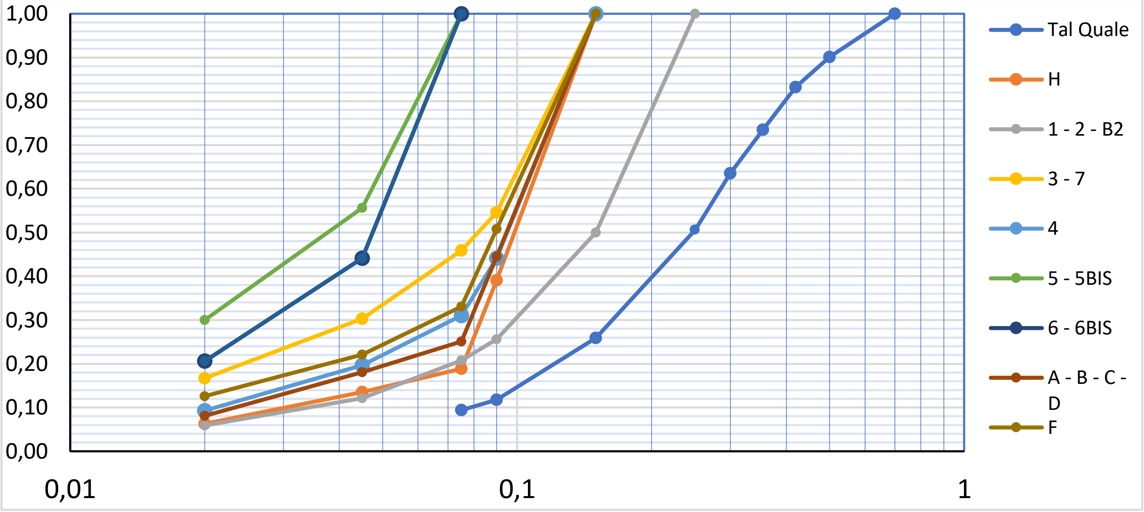
- Possibility of obtaining a final waste in which the concentrations of the analytes (in order of decreasing concentrations) Zn, Pb, As, Cd and Sb are lower than the CSC industrial sites.
- Possibility of obtaining a sulphide concentrate with 50% Zn (usual blende contents in Waelz metallurgical plants) and determine the number of Cleaner required.
- Need for de-sliming before oxide flotation;
- Benefits achievable from separate circuits by particle size.
- Benefits of alternative grindings at 250µm, 150µm or 75µm; i.e. determining the optimum d80.
- Possibility of obtaining an oxidised concentrate with marketable concentrations.
- Selection and dosing of reagents in the oxidate section

5.6 Grain size cuts and grinding

For 9 test groups, the feeds were subjected to size separation (at 250µm or 150µm) in order to check whether the differentiation in metal units between the coarser and finer fractions could be exploited to the full.

Table 5.8 Particle size analysis of Tal Which and after grinding (size in µm).

Particle size composition of feeds after size cutting and grinding												
Grain size cutting	Tal Quale	Tal Quale +75 µm	+250 µm	-250 µm	+250 µm	-250 µm	+150 µm	-150 µm	+150 µm	-150 µm	+150 µm	-150 µm
Grinding	----	-150 µm	-250 µm		-150 µm	-150 µm	-75 µm	-75 µm	-150 µm		-150 µm	-75 µm
Size (mm)	Cumulative weights of through fractions											
0.70	1.0											
0.50	0.9											
0.42	0.8											
0.36	0.7											
0.30	0.6											
0.25	0.5		1.00									
0.15	0.3	1.00	0.50		1	1			1		1	
0.09	0.1	0.39	0.26		0.546	0.441			0.445		0.508	
0.08	0.1	0.19	0.21		0.459	0.31	1	1	0.251		0.331	1
0.05		0.14	0.12		0.303	0.197	0.556	0.441	0.181		0.221	0.441
0.02		0.06	0.06		0.167	0.093	0.3	0.206	0.081		0.126	0.206
D80 (mm)	0.41	0.13	0.21		0.13	0.13	0.06	0.07	0.13		0.13	0.07
Test ID	-	H1, H2, H3, H4	1 - 2 - B2		3 - 7	4	5a – 5b	6a – 6b	A - B - C – D e E1, E2, α1,		F	G



In addition, all feeds (with or without particle size cut-off) were ground to one of three reference sizes 250µm, 150µm or 75µm. Finally, all feeds were subjected to particle size analysis. The results obtained, which represent the preparation phases of the feeds in each group of tests, are collected in Table 14 and referred to the size compositions (11 classes). Each column corresponds to a particle size cut, a milling and a particle size composition. The last two rows of the table show for each column the D80 values and the identification code of the tests performed.

An example of reading of Table 18 is as follows: for the group of tests ID=Hi, a sample obtained by eliminating the <75µm fraction from Tal Quale, grounded at 150 µm, whose particle size composition gives a D80=0.13mm.

5.7 Results

The results obtained are briefly discussed for each experimental objective.

5.7.1 Concentrations in final waste

The possibility of obtaining a final waste compliant with the heavy metal CSCs was addressed by performing the following 11 groups of tests: E1, E2, H1, H2, αβ, C, F, G, B, ϒ and δ. The final results obtained are represented in the histograms in Figure 7 in terms of Zn concentrations and metal units (g) in the final waste.

Figure 5.7 Histograms of Zn concentrations and metal units in final waste for 11 test groups

In the histogram of the yields, the intersection of the axes is placed at Zn= 0.15 to discriminate, also visually, in which cases the expected result (under the CSCs) has been obtained. Examination of the histograms reveals the following:

- The strongest reduction, both in terms of Zn concentration and metal units, occurs in sulphide and oxide roughing;
- The attainment of the CSC limit is conditioned by the way in which the Scavenger flotation takes place (reagent dosage) rather than by the effect of the reiteration of the process (for the same total of reagents used).

- Scavenger flotation in the sulphide circuit results in negligible effects (the flotation efficiency rarely exceeds 10%); whereas, de-sliming significantly reduces the concentration and metal units of Zn in the underflow.

Values ≤0.15 % Zn are reached by test groups H2, C and B after Scavenger I flotation; group F after Scavenger III flotation; the other 7 groups reach the following values in correspondence to the number of Scavenger flotations indicated as follows: αβ 0.16% Scavenger I, H1 0.19% Scavenger III, E1 0.18% Scavenger II, E1 0.17% Scavenger I, G 0.16% Scavenger I, γ and δ 0.17% Scavenger VI. The results obtained in these seven groups indicate the need for further flotation (increase in number) or/and increased concentrations of reagents (amine), also from Scavenger I flotation.

5.7.2 Grain size cutting effects and grinding

The analysis is carried out by comparing all the 22 groups of tests carried out and using as a parameter of judgement the overall efficiency (or inefficiency) of the two flotations roughing and scavenging of the sulphide circuit.

Table 5.9 Calculated sulphide circuit inefficiencies between Feeding and Roughing+Scavenging

ID	Cutting size	Grinding size	ηZn	ID	Cutting size	Grinding size	ηZn
1	TQ	250	0.406	3	+250	150	0.354
2	TQ	250	0.373	4	-250	150	0.388
B2	TQ	250	0.349	3 - 4			0.377
Aβ	TQ	150	0.381	7	+250	150	0.363
ϒ	TQ	150	0.376	4	-250	150	0.388
Δ	TQ	150	0.343	7 - 4			0.380
E1	TQ	150	0.330	**F**	**+150**	**150**	**0.267**
E2	TQ	150	0.337	G	-150	75	0.484
E1+E2	TQ	150	0.333	F+G			0.389
A	TQ	150	0.341	**5a**	**+150**	**75**	**0.236**
B	TQ	150	0.347	6a	-150	75	0.488
C	TQ	150	0.327	5a - 6a			0.315
D	**TQ**	**150**	**0.295**	**5b**	**+150**	**75**	**0.223**
H1	+75	150	0.342	6b	-150	75	0.448
H2	+75	150	0.344	**5b - 6b**			**0.295**

The objective is to evaluate the results that can be obtained through the differentiated treatment of two-particle size fractions (in two circuits), combined with the effects of three different choices in the subsequent grinding process [73] [84]. The assessment is carried out by comparing the ratio between the metal units contained in the tail scavenger and those contained in the Feed Rougher of the sulphide circuit. This ratio, indicated by the acronym ηZn and also defined as process inefficiency (obviously between 0 and 1), indicates the proportion of metal units lost, because they go into the waste, and therefore constitutes an element of negative judgement, the stronger the higher its value (close to one). This is true if it is looked at the flotation process as the production of a flotation concentrate, but it retains this meaning also in this case because inefficiency does not impoverish the waste, which is instead the fundamental objective of this work. Therefore, the best of the 23 solutions examined will be the one with the lowest Inefficiency Index (calculated on the two flotations of Roughing and Finishing).

The grain size hypotheses considered were 4: Tal Quale (abbreviation TQ, i.e. no cut) and the cuts at sizes 250, 150 and 75µm; the grinding hypotheses considered were 3: 250, 150 and 75µm. The combinations examined and the results obtained are shown in Table 15.

It should be noted that the lowest values are those (highlighted in bold) relative to tests D and 5b+6b; the others (F, 5a and 5b) highlighted in the Table refer to tests on single particle size classes which are not useful on their own for comparison.

In summary, the examination of the table shows that the best grinding size is that at 150µm and that there is indifference between the solution with a single circuit (test D) and a separate circuit for the two-particle size classes (5b+6b).

5.7.3 Concentrations in the final sulphide floatation

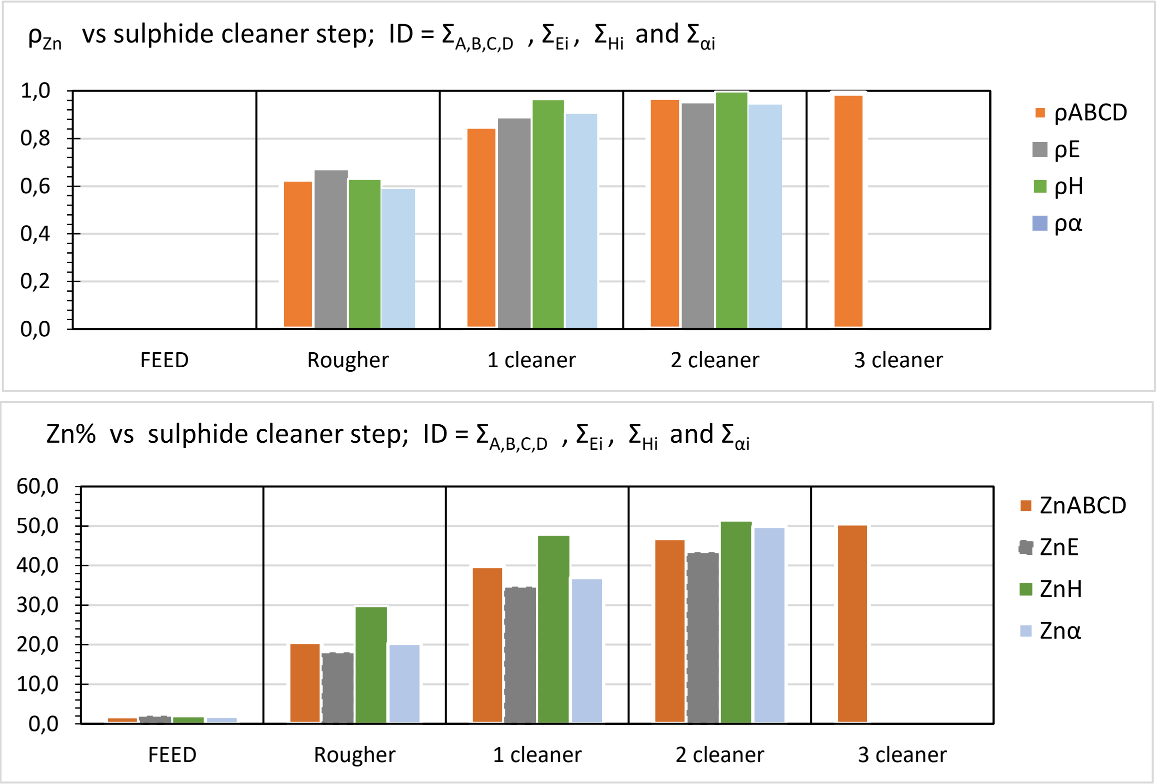


Figure 5.8 Yield and Zinc content in the float after each clean step.

The final Zn-sulphur concentrate is obtained after successive recleaning of the flotation fraction in the roughing phase. The groups of tests reconstructing this part of the flowsheet, see Figure 5.8 , were four and in all of them the material was previously milled at 150µm, however, it was considered that the final Zn-sulphur concentrate is the final flotation concentrate:

- A Tal Quale sample in the three groups identified with ID=(A, B, C, D), ID=Ei and ID=αi.
- The fraction of Tal Quale >75µm (equal to 90% of the total) for the group ID= Hi.

In order to reach the mass necessary to perform the sulphide Cleaner flotation, the fractions obtained from roughing operations performed on 4 samples in (A, B, C, D), Hi and αi, and on 2 samples for Ei, were combined in a single sample.

The results obtained in terms of weight yield ρZn and % Zn content are shown graphically in the two diagrams in Figure 5.9. The following comments can be made:

- Flotation of the sulphides is sufficiently selective to achieve the usual commercial concentrations (about 50% Zn), the elimination of the fraction below 75µm gives a slightly better result than the other cases and with only two Cleaner. Thus, although the target of 50% Zn is always reached (or achievable), the best results (in terms of the rapid increase in content) are obtained by excluding the 75µm fraction.

- Subsequent cleaning is accompanied by increases in yield (which tends to 1.0) and in Zn content which tends to the maximum value (for ρZn =1). In our case Znmax= 51.5%.

- Reiterating the cleaning phase beyond a certain limit, in this case, 3 or 2, brings no benefit either in terms of yield or in terms of useful species content.

5.7.4 Slime separation before oxidized flotation

The literature on oxidised flotation [59] [86] [77] amply justifies the usefulness of this operation, which is applied in our case in all flowsheets. In order to evaluate its effects and decide the size at which to apply the cut, two solutions were compared: screening at 20µm followed or not by cycloning with d50=3µm and re-introduction into the circuit of the 20µm - 3µm fraction. So the two sizes of de-sliming compared were 20µm and 3µm. By de-sliming, a particle size class that hinders flotation and generally has a higher Zn concentration is cut. The fraction that is removed is proportionally higher if the material is ground to smaller sizes (overproduction of fines), in our case the grinding sizes were: 250µm, 150µm or 75µm. The expected effect should be a change in yield in the subsequent oxidised roughing stage.
The tests compared were: B2, Ω, 5b, 2, 3, 4, 5a, 6a.

Table 5.10 Evaluation of the effects of de-sliming prior to oxidised roughing

ID	Grain size Sampling	Grinding	De-sliming	W_{slim}/W_A	ρ_{Zn}	um
B2	Tal Quale	250µm	-3µm	5.0	0.20	0.17
Ω	Tal Quale	150 µm	-3 µm	9.0	0.65	0.21
5b, 6b	>150µm/<150µm	75µm	-3µm	11.0	0.31	0.23
2	Tal Quale	250 µm	-20 µm	8.0	0.51	0.22
3,4	>250µm/<250µm	150µm	-20µm	13.0	0.60	0.29
5a, 6a	>150µm/<150µm	75µm	-20µm	20.0	0.58	0.30

The reagents used and their proportions in relation to slurry were the same in all tests (see Table 5.4).

Tests 3-4, 5a-6a and 5b-6b should be considered as paired, taking into account that the particle size fractions >250µm and >150µm are 49.4% and 74.1% respectively (weighted averages should be applied to the results obtained separately). The analysis was carried out by comparing the flotation yield of the oxidised roughing (ρZn), the percentage by weight (100-Wslim/WA) that the de-sliming subtracts from the roughing feed and the proportion of metal units subtracted from the roughing feed (um). The results are shown in the table and histogram in Figure 18. In terms of yield in the flotation concentrate of the oxidised roughing, the best results were obtained on the sample milled at -150 µm, with ρZn values exceeding 60%, with no particular differences due to the de-sliming cut. The same effect did not occur in the case of milling at -75 µm, for which a higher yield in the flotation concentrate was recorded in the case of de-sliming at 20 µm, confirming the fact that the flotation of oxidised Zn minerals is strongly penalised by the overproduction of fine particles. The comparison of the results obtained between the two samples milled at -250 µm cannot be considered valid because the flotation, in the oxide roughing stage, is vitiated by the use of a different collector (Flotigam S.A.) which proved to be not very effective. As can be seen from the histogram in figure 5.9, the removal of metallic units, evaluated with respect to the incoming feed, is greater in the case of de-sliming at 20 µm and, obviously, the fraction of material that escapes from the treatment circuit increases. The latter is a penalising aspect which should not be overlooked because the greater the portion eliminated, the lower the weight yield of the final waste. The choice of the optimum size cut must be made on the basis of a compromise between the three parameters considered. Referring to tests 3, 4 and Ω, it has therefore been decided not to evaluate negatively the lower removal of metallic units implied by de-sliming at 3 µm but, with the same excellent yields in the float, it has been decided to give more importance to the lower weight yield of the material subtracted from the feed, considering, therefore, the milling of the sample at -150 µm with de-sliming at 3 µm the ideal conditions for the treatment of the material inside the oxidised circuit.

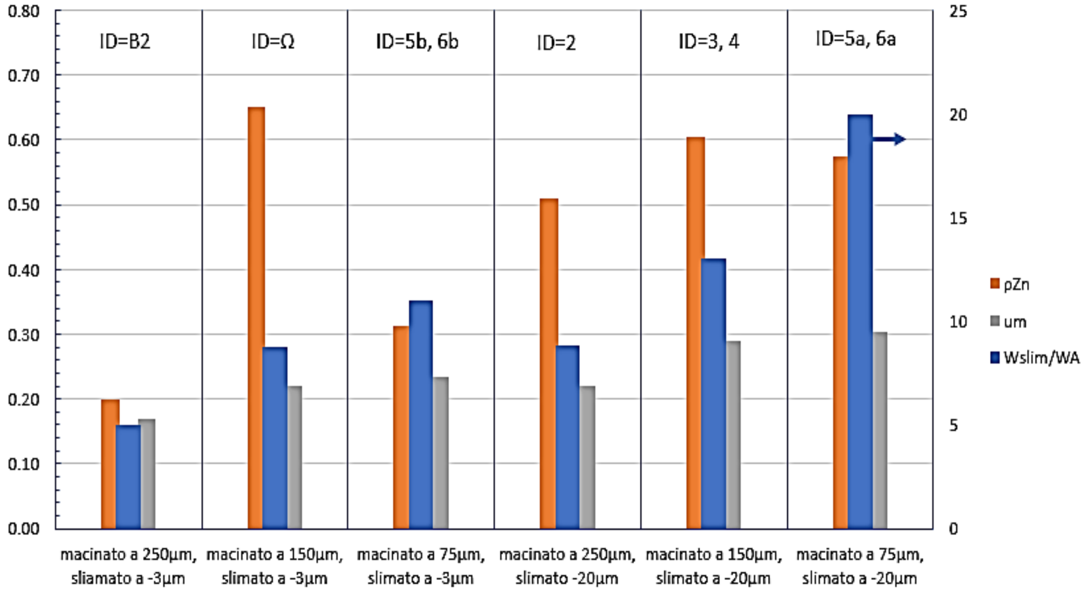


Figure 5.9 Oxidised roughing performance, Wslim/WA and UM subtracted from de-sliming to roughing

5.7.5 Amine dosage and usefulness of flotigam and flotinor reagents

The reagents used and their dosages correspond in all parts of the flowsheet to the usual choices indicated in the technical literature for sphalerite flotation. The only exception is the Roughing and Scavenger of the oxidised circuit. This is because these flotations, in particular, are intended to deplete the waste to a predefined limit and not to recover additional concentrate. This justifies the choice of high dosages and/or repeated flotation.

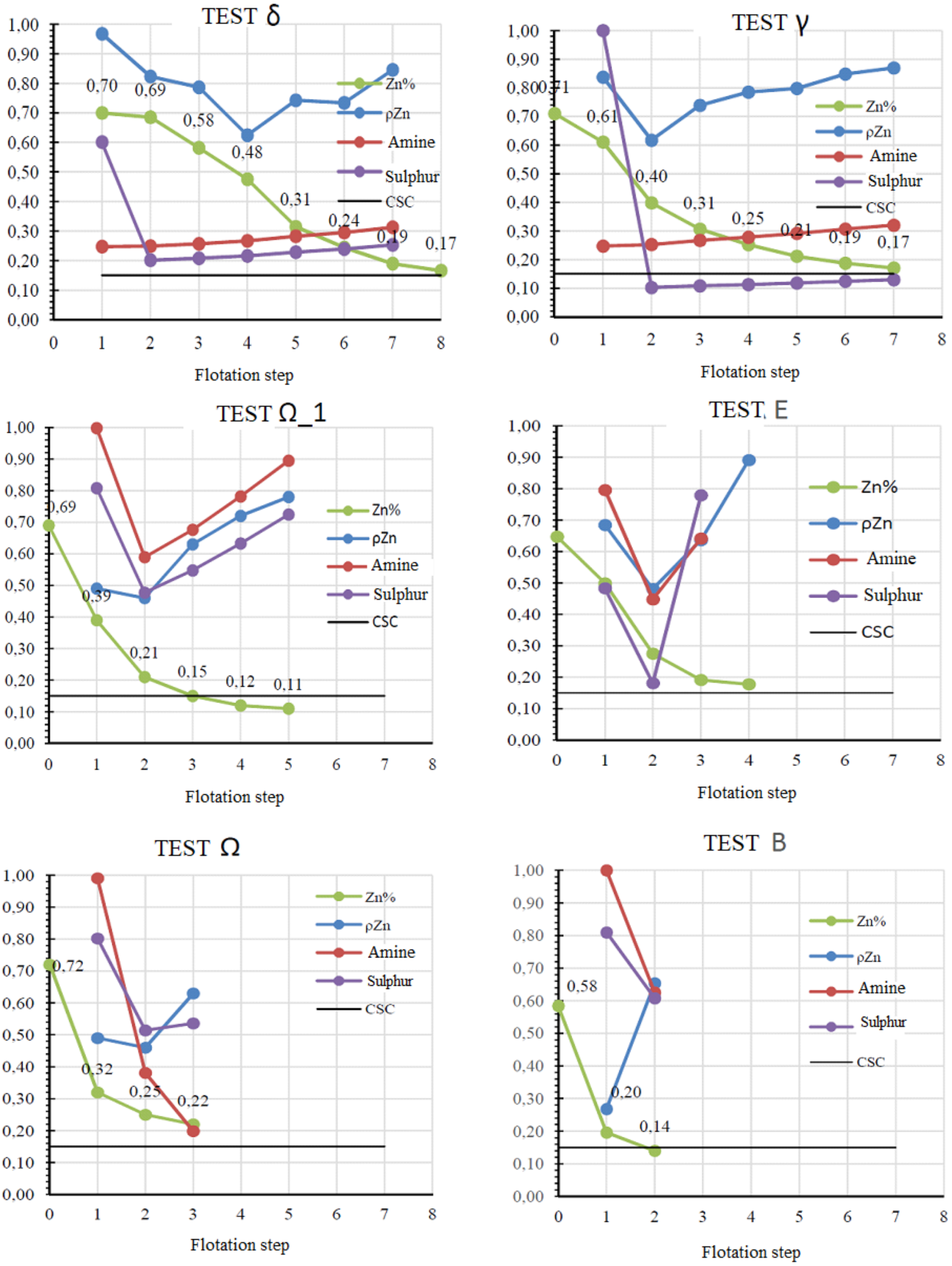


Figure 5.10 Amine dosage in the Ox circuit - The best results are those of tests Ω1 and B

The achievable results were evaluated according to the six tests with ID: δ, ϒ, Ω1, E, B and Ω. Judging elements were: Zn concentration (%) in the Final Waste and Inefficiency (% and equal to the Wtail/WFeed weight ratio). The evaluation is carried out not on the basis of a single final numerical value, but on the evolution of the kinetics expressed in terms of the number of scavenger carried out.

The results obtained are shown in the groups of diagrams that make up the Figure 5.9. The numbers shown in the abscissa indicate the Roughing Flotation (identified by number 1) and the subsequent Scavenger Flotations (indicated by numbers from 2 to 7 in tests δ and ϒ; from 2 to 5 in test Ω1; from 2 to 4 in test E; from 2 to 3 in test Ω; by number 2 alone in test B). The values reported in correspondence to the zero abscissa (tests Ω1 and Ω) indicate the concentration Zn% in the Under after cycloning (the phase that in the flowsheet precedes oxidised roughing).

The amine and sodium sulphide dosages are indicated by the two orange and yellow curves and expressed numerically as a dimensionless ratio between the adopted and the maximum concentration shown in Table 5.11 below. The silicate dosage remained constant and always equal to the maximum value indicated in the table and therefore not shown in the diagrams in Figure 5.9.

Table 5.11 Maximum reference doses used in the oxidised circuit

Reagent Maximum reference dosage (g/t)
Amina 240
Sodium sulphide (Na_2S) 5900
Sodium silicate (Na_2SiO_3) 2400

The diagrams show that:

- In all tests, the kinetics develop towards the CSC value (horizontal black line), which is reached in tests Ω1 and B.
- Dosage changes modify the kinetics: the inefficiency changes the sign of the gradient and the Zn concentration changes concavity.

- The high initial dosage allows a concentration of 0.15% to be achieved even after a single scavenging flotation.
- Repeating the scavenger flotation, even six times, but after low initial amine dosages lengthen the kinetics and make it difficult to reach the CSC.

5.7.6 Time evolution of the plant flowsheet.

In order to pursue the aims of the project, the tests on SDBF_07 have given results that lead to the construction of increasingly complex flowsheets, enriched by granulometric cuts and recirculations in several points of the plant sections. In the following paragraph, the most representative examples chosen from the 32 flowsheets will be indicated.

5.7.6.1 Tests 3 and 4

In these first tests, a variety of reasoning was given, so the variables that condition the structure of the following flowsheets are the best feed grain size option and the grinding size. The two images show the two options used in our sample.

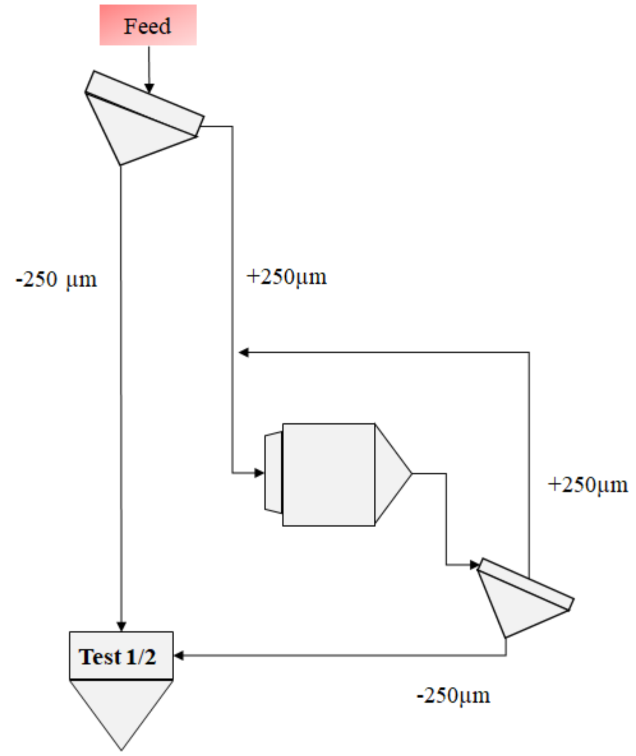


Figure 5.11 Particle size reduction scheme (-250 μm) of the feed Tal Quale to the Flotation procedure.

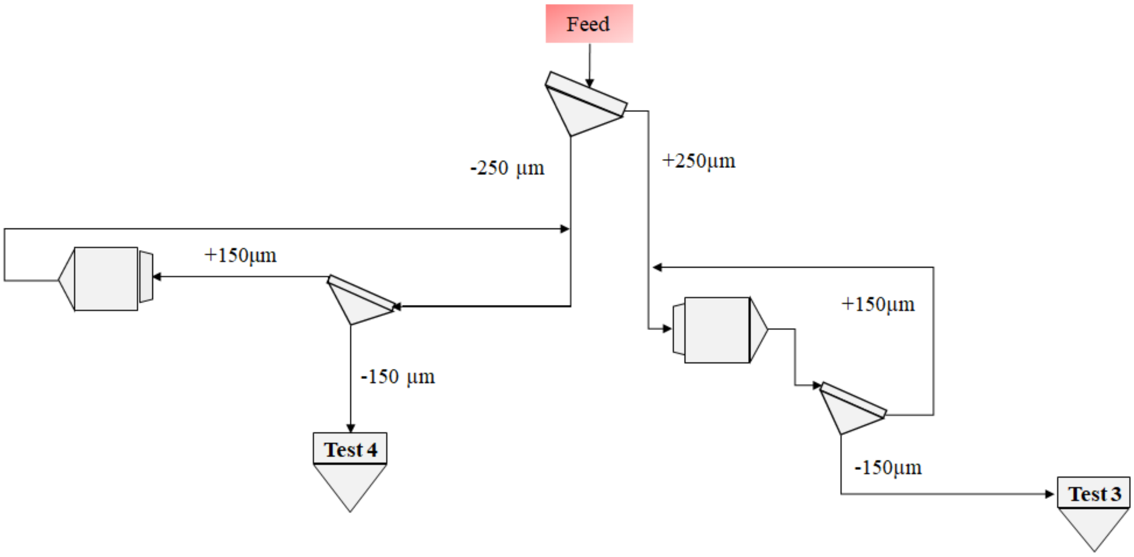
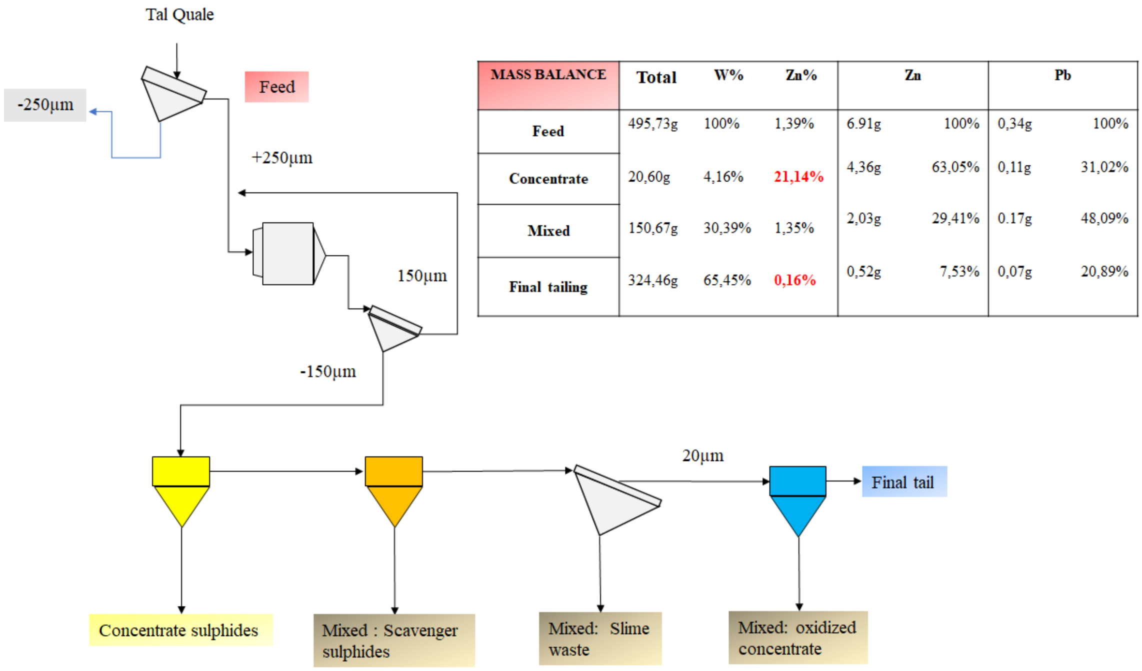


Figure 5.12 Particle size reduction scheme (-150 μm) of the feed Tal Quale to the Flotation procedure

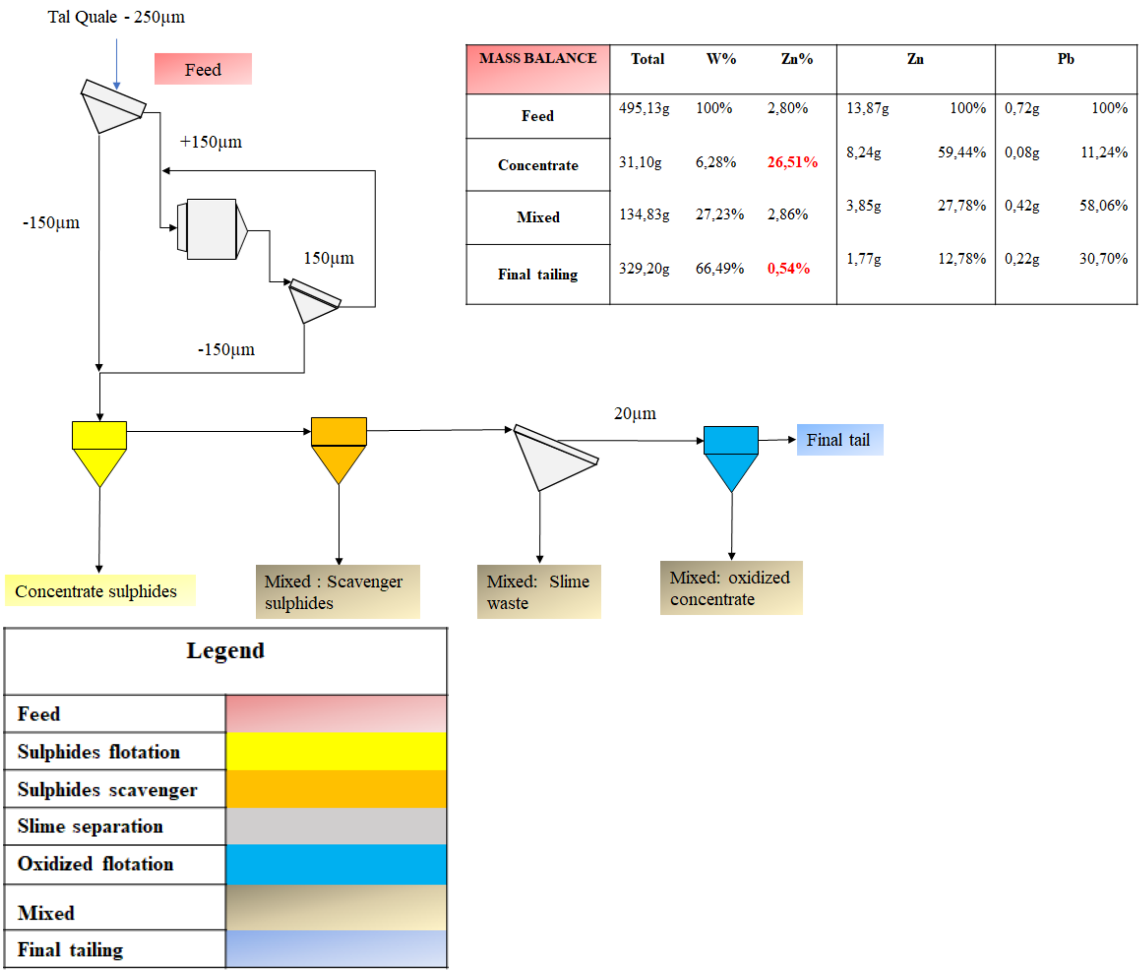
Initially, a simple scheme was used, the steps of which show the typical flotation procedure for Zn sulphide minerals and the procedure for calamine minerals.

The following diagrams represent the procedure used in tests 1, 2, 3 and 4. In tests 3 and 4, the two-particle sizes +250µm and -250µm were processed in two separate circuits. The figure shows the flowsheet for tests three and four.



MASS BALANCE	**Total**	**W%**	**Zn%**	**Zn**		**Pb**	
Feed	495,73g	100%	1,39%	6.91g	100%	0,34g	100%
Concentrate	20,60g	4,16%	**21,14%**	4,36g	63,05%	0,11g	31,02%
Mixed	150,67g	30,39%	1,35%	2,03g	29,41%	0.17g	48,09%
Final tailing	324,46g	65,45%	**0,16%**	0,52g	7,53%	0,07g	20,89%

Figure 5.13 Flowsheet of tests 3. The table shows the mass balance and concentration values for the analytes of interest.



MASS BALANCE	Total	W%	Zn%	Zn		Pb	
Feed	495,13g	100%	2,80%	13,87g	100%	0,72g	100%
Concentrate	31,10g	6,28%	**26,51%**	8,24g	59,44%	0,08g	11,24%
Mixed	134,83g	27,23%	2,86%	3,85g	27,78%	0,42g	58,06%
Final tailing	329,20g	66,49%	**0,54%**	1,77g	12,78%	0,22g	30,70%

Legend	
Feed	🟥
Sulphides flotation	🟨
Sulphides scavenger	🟧
Slime separation	⬜
Oxidized flotation	🟦
Mixed	🟫
Final tailing	🟦

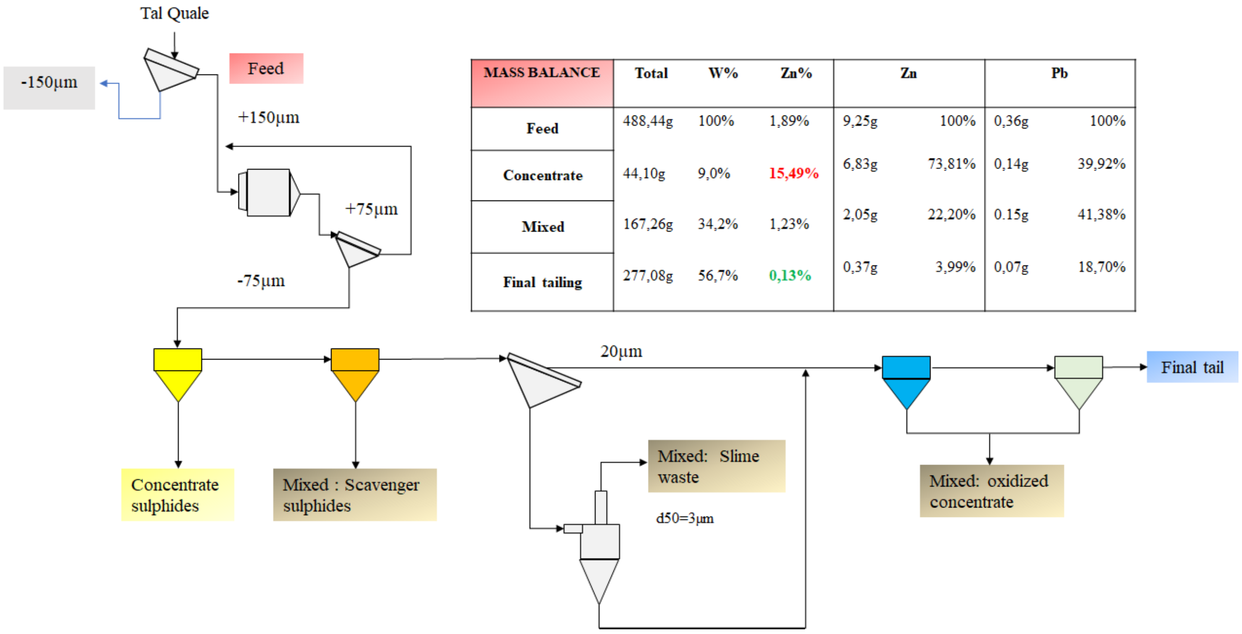
Figure 5.14 Flowsheet of tests 4. The table shows the mass balance and concentration values for the analytes of interest.

These first tests revealed several problems: the heavy metal content in the mixed waste and in the final waste (with the same reagents) is too high, accumulating mainly in only one of the two circuits, the one from the -250µm fraction.

In the following tests, a further reduction of feed particle size +75µm and -75µm was tested.

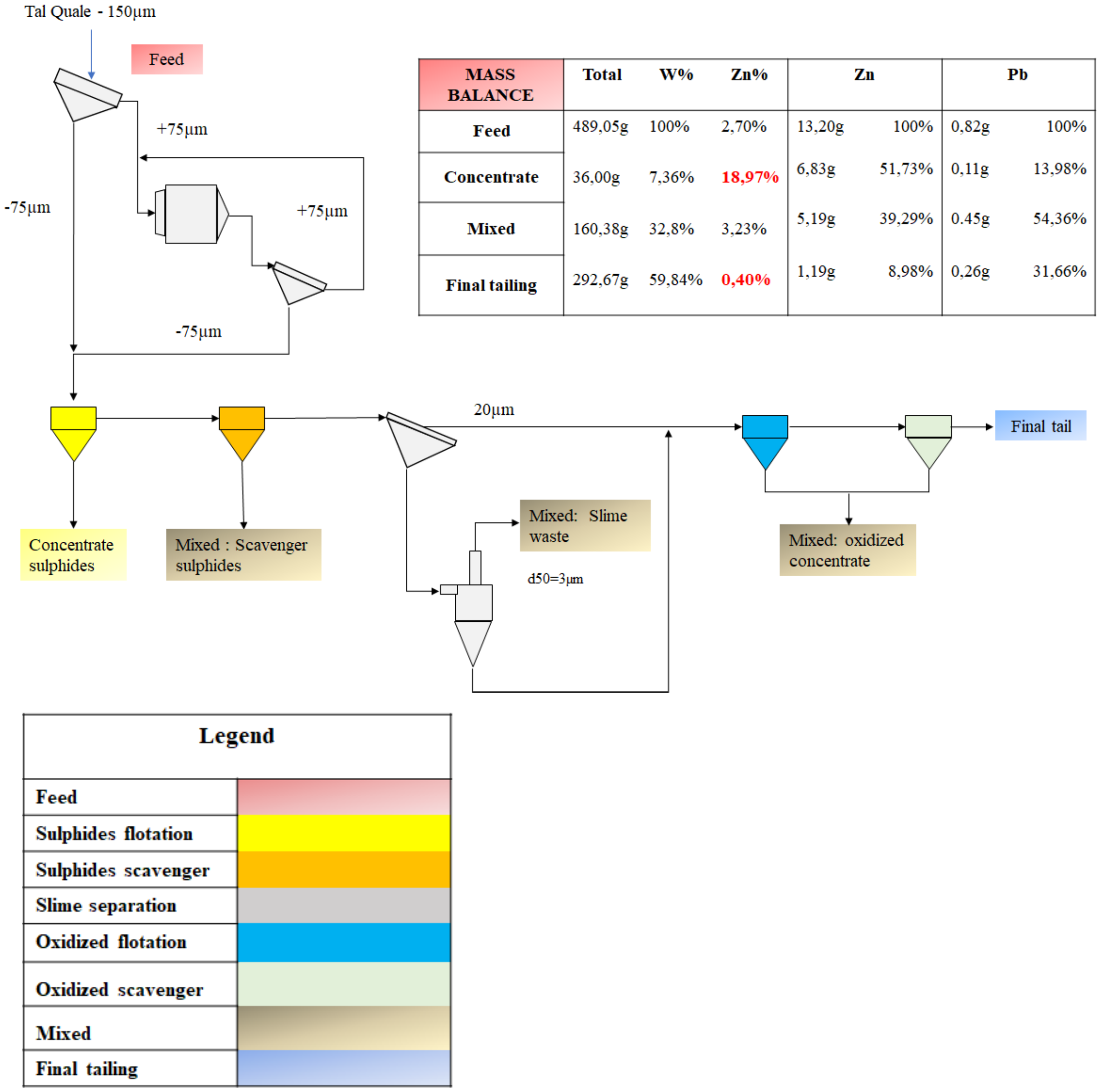
5.7.6.2 *Tests 5 and 6*

In the tests, the two-particle sizes +150µm and -150µm were processed in two separate circuits. In order to overcome the overproduction of fines, a particle size cut was introduced, via hydrocyclone, before flotation of the oxidised minerals; the following mass flow diagrams, representing tests 5 and 6, characterise an example.



MASS BALANCE	Total	W%	Zn%	Zn		Pb	
Feed	488,44g	100%	1,89%	9,25g	100%	0,36g	100%
Concentrate	44,10g	9,0%	15,49%	6,83g	73,81%	0,14g	39,92%
Mixed	167,26g	34,2%	1,23%	2,05g	22,20%	0.15g	41,38%
Final tailing	277,08g	56,7%	0,13%	0,37g	3,99%	0,07g	18,70%

Figure 5.15 Flowsheet of tests 5. The table shows the mass balance and concentration values for the analytes of interest.



MASS BALANCE	Total	W%	Zn%	Zn		Pb	
Feed	489,05g	100%	2,70%	13,20g	100%	0,82g	100%
Concentrate	36,00g	7,36%	18,97%	6,83g	51,73%	0,11g	13,98%
Mixed	160,38g	32,8%	3,23%	5,19g	39,29%	0.45g	54,36%
Final tailing	292,67g	59,84%	0,40%	1,19g	8,98%	0,26g	31,66%

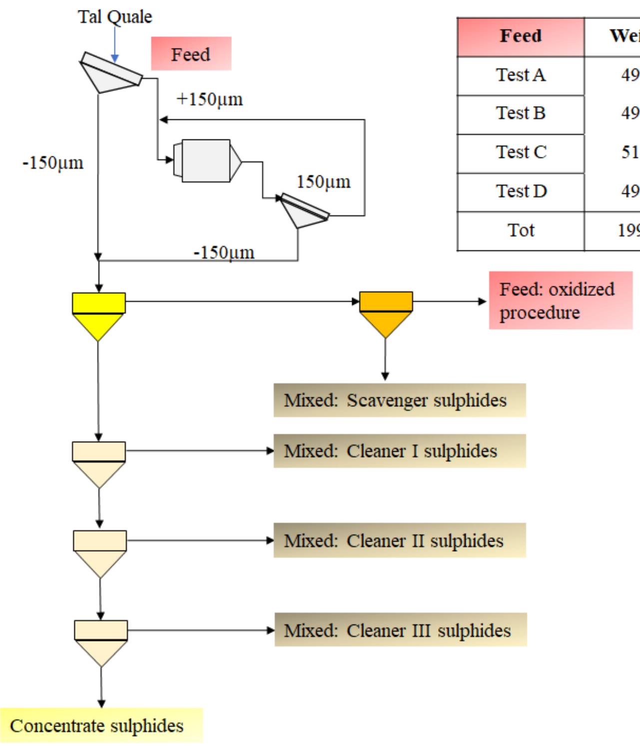
Legend	
Feed	🟥
Sulphides flotation	🟨
Sulphides scavenger	🟧
Slime separation	⬜
Oxidized flotation	🟦
Oxidized scavenger	🟩
Mixed	🟫
Final tailing	🟦

Figure 5.16 Flowsheet of tests 6. The table shows the mass balance and concentration values for the analytes of interest.

Again, the use of two separate particle size circuits makes it difficult to manage one of them, in fact, a Zn content below the legal limits is only achieved in the balance coming from the +150µm. It is also observed that the content of Zn sulphide concentrate is not satisfactory. It was therefore decided to include a test in which three steps of cleaning were carried out in the section of the sulphide circuit in order to increase the content in the float, and not to separate the feed by particle size cut, thus trying not to hinder the procedure with the overproduction of fines. To be able to carry out the cleaning of the sulphide concentrate, sufficient mass of the feed was required, which is why the sulphide concentrates from four related tests were mixed.

5.7.6.3 Tests ABCD

The next tests are A B C and D although independent they are very similar as they are the first attempt to rewash the flotation concentrate, also evaluating the difference in the effectiveness of two different collectors. The tests have the same feed (Tal Quale <150µm); tests C and D differ from the others the first for one oxidised flotation concentrate cleaner and the second for three more oxidised waste scavengers. From the tests, it was found that the best collector was amine. Changes were made in the type and dosage of reagents in the oxide circuit section to improve selectivity and recover galena and sphalerite. Flotation concentrates from tests A B C D were mixed and after three cleanings a marketable concentrate was obtained. An example is shown in the following flow chart.



Feed	**Weight g**	**Zn %**
Test A	495,50	2,08
Test B	493,30	1,70
Test C	514,10	1,78
Test D	495,90	2,07
Tot	1998,80	1,90

Sulphides Rougher	**Weight g**	**Zn %**
Test A	30,0	21,61
Test B	30,0	17,21
Test C	29,60	19,68
Test D	28,50	23,65
Tot	118,10	20,50

MASS BALANCE	**Total**	**W%**	**Zn%**	**Zn**	
Feed	1995,3g	100	1,88	37,51g	100%
Concentrate	38,4g	1,92	50,61	19,43g	51,81%
Mixed	118,1g	5,92	4,8	5,65g	15,06%
Final tailing	1838,8g	92,16	0,68	12,43g	33,13%

Legend	
Feed	🟥
Sulphides flotation	🟨
Sulphides scavenger	🟧
Sulphides Cleaner	⬜
Mixed	🟫
Final tailing	🟦

Figure 5.17 Flowsheet of tests ABCD. The tables shows the weight of the individual feeds and concentrates, the mass balance and concentration values for the analytes of interest.

5.7.6.4 *Tests α and β*

Tests α and β characterise two sets of five flotation tests forming a single experiment (10 tests in total). The two sets represent the two circuits, sulphides and oxides, separately so as to be able to observe the course of the experiment and the various aspects that characterise it. In the circuit α (sulphides) shown in the figure, the composition of the feed to the flotation stages is observed. The first concentrate of section α is obtained from the sum of the concentrates of tests α1 α2 α3, while the second float is made up of the sum of the concentrates of tests α4 α5; the sum of the two floats constitutes the sulphide concentrate of the experiment. The scavenger flotation stages of the three tests, combined, also gave products which, when added together, constitute part of the mass of the mixed waste and of the sulphide waste of the experiment.

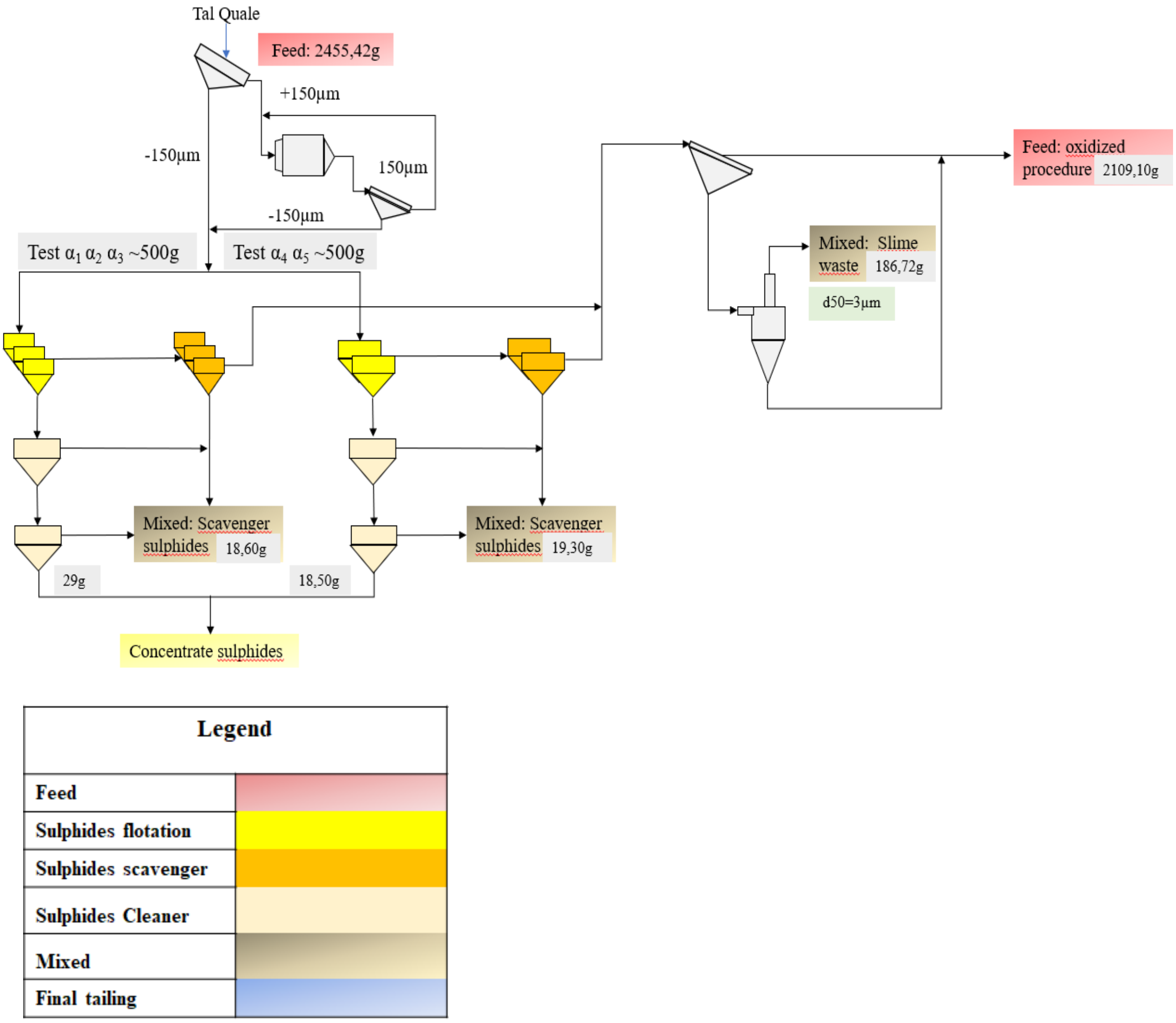
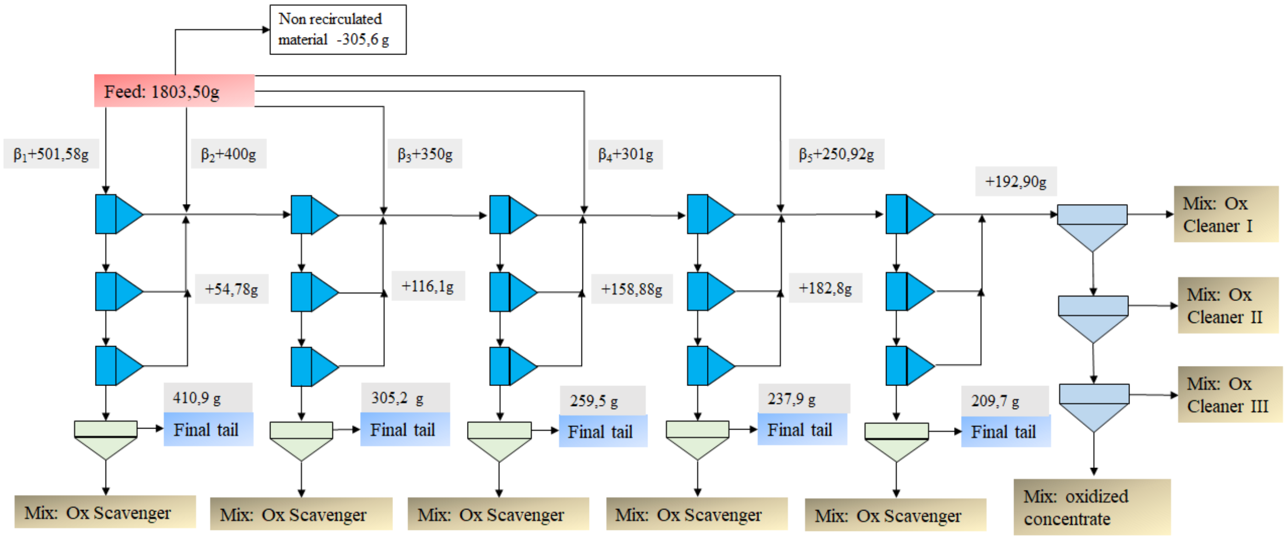


Figure 5.18 Flowsheet of tests α.

In the β circuit (oxidates) shown in the figure, the effect on the mass balance caused by recirculations involving the flotation concentrate in the oxidates scavenger was also tested for the first time. In this case, the feed upstream of the oxidates flotation procedure, β1 β2 β3 β4 β5, consists of the sum of all the +20 µm of the screening and the +3 µm of the hydrocyclone. The feeds of each flotation inside the closed circuit are about 500g each and after the first one obtained entirely from the total mass, the following ones are obtained by implementing smaller and smaller fractions of the total mass to the products obtained from the two scavenger phases; lastly the test ends with the oxidates cleaner.



Legend	
Feed	🟥
Oxidized flotation	🟦
Oxidized cleaner	🟦
Oxidized scavenger	🟩
Mixed	🟫
Final tailing	🟦

Figure 5.19 Flowsheet of tests β.

Table 5.12 Mass balance and concentration values of tests α-β for the analytes of interest.

MASS BALANCE	**Total**	**W%**	**Zn%**	**Zn**		**Pb**	
Feed	2455,42g	100%	1,88%	46,28g	100%	2,43g	100%
Concentrate	47,50g	1,93%	49,90%	23,70g	51,2%	0,19g	7,76%
Mixed	679,12g	27,66%	2,70%	18,36g	39,7%	1,56g	64,14%
Final tailing	1423,20g	57,96%	0,15%	2,20g	4,8%	0,50g	20,56%
Non-recirculated material	305,60g	12,45%	0,66%	2,1g	4,4%	0,18g	7,54%

The resulting mass balance, table, indicates the achievement of the desired concentration targets; it also highlights two fundamental aspects of the use of recirculation:

- The graph shows the ratio between the mass of the flotation concentrate obtained for each step of the flotations in the oxidised circuit M and the output mass directed to the scavenger section R. As can be seen from the graph, (5.7.6.4-4), the trend of R is decreasing as one goes on with the addition of recirculated material.

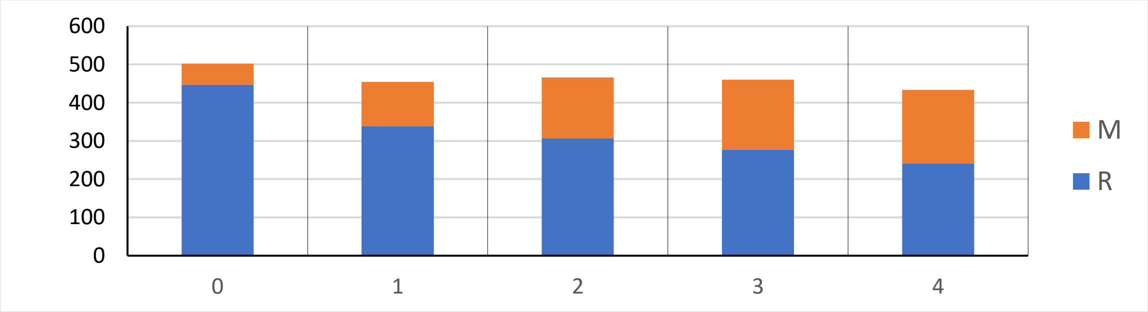


Figure 5.20 Ratio between the floated mass obtained for each step and the output mass.

- On the other hand, the graph shows the quantities of each product that make up the feed of each flotation. AN indicates the g of feed added from the main mass, while RC indicates the g of oxidised concentrate obtained in each flotation and recirculated. In this case, we highlight the increasing figure, RC, which indicates a constant increase in the mass of oxidised concentrate until it reaches a quantity useful for the flotation concentrate cleaning phases.

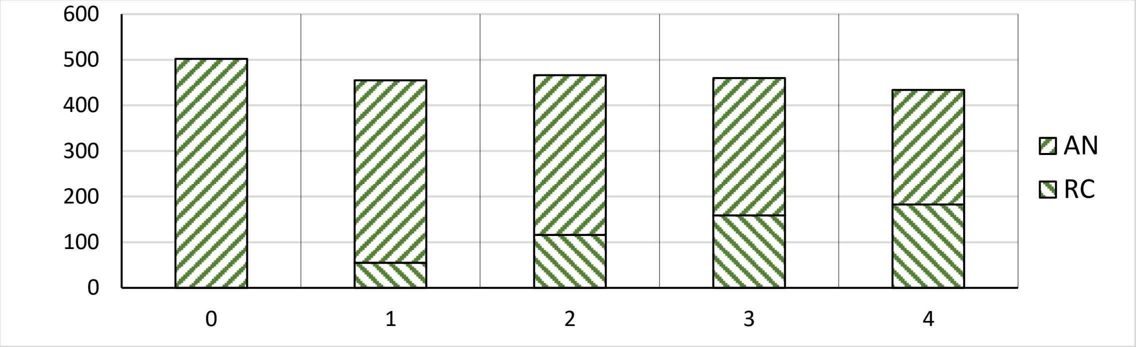
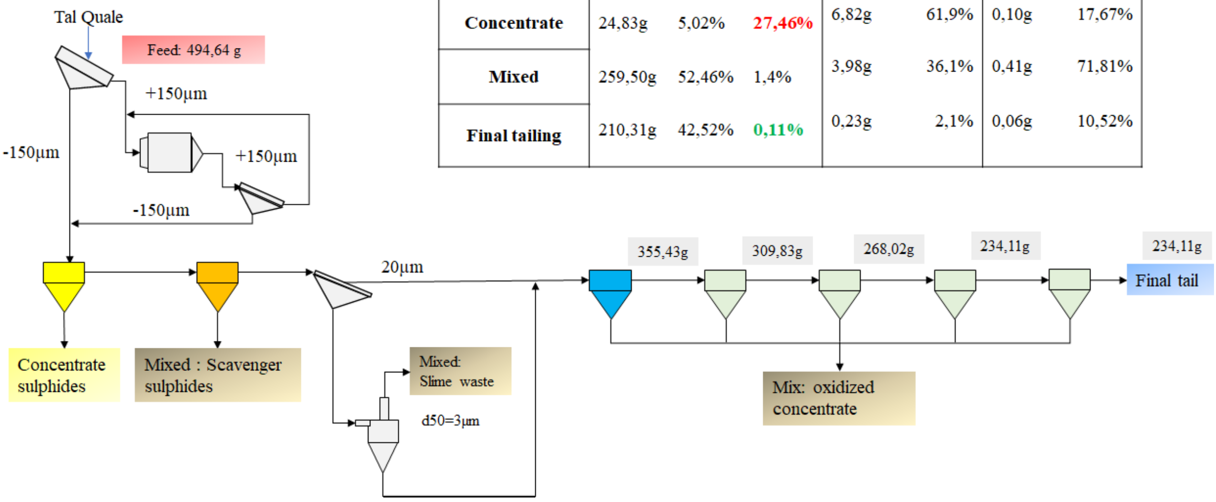


Figure 5.21 Trend of feed masses and concentrated oxidazed

5.7.6.5 Test *Ω1*

Considering the possible hypothesis of arriving at a marketable oxide concentrate, the final tests were based on a scheme consisting of multi-stage roughing in the oxide circuit section. The tests are 4, γ δ Ω Ω1, are similar and differ only in the number of cleaning stages, while in the first one 7 Cleaner were carried out with amine dosages lower than the first one, in the last two we opted for a lower number of rewash, 5 and maintaining the initial amine dosage. The figure shows the omega test, which was the best of the four, achieving an optimum waste content.

MASS BALANCE	**Total**	**W%**	**Zn%**	**Zn**		**Pb**	
Feed	494,64g	100%	2,23%	11,02g	100%	0,57g	100%
Concentrate	24,83g	5,02%	**27,46%**	6,82g	61,9%	0,10g	17,67%
Mixed	259,50g	52,46%	1,4%	3,98g	36,1%	0,41g	71,81%
Final tailing	210,31g	42,52%	**0,11%**	0,23g	2,1%	0,06g	10,52%



Legend	
Feed	🟥
Sulphides flotation	🟨
Sulphides scavenger	🟧
Slime separation	⬜
Oxidized flotation	🟦
Oxidized scavenger	🟩
Mixed	🟫
Final tailing	🟦

Figure 5.22 Flowsheet of tests Ω1. The tables shows the weight of the individual feeds and concentrates, the mass balance and concentration values for the analytes of interest.

5.7.6.6 Experimental plan

The choice of these representative tests determined the construction of a hypothetical experimental plan through the application of the best resulting strategies. Considering that in an eventual mineralurgical plant the recirculations would be applied in more than one point, the basic flowsheet to which all the tests carried out can be traced is as follows.

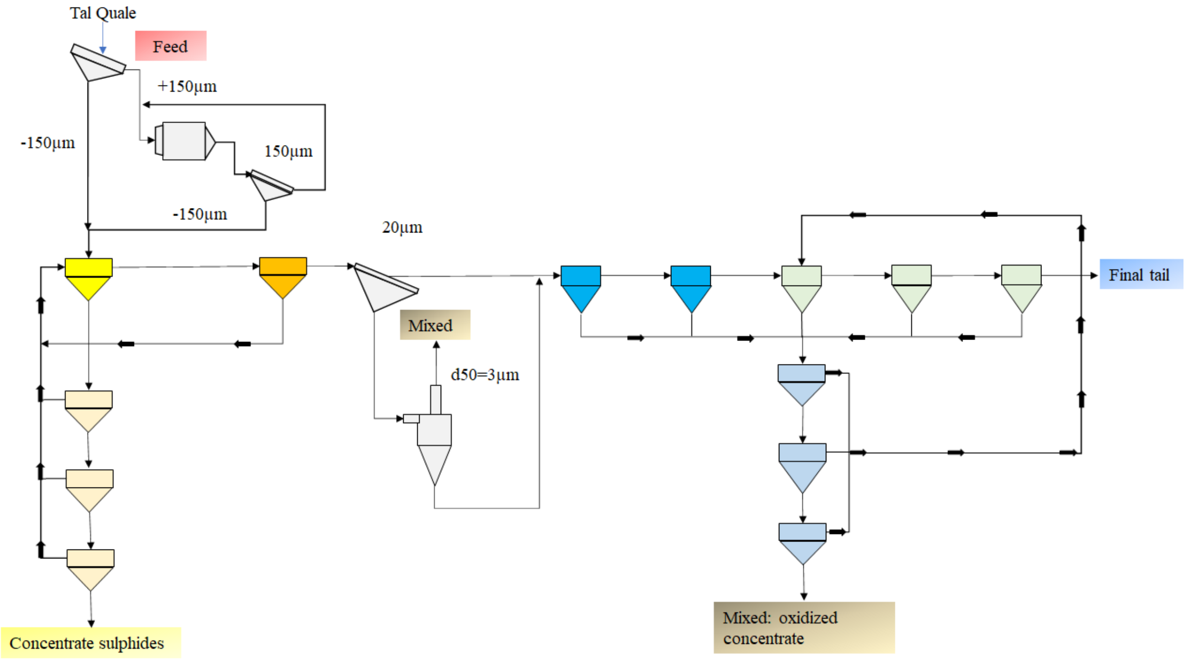


Figure 5.23 Flowsheet of the Experimental Plan

The study also looked at the effect on the mass balance caused by recirculation in all sections of the plant. In particular, the flotation concentrate in the scavenger stage, the waste produced in the sulphide cleaning stage, the flotation concentrate in the oxide scavenger stage and the waste in the oxide cleaning stage. These masses must be reintroduced at points in the circuit upstream (from the point of production) in a consistent manner, taking into account the section of the plant considered and the collectors used. Finally, it has been considered that the final oxidised concentrates, which does not have commercial characteristics, should be inerted and/or reused (for backfilling); alternatively, it could also be recycled at upstream points in the plant.

5.8 Comments and Conclusions

The results obtained from the research carried out on the SDBF_07 sample make it possible to draw a series of conclusive evaluations according to three different aspects: a brief summary of the results, a description of the process by which the final residue complying with the CSCs of Legislative Decree 502/2006 is obtained, a proposal for a plant flowsheet.

5.8.1 Summary of experimental results

Bearing in mind that the useful species considered is essentially Zn sulphide, it can be concluded, in schematic form, that:

- It is possible to obtain a final waste in which $C_{Zn} \leq CSC_{Zn}$, industrial sites. This is also valid for the other analytes Sb, As, Cd, Pb, which are part of the mineralogical equipment accompanying and the following sphalerite.
- It is possible to obtain a sulphide concentrate with about 50% Zn after roughing and 2 - 3 cleaning.
- It is necessary to de-slime the waste from the sulphide circuit before oxide flotation. The two sizes adopted, 3μm or 20μm, are <(already discussed).
- It is irrelevant whether the waste is treated separately according to two-particle size classes or according to a single circuit. Grinding at 150μm has proved preferable.
- It is more efficient in the oxidised circuit to concentrate the amine reagent (about 50% of the total) on the roughing and to limit the number of scavenger to no more than 2 to 3.

5.8.2 Reconstruction of the mining waste treatment process

Having demonstrated the possibility of achieving the proposed objective, it is useful to retrace the treatment process by examining it as a progressive depletion in pollutant species (in this case Zn) and highlighting the most important stages of the process. It should be pointed out first of all that the fundamental contribution is provided by the action of the anionic collectors (xanthates) [87] that operate an effective selection of Zn sulphide from the siliceous gangue, depleting the Zn feed; moreover, thus isolating a Zn concentrate with commercial characteristics.

The critical part of the process is the so-called oxidised circuit due to the low selectivity of the cationic collectors (amines), which cause a low reduction in Zn content and a high reduction in mass of the waste with each flotation.

The mechanism develops in two stages: a preventive de-sliming (which produces a non-recyclable OVER waste with CZn>CSCZn), roughing and scavenger step in several stages (at least three); appropriate dosages.

5.8.3 Proposed flowsheet

The optimum conditions for the flowsheet are as follows:

- feeding by Tal Quale (without particle size division and separate circuits);
- milling under 150µm controlled in a closed circuit;
- roughing and sulphide scavenger; two sulphide rewash for the production of the final concentrate;
- de-sliming, preferably at 3µm or 20µm [88];
- oxide roughing (with high amine concentration) and two to three scavenger flotations (with low collector concentration).

For a hypothetical plant flowsheet, the breakdown in terms of Zn content, metal units and masses can be summarised in the following table.

Table 5.13 Breakdown of products in a theoretical flowsheet.

ID-Sample	%Zn	Distribution UM%	Distribution Mass %
Feed	2,2	100	100
Sulphide concentrate	50	63	3
Oxidised concentrate	2,5	31	27
OVER De-sliming	1	1	2
Final waste	0,15	5	68

However, the final choice of the optimal flowsheet depends on economic evaluations (the possible market for oxidised concentrate) and on other specific situations related to reuse and required quantities of CSC non-compliant products (for surface or deep fillings) that should be delivered to collection sites, previously submitted or not to inertisation.

The choices could also be conditioned by the capacity of the plant and its location in relation to the materials with which it should be fed (not only those from the Montevecchio Levante Sludge Basin).

Chapter 6: Procedures performed on Power feeds in GTK

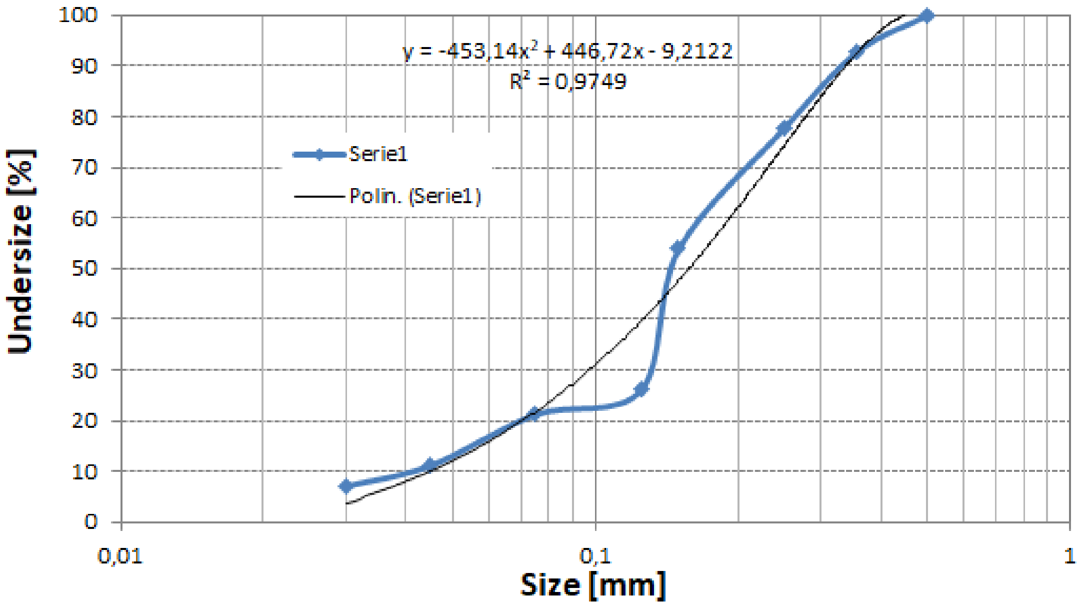
During the 4-month internship period at the Geological Survey of Finland, GTK, the SDBF_07 sample was analysed with the aim of achieving the objectives, integrating the analyses carried out at the laboratories of the University of Cagliari with additional data obtained by applying innovative techniques. The flotation tests such as the determination of the analytes by XRF and the mineralogical investigations were carried out at Outokumpu mineral processing pilot plant and laboratories - GTK Mintec, while the ICP-MS analyses and critical data analysis were performed at the Kuopio site.
Approximately 12 kg of Tal Quale sample from SDBF_07 was sent for the project.

6.1 Samples characterization

The material was quartered and 16 samples of approximately 500 g were obtained. Of these, ten were used as feeds to the flotation procedures, while the others were used for mineralogical and chemical characterisation analyses. The table shows the particle size analysis. The resulting D80 is 0.20 mm.

Table 6.1 Particle size analysis of SDBF_7 Tal quale

PARTICLE SIZE CLASS	**SDBF-07**		
	Weight (g)	**Passing (%)**	**Retained (%)**
(µm)		**100,0**	
500	6,1	92,7	7,3
355	12,5	77,7	15,0
250	19,9	53,9	23,9
150	23,2	26,1	27,8
125	4,0	21,3	4,8
175	8,4	11,1	10,1
45	3,4	7,1	4,0
32	0,9	6,0	1,1
-32	5,0		6,0
TOT	83,3		100,0



6.1.1 XRF analysis

Major and minor elements are determined by wave-length dispersive XRF-analyzer, PANalytical AXIOS. The method is based on the principle that atoms of the sample are exited by X-ray radiation. Exited atoms produce the characteristic fluorescence radiation. The intensity of the emitted fluorescence radiation of each element is the measure of its amount in the sample.

Samples are ground to <10 micron particles in size in a tungsten carbide (WC) bowl and pressed to pellets. The XRF measurement uses for matrix corrections the unique RR-fundamental parameters programme which enables the analysis of major, minor and trace components from the same pellet. As fundamental correction program no matrix depending additional corrections are needed and all the different types of samples are analyzed by the same basic correction. The calculated detection limits for determination lie between 4 ppm and 100 ppm depending on the element to be measured.

Table 6.2 Analysis of the Major Sample SDBF-07 at GTK

Major	W%	Major	W%
Al_2O_3	5.38	K_2O	1,40
Fe_2O_3	10.0	Na_2O	0,00
MnO	0.451	TiO_2	0,265
MgO	0.52	P_2O_5	0,04
CaO	0.486	SiO_2	69,7
Cr_2O_3	0.0061	V_2O_3	0,0060
Rb_2O	0.0048	SrO	0,0090
BaO	0.307	ZrO_2	0,012
TOT			88,6

For the determination of minor components, ICP-Ms analysis was used on the products of the grain size analysis, and on the products of the first flotation test.

Table 6.3 Minor element concentration of sample SDBF-07 at GTK.

Minor element in %										
Cu	**Ni**	**Co**	**Zn**	**Pb**	**Ag**	**S**	**As**	**Sb**	**Bi**	**Te**
0.015	0,006	0,011	2,01	0,155	0,000	1,40	0,002	0,015	0,002	0,001
Y	**Nb**	**Mo**	**Sn**	**W**	**Cl**	**Th**	**U**	**Cs**	**La**	**Ce**
0.0035	0,0010	0,0000	0,003	0,001	0,013	0,0009	0,0000	0,000	0,010	0,010
Ta	**Ga**	**Si**	**Ti**	**Cr**	**V**	**Fe**	**Mn**	**Mg**	**Ca**	**Ba**
0.001	0,0019	32,6	0,159	0,0042	0,0041	7,81	0,349	0,31	0,347	0,275

6.1.2 Precious metal analysis: Fire Assay and gravimetric determination of Au,Ag.

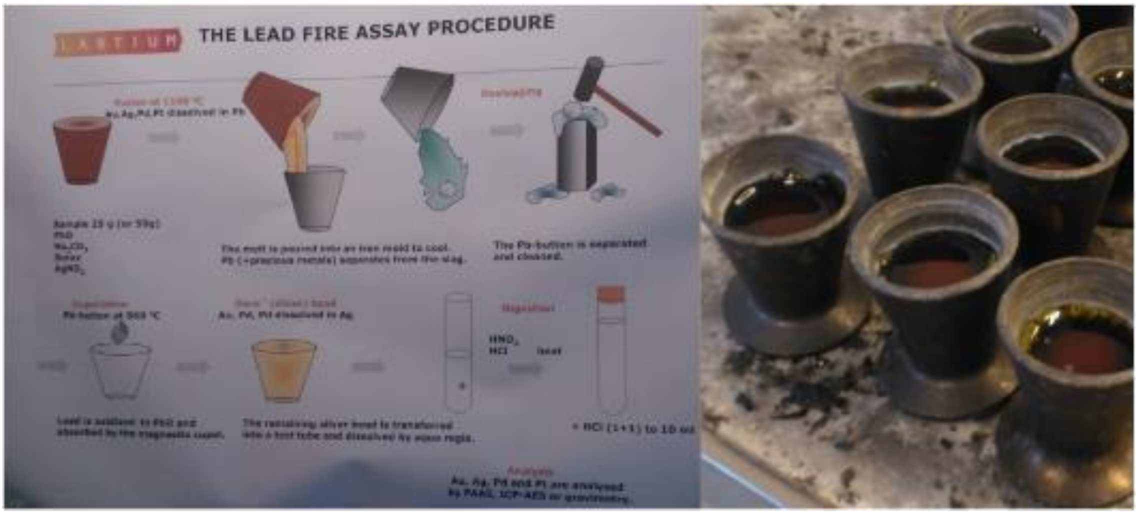


Figure 6.1 Fire Assay and gravimetric determination of Au,Agcarried out at GTK.

For the Au and Ag ore analyses, the loss-in-fire procedure with gravimetric finishing was performed. The step-by-step procedure is listed in the picture.

The sample weight varied from 5-30 g. For sample preparation, representative sub-sampling was performed using a precision rotary splitter. The concentration range is 0.1-50 % Au. The analyses for the determination of Au and Ag were carried out by flame atomic adsorption spectroscopy (FAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) or by gravimetry.

The table below shows the precious metal concentrations obtained for SDBF-07. The data from the fire assay and the gravimetric determination of Au and Ag analysis, exhibit a discreet presence of golds and silver in the mining waste sample from Montevecchio.

Table 6.4 concentrations of precious metals (Ag Au) carried out at GTK.

Analytical method code	**711G**	**711G**
Parameter	**Ag**	**Au**
Unit	**g/t**	**g/t**
Sample id / LIMS sample id / Sample description		
SDBF-07 / S19064309 /	3,88	0,09

6.1.3 MLA analysis

The studied sample is zinc-lead-tailing from Italy named SDBF_07. The particle size is -250 µm. One vertical polished section was prepared, and it was measured on the MLA device. Scanning electron microscope was Quanta 600. The mineral contents were measured by XMOD_std method. XBSE method was used for measuring the liberation and particle size of sphalerite.

The densities used for the calculation of the mineral contents are shown in Table 6.6.

Table 6.5 Mineral densities.

Mineral	Density	Formula
Quartz	2,63	SiO_2
Albite	2,62	$NaAlSi_3O_8$
K_feldspar	2,56	$KAlSi_3O_8$
Epidote	3,45	$Ca_2Al_2(Fe^{3+},Al)(SiO_4)(Si_2O_7)O(OH)$
Muscovite	2,83	$KAl_3Si_3O_{10}(OH)1.9F0.1$
Chlorite	2,95	$(Mg,Fe)3_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$
Kaolinite	2,60	$Al_2Si_2O_5(OH)_4$
Siderite	3,96	$FeCO_3$
Ankerite_Mg	3,05	$Ca(Fe,Mg,Mn)(CO_3)_2$
Calcite	2,71	$CaCO_3$
Zincian_siderite	4,20	$(Zn,Fe)CO_3$
Smithsonite	4,45	$ZnCO_3$
Monazite	5,15	$REE(PO_4)$
Apatite	3,19	$Ca_5(PO_4)(F,Cl,OH)$
Rutile	4,25	TiO_2
Pyrite	5,01	FeS_2
Galena	7,40	PbS
Chalcopyrite	4,20	$CuFeS_2$
Sphalerite	4,00	ZnS
Goethite_Zn	3,80	$FeO(OH)$
Barite	4,48	$BaSO_4$
Synchysite-(Nd)	4,02	$CaREE(CO_3)2F$
Unknown	2,60	

In this sample exists zinc-iron-carbonate which is named as zincian siderite ($(Zn,Fe)CO_3$). The Raman study shows that the spectrum of zincian siderite is almost identical with siderite and smithsonite. Siderite ($FeCO_3$) and Smithsonite ($ZnCO_3$) form solid solution. The both end members of this solid solution exist also in studied tailing sample.

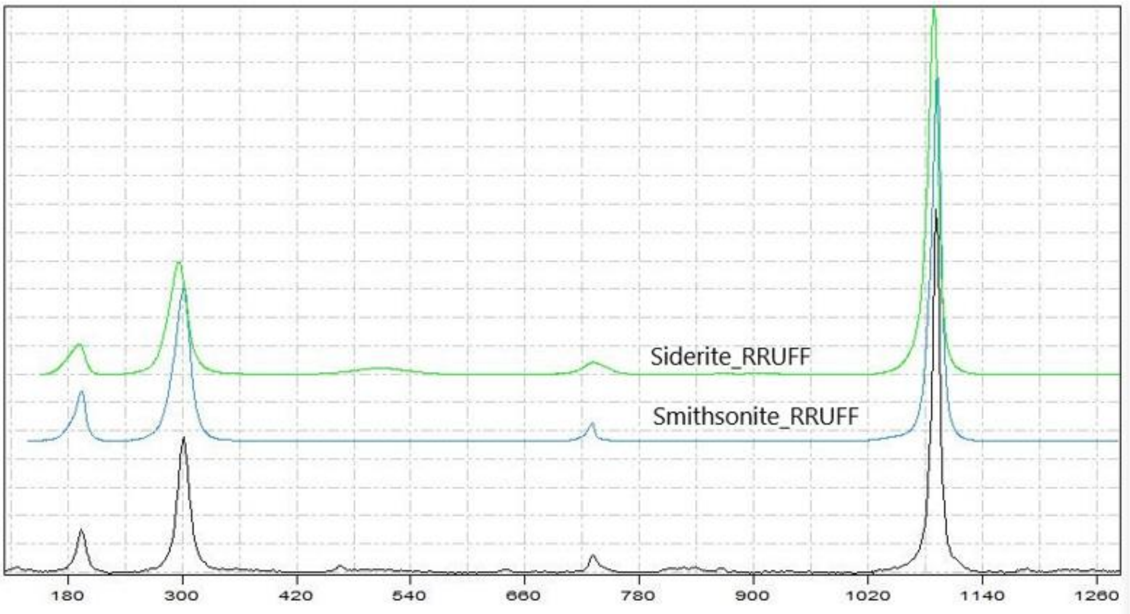


Figure 6.2 Raman spectrum of Zincian siderite((Zn,Fe)CO3) and its comparison to siderite (FeCO3) and smithsonite (ZnCO3).

The main silicates are quartz (60.4%), muscovite (7.5%) and K-feldspar (5.9%). Siderite is the most common carbonate (13.7%). Sphalerite content is 2.5%. Galena and chalcopyrite contents are less than 0.1 %.

Table 6.6 Mineral contents.

Mineral	Wt%
Quartz	60,37
Albite	1,42
K_feldspar	5,89
Epidote	0,00
Muscovite	7,48
Chlorite	0,40
Kaolinite	0,01
Siderite	13,68
Ankerite	0,06
Calcite	0,00
Zincian_siderite	1,45
Smithsonite	0,24
Monazite	0,02
Apatite	0,01
Rutile	0,02
Pyrite	2,23
Galena	0,08
Chalcopyrite	0,05
Sphalerite	2,54
Goethite_Zn	3,45
Barite	0,48
Synchysite	0,01
Unknown	0,12
Total	100,00

Number of measured points	20221

The distribution of zinc to different minerals is roughly calculated in Table 21. Sphalerite carries about 75% of zinc and carbonates 22%. The rest of zinc is in the lattice of goethite (3%). This calculation based on standardless EDX-analysis and modal mineralogy data.

Table 6.7 Distribution of zinc.

Mineral	Zn (%)
Quartz	
Albite	
K_feldspar	
Epidote	
Muscovite	
Chlorite	
Kaolinite	
Siderite	
Ankerite	
Calcite	
Zincian_siderite	17,1
Smithsonite	5,4
Monazite	
Apatite	
Rutile	
Pyrite	
Galena	
Chalcopyrite	
Sphalerite	74,5
Goethite_Zn	3,0
Barite	
Synchysite	
Unknown	
Total	100,0

XBSE method was used for measuring the liberation and particle size of sphalerite d80 passing value of sphalerite is about 170 µm. The liberation value of sphalerite is over 85%.

Particle images of sphalerite is presented in Figure 6.4.

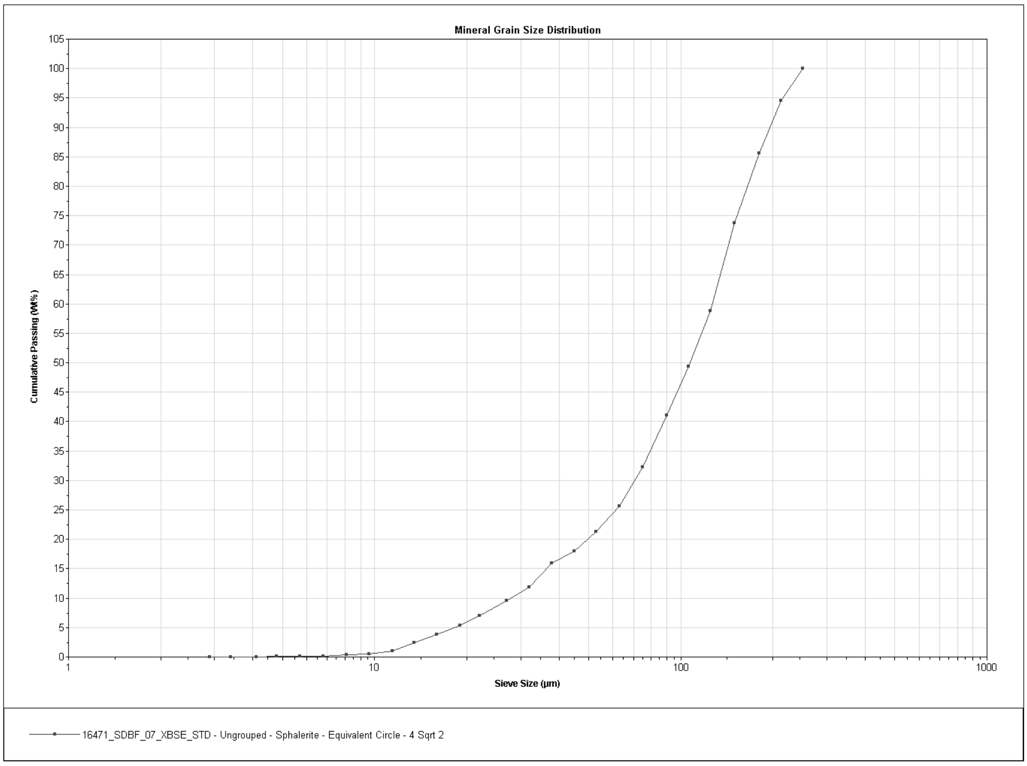


Figure 6.3 Measures of the liberation and particle size of sphalerite

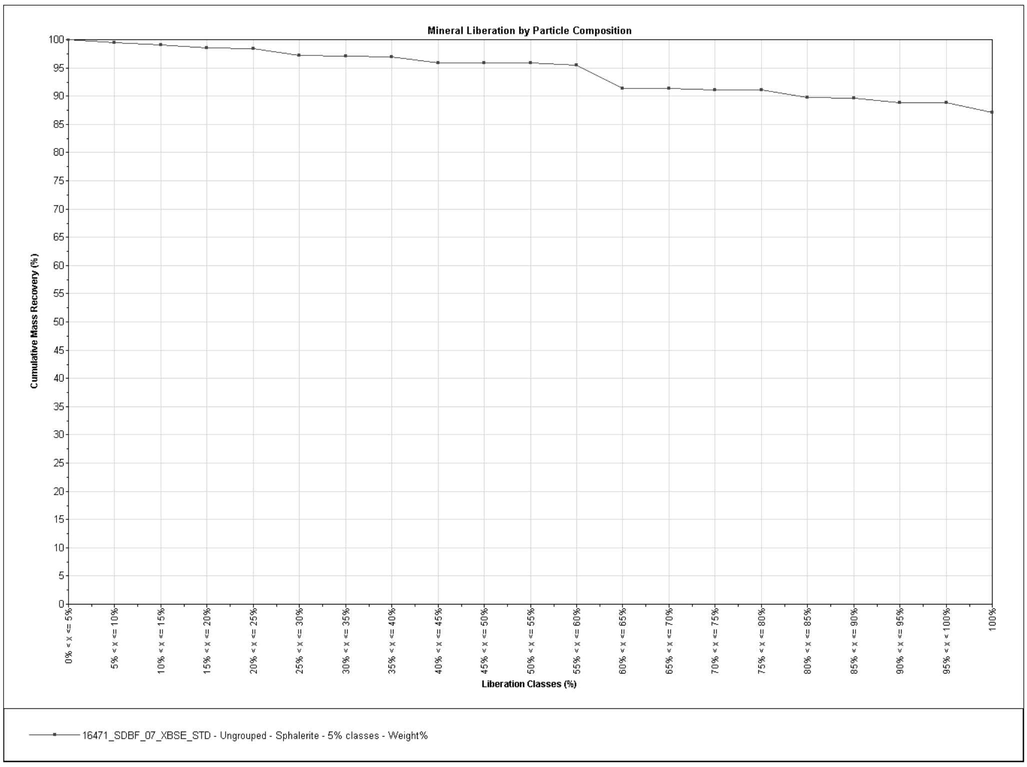


Figure 6.4 Liberation of sphalerite.

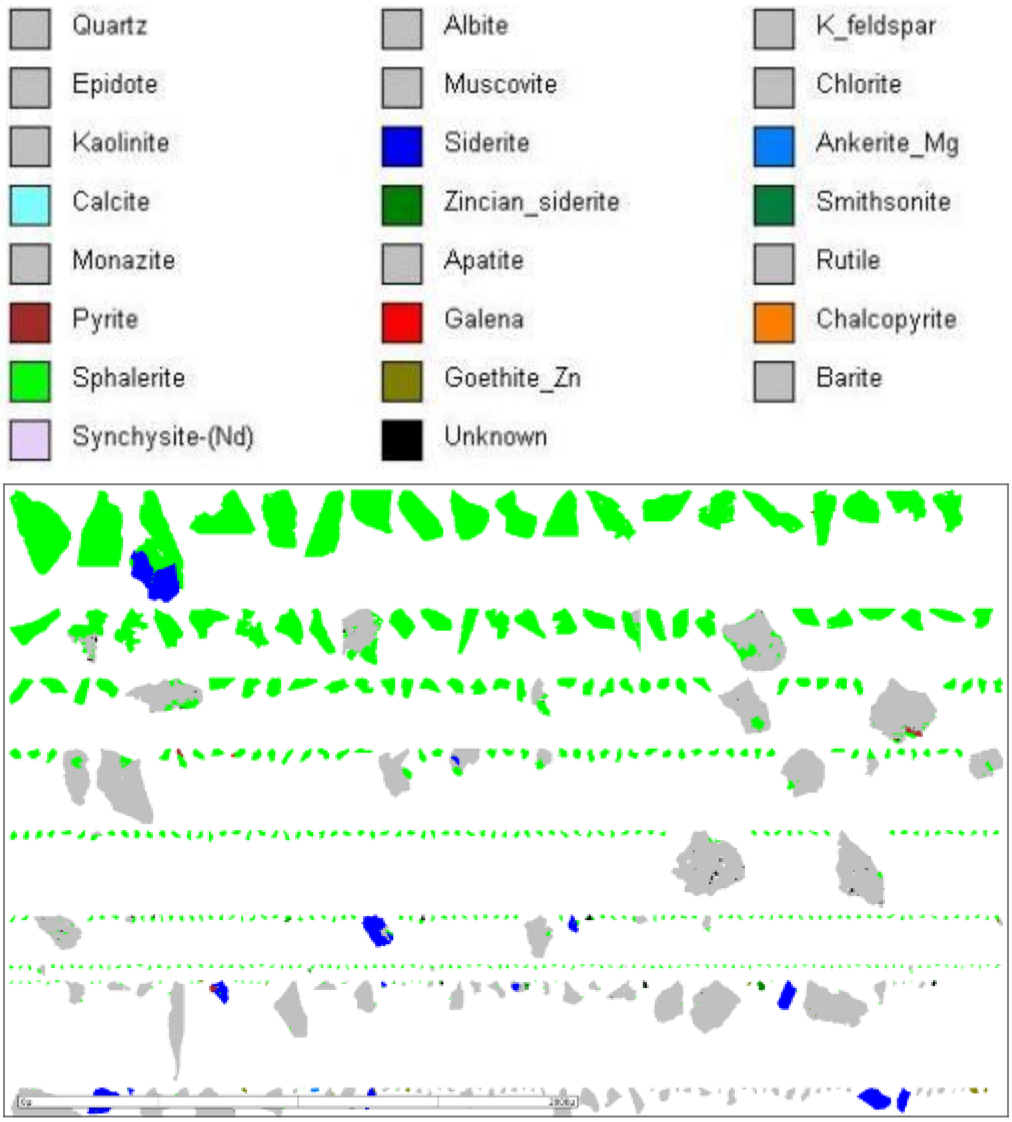


Figure 6.5 Sphalerite particles and minerals legend.

6.2 Sequential Extraction and comparison with MLA

Sequential Extraction was performed on the SDBF-07 mineral residue at the Environmental Chemical Analysis Laboratory of the Department of Civil-Environmental Engineering and Architecture (DICAAR) of the University of Cagliari. The results showed that most of the total Zn and Pb content is contained in the form of carbonate, bound to oxidisable forms such as sulphide.

The mineral contents calculated from the MLA analysis show that the main silicates are quartz (60.4%), muscovite (7.5%) and K-feldspar (5.9%). Siderite is the most common carbonate (13.7%). The sphalerite content is 2.5%. The content of galena and chalcopyrite is less than 0.1%. The distribution of zinc to different minerals is roughly calculated in Table 6.10, sphalerite carries about 75% Zn and carbonates 22%. The rest of the Zn is in the goethite lattice (3%).

Table 6.8 Pb and Zn distribution (%) in different mineral fractions by SE analysis.

ID Sample		**% Sequential Extraction on total**						**Tot ES**	**1 step**
		step1	step2	step3	step4	step5	step6	%	
AF51 5B	Cu	0,2	0,4	6,6	0,9	27,1	64,8	0,04	0,03
	Cr	0,0	0,0	1,1	0,6	1,9	96,4	0,01	0,01
	Pb	0,5	3,7	32,5	11,2	34,9	17,3	2,01	1,55
	Zn	2,5	3,5	18,7	12,5	20,6	42,1	1,35	1,15
	Cd	12,3	19,4	13,4	6,7	16,6	31,6	0,01	0,01
	Ag	Dl	11,7	2,6	1,4	Dl	71,3	0,00	0,00
SDBF 7		step1	step2	step3	step4	step5	step6		
	Cu	0,2	0,6	5,5	3,3	21,5	68,8	0,02	0,02
	Cr	dl	dl	3,2	0,7	5,0	91,1	0,01	0,01
	Pb	0,7	1,6	35,0	12,5	37,1	13,1	0,13	0,10
	Zn	3,8	1,9	16,6	8,9	29,6	39,2	1,97	2,14
	Cd	12,6	6,9	13,5	2,2	14,6	50,2	0,02	0,02
	Ag	Dl	10,2	5,3	19,2	2,7	62,5	0,00	0,00

Table 6.9 Pb and Zn distribution (%) in SDBF_7 different mineral fractions by MLA analysis

SDBF_7 Mineral fractions	**Wt%**	**Zn%**	**Mineralogical classes**	**Wt%**
Quartz	60,37		Silicate	75,57
Albite	1,42			
K_feldspar	5,89			
Epidote	0,00			
Muscovite	7,48			
Chlorite	0,4			
Kaolinite	0,01			
Siderite	13,68		Carbonates	15,44
Ankerite	0,06			
Calcite	0,00			
Zincian_siderite	1,45	17,1		
Smithsonite	0,24	5,4		
Synchysite REE	0,01			
Monazite REE	0,02		Phosphates	0,03
Apatite	0,01			
Rutile	0,02		Oxides/hydroxides	3,47
Goethite_Zn	3,45	3		
Pyrite	2,23		Sulfides	4,9
Galena	0,08			
Chalcopyrite	0,05			
Sphalerite	2,54	74,5		
Barite	0,48		Sulphate	0,48
Unknown	0,12			0,12
Total	**100**			100,01

6.3 Flotation procedure

Based on these analyses, flotation tests were carried out on sample SDBF_07 from the Montevecchio mine. The aim is to compare the starting data and to find new and efficient procedures aimed at recovering useful species.

The chosen particle size of the flotation feed is 150 µm. The choice has been based on the comparison between the MLA analysis and the results obtained from the inefficiency analysis in Italy. the MLA analysis resulted in a sphalerite d80 of 170 µm, while the inefficiency analysis showed that the particle size at around 150 µm gives less problems during the flotation procedure. This grain size has been retained for all tests. Each flotation procedure performed at Outokumpu's laboratory required wet grinding of the feed: after wet screening, of approximately 500g of Tal Quale feed, the +150 µm was ground using a rod mill. All steps in the sulphide circuit were carried out using the same reagents; in the oxide circuit, 4 different collectors were tested. The reference flowsheet for all the tests is shown in the figure.

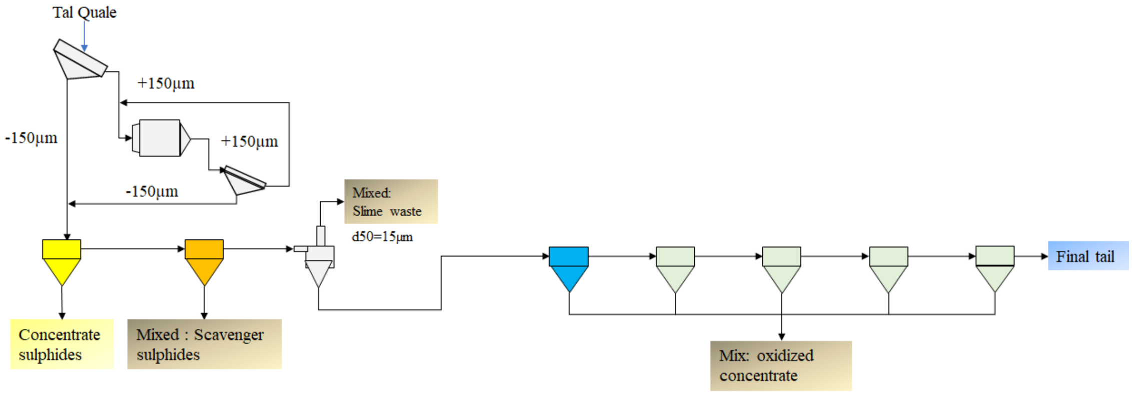


Figure 6.6 Flotation test flow sheet.

6.3.1 Experimental Plan

The flotation tests, 10, were carried out on the basis of a plant circuit consisting essentially of the 3 phases indicated in the table 6.10: Roughing and scavenging of the sulphide circuit, removal of fines less than 15 µm from the oxidation circuit and roughing and scavenger of the oxidation circuit. The concentrations of Zn, Pb, Cu, Fe, SiO_2, Al_2O_3 and As were determined on each sample taken.

Repeated scavenger steps (re-scavenger) were introduced into the oxidation circuit.

Table 6.10 Experimental batch test plan

ID_TEST	**Particle size**	**Grinding**	**Solphur flotation**		**De-sliming**	**Oxidized flotation**						
	Tal Quale	>150µm	Rugher	Scavenger	hydrocyclon d50=15 µm	Rugher	Scavenger					
						1	1	2	3	4	5	6
1	▨	▨	▨	▨	▨	▨	▨					
2	▨	▨	▨	▨	▨	▨	▨					
3	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
4	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
5	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
6	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
7	▨	▨	▨	▨	▨	▨	▨	▨				
8	▨	▨	▨	▨	▨	▨	▨	▨				
9	▨	▨	▨	▨	▨	▨	▨	▨				
10	▨	▨	▨	▨	▨	▨	▨					

6.3.2 Reagents employed

The following table, 6.12, lists the reagents used, distinguishing between: products, concentrations, section of plant, function performed and identification code of the tests performed.

Table 6.11 Overview of reagents used

Products	**Concentrations**	**Plant sections**	**Roles**	**ID_Test**	
CuSO4	400 g/t	Sulphides Rougher, Scavenger and Cleaner	Sphalerite Activator	All	-
Na Isopropil xanthate	100 g/t		Sphalerite Collector	All	-
Dowfroth 250	20+20 g/t		Frother	All	-
Na2SiO3	2000 g/t	Oxides Rougher (primary and secondary), and Cleaner	Gangue Depressant	All	-
Na2S	4000-9000 g/t		Oxides Zn Activator and pH controller	All	-
Aeromine 3000 C	200 g/t 350 g/t 400 g/t		Oxides Zn Collector	-	1-2 3 11
Armac C	350 g/t 800 g/t				4 5
Armac T	800 g/t 900 g/t				6 7
Aeroammina 3030	900 g/t				8-9
Dowfroth 250	40 g/t 280 g/t 120 g/t			-	1-2-11 3-4-5-6 7-8-9
Na2S	4000 g/t	Oxides Scavenger	Oxides Collector	-	1-2
Aeromine 3000 C	100-200 g/t 400 g/t				1-2 11
Dowfroth 250	60 g/t			-	1-2-11

All the tests carried out, the roughing, cleaning and scavenger phases of the sulphide circuit were performed using the same reagents; the differences were introduced in the oxidised circuit; during the course of the tests, various collectors from the collection of reagents made available by GTK were tested.

6.4 Results

From the results obtained, it is possible to state that the starting information coincides, and new alternatives are needed to obtain a procedure that increases recovery while reducing losses and maintaining a final waste with the csc limits of heavy metals.

6.4.1 Summary of the experimental results

During the month of September, all data obtained from flotation tests were processed and tabulated to obtain trend curves.

- Total Zn grades and recoveries

The graph below shows the Zn values achieved in the waste from the 10 tests.

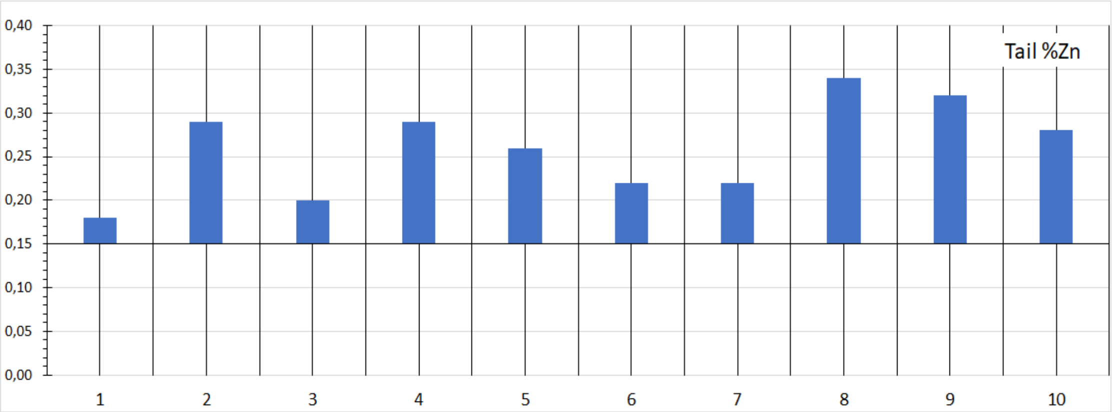


Figure 6.7 Total Zn grades in Tail

The following scatter diagram shows the % Zn content achieved in the sulphide concentrate in relation to the weight percentage yield data ρZn .

The flotation of the sulphides is not selective enough to reach commercial concentrations (about 50% Zn), cleaning stages of the flotation concentrate would increase the yield. The best recovery results were obtained in tests 1, 2 and 3.

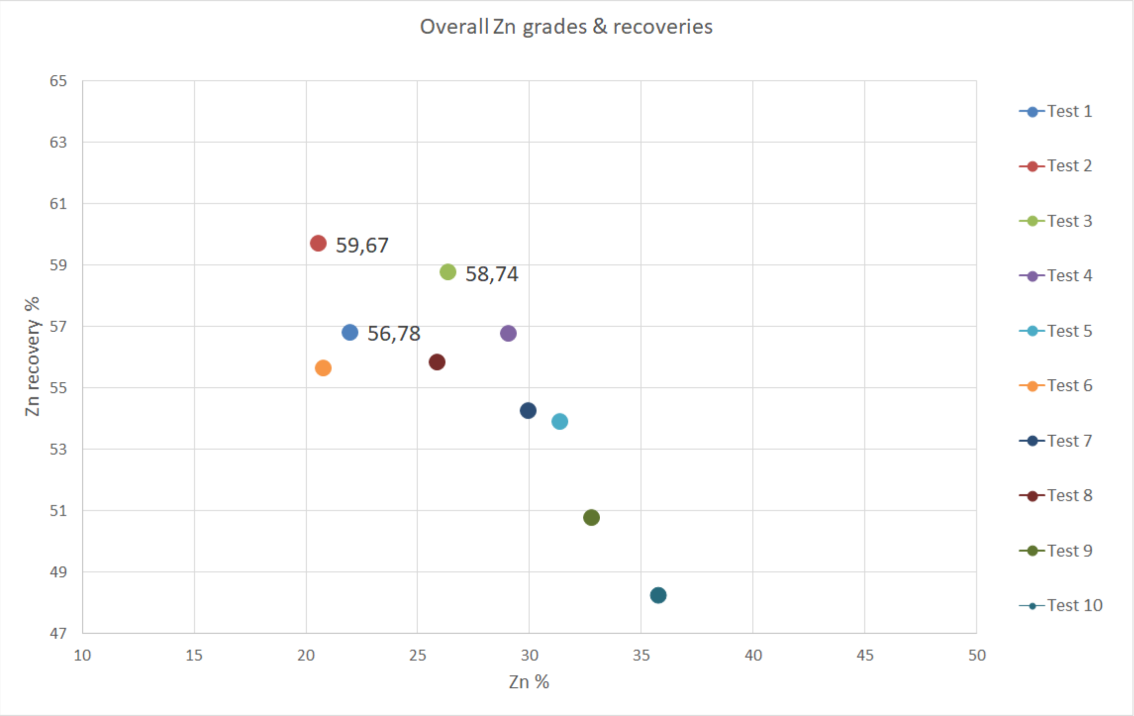


Figure 6.8 Zn% grade in concentrate and recoveries

- Zn content in the oxidised circuit

The results obtained from the tests made it possible to reason about the performance of the tests in the oxidised circuit considering that the main objectives were to test various types of collector used in the tests and to increase the number of scavengers in the oxidised circuit.

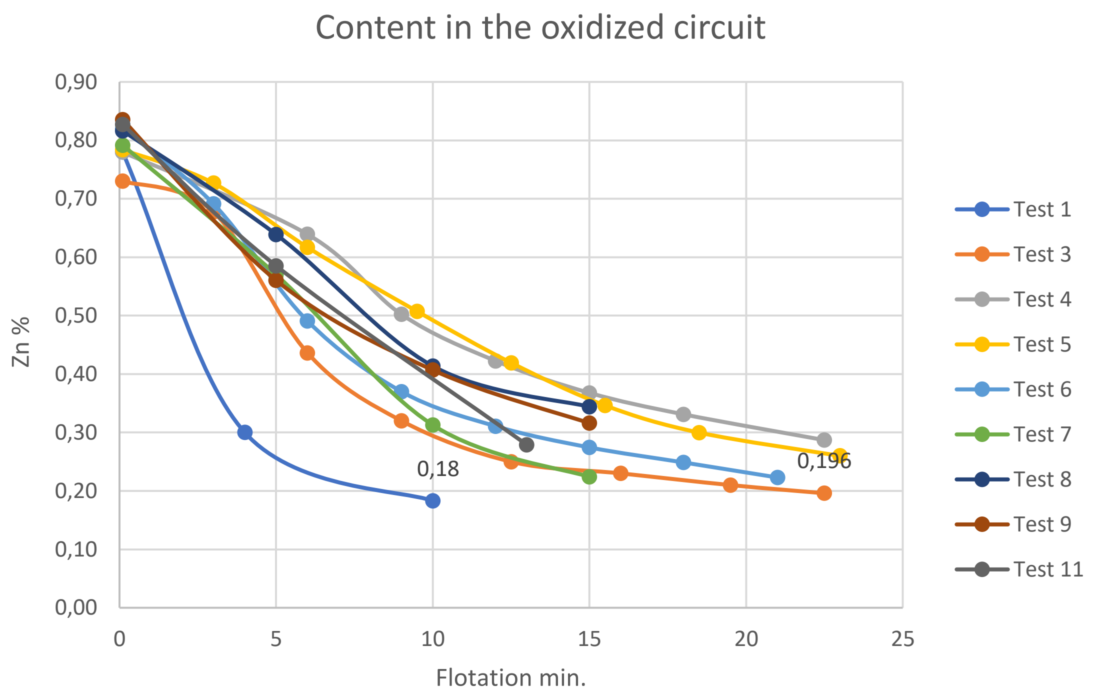


Figure 6.9 Zn content in the oxidized circuit

The graph shows the development of the Zn content in the oxidised circuit. The starting values for all tests lie in a range between 0.70 and 0.85. The trend of this flotation kinetics shows that the tests which had the most convincing results were test 1 which reached 0.18% with only 2 scavengers in the oxidised circuit, while the subsequent tests obtained less satisfactory results despite a greater number of scavengers.

In no test did a final rejection in accordance with the CSCs for heavy metals occur.

- Oxidised circuit inefficiency

The tests which had an irregular pattern are highlighted in the following graph, excluding tests 1, 9 and 11 which show an increasing regular pattern. This may be due to the irregular tests being those in which the type of collector was varied, whereas in the tests characterised by more regular behaviour the collector used was the same for all three tests.

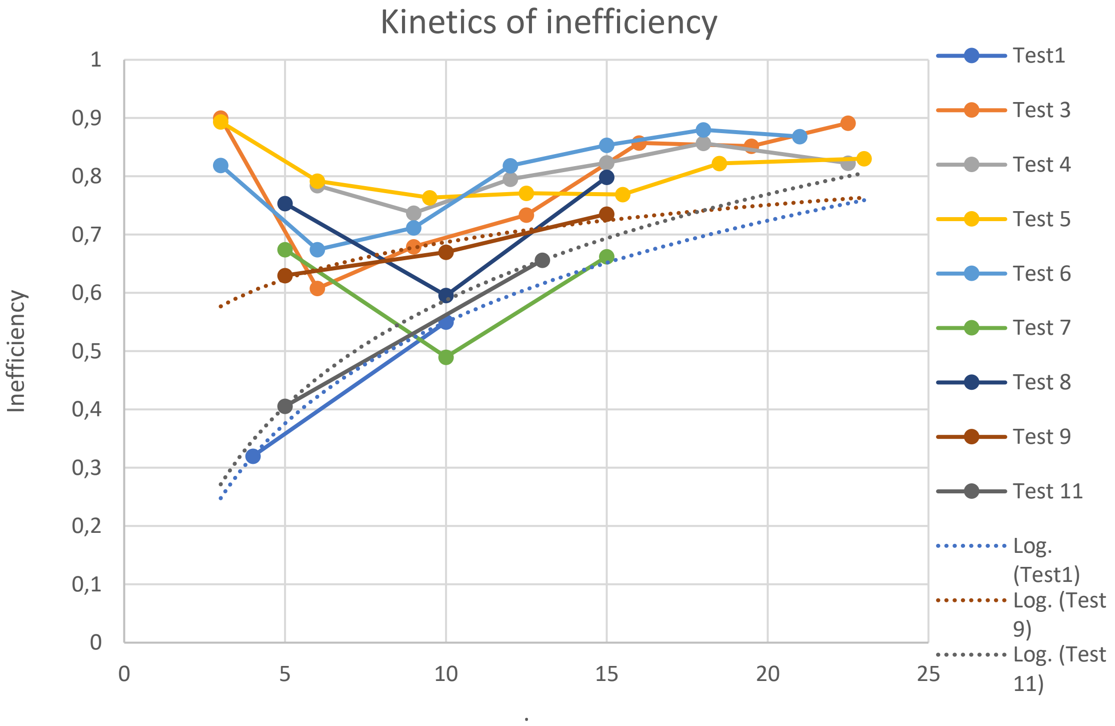


Figure 6.10 Oxidized circuit inefficiency

- Recovery of Zn in the oxidised circuit

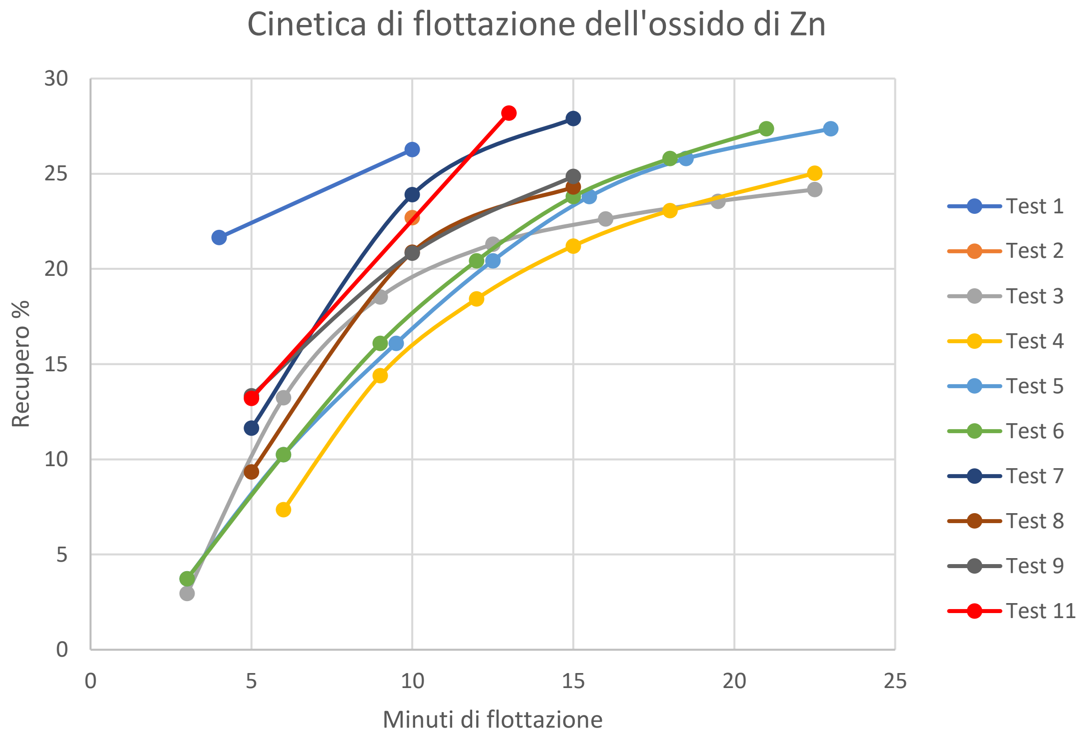


Figure 6.11 Recovery of Zn in the oxidized circuit

The graph in figure 6.10 shows that the test that gave the best result in terms of time is the first one, since in only 3 minutes and a single flotation it obtained values similar to those of roughing plus scavenger (ox-RC+SC) of the other tests; while in terms of final recovery, test 11 reaches the maximum obtainable value of RC+SC in half the time of all the other tests.

The higher the recovery in roughing, the more the line will assume a vertical trend; the lower the recovery in scavenger, the more the line will assume an asymptotic trend.

- Distribution of metal units

The distribution of the metal units obtained in the circuit phases for all the tests is represented by the histogram in fig. It is evident that test 3 obtained the highest value in g of the Zn content, but this is still not sufficient to be saleable to the metallurgical sector. Test 9 shows a Zn concentration after roughing of 33%, so more scavengers were needed to reach the required content.

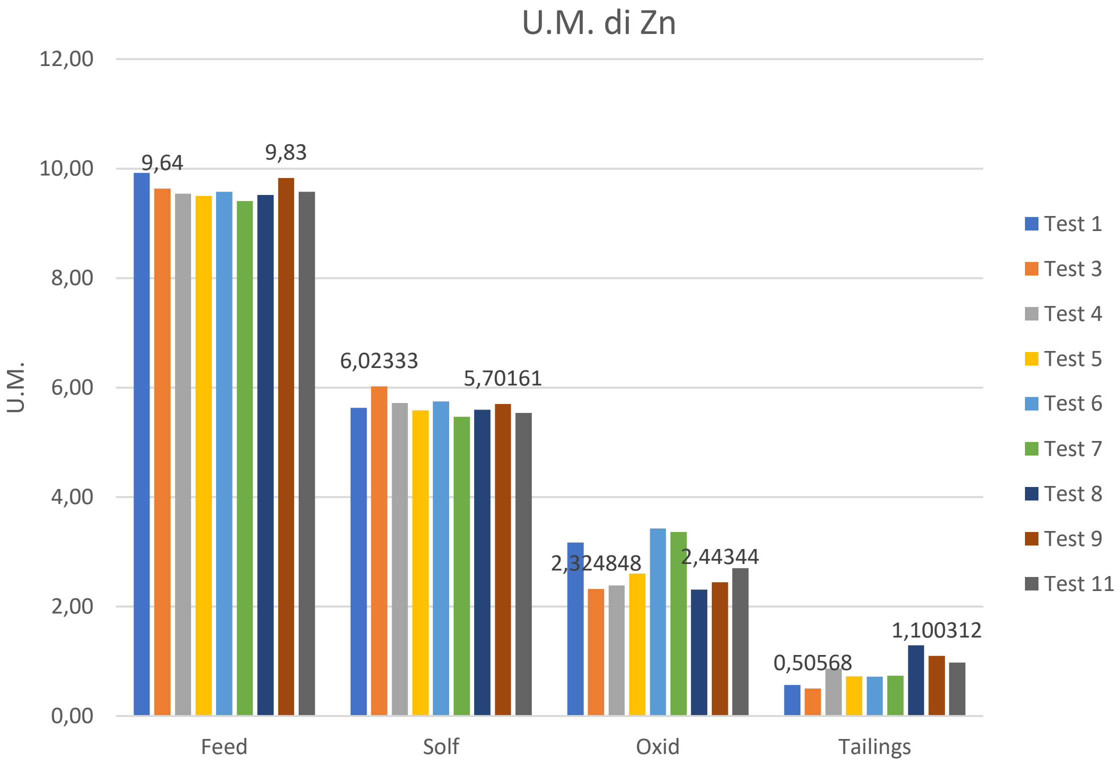


Figure 6.12 Distribution of metal units.

6.4.2 Mineralogical characteristic of Montevecchio mining tailings

Using the methodologies provided by the GTK company, such as the ICP-MS atomic mass spectrometer and the Mineral Liberation Analyzer, the concentrations of heavy metals and minor elements distributed for the various products of the first flotation were measured (Table 6.13); it was also possible to quantify the distribution of zinc bound to the various mineralogical formations. The investigation, whose data are shown in Tables 6.15-6.16, was performed on the final waste of the first test since it obtained the best result in terms of Zn content.

Table 6.12 Analysis of the minor elements of the products in the first flotation

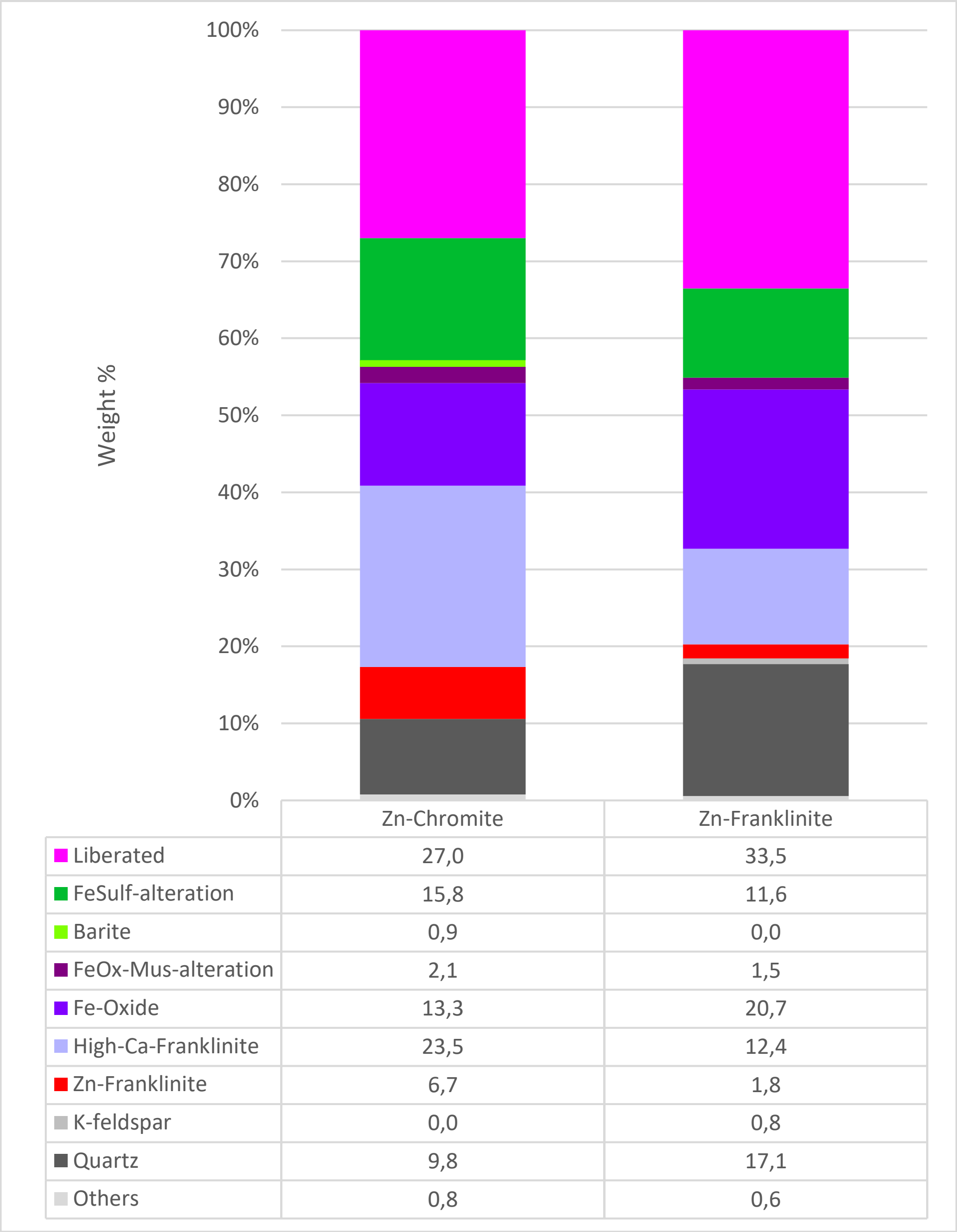
ID-Sample	**Cu**	**Fe**	**Zn**	**Pb**	**WEIGHT**
	mg/kg	mg/kg	mg/kg	mg/kg	g
Sulph RC	2150	157000	231000	2930	25,6
Sulph Sc	1150	130000	38700	3400	11,6
-15 µm	625	70500	14200	2840	43,1
Oxidized RC	127	146000	28100	1300	66,5
Oxidized SC	145	263000	11600	1020	32,0
Tails	79	39300	1950	532	308
CSC	600	-	1500	1000	486,80

According to the modal mineralogy main mineral of the sample is quartz (76.6 wt%), with low amounts of K-feldspar (5.3 wt%) and muscovite (4.7 wt%). Accessory minerals are franklinite – Mn magnetite with possible content of Zn (6.8 wt%) and iron oxide – goethite-hematite (3.9 wt %). The only Zn containing minerals are Zn-franklinite (specially separated from franklinite mass) and Zn-chromite. Remarkable that some franklinite contains Ca and sometimes Si.

Table 6.13 Modal mineralogy

Mineral	Wt%	Particle Count
Quartz	76,58	107818
Albite	0,06	399
Bytownite silic	0,01	45
K_feldspar	5,27	8914
Muscovite	4,66	7404
Illite	0,06	268
Phlogopite silic	0,22	2127
Chamosite silic	0,01	196
Cummingtonite silic	0,02	519
Tschermakite silic	0,03	507
Zircon silic	0,02	94
Calcite	0,00	44
Ankerite dolomite	0,08	228
Apatite	0,05	498
Monazite REE	0,01	137
Goyazite	0,00	122
Zn_Franklinite	0,14	541
Zn_chromite	0,02	180
Cr_Magnetite	0,02	329
HighCa_Franklinite	6,83	2966
Fe_Oxide	3,91	5873
FeOx_Mus_alteration	0,62	5563
Rutile	0,20	1863
Barite	0,47	952
Pyrite	0,08	301
FeSulf_alteration	0,53	3931
Unclassified	0,08	1418
Total	100,0	136988

Table 6.14 Zn bearing minerals association.



	Zn-Chromite	Zn-Franklinite
🟪 Liberated	27,0	33,5
🟩 FeSulf-alteration	15,8	11,6
🟩 Barite	0,9	0,0
🟪 FeOx-Mus-alteration	2,1	1,5
🟪 Fe-Oxide	13,3	20,7
🟪 High-Ca-Franklinite	23,5	12,4
🟥 Zn-Franklinite	6,7	1,8
⬜ K-feldspar	0,0	0,8
⬛ Quartz	9,8	17,1
⬜ Others	0,8	0,6

According to cumulative liberation graph (Figure 6.13) the P80 of Zn-chromite is in 0-5wt% segment and of Zn-franklinite is in 15-20 wt%. It means that there is valuable portion of the minerals, which are locked almost totally inside other phases. Grain size distribution, shown in Figure 6.14, clearly pointing that Zn bearing minerals are small – 80 wt% of Zn-chromite is below 30µm and of Zn-franklinite is less than 60µm.

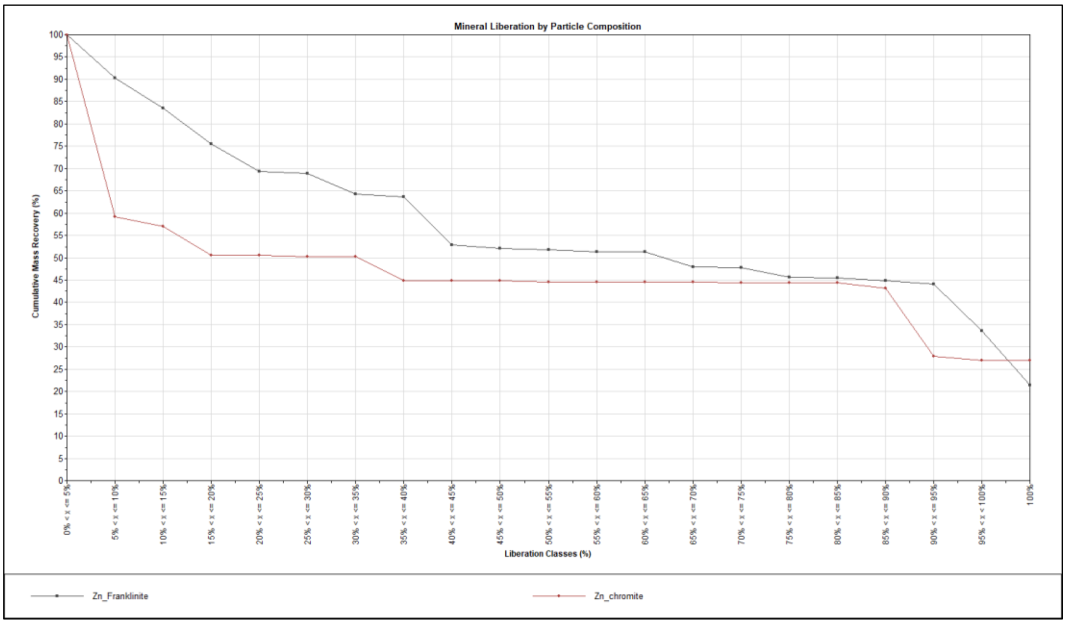


Figure 6.13 Cumulative liberation diagram.

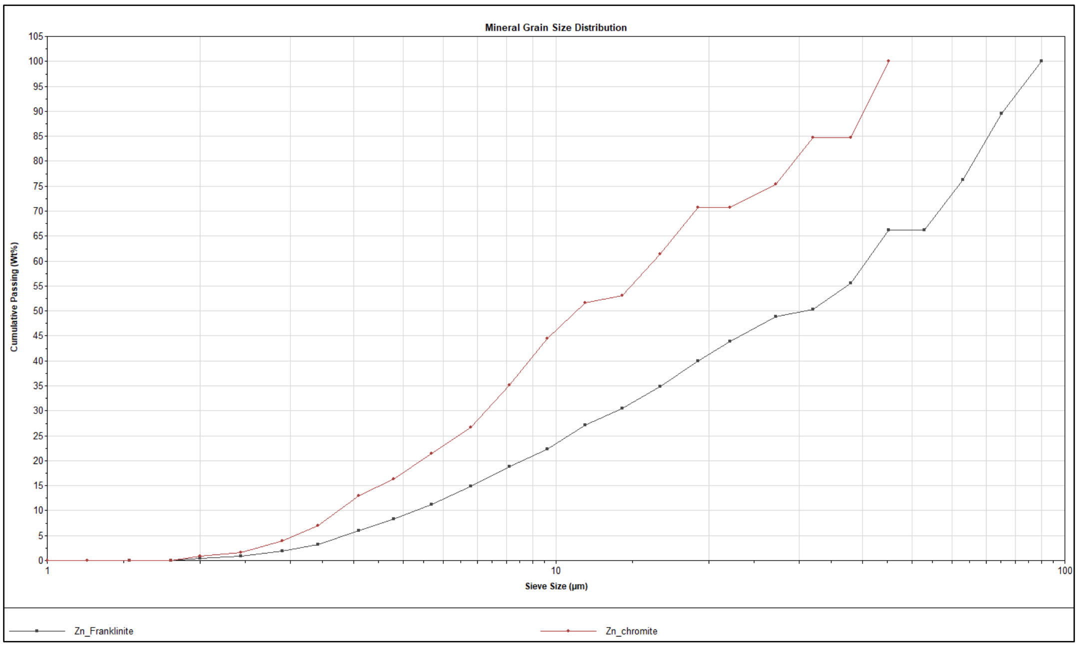


Figure 6.14 Cumulative grain size distribution diagram.

- ICP-MS analysis

Analyses carried out using ICP-MS revealed interesting data on some of the contents of elements in the rare earth group and other elements of economic value. The minor concentrations indicated in the table 6.16 and their representation in the histogram in the figure 6.15 show the distribution of the metallic units contained in the feed. The contents show a tendency to increase in scavenger. It can also be seen that the richest particle size fraction is the -15µm. Some elements such as Titanium, Lanthanum, Cerium and Neodymium have economically interesting sulphide and oxide scavenger contents.

Table 6.15 ICP-MS ANALYSIS: SDBF_7 Rare earths and other elements of economic value.

ID_sample	**Li**	**Mg**	**Sc**	**Ti**	**Sr**	**Y**	**Sn**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Ta**
	mg/kg														
Zn Sulphide rougher	57	1780	3,5	679	67,6	28,6	25.6	65,5	118	13,8	53,8	12,6	4,51	12,3	0,28
Zn Sulphide Scavenger	98	3500	7	**1240**	136	57,5	6.72	**117**	**207**	24,1	**93,3**	21,6	7,74	21	0,25
<15µm	100	3840	8,8	1520	119	69,2	4.62	97,6	172	20	77,3	17,7	6,35	17,1	0,43
Zn Oxide rougher	35	6480	8,2	1340	126	50,7	<2	65,2	126	14,9	57,3	13,5	4,78	13,1	<0,2
Zn Oxide Scavenger	38	9540	4,9	506	63,8	22,8	<2	**75,1**	**143**	17,1	**66,8**	16,3	5,74	16,2	<0,2
Tails	74	2170	3	762	85,3	23,2	<2	43,6	78,2	8,85	34,4	7,42	2,64	6,86	<0,2

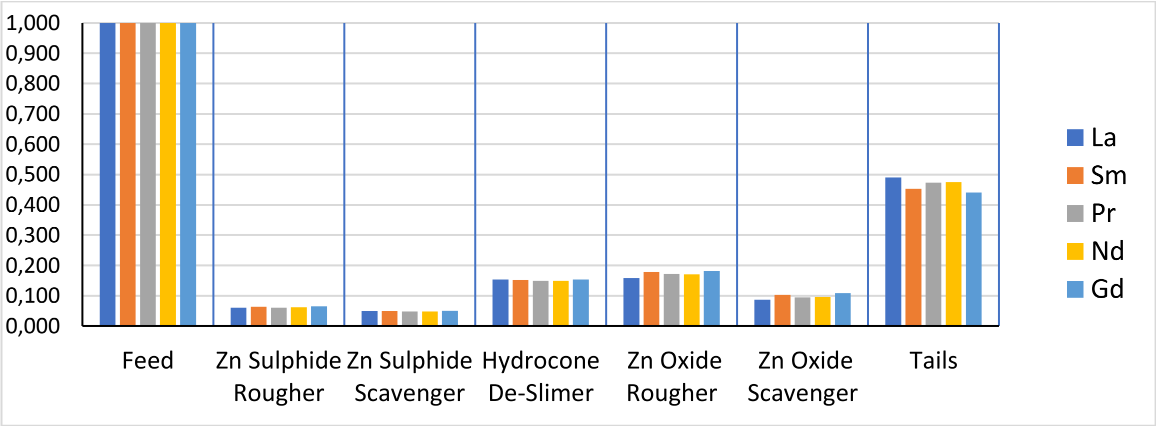


Figure 6.15 Distribution of metal units contained in the UM feed [mg].

6.5 Discussion

Many observations were made.

- From the results of the mineralogical analyses, given the proximity of the values obtained, it was possible to give value to the quality of the methodologies used.

- Based on the analyses carried out in Italy, the first flotation tests were carried out on the SDBF_7 sample from the Montevecchio mine at the GTK laboratories in Finland. The aim was to compare the starting data and find new procedures for the recovery of useful species.

- Thanks to the use of the methodologies provided, such as XMOD and XBSE of the Mineral Liberation Analyzer device, it was possible to quantify the distribution of zinc linked to the various mineralogical formations. The data obtained through MLA also confirmed the values of the granulometric analyses carried out in our laboratories.

- During the flotation tests several collectors were used for the oxidized circuit. The results showed no obvious improvements. The Aeroamine 3000 was the collector that gave Zn levels closer to the predetermined result for the same dosage.

- As far as the sulphur circuit is concerned, the best results were those of tests 5 and 9 which reached higher values than those obtained in Cagliari.

- The analysis carried out at the ICP-MS shows an enrichment of the content of some elements of strong economic interest. These data deserve an in-depth analysis of the mass icp present in our department.

Comment and conclusion

The condition of the tailings from the Montevecchio mine does not compromise their reprocessing. The waste has a high floatability even in cases of complex mineral composition. The methods used are the same as those adopted for primary ore, not only for pH adjustment and reagent dosage, but also for the number of cleanings, scavengers and recirculation of the mixed waste. This evidence suggests its use as a reclamation technique for the same type of materials in which Zn and associated metals are the sources of pollution.

The results show that although starting with zinc contents of less than 2%, concentrates with contents of ranging from 15% to 26% and 50% have been obtained (after the inclusion of several phases of cleaning of the float). In addition, recovery values of up to 70% or more have been recorded for the blended flotation concentrate. Differences in feed content produce different weight yields but do not affect metal recoveries [80]. What affects the feasibility of treatment is therefore not the low content, which in any case makes the material characterisation phase difficult, but other characteristics. The choice of collector or even the inclusion of several stages of cleaning and scavengers of the material characterise the feasibility of the process.

The flotation of oxidised minerals, which are widely present in the Montevecchio and Ingurtosu areas, such as calamine and smithsonite, shows better recovery at basic pH (10-11) using different types of collectors from xanthates to amines, with recovery rates of between 30 and 40% [59]. The rise of smithsonite can also be enhanced during the process by the combination of sodium sulphide Na_2S and the Pb^{2+} ion. These, through chemical processes, such as the formation of PbS galena involving the mineral lattice, enable the mineral to float [89]. The concentration targets in the final waste were achieved in the tests carried out at the DICAAR department where the inclusion of two roughing stages and three or more scavenger stages was necessary. The reagents tested in the GTK laboratories, Armac C, Armac T, Aeroamine 3030 as collectors in the roughing and scavenger phases did not contribute to the attainment of the content objectives despite the fact that the number of scavenger phases was increased up to seven times; on the other hand, the use of Aeromine 3000 achieved a content in the final waste close to the legal limits.

Another aspect that alters the flotation mechanism is the grain size of the material. The release of galena, sphalerite and smithsonite occurs with a particle size varying between 30-40 µm and 160 µm. [84]. From the analysis of the particle size curves, it is possible to determine the degree of assortment. Mine waste has classes ranging from a coarse grain size characteristic of gravel to a very fine grain size such as silt. The materials from the Montevecchio Ponente and Levante areas show a difference in grain size despite the fact that AF51_5B and SDBF_7 both originate from areas of fine gravel. The d80% of SDBF_7 tends more towards 1 showing a greater uniformity. This is because the flotation residues were mainly disposed of in the Levante sedimentation basin, which currently contains about 4.3 million cubic metres of sludge. In the Ponente settling basin, the Laveria Sanna, the material is not homogeneous and presents poor management of processing waste.

The results of SDBF_7 are in agreement with the literature data on the mineralisations present in the Montevecchio seams, those of Zn sulphide prevailing over Pb sulphide; in addition, smaller proportions of oxidised forms of Zn and Pb (calamine or hemimorphite, $Zn_4[(OH)_2Si_2O_7]\ldots H_2O$; PbO) and carbonate (smithsonite, $ZnCO_3$; Cerussite $PbCO_3$) are found. In the samples examined, the carbonates have three distinct compositions: siderite, Zn-rich carbonate and calcite.
Mineralogical analysis of MLA release was performed on a small part of the sample representing the feed of the flotation procedure. The results of the analysis showed an affinity with the data obtained in Italy from a different mineralogical characterisation procedure. Undoubtedly, the MLA analysis provided more specific information and, above all, provided QUANTITATIVE data on the mineralogical composition. The distribution of sphalerite highlighted by the MLA analysis, in apparent contrast to the sequential extraction analysis of Zn, is explained by the presence of Zn as a sulphide (sphalerite) in fractions >250µm, and as an oxidate and carbonate in fractions <250µm. The analysis revealed the presence of a zinc-iron-carbonate mineral called Zincian siderite ($(Zn,Fe)CO_3$). This mineral was studied with Renishaw's InVia Contor Raman microscope. Recent studies confirm the presence of abundant Zincian siderite in Sardinia [2]*:" Siderite contains variable amounts of Mg, Mn and Zn. Zinc carbonates range between end member smithsonite and, most frequently, intermediate compositions with siderite. The latter are recorded in the S. Antonio vein system, at Sanna and Casargiu-Brassey, and correspond to the different growth zones in the ore-stage Zn carbonates*

predating quartz and sphalerite crystallization”..”The computation of CO2 highlighted a tendency to a total oxide sum substantially less than 100 wt% (Table 5g ESM). Such imbalance is affecting carbonate compositions with a combination of high Zn and Mn contents and is maximum (up to 8.9 wt%) in Zn-rich carbonates.”

Sequential Extraction performed on samples AF 51-5B and SDBF-7 showed that most of the total Zn and Pb content is present in carbonate form, bound to oxidisable forms such as sulphide. The ES shows that a large proportion of the Zn is related to silicate forms that were not detected by the MLA. From both analyses, the sum of the Zn contents of oxidised carbonates and hydroxides from SDBF-07 was calculated, both of which repeat and confirm that 25.5 % of the Zn content is transported in these forms.

In terms of content in the final waste, the studies collected in this thesis show that it is possible, through specific measures, to obtain a final product with concentrations of the analytes Sb, As, Cd, Pb, as CZn < CSCZn, industrial sites. The data obtained so far have shown the feasibility for residues from Montevecchio Ponente DM_051 and DM_091 (galena and sphalerite) and a sample from Montevecchio Levante SDBF_7 rich in Zn (sphalerite recovery). In the meantime, the investigations on AF51_5B, which shows significant concentrations of both Zn and especially Pb, are proceeding at the laboratories of the DICAAR department and new samples are to be tested.
As explained in more detail in the work reported, achieving the concentration goals required the introduction of targeted strategies, and in particular various types of particle, size cuts were tested upstream of the plant on the Tal Quale feed or on the feed of the "oxidised circuit" through hydrocyclones, the reprocessing of the flotation concentrates in the "sulphide circuit", and the increase in the scavengers of the "oxidised circuit": Solid particles of larger particle size are better suited to the flotation procedure, which is also demonstrated by the zinc content values in the waste which are very close to the CSC limit. For the finer particles, the waste must be exhausted in order to have waste that meets the requirements defined by the 152/2006 regulations for industrial sites.

The flowsheet reconstruction of the circuit evolution demonstrates how the complexity of the plant can vary depending on the different material composition. The introduction of cleaning phases of the flotation concentrate in the sulphide section, a de-sliming with a hydrocyclone, having d50 of 3 µm and different scavenger procedures of the oxidised waste have been investigated and led to the development of a strategic proposal. The hypothesis of the effect determined by mixed waste recirculation in the mass balance is very interesting, in particular, the mixed waste produced during the entire process phase affects all sections of the plant. Finding the most convenient solution between freeing the circuit from constant leakage of material while maintaining a product content and at the same time eliminating the production of waste to be inerted will be the subject of future tests.

Loss on ignition analysis and Au and Ag determination carried out on sample SDBF-07, in GTK's laboratories, demonstrated the presence of particularly interesting levels if compared to the amount of mining waste present in the Montevecchio Levante areas. The liberated native coarse gold particles could be recovered by gravity separation. After the crushing and grinding the ore is fed, for example to spirals, to produce rougher concentrate and then the rougher concentrate could be cleaned for instance with the shaking table. Also, the ground ore could be fed straight to the Knelson concentrator which is a gravity concentrator based on centrifugation. GTK has centrifugal gravity separators, a 3" and a 4" Knelson Concentrators that are modified for pre-concentration of heavy ores of varying densities and sizes. Besides, it is also often used the combination of gravity separation and flotation to improve the overall recoveries. Concentration can be further processed by manually using nuggets and/or heavy liquids to increase the volume of gold nuggets or indicator minerals relative to the tailings. Thus, it is easier to collect mineral particles for mineralogical analysis. The collection is usually carried out using the stereomicroscope. Anyhow, the suitable process combination should always be designed for the specific ore.

Rare Earths, which represent elements of the Earth's crust that are difficult to extract, are a topic that can hardly be ruled out by looking at data from ICP-MS analyses.
The interest arising from the observation of the data obtained through the MLA-EPMA survey is justified by the consequent reflection on the abundance of mining waste in Sardinia. Looking at this waste with fresh eyes, encouraged by recent global legislation aimed at sustainable waste management and conservation of raw materials, we could investigate further the procedures that lead to a concentration of rare earth in the various flotation products and consider their contained value.

The results obtained so far appear to be important both in terms of technological feasibility and in terms of costs compared to Permanent Safety. Flotation is a good compromise between time and costs compared to phytoremediation methods (which are longer) and biodepuration (which are expensive); in the light of this information, further research will include the transition from laboratory-scale to industrial-scale tests for a more complete framework; in this regard, it should be noted that there is already a plant that could amortize the costs of the pilot plant whose construction is planned by Cesa.

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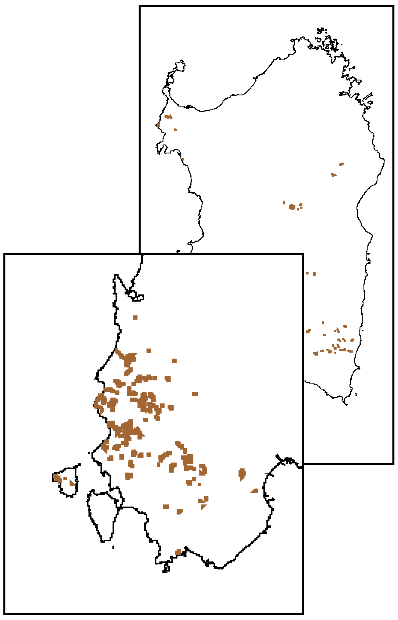
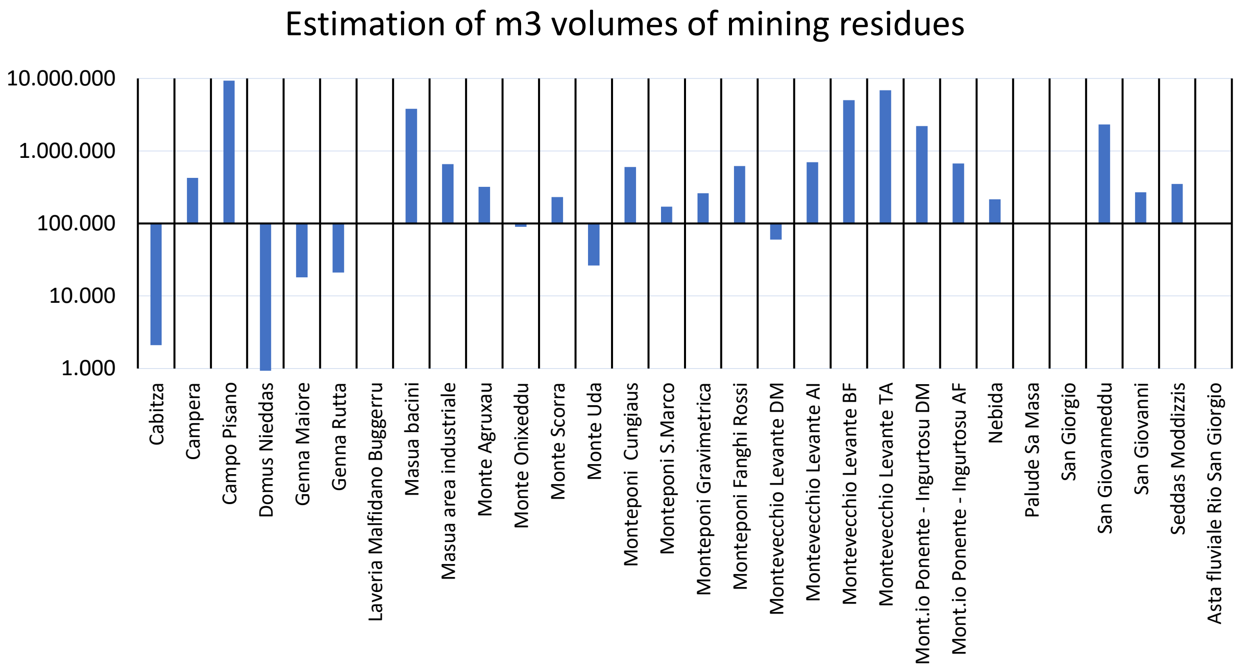
Appendix 1

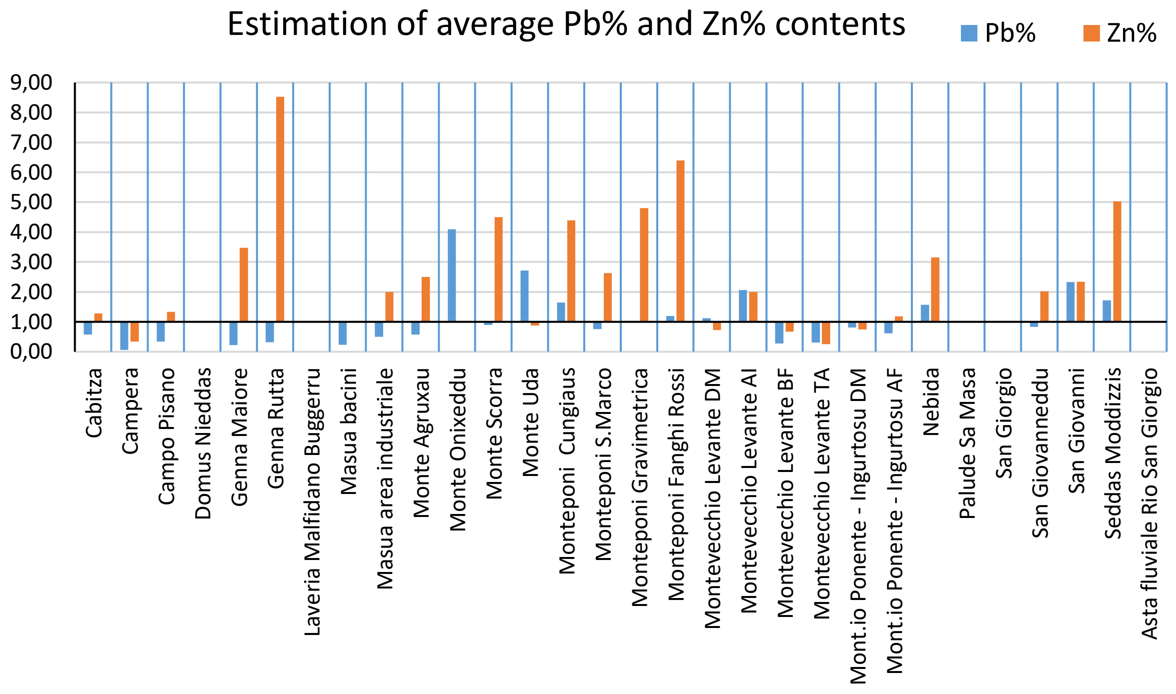
Sites of greatest interest for volume and residual content



N.	Sito	volumi, m^3	Sub-aree	volumi, m^3	Pb%	Zn%
1	Cabitza	2,100		2,100	0.58	1.28
2	Campera	424,000		424,000	0.06	0.34
3	Campo Pisano	9,340,000		9,340,000	0.34	1.33
4	Domus Nieddas	0		0		
5	Genna Maiore	18,000		18,000	0.22	3.47
6	Genna Rutta	21,000		21,000	0.32	8.53
7	Laveria Malfidano Buggerru	0		0		
8	Masua bacini	4,460,000	bacini	3,800,000	0.23	0.98
	Masua area industriale		area industriale	660,000	0.50	2.00
9	Monte Agruxau	320,000		320,000	0.58	2.50
10	Monte Onixeddu	90,000		90,000	4.10	0.98
11	Monte Scorra	231,000		231,000	0.90	4.50
12	Monte Uda	26,300		26,300	2.71	0.87
13	Monteponi Cungiaus	1,650,000	Cungiaus	600,000	1.64	4.40
	Monteponi S.Marco		S. Marco	170,000	0.76	2.63
	Monteponi Gravimetrica		Gravimetria	260,000	1.00	4.80
	Monteponi Fanghi Rossi		Fanghi rossi	620,000	1.20	6.40
14	Montevecchio Levante DM	12,660,000	discariche	60,000	1.12	0.73
	Montevecchio Levante AI		area industriale	700,000	2.06	2.00
	Montevecchio Levante BF		bacino	5,000,000	0.28	0.67
	Montevecchio Levante TA		tailings	6,900,000	0.31	0.25
15	Mont.io Ponente - Ingurtosu DM	2,870,000	discariche	2,200,000	0.81	0.75
	Mont.io Ponente - Ingurtosu AF		Abbancamenti Fini	670,000	0.62	1.19
16	Nebida	215,000		215,000	1.57	3.15
17	Palude Sa Masa			0		
18	San Giorgio			0		
19	San Giovanneddu	2,320,000		2,320,000	0.83	2.02
20	San Giovanni	270,000		270,000	2.33	2.34
21	Seddas Moddizzis	350,000		350,000	1.72	5.03
22	Asta fluviale Rio San Giorgio			0		
TOTALE m^3 =		35,267,400				
TOTALE t =		56,427,840				

Spatial distribution of residues and variability of residual concentrations.





Appendix 2

The following tables show the readings by ICP-OES, of the concentrations of heavy metals in solution, present in the samples produced during the separation procedures.

ICP-OES 1 Test 1-2

Id_sample	**Cr**	**Fe**	**Co**	**Ni**	**Zn**	**As**	**Pb**	**Cd**	**Ag**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB1	51	0	2739	382666	-DL	2909	307	-DL	69740
FB2	56	0	2775	259651	-DL	1726	496	-DL	113374
SV1	94	0	2175	130969	-DL	961	921	-DL	194225
SV2	128	0	3033	41304	-DL	325	1121	-DL	215528
T1	28	42	686	9237	-DL	32	66	-DL	81382
OS2	56	0	4058	22913	-DL	184	310	-DL	77143
FA2	48	0	1550	27052	-DL	59	193	-DL	104970
TA2	10	16	330	4048	-DL	8	24	-DL	66112
CSC	**800**	**-**	**250**	**500**	**1500**	**50**	**1000**	**15**	**-**

FB1= floated blenda 1

FB2= floated blenda 2

SV1= scavenger 1

SV2= scavenger 2

T1= Tail 1

OS2= over de-sliming 2

FA2= floated amina 2

TA2= tail amine 2

ICP-OES 2 Test B2

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Cd**	**Ag**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	105608	2097,7	243285	392,5	3476,6	2061,8	10,4
SV	179053	1409,4	53419	794,9	1858,3	494,0	6,4
OS	78968	1047,587	26635	412,08	4673,77	265,05	3,52
FF1	81029	198,198	19921	73,76	1907,72	79,06	0,17
FF2	61701	122,9374	10189	35,96	1213,10	47,32	-0,04
T	73453	54,65176	5437	-DL	453,29	23,38	-0,74
CSC	**-**	**600**	**1500**	**50**	**1000**	**15**	**-**

FB= floated blenda

SV= scavenger

OS= over de-sliming

FF1= floated flotigam 1

FF2= floated flotigam 2

T= Tail

ICP-OES 3 Test 3

Id_sample	**Cr**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +250	45,81	52726	15,74	23,96	121,10	14764	73,53	888	1,85	115,24
FB	90,57	98270	73,25	83,92	2745,38	211429	381,40	5174	25,10	1647,04
SV	116,08	115392	51,88	102,92	1299,21	20075	553,97	2695	5,91	252,69
FA	69,40	67184	33,68	47,51	103,87	14698	112,19	726	0,81	53,63
OS	78,63	64644	21,86	40,14	474,39	10584	122,96	1545	1,28	102,13
T	28,42	38682	7,17	10,98	26,90	1604	12,33	221	-DL	15,16
CSC	**800**	**-**	**250**	**500**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

FA= floated amine

OS= over de-sliming

T= Tail

ICP-OES 4 test 4

Id_sample	**Cr**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed -250	46,91	107565	25,75	36,30	211,52	29755	134,13	1255	2,73	228
FB	74,39	140208	81,01	74,71	2345,55	265079	575,99	2600	19,20	1917
SV	113,24	253038	62,34	133,27	1686,05	34057	1112,51	2363	13,03	375
FA	63,62	127590	42,50	61,94	212,43	29528	156,70	1932	1,23	101
OS	103,14	98891	55,41	62,88	835,34	27195	314,13	4148	3,27	241
T	31,97	98502	13,89	18,73	70,83	5385	32,84	671	0,03	36
CSC	**800**	**-**	**250**	**500**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

FA= floated amine

OS= over de-sliming

T= Tail

ICP-OES 5 Test 5a

Id_sample	**Cr**	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +150	50,5	65810	152,7	19541	71,2	841	2,43	134
FB	84,9	112485	1432,5	130411	279,9	3073	16,87	1005
SV	111,0	128543	975,4	24237	506,8	2421	9,92	235
FA	60,6	80863	95,6	15801	63,6	693	0,90	42
OS	69,7	62891	275,5	7193	78,1	995	0,97	56
T	28,9	58763	34,4	1827	9,3	248	0,09	12
CSC	**800**	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda
SV= scavenger
FA= floated amine
OS= over de-sliming
T= Tail

ICP-OES 6 test 6a

Id_sample	**Cr**	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed -150	126	153979	1739	142877	726	3272	19,0	1214
FB	71	363204	987	31259	1596	1292	16,9	265
SV	72	107465	194	35844	209	3921	3,3	109
FA	93	105376	441	20342	288	3381	58,9	149
OS	36	107387	94	8666	54	897	0,2	36
T	29	58763	34	1827	9	248	0,1	12
CSC	**800**	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

FA= floated amine

OS= over de-sliming

T= Tail

ICP-OES 7 test 5b

Id_sample	**Cr**	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +150	N.D.	4,97	N.D.	1,89	N.D.	0,07	N.D.	N.D.
FB	96,6	106971,3	1601,7	154857,9	226,5	3268,0	18,1	1098,4
SV	92,2	167098,6	1238,2	22703,5	627,5	1100,6	6,5	188,6
FA	78,7	102491,4	171,0	14014,9	52,7	634,2	0,5	43,3
OS	353,4	51642,4	532,2	6597,8	86,9	1361,5	1,3	47,3
T	29,6	49459,6	47,1	1885,1	2,8	266,0	-DL	10,9
CSC	**800**	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

FA= floated amine

OS= over de-sliming

T= Tail

ICP-OES 8 test 6b

Id_sample	**Cr**	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed -150	N.D.	10,67	N.D.	2,70	N.D.	0,17	N.D.	N.D.
FB	129	133267	1898	189653	625	3190	19	1446
SV	86	282269	1160	30935	1073	980	9	313
FA	75	119055	205	38078	235	2777	3	126
OS	401	93869	1016	22357	386	5662	4	184
T	38	108377	102	8909	37	1046	0	35
CSC	**800**	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda
SV= scavenger
FA= floated amine
OS= over de-sliming
T= Tail

ICP-OES 9 test 7

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	787,0	27,8	2022,8	4,0	52,3	0,1	16,1
OS	608,1	6,5	139,4	2,1	24,1	0,0	1,3
FA	1027,2	3,9	270,3	5,8	21,4	0,0	0,8
FO	2471,3	1,4	264,2	-DL	5,9	0,0	0,8
TF	92,6	0,4	7,0	0,3	1,9	0,0	0,1
FR	2720,2	1,8	105,1	-DL	8,6	0,0	0,4
TR	778,7	0,6	60,3	0,1	3,3	0,0	0,3
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

OS= over de-sliming

FA= floated amine

FO= floated oleina

TF= tail flotinor

FR= floated re-wash

TR= Tail re-wash

ICP-OES 10 test A

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +Tal Qual	74397	N.D.	20752	84	1043	2,23	154
FB	101354	2219	216095	374	3416,0	26,63	1901
SV	208517	1176	30950	1326	2202,2	8,76	347
OS	64201	N.D.	19554	272	3851,79	4,03	166
FF1	71064	N.D.	24700	92	1798,90	1,25	60
FF2	84752	N.D.	14366	64	1105,65	0,76	58
T	69781	N.D.	4703	12	492,91	0,09	21
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

OS= over de-sliming

FF1= floated flotigam 1

FF2= floated flotigam 2

T= Tail

ICP-OES 11 test B

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +Tal Qual	72871	277	16993	94	944		137
FB	93050	2416	172132	558	3130	15,5	1625
SV	169389	1136	28999	1003	2076	4,9	328
OS	58468	655	13638	237	3066	1,3	139
FA1	130729	154	21325	99	1173	-DL	72
FA2	151056	149	7950	19	1084	-DL	46
T	45869	42	1397	5,9	381	0,0	11
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

OS= over de-sliming

FA1= floated MFA-15_1

FA2= floated MFA-15_2

T= Tail

ICP-OES 12 test C

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +Tal Qual	75032	N.D.	17781	N.D.	N.D.	N.D.	N.D.
FB	95958	N.D.	196753	N.D.	N.D.	N.D.	N.D.
SV	197351	N.D.	33076	N.D.	N.D.	N.D.	N.D.
OS	65743	736	16203	253	3435	6	159
FA1	143753	218	33525	113	1519	-DL	105
TF	20124	69	1158	-DL	304	3	9
AF	288441	187	8123	-DL	1189	4	32
T	127357	97	5407	-DL	442	2	14
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda
SV= scavenger
OS= over de-sliming
FA1= floated amina
TF= tail amina
AF= acid floated
T= Tail

ICP-OES 13 Test D

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Feed +Tal Qual	71664	264	20675	N.D.	991	N.D.	153
FB	98659	2302	236537	645,6	4388	5,3	1929
SV	193647	1260	41468	847,2	2123	9,7	397
OS	61898	807	15950	223,9	3587	2,1	155
FF1	81209	173	19490	149,7	1212	0,5	60
FF2	147635	255	34520	203,5	1415	5,7	110
FF3	101245	127	15644	-DL	1015	4,9	63
FF4	108670	88	17148	-DL	799	-DL	60
T	59972	40	3239	-DL	433	-DL	18
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= floated blenda

SV= scavenger

OS= over de-sliming

FF1= floated flotigam 1

FF2= floated flotigam 2

FF3= floated flotigam 3

FF4= floated flotigam 4

T= Tail

ICP-OES 14 Test E1_E2

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
BC	159130	3161	**434121**	521	3745	36	3351
1°-2° CB	99139	1268	38943	360	4130	5,8	401
3°CB	111914	1773	74897	515	6009	7,8	676
Over	66625	774	17214	288	3439	2,9	164
1°OC	122385	234	37031	358	2709	1,7	111
1°-2°CB_1°OC	64981	162	7565	60	999	-DL	46
3°CB_OC	55697	132	10430	58	920	-DL	51
2°OC	155945	183	38515	212	1459	-DL	97
1°-2°CB_2°OC	76729	116	6394	45	789	-DL	35
T1	65595	52	2752	5,6	433	-DL	17
T2	72486	56	3214	21	474	-DL	18
FA_E1	144073	143,4	11742	8,6	959	24,45	49,3
FF+Ol_E1	225157	85,5	5180	-DL	876,2	1,27	31,2
FT_E1	53610	50,5	**1777**	-DL	313	0,3	12
FA+F_E1	136792	130,3	12057	58,7	877,1	2,33	46,5
FT_E2	52066	41,2	**1679**	-DL	317,8	0,52	11,1
CSC	**-**	**600**	**1500**	**50**	**1000**	-	**15**

BC=Blend Concentrate

1°-2° CB=1°-2° sulphur cell bottom

3°CB= 3° sulphide cell bottom

O= Over

1°OC= 1°oxidized concentrate

1°-2°CB_1°OC= 1°-2°cell bottom of 1° oxidized concentrate

3°CB_OC= 3° cell floor of 1° oxidized concentrate

2°OC= 2° oxidized concentrate

1°-2°CB_2°OC= 1°-2°cell bottom of 2° oxidized concentrate

T1=Tail 1

T2=Tail 2

FA_E1=Floated amine test E1

FF+Ol_E1= Floated flotinor + olein E1 test

FT_E1= Final tail test E1

FA+F_E1= Floated amina+ flotinor_test E2

FT_E2=Final tail test E2

ICP-OES 15 Test F

Id_sample	**Fe**	**Cu**	**Zn**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	110295	2708	**275470**	3574	30,5	2371
SV	143191	1249	28786	2875	7,7	303
O	58947	605	12039	2357	2,3	120
1° F_MFA	127384	195	**29808**	1278	1,2	87
2° F_MFA	165660	138	20133	774	-DL	75
1° FF=	199354	103	5418	720	-DL	33
T	41971	40	1619	474	-DL	9
2° FF	195241	170	6251	1510	-DL	50
FT	33979	32	**1334**	370	-DL	9
CSC	**-**	**600**	**1500**	**1000**	**-**	**15**

FB= Floated Blenda F
SV= Scavenger F
O= Over F
1° F_MFA= first floated MFA-15
2° F_MFA= Second Floated MFA-15 F
1° FF= first floated Flotinor F
T=tail F
2° FF= Second Floated flotinor F
FT= Final tail F

ICP-OES 16 Test G

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	183303	1966	179973	792	1519,2	18,3	1526
SV	216343	955	40333	1480	1560,1	8,2	447
O	90711	613	24888	441	5019,6	3,5	237
UC	106296	171	15369	181	1448,0	-DL	82
1° F_MFA	137591	176	41243	468	3199,7	2,1	140
2° F_MFA	156349	144	39294	335	2151,4	0,0	128
FT	28462	50	1634	237	551	-DL	12
FA	341226	208	11915	248	5182	-DL	51
AT	159275	97	10582	101	861	-DL	32
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**

FB= Floated Blenda G

SV= Scavenger G

O = Over cyclon G

UC= Under cyclon G

1° F_MFA= first floated MFA-15 G

2° F_MFA= second floated MFA-15 G

FT= Final tail G

FA= acid floated G

AT= acid tail G

ICP-OES 17 Test H1-H2

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**	***Sb***
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	***mg/kg***
Zn_C	86601	3768	**513590**	312	3845	5,71	3936	N.D.
SV	151568	1215	33625	553	2211	12,51	353	N.D.
1°- CB_S	96960	1240	26005	301	3282	6,67	283	N.D.
2°- CB_S	139594	192	17958	121	1094	1,58	87	N.D.
O_H1	69474	797	17224	250	3222	5,11	160	N.D.
O_H2	51180	847	17078	287	3522	N.D.	155	66
OC	192451	205	**46624**	336	1537	3,70	123	N.D.
1° CB_ox	49342	117	3917	37	700	1,12	32	N.D.
2° CB_ox	139625	192	17965	121	1094	1,58	87	N.D.
3° CB_ox	143393	271	28845	120	1624	2,19	148	N.D.
FF_H1-H2	192001	106	8359,3	-19	1001	-DL	48	N.D.
FA_H1	89439	123	12546	61	884	1,48	51	N.D.
FF_H1	146561	111	6105	1,87	1048	0,66	37	N.D.
FA_H2	104438	99	11050	42	873	1,42	43	N.D.
FF_H2	116490	71	3883	5,4	744	0,27	26	N.D.
T_H1	53372	31	**1916**	10	347	0,54	11	N.D.
T_H2	47819	37	**1857**	14	362	0,35	12	N.D.
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**	**30**

Zn_C= zinc concentrate ZnS test H

SV= Scavenger test H

1° CB_S= first solphur cell bottom test H

2° CB_S= second solphur cell bottom test H

O_H1= Over cyclon H1

O_H2= Over cyclon H2

OC= oxidazed concentrate H1 – H2

1° CB_ox= first oxidazed cell bottom test H1-H2

2° CB_ox= first oxidazed cell bottom test H1-H2

3° CB_ox= first oxidazed cell bottom test H1-H2

FF_H1-H2= Floated Flotinor H1-H2

FA_H1= Flottato ammina H'_1

FF_ H1= Flottato flotinor H'_1

FA_H2= Flottato ammina H"_1

FF_H2= Flottato flotinor H"_1

T_H1= Tail H1

T_H2= Tail H2

ICP-OES 18 Test H3-H4

Id_sample	**Fe**	**Cu**	**Zn**	**As**	**Pb**	**Ag**	**Cd**	**Sb**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
O_H3	51699	865	16916	286	3558	N.D.	164	66
O_H4	51675	867	17480	304	3597	N.D.	165	67
OC	196479	179,5	46846	205	1965	4,6	113	N.D.
1° CB_ox	58202	133	4737	73	1085	N.D.	37	20
2° CB_ox	82759	132	8147	83	1397	N.D.	51	22
3° CB_ox	88414	117	11518	83	1396	N.D.	58	24
FF_H3-H4	219676	84,5	6308	-DL	840	0,1	36	N.D.
T_H3	29711	32	1447	28	460	N.D.	11	9,8
T_H4	34583	33	1636	31	492	N.D.	12	9,6
CSC	**-**	**600**	**1500**	**50**	**1000**	**-**	**15**	**30**

O_H3= Over cyclon H3
O_H4= Over cyclon H4
OC= oxidazed concentrate H3 – H4
1° CB_ox= first oxidazed cell bottom test H3-H4
2° CB_ox= first oxidazed cell bottom test H3-H4
3° CB_ox= first oxidazed cell bottom test H3-H4
FF_H3-H4= Floated Flotinor H3-H4
T_H3= Tail H3
T_H4= Tail H4

Appendix 3

ICP-OES 19 Test α

Id_sample	**Fe**	**Cu**	**As**	**Zn**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
SC α1_α2_α3	85481	3565	245	**512725**	4062	8,4	4023
1° CB α1_α2_α3	98828	1228	331	40674	1838	6,6	234
2° CB α1_α2_α3	106151	1807	761	74407	2660	4,6	701
SV_α1_α2_α3	166964	1166	604	41105	1825	10,2	421
SC_α4_α5	78168	3529	72	**477419**	3806	0,0	3669
1° CB_α4_α5	87313	1013	314	32468	3399	0,0	348
2° CB_α4_α5	81431	1255	297	50381	2153	0,0	445
SV_α4_α5	144937	1363	538	64533	1718	0	587
OC_α1	65768	726	228	17415	3444	3,6	178
OC_α2	67100	711	266	17466	3491	3,6	178
OC_α3	70269	669	216	17842	3337	4,1	165
OC_α4	78301	810	271	20008	3877	0,0	191
OC_α5	102343	1227	405	27518	5349	0,0	261
U	71915	186	19	9788	1062	0,9	53
CSC	**-**	**600**	**50**	**1500**	**1000**	**-**	**15**

SC α1_α2_α3 = Sulfide Concentrate Zn - α1_α2_α3

1° CB α1_α2_α3= First sulfides cell bottom Zn - α1_α2_α3

2° CB α1_α2_α3= Second sulfides cell bottom Zn - α1_α2_α3

SV_α1_α2_α3= Scavenger sulfides Zn - α1_α2_α3

SC_α4_α5= Sulfide Concentrate Zn - α4_α5

1° CB_α4_α5= First sulfides cell bottom Zn - α4_α5

2° CB_α4_α5= Second sulfides cell bottom Zn - α4_α5

SV_α4_α5= Scavenger Solfides Zn - α4_α5

OC_α1= Over - α1

OC_α2= Over - α2

OC_α3= Over - α3

OC_α4= Over - α4

OC_α5= Over - α5

U= Under - α3

ICP-OES 20 Test β

Id_sample	**Fe**	**Cu**	**As**	**Zn**	**Pb**	**Ag**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FSV_β1	257162	128	-DL	9250	1185	0,0	48
FSV_β2	221079	104	-DL	7857	1187	0,0	43
FSV_β3	187209	104	-DL	7019	1132	0,0	40
FSV_β4	193055	109	-DL	7499	1161	0,0	43
FSV_β5	180341	121	-DL	7974	1204	0,0	44
T_β1	34609	38	-DL	1580	350	0,0	11
T_β2	39372	39	-DL	1539	362	0,0	11
T_β3	33761	40	-DL	1448	333	0,0	11
T_β4	37023	47	-DL	1594	358	0,0	12
T_β5	35947	39	-DL	1551	347	0,0	12
OC	183730	212	233	45376	1860	0,0	136
1° CB_ox	99385	259	33	17330	1468	0,0	101
2° CB_ox	127282	344	69	26134	1952	0,0	141
3° CB_ox	185148	277	83	41777	2432	0,0	164
CSC	**-**	**600**	**50**	**1500**	**1000**	**-**	**15**

FSV_β1= Flottato scavenger β1

FSV_β2= Flottato scavenger β2

FSV_β3= Flottato Scavenger β3

FSV_β4= Flottato Scavenger β4

FSV_β5= FlottatoScavenger β5

T_β1= Tail β1

T_β2= Tail β2

T_β3= Tail β3

T_β4= Tail β4

T_β5= Tail β5

OC= Oxidated concentrate Zn - β1_β2_β3_β4_β5

1° CB_ox= first oxidazed cell bottom Zn - β1_β2_β3_β4_β5

2° CB_ox= second oxidazed cell bottom Zn -β1_β2_β3_β4_β5

3° CB_ox= third oxidazed cell bottom -β1_β2_β3_β4_β5

Appendix 4

ICP-OES 21 test γ

Id_sample	**Cu**	**Ag**	**Fe**	**Zn**	**As**	**Pb**	**Cd**	**Sb**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	2627	30	126689	279167	478	3442	2185	288
SV	1417	15	236906	39333	1597	2550	395	243
O	784	4	76856	21709	323	4340	197	72
1° FA	666	7	170349	53312	540	3681	188	140
2° FA	228	0	143522	43280	151	1894	123	44
3° FA	163	0	126228	26250	75	1598	88	41
4° FA	107	0	105759	14210	46	1171	55	39
5° FA	79	0	111137	10389	59	1048	26	39
6° FA	77	0	105973	7690	58	874	38	32
7° FA	60	0	90772	5398	37	784	28	23
FT	30	0	54926	1706	27	410	12	12
CSC	**600**	**-**	**-**	**1500**	**50**	**1000**	**15**	**30**

FB= Floated Blenda
SV= Scavenger
O = Over
1° FA= first floated amina
2° FA= second floated amina
3° FA= Third floated amina
4° FA= Fourth floated amina
5° FA= fifth floated amina
6° FA= sixth floated amina
7° FA= seventh floated amina
FT= Final tail

ICP-OES 22 test δ

Id_sample	**Cu**	**Ag**	**Fe**	**Zn**	**As**	**Pb**	**Cd**	**Sb**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	2631	18	132390	307788	652	3553	2245	280
SV	1469	15	282072	52441	1202	2942	464	262
O	872	5	86002	24601	323	4290	205	68
1° FA	836	6	147575	37737	591	4945	196	127
2° FA	424	3	116524	40325	362	2898	140	47
3° FA	249	2	111193	33050	133	1872	97	26
4° FA	170	2	136747	32253	130	1597	92	31
5° FA	145	0	134364	18579	112	1291	69	30
6° FA	128	0	137608	11469	97	1147	53	21
7° FA	126	0	137230	8790	45	1078	46	5
FT	38	2	52932	**1661**	-DL	399	12	-DL
CSC	**600**	**-**	**-**	**1500**	**50**	**1000**	**15**	**30**

FB= Floated Blenda
SV= Scavenger
O = Over
1° FA= first floated amina
2° FA= second floated amina
3° FA= Third floated amina
4° FA= Fourth floated amina
5° FA= fifth floated amina
6° FA= sixth floated amina
7° FA= seventh floated amina
FT= Final tail

ICP-OES 23 Test Ω

Id_sample	**Cu**	**Ag**	**Fe**	**Zn**	**As**	**Pb**	**Cd**	**Sb**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	2867	28	126124	**310598**	450	3387	2458	282
SV	1268	9,7	169410	34643	671	2667	382	145
O	977	4,0	86064	25709	339	4588	249	73
1° FA	135	0,0	113541	21433	98	1396	73	32
2° FA	146	0,0	121351	20366	92	1202	72	30
3° FA	139	0,0	134555	12815	35	1196	60	24
FT	39	0,0	66284	**2216**	4	430	15	8
CSC	**600**	**-**	**-**	**1500**	**50**	**1000**	**15**	**30**

FB= Floated Blenda
SV= Scavenger
O= Over
1° FA= first floated amina
2° FA= second floated amina
3° FA= Third floated amina
FT= Final tail

ICP-OES 24 Test Ω1

Id_sample	**Cu**	**Ag**	**Fe**	**Zn**	**As**	**Pb**	**Cd**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
FB	2389	23	129792	**274584**	412	4033	2181
SV	1109	6	164883	36601	674	3030	397
O	826	4	80897	23473	297	4293	211
1° FA	149	0	108653	23027	106	1475	72
2° FA	117	2	132177	16535	66	1060	56
3° FA	78	2	109156	5779	15	778	29
4° FA	56	0	86239	3354	-DL	562	19
5° FA	53	2	83677	2733	5	479	16
FT	36	2	37091	**1081**	-DL	283	7
CSC	**600**	**-**	**-**	**1500**	**50**	**1000**	**15**

FB= Floated Blenda
SV= Scavenger
O= Over
1° FA= first floated amina
2° FA= second floated amina
3° FA= third floated amina
4° FA= fourth floated amina
5° FA= fifth floated amina
FT= Final tail