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# A flow-sheet approach to the issue of sulfide-rich tailings

## The beneficiation process as a key to the environmental management of copper mines

Ph.D. Thesis

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*Nothing is to be thrown away*

# Abstract

The present work is meant to evaluate the effect of separation of pyrite-rich fractions of tailings for both economic and environmental benefit. The project was focused on two tailing dumps in the former mining and processing site of Reps (Northern Albania). In-situ and laboratory investigations were conducted (i) to outline the main environmental characters of the selected dumps with an emphasis on heterogeneities within and between dumps and (ii) to evaluate the concentration potential of commodities, namely pyrite, from the waste materials. Mineralogical and geochemical data were collected and the Acid-Base account procedure was performed in order to evaluate the Acid Drainage (AD) potential of the selected tailing dumps. A quantitative flowsheet was devised in order to relate quantitatively the available information on processing and the collected data. Gravity separation tests were performed by a water shaking table method and the re-processing potential was evaluated through mineralogical and geochemical analyses.

The site is subject to long-lasting ($10^3$ years) AD processes with significant release of Potentially Toxic Elements into the local environment. Two different classes of tailings have been recognized, based on the sulfide S content. The high- sulfide (S>10%) content material (hS) accounts for about 82% of the total potential $H_2SO_4$ production, despite it represents less than 20% of the whole tailing discard. On the contrary, the remnant low- sulfide (S<3%) content material (lS) is the most abundant fraction, yet responsible of a much lower environmental footprint. The two types of tailings are interpreted as by-products of two different mineral processing chains. A single-stage flotation stream yielded to discard lS+hS tailings. On the other hand, a double-stage flotation chain, when active, included a secondary flotation of the tailings produced by the primary Cu flotation. The latter flowsheet yielded to obtain a pyrite concentrate and to discard lS materials. The S content of tailings was thus reduced by over 50%. Re-processing via gravity concentration is an effective method for pyrite recovery from tailings. Tabling tests recovered 29 to 52% of the total sulfide S of the R2 dump, the hS material reworking being the most cost-effective procedure. The final concentrate may also become a sealable product and the gold content may increase the value of pyritic concentrates, given a measured selection of the separation input and parameters. Separation can therefore be used to both confer value to wastes and create smaller sulfide-rich dumps, with lower reclamation costs.

# Summary

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CHAPTER 3

## CHAPTER 1

# Introduction

## 1.1 Aims and novelties

The aim of this work is to provide a contribution to the characterization and management of tailing dumps. In particular, the overall study is meant to evaluate the separation of pyrite-rich fractions of tailings with either economic or environmental purposes. The project was focused on former mining districts of Northern Albania, where few mining activities are currently operative. This choice is motivated by the socio-political and economical transition that Albania is going through.

The study takes shape from an overview of six dump sites, conducted in order to select target sites and materials. Among others, a tailing dump site of the Mirdita District was selected. In-situ and laboratory investigations were thus conducted with the following objectives:

- To outline the main characters of the selected dumps, including the estimation of volumes and evaluation of the actual environmental hazard.
- To provide a viable method for reprocessing tailing.
- To evaluate the concentration potential of commodities, namely pyrite and Au from the waste materials, by applying a mechanical separation method.

The analytical approach takes into consideration: (i) the existing heterogeneities of tailing dumps as a key for effective reclamation; (ii) the former processing flowsheet as a tool for a good characterization of the tailing materials; (iii) the separation method as a good opportunity for dealing with large volumes of potentially hazardous tailings.

The overall study deals with a major issue of waste reclamation: the heterogeneity of the discarded materials. When former processing data are available, the reconstruction of a *quantitative flow-sheet* can provide a useful insight for remediation planning. In fact, such a quantitative approach constitutes the basis of a rationale separation of tailings that can lead either to a more effective management or to recycling.

## 1.2 Mining impact and regulation: the Albanian case

Mining operations always imply some impact on environment, population and economics of the region where they take place. The effects can be long-lasting and manifold. Among the significant concerns are accidents involving workers, waste accumulation, water and energy consumption, acoustic disturbance. Gas (i.e. $SO_2$ and $NO_x$) and dust release cause atmospheric pollution and elevated concentrations of various contaminants can accumulate in soils and water systems, thus causing severe threats to land use and biodiversity. After closure, despite a reduction of air emission, resources consumption and noise, significant issues need to be coped with, mainly concerning landscape and environmental impact. One main matter of concern is the considerable volumes of mining wastes that are often left behind. These in fact are likely to interact with the environmental matrixes, leading to lasting environmental and socio-economic consequences.

Across centuries, absent or inadequate closure practices have been leaving potentially hazardous sites all around the world. Therefore, most developed countries established regulatory guidelines for monitoring mining activities, for closing procedures and for management of closed sites. New scientific knowledge and the occurrence of accidents lead to continuous implementation of regulations. In the last fifty years and especially from the Nineties forward there has been an increasing social demand on environmental aims and on sustainable approaches to the mining sector, also in developing countries. The idea behind is that the economic and social benefits of mineral resources exploitation can be maximized by applying preventive policies based on planning and responsible practices (Azapagic, 2004; ENVSEC, 2005; Driussi and Janz, 2006; Verburg et al., 2009; Mc Mahon, 2010; Vierendeels, 2011).

### *Mining and environmental regulation in Albania*

The mineral extraction industry has played a key role in Albanian history and economy up to the early Nineties. The 45 years-long communist regime led to inappropriate investments and inefficient approaches to production, other than social and economic serious consequences. Moreover, most mining and industrial activities took place without proper planning. Yet, Albania is well-endowed in natural resources such as chromite, nickeliferous iron ore, bitumen, olivine, natural gas, lignite and crude oil (Tab. 1) and used to be a major exporter of some raw and semi-finished materials (ENVSEC, 2009; Demi, 2010; USGS, 2015). For instance, before 1990 Albania was the world's third largest producer of chrome ore (ENVSEC, 2009). After the economic collapse of the Nineties, most mining activities were suddenly abandoned without undergoing proper closing, nor post-closure procedures. Therefore, many of the former mining and processing sites constitute a matter of concern for their potential hazard. Albania signed the Stabilization and Association Agreement with the EU in 2006 and presented its application for membership in 2009. By June 2014 the Country achieved the candidate status. Albania is monitored for specific parameters, including political and economic criteria and the ability to take on the common rights and obligations (SWD, 2014). The basis for the accession process is in fact adopting the community *acquis*, that include issues such as movement of capital, transport policy, environment and many others. Therefore, in the last ten years, the Albanian scientific community and authorities developed a growing interest towards methods and rules for dealing with the environmental issues, in order to align to the European standards. As a matter of facts, the major regulations governing the Albanian mining sector date after 2010 (ICLG, 2015). In particular, the 304/2010 law regulates the provisions needed for the closure of mines, including rehabilitation plans to be submitted in order to obtain a mining permit. On the other hand, the 2014 Progress Report of the European Commission (SWD, 2014) claims that further work is needed to meet the EU criteria, focusing in particular on the Environmental Impact Assessment. The mining waste management in Albania is mainly directed on cleanup and remediation at specific "hot spots", but there is no complete data available on the actual situation. In general, the waste management suffers for practical lacks in monitoring and inspection and a weak central coordination (UNECE, 2012). The quite recent mining policy update (ICLG, 2015) suggests that the government considers the mineral asset as an opportunity to promote development. At the present time few active sites operate and faint attempts have been lately made in order to revitalize the national mine industry. Yet, Albania is rich of unexploited metal-bearing and industrial mineral resources, (ENVSEC, 2009). Therefore, a good opportunity would be developing a solid regulatory, technical, financial and administrative framework to support risk reduction and new sustainable mining practices. In such a frame a suitable option for dealing with the existing legacies would be finding other uses/economic value from former sites. Moreover, re-mining and recycling chains could represent good opportunities for coping with the challenge of a sustainable economic growth.

| Commodity | U.m. | 2009 | 2013 |
|---|---|---|---|
| | | | |
| Chromite ore (18-42% $Cr_2O_3$) | t | 283 558 | 529 592 |
| Cu ore ( 1.45% avg) | t | 114 286 | 507 105 |
| Fe, Fe alloys, Fe-chromium | t | 7 556 | 24 692 |
| Ni ore | t | 6 884 | 215 086 |
| | | | |
| Clay, caolin | $10^3$ t | 796 | 1 181 |
| Gypsum | t | 71 276 | 126 399 |
| Lime | t | 25 000 | 23 007 |
| Limestone | $m^3$ | 3 271 617 | 3 257 513 |
| Silica sand | t | 12 000 | 150 |
| | | | |
| Natural gas | $10^3$ $m^3$ | 8 000 | 18 300 |
| Crude petroleum | $10^3$ 42-gallon barrels | 3 798 | 7 937 |
| Bitumen | t | 80 000 | 169 800 |
| Coke | t | 72 000 | 10 000 |

**TABLE 1:** PRODUCTION OF MINERAL COMMODITIES IN ALBANIA (USGS, 2013).

## 1.3 Issues related to processing tailings

Mining and beneficiation operations produce huge amounts of wastes which include mining and processing discards, smelter slags, particulate and gaseous emissions processing solutions and drainage water. (Fig. 1). Metal production generates a major waste stream because a large amount of material must be discarded to obtain the mineral resource and afterwards break it down to metal. Producing 1t of pure copper, for instance, requires the extraction of over 100t of rock, most of which is discarded alongside the processing chain (Ayres, 1997; Blowes et al., 2003; Demi, 2003; Hudson-Edwards, 2011). Part of the waste fractions may contain contaminants that tend to become chemically more available through processing. Comminution and separation, in particular, produce fine grained (typically 25µm – 1mm) wastes known as tailings that typically contain high concentrations of trace elements (Blowes et al., 2003). Tailings are often discarded along with processing fluids that may contain processing chemicals like xanthate, cyanide and metallic mercury (Ayres, 1997; Macklin, 2006; Sousa et al., 2010). In the past tailings were commonly poured into streams, rivers, lakes and wetlands. Currently they are pumped into ponds, often covered with water and retained by means of dams, or dried and stacked in heaps, or stored in open pits. In some modern plants tailing ponds are insulated by the use of clay or plastic materials, but in most districts they are stored within valley bottom impoundments. (Blowes et al., 2003; Willis and Napier-Munn, 2006; Hudson-Edwards, 2011). The risk related to waste processing is due to their contamination potential on one hand and to physical issues, on the other. The enormous tailing piles and impoundments constitute a threat to landscape, they are often vulnerable to erosion and seepages and they can release toxic and bioavailable substances to the environment. Several cases of major structural failures are reported worldwide (WISE, 2015). Among the notorious disastrous accidents in Europe is the rupture that affected two tailing dams in Val di Stava (Northern Italy), in 1985. The collapse originated a 180 000 $m^3$ mudflow that beat from the storage basin down on the village of Stava, destroyed over 60 buildings and, caused 268 human victims (Luino and Graff, 2012). The largest European reported case was a tailing dam burst at Los Frailes mine (Southern Spain), in 1998. The dam failure caused over 4 million $m^3$ of acidic sludge to poure into the Guadiamar river, with a load of Zn, Cu, Cd, As, Pb and Tl. Thousands of hectares of farmland were covered with slurry and the overall consequences for water quality, agriculture and wildlife were severe (Macklin, 2006, Domíniguez et al, 2008; Nikolic et al., 2011; Martín et al., 2015). In 2000 two tailing dams broke at Baia Mare and Baia Borsa (NW Romania) respectively, due to extreme weather conditions. The two dam failures spilled 200 000 $m^3$ of contaminated water and 40 000 tons of tailings into a major tributary of the Danube. Therefore cyanide and heavy metals spread downstream within a large area, including territories of Romania, Hungary, Serbia and Bulgaria. Four weeks later, the cyanide plume was even detected at the Danube Delta, at the mouth on the Black Sea. The drinking water of more than 2 million of people in Hungary was poisoned, besides the contamination of river waters caused eradication of flora and massive deaths of fishes, with remarkable economic consequences (UNEP, 2000; Macklin et al., 2003; Vierendeels et al., 2011).

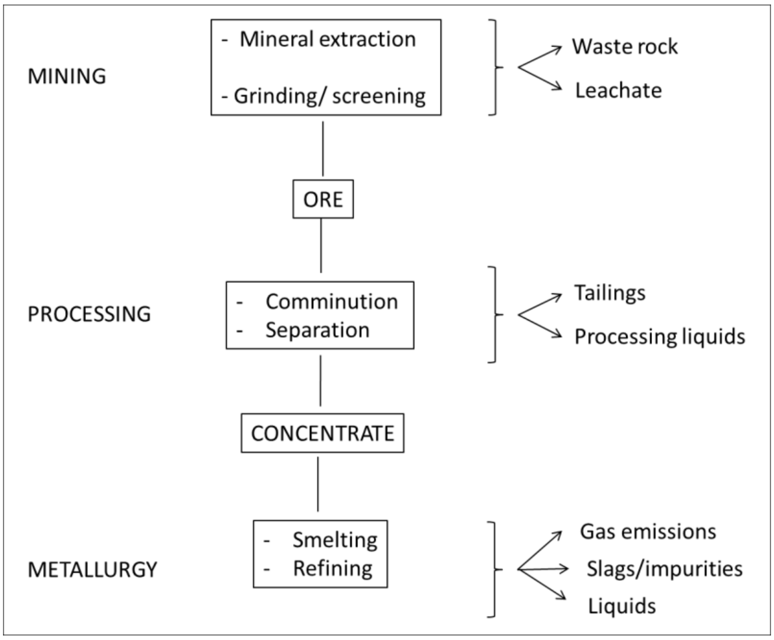

**FIGURE 1**: MAJOR STAGES OF METAL EXTRACTION.
MODIF. AFTER AYRES, 1997 AND MACKLIN ET AL, 2006

Apart from the most striking events, the impact of tailings mainly arise from the dispersion of potentially toxic components into the environment by means of water and wind. The associated risk is related to the mechanisms of release, transport and interaction with biota. As a matter of facts, water pH values at mine and dump sites are typically altered by the solution and precipitation reactions occurring in such environments. Mine drainage can be acidic to basic, it is usually mineralized and may be corrosive, radioactive and toxic. Besides, acidic to circumneutral (pH= 0-7) drainage often contain high concentration of trace elements, either in solution or as particulate, that can be thus delivered to the surficial and ground waters (Nordstrom, 2011b). Widespread consequences are the accumulation of metals with prolonged residence time (hundreds to thousands of years) in sediments and soils and the bioaccumulation of elements in flora and fauna (Macklin et al., 2006; Hudson-Edwards, 2011). Humans can be exposed to potentially toxic substances by various pathways, via either occupational or environmental means (Plumlee and Morman, 2011).

### *Acid Mine Drainage*

Mining and mineral processing expose mineralized materials to oxidizing agents. The supergenic interaction between air and/or water (either meteoric, superficial or ground-) and minerals in an oxidizing environment can trigger a series of reactions known as Acid Drainage (AD). The expression Acid Mine Drainage (AMD) refers to mining and mineral processing sites, but in unmined areas mineralized rocks undergo acidic drainage (Acid Rock Drainage, ARD) as well. The AD is a complex hydrogeochemical process whereby low pH (<5.6) waters form and mobilize components from mineral sources. The geochemical weathering of minerals, namely sulfides, in fact, leads to the formation of sulfate-rich acidic solutions, which can mobilize ions such as Zn, Pb, Cu, Ni, Cd, Hg, Mo, Cr, Co, As, Se. The mobility of ions depends on the occurrence and abundance of the mineral sources, on the vector flow paths and on reactivity. The latter includes the overall energetics of the dissolution/precipitation mechanisms. Reactivity is function of several parameters such as pH, solution composition, redox chemistry, temperature, flow rate, microbiology, besides inherent features of the single elements (Nordstrom, 2011a). Yet, the attributes governing chemical reactivity within a tailing dump are largely inherited from the mineral deposits and the processing methods. Mineralogy, trace element association, grain size and textures of the mineral sources, in fact, are determining factors. In particular, the balance between acid generating and acid neutralizing minerals strongly influence reactivity and the subsequent evolution of the AD processes (Jamieson, 2011). As a matter of facts, the presence of sulfidic minerals is a controlling factor of AMD processes due to the high reactivity of these mineral phases, pyrite, pyrrhotite, arsenopyrite, and sphalerite above all (Tab. 2). Besides, grain size reduction, sorting and liberation processes expose the grains to reaction and increase the surface : volume ratio, thus favoring the interaction with the circulating waters (Marescotti et al., 2008). Oxidation and related processes last until the sulfides are completely weathered, which can take hundreds to thousands of years (Nordstrom, 2009). The oxidation processes are mainly driven by oxygen, but ferric iron and hydrogen peroxide ($H_2O_{2)}$ also play a key-role in certain reactions (Ma and Lin, 2013; Nooshabadi and Rao, 2104). The initial oxidation of pyrite, that is the most common and most susceptible to AD among sulfides, generates acid, sulfate and aqueous $Fe^{2+}$ (eq.1, Tab. 2). The $Fe^{2+}$ is further oxidized to $Fe^{3+}$(eq.2, Tab. 2), which can accelerate further oxidation of sulfides at low pH ranges (Nordstrom 1982; Smuda et al., 2007; Ma and Lin, 2013). Although the reaction expressed by eq.(2) (tab. 2) is slow under acidic conditions, it can be catalyzed by microbial activity. Acidophilic Fe- oxidant and S-oxidant organisms and chemolithoautotrophic bacteria, in fact, strongly increase the oxidation rates. *Acidithiobacillus ferrooxidans*, for example, rapidly oxidizes $Fe^{2+}$ to $Fe^{3+}$ at pH below 3.5, oxidizes reduced sulfur phases and plays a rate-determining role (Nordstrom, 1982; 2011b).

| **Reactant minerals** | **Reactions** | **Eq. N.** |
|---|---|---|
| Pyrite | $FeS_{2(s)} + H_2O + 7/2\ O_{2(aq)} \rightarrow Fe^{2+} + 2SO^{2-}_4 + 2H^+$<br>$FeS_{2(s)} + 8H_2O + 14Fe^{3+} \rightarrow 15Fe^{2+} + 2SO^{2-}_4 + 16H^+$<br>$4FeS_{2(s)} + 15O_2 + 14H_2O \rightarrow 4Fe\ (OH)_3\ S + 8SO^{2-}_4 + 16H^+$<br>$2FeS_{2(s)} + 15H_2O_2 \rightarrow Fe^{3+} + 4SO^{2-}_4 + 14H_2O + 2H^+$ | (1)<br>(2)<br>(3)<br>(4) |
| Pyrrhotite | $Fe_{(1-x)}S + (2-x/2)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO^{2-}_4 + 2xH^+$<br>$Fe_{(1-x)}S + (8-2x)\ Fe^{3+} + 4H_2O \rightarrow (9-3x)Fe^{2+} + SO^{2-}_4 + 8H^+$ | (5)<br>(6) |
| Arsenopyrite | $FeAsS_{(s)} + H_2O + 7/2\ O_{2(aq)} \rightarrow Fe^{3+} + SO^{2-}_4 + H_2AsO^-_4$<br>$FeAsS_{(s)} + 14\ Fe^{3+} + 10H_2O \rightarrow 14Fe^{2+} + FeAsSO_4\ 2H_2O + SO^{2-}_4 + 16H^+$ | (7)<br>(8) |
| Chalcopyrite | $CuFeS_{2(s)} + 4O_{2(aq)} \rightarrow Fe^{2+} + 2SO^{2-}_4 + Cu^{2+}$<br>$CuFeS_{2(s)} + 16Fe^{3+}\ 8H_2O_{(aq)} \rightarrow 17Fe^{2+} + 2SO^{2-}_4 + Cu^{2+} + 16H^+$ | (9)<br>(10) |
| Sphalerite | $ZnS_{(s)} + 2O_{2(aq)} \rightarrow Zn^{2+} + SO^{2-}_4$<br>$ZnS_{(s)} + 8Fe^{3+} + 4H_2O_{(aq)} \rightarrow Zn^{2+} + SO^{2-}_4 + 8Fe^{2+} + 8H^+$ | (11)<br>(12) |
| Galena | $PbS_{(s)} + H^+ \rightarrow Pb^{2+} + HS^-$ | (13) |
| Calcite | $H^+ + CaCO_3 \rightarrow Ca^{2+} + HCO^-_3$ | (14) |
| Dolomite | $2H^+ + CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 2HCO^-_3$ | (15) |
| Siderite | $FeCO_3 + H^+ \rightarrow Fe^{2+} + HCO^-_3$ | (16) |
| Albite | $2NaAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow 2Na^+ + 4H_4SiO_4 + Al_2SiO_5\ (OH)_4$ | (17) |
| Muscovite | $2KAlSi_3O_8 + 2H^+ + 3H_2O \rightarrow 3Al_2Si_2O_5\ (OH)_4 + 2\ K^+$ | (18) |
| Goethite | $FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O$ | (19) |
| Gypsum | $CaSO_4 + 2H_2O \rightarrow Ca^{2+} + SO^{2-}_4 + 2H_2O$ | (20) |
| Jarosite | $KFe_3(SO_4)_2\ (OH)_6 + 6H^+ + 2H_2O \rightarrow K^+ + 2SO^{2-}_4 + 3Fe^{3+} + 6H_2O$ | (21) |
| Schwertmanntite | $Fe_8O_8(OH)_6SO_4 + 22H^+ \rightarrow 8Fe^{3+} + SO^{2-}_4 + 14H_2O$ | (22) |

**TABLE 2:** MAJOR GEOCHEMICAL REACTIONS INVOLVING SULFIDES AND NON-SULFIDE MINERALS IN AD ENVIRONMENT. MODIF. AFTER ANAWAR (2015).

Dissolution reactions involving some non-sulfide minerals have a potential to neutralize acidity produced by the oxidation of sulfides, nevertheless the effects depend on the relative abundance of the mineral phases. Carbonate phases, in particular are effective buffers, also due to their high reactivity. Reactions involving carbonates increase the alkalinity of waters and release cations like Ca, Mg, Fe and others. Aluminosilicates, such as chlorites, pyroxenes, micas, plagioclase, amphiboles have lower reactivity rates and dissolve at lower pH, but their dissolution provides some consumption of $H^+$. Dissolution of aluminum-bearing hydroxide phases, on the other hand, has the potential to lower the pH to 4.0–4.5, while dissolution of ferric oxyhydroxide minerals typically maintains pH values in the range of 2.5–3.5 (Blowes et al., 2003). The reactions involving both acid producing and acid consuming minerals lead to liberation of cations into circulating solutions. These may subsequently precipitate in secondary phases mainly due to oversaturation, pH variations, redox reactions, mixing or evaporation. In AD environments a wide range of secondary minerals precipitate, with variable timing and at different pH conditions. The precipitates are often mixtures of phases of low crystallinity and sub-micrometer to nanometer size. They may occur as colloidal precipitates or suspensions and coatings on primary minerals, while on a macroscopic scale they often form consolidated crusts and efflorescent salt deposits. The precipitation of coatings and patinas on the surfaces of minerals provides a shield effect that prevents further oxidation. The secondary phases can selectively concentrate and store several metals and metalloids from solutions through various mechanisms such as structural incorporation, co-precipitation and adsorption. After precipitation, the stability of each phase determines the mobility of the scavenged elements. In fact, changes in physical and chemical parameters of the circulating solutions can trigger dissolution, precipitation and solid state transformations, which determine either release or retention of elements. Among the most abundant and widespread secondary phases are hydrous sulfates, oxides, oxy-hydroxides, but carbonates, phosphates and secondary sulfides are also reported (Gade et al., 2001; Blowes et al. 2003; Marescotti et al., 2008; Nordstrom, 2011b; Carbone et al., 2012; Marescotti et al., 2012; Carbone et al., 2013).

Seasonal variations between rainfall events and droughts can strongly affect the fate of secondary minerals and the element storage. During dry periods, in fact, efflorescent salts often form on the dump surfaces and soils. The soluble secondary phases may dissolve during the next major runoff and pour into the receiving water bodies. These events can cause the metal and $SO_4^{2-}$ load in water to increase substantially in a short time laps (Smuda et al., 2007; Nordstrom, 2011a; Carbone et al., 2013).

### *Protection and reclamation strategies*

Even though mining is an ancient practice, the relative environmental issue has arisen only in the last decades. Several techniques have been developed in the past years and today reclamation is considered as part of the plans of mine development and closure (Brown, 2002). Furthermore, nowadays new technological tools are available that allow to minimize both energy consumption and waste production (Driussi and Janz, 2006). The ideal goal of reclamation is to restore the pre - mining conditions with sustainable, cost-effective and possibly preventive methods (Brown, 2002; Johnson and Halberg, 2005; Lottermoser, 2011; Nordstrom, 2011a; Anawar, 2015). In order to correctly estimate the ultimate cleanup costs, remediation should take start from and be commensurate with (i) the weathering and contaminant release potential of the waste materials; (ii) the natural background, that means gaining quantitative information on water, soils, rocks and biota pre-mining conditions. Therefore, the most effective remediation plans are those included into the pre-mining procedures (ENVSEC, 2009). An environmentally effective approach is to base the reclamation plans on the worst-case scenarios. Moreover, effective plans should consider seasonal variations of the AD processes and even the medium to long term variations due to climate changes (Nordstrom, 2011a,b). Preventive strategies are usually based on *source control* measures that are aimed at either inhibit oxidation or produce benign reactions within the tailing dump (Johnson and Halberg, 2005). Pyrite-rich mining wastes, for instance, are usually put under water level, either ground-or surface in order to prevent contact with oxygen. As an alternative, solutions like dry covers and sealing layers are used. At the mineral scale, microencapsulation technologies can be applied to produce precipitation of coating minerals on pyrite surfaces, thus providing insulation from oxidant agents. Besides, blending acid generating wastes with buffering materials allows to reduce the acid drainage effects. Finally, biocides can be used to inhibit the activity of oxidizing bacteria (Brown, 2002; Johnson and Halberg, 2005; Anawar, 2015). On the other hand, remediation options are aimed at control AD migration from sources, by means of water treatment. The so called *active* remediation methods, mainly involve continuous addition of neutralizing reagents or bioreactors. Otherwise, *passive* methods usually apply drains, reactive barriers and wetlands (Johnson and Halberg, 2005). After closure, decommissioning and reclamation of a processing site, proper procedures provide for periodic monitoring of water quality, ongoing consolidation of the tailings, state of the structures that may be subjected to deterioration (Brown, 2002). At already closed or abandoned sites reclamation projects are usually motivated by severe environmental situations in act, due to negligent disposal, abandon and disrepair. Such cases require background studies that take into account the age of the site and the evolution stage of the AMD processes. Geo-environmental modeling and risk assessment thus constitute the base for rehabilitation plans (Servida, 2008). Emergency remediation at historic sites can be extremely difficult and costly. Therefore, the main goal is to rapidly reduce the existing environmental impact and prevent further contamination with limited budgets.

## 1.4 Reuse and recycling

In the recent years the industrialized countries have been developing strategies for economic growth based on limited resources and environmental awareness. The ultimate achievement of environmental protection would be the total resource utilization and zero waste production (Lottermoser, 2011). Among the modern strategic tools for reducing both costs and environmental impact is the so-called Industrial Symbiosis that is the sharing of services, utilities, and by-product resources among industries (Laybourn and Lombardi, 2012). For example, today a diffuse practice is to recover sulfur in non-ferrous sulfide processing and refinery industry in order to produce sulfuric acid (USGS, 2015). Nowadays the conversion of actual wastes into valuable resources, either by complete utilization (reuse) or extraction of valuables (recycling) is a feasible and adopted option (Ayres, 1997; Lottermoser, 2011). Recycling and reuse ideally lead to both economic benefits and reduction of waste volumes, which can be favorable especially in disadvantaged regions where historic mining has occurred (Vieira, 2006; Sousa et al., 2010; Geise et al., 2011). Some mine wastes can turn into commodity thanks to new emerging markets or technologies. The latter are critical for effective extraction of resources that were previously neglected (for instance gangue minerals or low-grade ore) (Lottermoser, 2011). Beyond technical and environmental parameters, economical requirements must also be met for effective recycling, as economic cost-benefit performance is the ultimate evaluating parameter (Bian et al., 2012). In general, recycling is profitable on smaller scales than mining and metallurgical industries, and in many cases it may be less profitable at all (Ayres, 1997). Therefore, such investments make sense if the recyclable value is at least comparable with reclamation costs (Smith and Williams, 1996). Among the explored options is for instance the exploitation of the milling/beneficiation discards. The latter, in fact, can be profitable as they do not require major investments in mining and comminution operations. As a matter of facts, mining implies both an initial capital effort and high operating costs, while comminution can represent more than 45% of the costs per tonne of the final product. Tailings, on the other hand, constitute already mined and partially processed potential resources (Willis and

Napier-Munn, 2006), even though the extraction of valuables requires some reprocessing. Extraction of metals, in particular precious metals, from tailings is practiced and new methods have been lately explored (Zheng et al., 2006; Antonijevic et al., 2008; Valderrama and Rubio, 2008; Dehghani et al., 2009; Sousa et al., 2010; Chen et al., 2014; Hatayama et al., 2015). Tailings are also applied as filling and building materials, as well as for several other applications(Zheng et al., 2006; Geise et al., 2011; Schellenbach and Krekeler, 2011). Where the mineral content is variable, selective reprocessing could partially cover the high reclamation costs (Smith and Williams, 1996). Mineralogical, mechanical and geochemical characters of the waste materials are critical for implementing recycling or reuse. These factors, in fact, determine the target market, the packaging and the safety (i.e. presence and speciation of contaminants) of the product (Williams et al., 2006; Geise et al., 2011).

**CHAPTER 2**

# The study area

## 2.1 Overview of the study area

On the spot overviews have been performed between November 2011 and April 2015, at six different sites in Northern Albania, namely in the Mirdita and in the Puka municipalities (Tab. 3). Two tailing dumps of the Reps site were selected for further investigations based on the grain size, mineralogical and geochemical characters of the collected samples. Moreover, the two tailing dumps (R1 and R2 respectively) have been dry-stacked as separate hips with clear geometric features, which allow to better estimate the volumes. The former processing site of Reps is located in the valley of the Fan I Vogel river, in the Mirdita municipality (Northern Albania) about 90km NE of Tirana. The activity at Reps began in 1971. The plant treated ore coming from several sulfide mines of the Mirdita district, but, at the same time the site hosted a minor mine, with mining operations occurring about 1 km SE of the plant.

| | **Mining district** | **Solid samples** | **Sampling period** |
|---|---|---|---|
| **Kulme Derven** | Mirdita | WR | aug. 2012 |
| **Rreshen** | | WR; T | aug. 2012 |
| **Spač** | | WR | aug. 2012 |
| **Prosek** | | WR | aug. 2012 |
| **Reps** | | T | aug. 2012; may 2013; nov. 2013; apr. 2015 |
| **Fushe Arrez** | Puka | T | nov. 2011; apr. 2015 |

TABLE 3: LIST OF THE OVERVIEWED SITES OF NORTHERN ALBANIA. TYPOLOGIES OF SAMPLED WASTES ARE INDICATED: WR = WASTE ROCK; T=TAILING

## 2.2 Geographic setting

Northern Albania is largely hilly and mountainous, with the exception of a narrow coastal plan that extends along the Albania-Montenegro boundary. The reliefs are the prosecution of the Alpine-Dinaride chain and reach altitudes of over 2 500m, being the Mount Korab (2 765m) the highest peak. On the north-westernmost edge of the Albanian territory is the trans-boundary (Albania-Montenegro) lake Skadar which is the major lake of the area. Its outflow is a tributary of the Drin river. The latter is barycentric to the main hydrologic system of Albania. The Drin river originates in the Kukës area and has two distributaries that flow into the Adriatic sea (Rivaro et al., 2004). The other major drain system is formed by the Fan and Mat rivers (Fig.2), that flow in convergent directions. The Fan stream becomes tributary to the Mat approximately 7km downstream of the Rubik town (Nicandrou 2010). The River Mat then flows through the alluvial coastal plain, towards the Adriatic Sea. Three underlying aquifers are connected to an alluvial fan at the entry of the river into the plain. Such aquifers supply water for about 240˙000 people (Kumanova et al., 2014 and ref.

therein). The people mainly live in small villages and towns, the main urban area being that of Shkoder. Other important urbanized centers are Lezha, Puka, Kukes, that are administrative centers of the respective municipalities (administrative divisions, called *districts* before law 115/2014 was introduced) bearing the same names. The Reps site is located in the Mirdita municipality, which administrative center is the town of Rreshen. The communication routes are few, but in the last ten years the two major arteries – the coastal Tirana-Podgorica road and the SW-NE highway to Kosovo have been significantly improved.

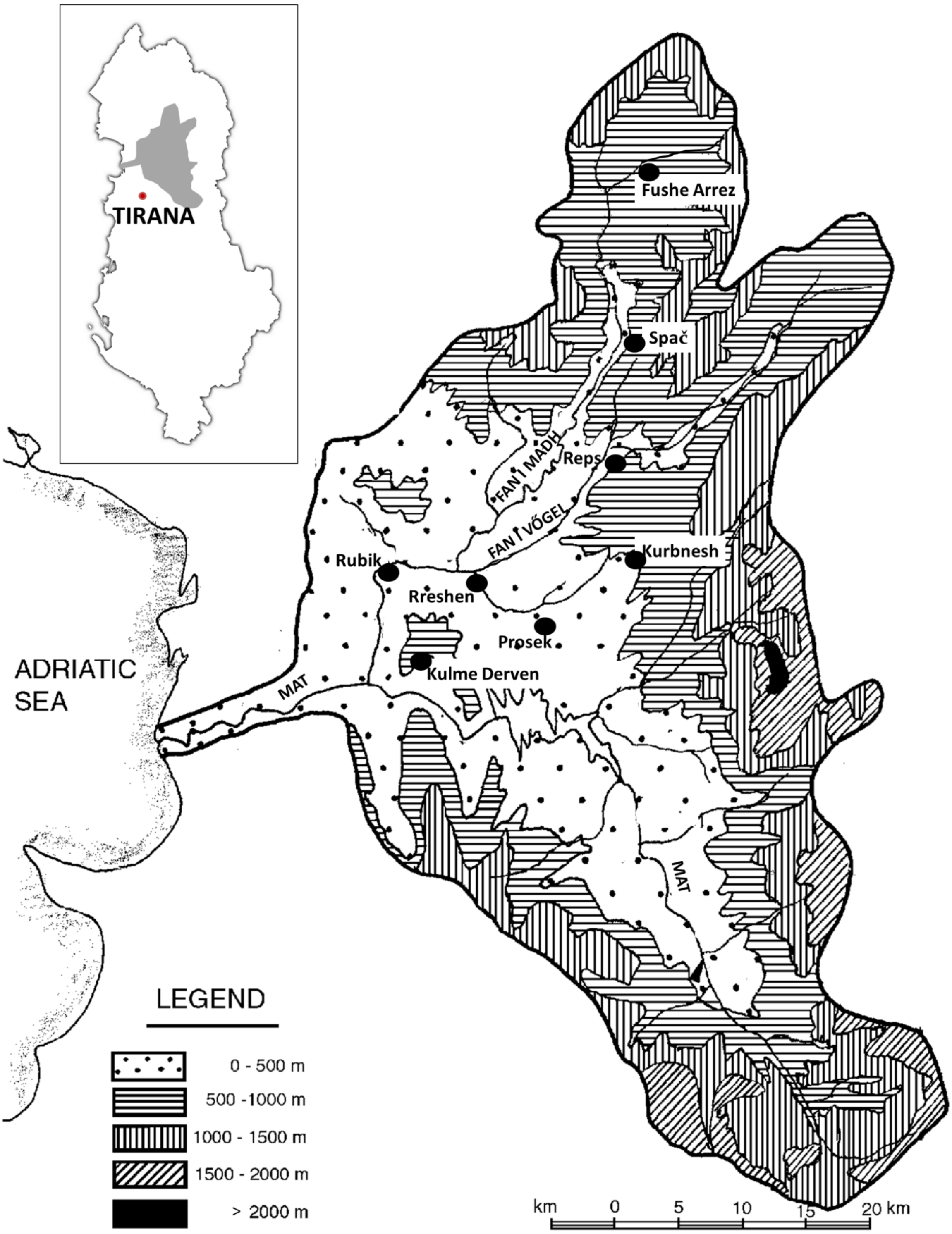

**FIGURE 2**: LOCALIZATION OF OVERVIEWED SITES IN THE FAN-MAT HYDROLOGICAL BASIN. MODIF. AFTER NICANDROU (2010)

*The Fan river Valley*

The River Fan flows entirely within the Albanian territory and has two main tributaries, named Fan I Madh (Great Fan) and Fan I Vogël (Small Fan), respectively (fig 2). The latter originates at Maja I Runes, 1856m above the sea level, flows through symmetrical valleys, in NE-SW directions and join the Fan I Madh stream about 2km W of Rreshen (200m a.s.l). The source of the Fan I Madh is Qafa e Malit, at an altitude of 1397 m and the stream flows in the same general direction as the Fan I Vogël, except for a NS segment in the lee of the Puka massif. Seasonal tributaries pour down the sides of the valleys and contribute to the flow of the two rivers, that is continuous (the annual mean streamflow of the Fan I Vogël is 11.7 $m^3/s$) but with differences between the dry and the humid seasons. From the confluence, he Fan river runs south-westwards and joins the Mat River downstream of Rubik. (Nicandrou 2010 and ref. therein; Daci and Sinojmeri 2011; Daci 2013).
In the Fan river valley the climate is continental, with warm summers and frequent frost events during the winter. The mean annual temperatures in the Reps area range between 10° and 12°C. Annual precipitation rates vary from 800 to 1400mm along the section of River Fan. Nevertheless, data updated to 1991 report that in the Reps area the annual precipitations can exceed 1700mm. More than 80% occur from October to March and the most rainy area are the highlands, that reach 2000m a.s.l. (Cullaj et al., 2005; Abazi & Astrit, 2008; Nicandrou 2010; Daci and Sinojmeri 2011). The valley is locally known to be particularly windy, either in winter or in summer (Daci, 2013).

## 2.3 Geological setting

*Geology*

The geology of northern Albania is dominated by the units of the Mirdita Zone (Fig. 3 ). The latter is a ~40 km wide, SW-NE trending segment within the Dinaride-Helenide sector of the Alpine orogenic system. The Mirdita Zone includes part of the Albanian ophiolite belt. These ophiolites represent an ocean-floor evolution that took start in early Middle Triassic with the thinning of a continental margin (Bortolotti et al., 2004; Gawlick et al., 2008). Notwithstanding the Mirdita ocean is commonly thought to have formed from Jurassic, recent studies support an early (from Middle Triassic) formation of the oceanic crust, based on radiolarites enclosed within the Jurassic melanges (Gawlick et al., 2008). The Triassic limestones of the Apulian margin and the Pelagonian Platform that bound the ophiolites to the west and to the east respectively, are interpreted as the margins of the Mesozoic ocean (Bortolotti et al., 2005). Most of the ophiolitic sequence witnesses the evolution of an oceanic litosphere in Early to Middle Jurassic. These upper mantle and crustal units show features in thickness, internal stratigraphy and chemical compositions varying from the west to the east. In particular, the Western Mirdita Ophiolites (WMO) show a lherzolitic-harzburgitic-dunitic upper mantle unit, overlain by a plutonic sequence and extrusive rocks characterized by MORB affinity. On the other hand, in the thicker Eastern Mirdita Ophiolites (EMO) sequence the basement is mainly constituted by harzburgites and dunites, overlain by a plutonic sequence. The sheeted dyke complex is well-developed and the extrusive unit show affinities of the supra-subduction zone type. (Shallo and Dilek 2003; Dilek et al. 2007; Phillips-Lander and Dilek 2009). Such differences are thought to derive from a Middle to Late Jurassic westward convergence that produced obduction on the western margin and created an intra-oceanic subduction. An island arc thus evolved above the subduction zone, between 170 and 160 My (Shallo & Dilek, 2003). The ocean closure occurred in a scissor-like manner, from south to north, between 174 and 160 My. The Mesozoic and Cenozoic collisional events strongly modified the contacts, both within the ophiolitic belt and between ophiolites and the bounding sedimentary units. The main tectonic event was the westward ophiolite emplacement onto the Triassic-Liassic carbonate platforms, that created the metamorphic sole. Subsequently the carbonate platform units migrated onto the Early Cretaceous flysch and again onto the Eocene flysch (Beccaluva 1994; Hoxha 2001). Moreover, Late Cenozoic thrust faults locally juxtaposed the EMO against the WMO (Dilek et al. 2007; Phillips-Lander and Dilek 2009)

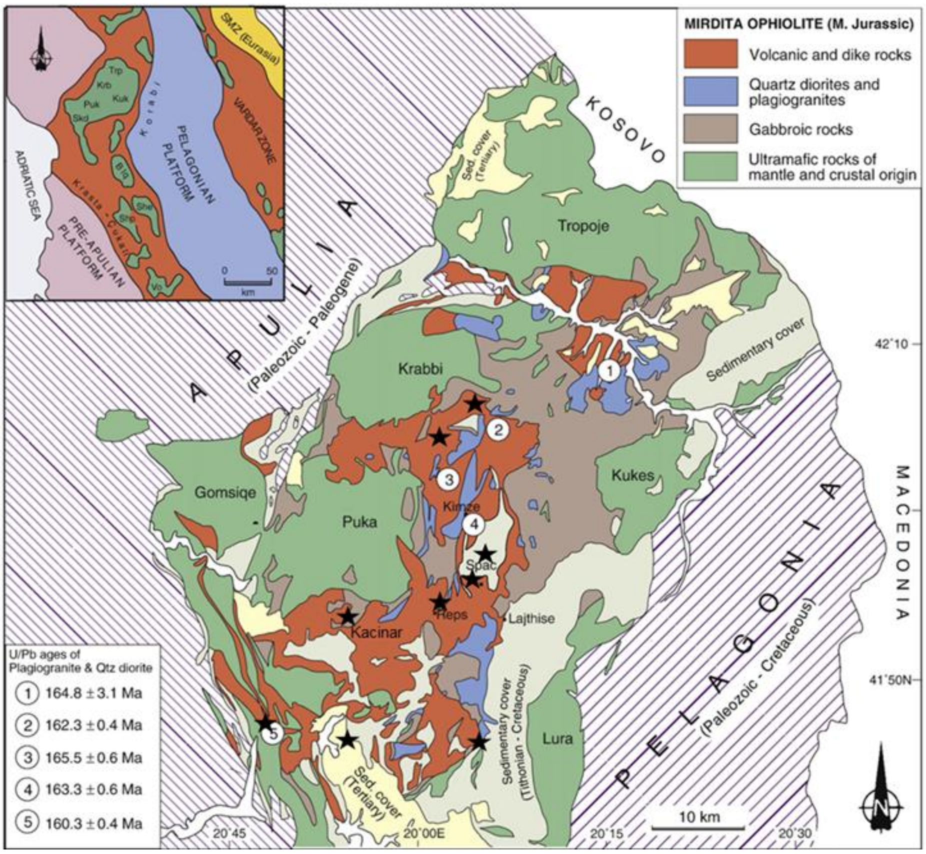

**FIGURE 3:** SIMPLIFIED GEOLOGICAL MAP OF THE NORTHERN MIRDITA ZONE, MODIFIED AFTER PHILLIPS-LANDER AND DILEK (2009). THE BLACK STARS LOCATE THE MAIN MINES. THE INSERT MAP SHOWS THE LOCATION OF THE BELT BETWEEN THE PELAGONIAN PLATFORM AND THE PRE-APULIAN PLATFORM. THE PERIDOTITE MASSIFS ARE NAMED: TRP - TROPOJA; KRB - KRRABI; KUK -KUKES; PUK – PUKA

*Ore minerals*

In northern Albania, sulfide orebodies occur both in the WMO and in the EMO. In the western belt massive sulfides and stockwork veins are mainly hosted into the volcanosedimentary series (volcanites, melanges, with variable content of shales, slates, cherts). Within the eastern belt a NNE-trending, 25km long belt between Chafe Mal and Reps hosts the majority of the important deposits (fig. 3). Major orebodies are distributed along a discontinuous line and minor occurrences lie along sub parallel orientations. Host rocks are massive lava flows, pillow basalts, pyroclastites and, in few cases, also intrusions and melanges (Economou-Eliopoulos et al., 2008; Hoxha 2001; Hoxha et al. 2005). Massive pyrite deposits are also documented within the rhyolitic dyke complex (Phillips-Lander and Dilek 2009). Pyrite is the dominant sulfide throughout. The copper ores comprise chalcopyrite, bornite, tennantite. Sphalerite and, to a lesser extent, covellite, chalcocite, arsenopyrite and galena, are also found in the mineral associations. Variable quantities of magnetite, hematite, mushketovite and native gold are reported. Chlorite and epidote gangue minerals represent the dominant hydrothermal alteration, but quartz, carbonates, sericite and zeolites are also found. Among secondary minerals, mainly formed in supergene zones, are malachite, azurite, smithsonite, cerussite. The main sulfide-related metals are Cu, Zn, Au, associated to variable contents of Pb, Ag, As, Cd, Ge, Sb, In (Sinojmeri, 1994; Hoxha et al. 2005; Economou-Eliopoulos 2008; Daci 2013). Other mineralized systems documented in the district are Mn bearing cherts (Rubik area), V and Ti-rich gabbros (in the Kacinari area) and exstensive chromite deposits associated to the EMO peridotites (Hoxha et al. 2005; Dilek, 2007).

## 2.4 Copper industry in Northern Albania

The most widespread mine industry in Norther Albania was that of copper. The copper deposits are located in the municipalities of Mirdita, Puka, Shkodra, Kukes and Has. The first mine to open, in 1935, was located in the Rubik area, while most of the sites began their activity between the Fifties and the Eighties. When the production peak was reached, more than 25 mines were operating.

The processing sites that received the mined ore were dislocated in the municipalities of Puka (Fushe-Arrez plant), Has (Golaj plant) and Mirdita (Reps, Rreshen and Kurbnesh plants). The dressing plants concentrated copper to a grade of over 18%, with a recovery of 88% (Demi, 2003). Some of these sites comprised several mining and concentration facilities. Rreshen, for instance, was a major center for copper industry, with several mining and concentration operations located on both arms of the Mat- Fan river system (ENVSEC, 2005). The concentrates coming from the processing facilities were then sent to either the Gjegjan (municipality of Kukes), Lac, or Rubik (municipality of Mirdita) pyrometallurgy primary smelters for thermal and electrolytic refinement (Demi, 2003; ENVSEC, 2005; Daci et al.,2007). Following the economic collapse, between 1990 and 1997 most of the mining, processing and smelting operations were interrupted (Demi, 2003), leaving behind crumbling structures, large volumes of waste materials and a generally depressed economy. Nowadays, the only active mine site is Munella, which feeds the processing plant of Fushe Arrez (Fig. 4A, B; Fig. 5).

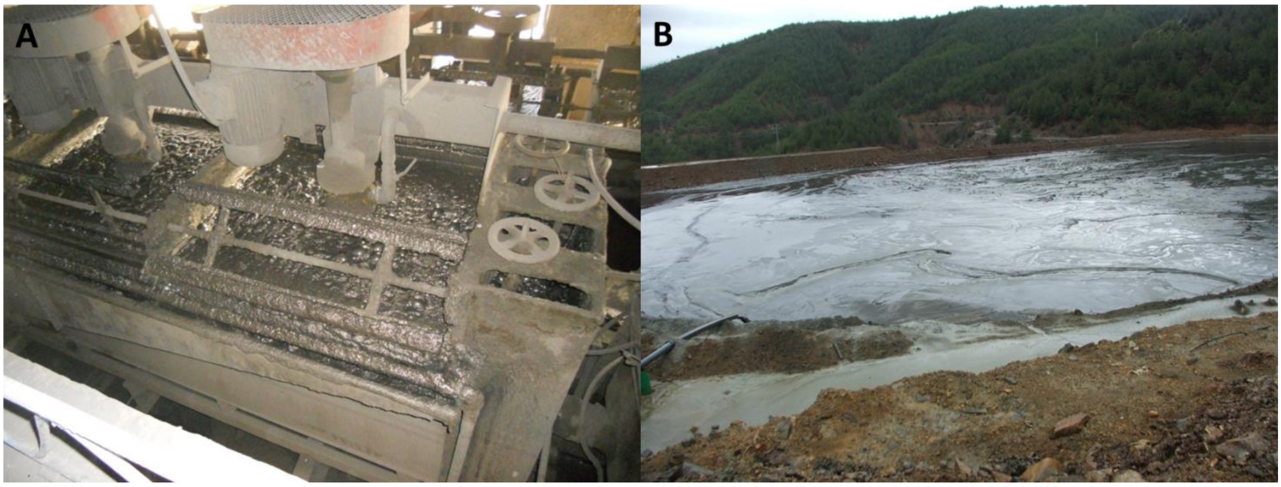

**FIGURE 4:** IMAGES OF THE FUSHE ARREZ PLANT **A)** FORMER FLOTATION CELLS (NOVEMBER 2011); **B)** TAILING IMPOUNDMENT (APRIL 2015)

*Processing methods*

Given the nature and the low grade of the mined Cu-ore, froth flotation was chosen as the concentration method in all the Albanian dressing plants (Demi, 2003). Such a method, in fact, was developed to achieve specific separations from complex ores, namely sulfide ores, and moreover it allows to reduce further losses to tailings (Willis and Napier-Munn, 2006). Flotation is a physico-chemical separation method that takes advance of the surface properties of particles. In particular, the froth flotation method utilizes the relative behaviour with respect to water/air for separating the hydrophobic (aerophilic) particles from the hydrophilic ones. Particles with water-repellent surfaces, in fact, attach to air bubbles that lift them up to the surface. The formation of a stable froth prevents the burst of the air bubbles, thus supporting the flotation of mineral particles at the surface, where the metal-rich froth can be removed (Fig. 4A). To achieve the desired selectivity several chemical reagents are added to the water-air mixture. In particular, the collectors adsorb at the mineral surfaces, thus increasing hydrophobicity. Regulators control the pH of the system and regulate the attachment of particles to air bubbles. Finally, frothers are used to create and maintain a stable froth (Willis and Napier-Munn, 2006; Alam & Sheng, 2012). The processing plants of Northern Albania operated, at least during some periods, with two separation steps. After the reparation of the copper concentrate at pH 11.5, in fact, a further pyrite concentration was performed at pH 5-6. The regulation of pH in the pulp was performed by adding either lime or sulfuric acid. (Demi, 2003). An insight of the present and former methods of concentrations is provided by the still active Fushe Arrez processing site (Fig. 5). The latter used to be the country's major copper mining and beneficiation complex, with a production of over 320 000 t of copper ore per year, when operating at full capacity (ENVSEC, 2005). After a period of inactivity (2000-2004), the plant now processes the ore coming from the nearby mine of Munella. At the present time, the input of the Fushe Arrez plant is 1-2% Cu, 40% S. 30-33% Fe, 5-10%$SiO_2$,. A Cu- concentrate output of 17-18% Cu is obtained and the metal recovery is 80-85%. The overall weight reduction (total input/concentrate) is about 90%. The processing tailings 30-35%S containing 10% water are poured through a pipe-line into an impoundment (fig.4b). Before 2000 a pyrite concentrate was also obtained at pH 5-6.5 from the Cu-flotation residuals. The secondary flotation was performed exclusively on lots of ore characterized by massive pyrite and S concentration over 15%. This process led to obtain tailings characterized by 15%S, or less (personal communication, 2$^{nd}$ of April 2015). Due to the recent four- years suspension of the operations, it was possible to sample the two types of tailings (double-flotation and single-flotation discards) separately (see Appendix 1).

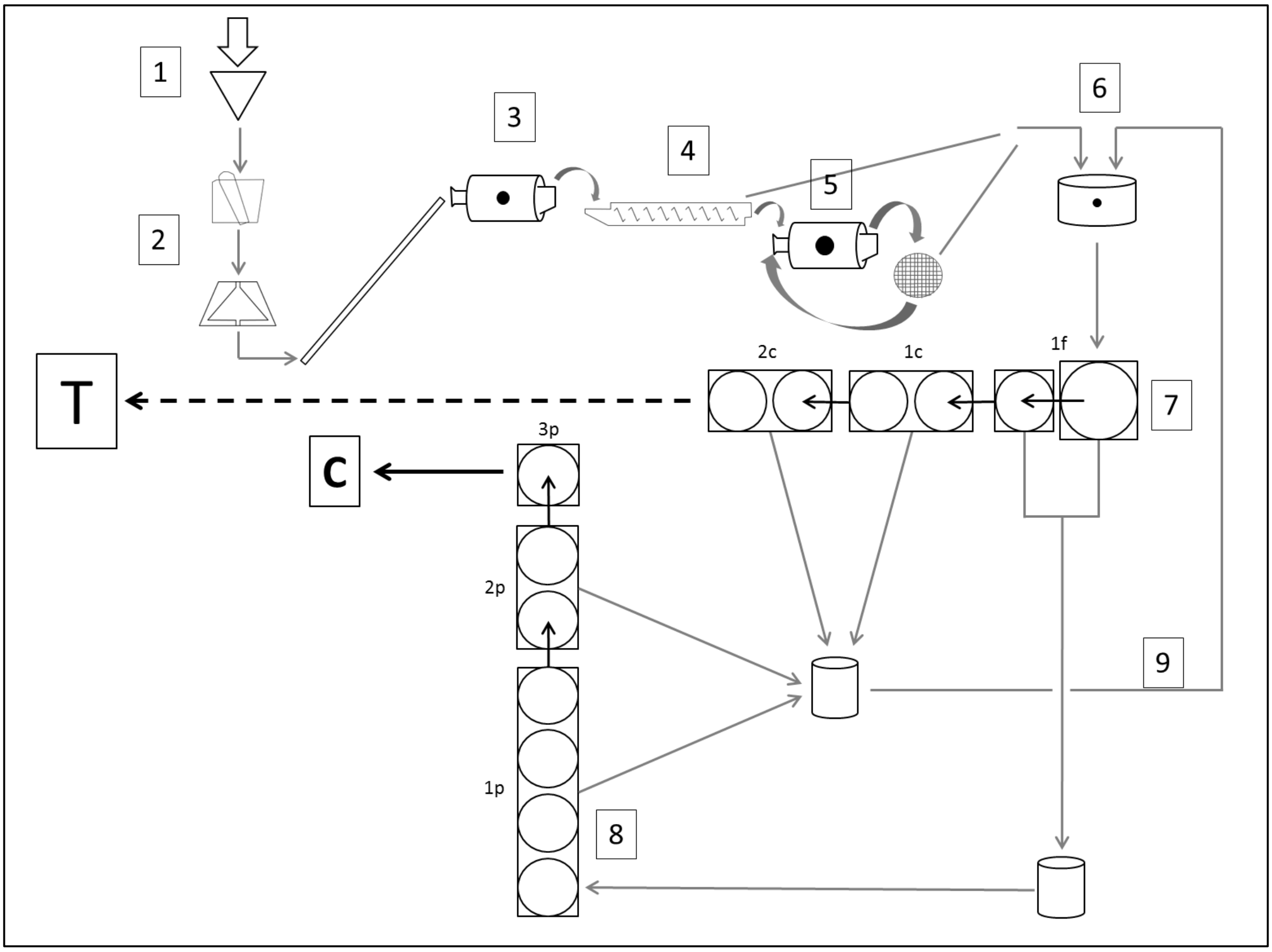

**FIGURE 5:** FLOWSHEET OF THE ACTIVE PROCESSING SITE OF FUSHE ARREZ. (1) FEED; (2) JAW+CONE CRUSHERS; (3) HORIZONTAL BALL (40MM) MILLS ; (4) HYDROCLASSIFICATOR; (5) HORIZONTAL BALL (80MM) MILLS – CLOSED CIRCUIT REGRIND; (6) VERTICAL BALL (2MM) MILL; (7) FIRST FLOTATION LINE- 1 FLOTATION AND 2 CONTROL STAGES; (8) PURIFICATION LINE – 3 STAGES; (9) RE-CIRCULATION; T= TAILING; C= CONCENTRATE

## 2.5 Environmental issues related to waste piles

As a consequence of the intense mineral exploitation, large volumes of discard materials were left behind and are still produced by the few ongoing activities, without undergoing proper security operations. At some processing sites (i.e. at Reps, Kurbnesh, Rreshen) the tailings were dumped just next to or even poured into the river beds (ENVSEC, 2005, Daci et al., 2007). Moreover, numerous dump sites lie in the vicinity of inhabited areas. At Fushe Arrez, for instance, the processing and tailing facilities are located just uphill to the village (Fig. 6A). The actual concern is due to the general state of neglect of the discard facilities and to the nature of the waste materials. Processing tailings, in particular, contain variable amounts of pyrite and other sulfide minerals and are therefore susceptible to Acid Drainage processes (Demi, 2003; Daci et al., 2007). Moreover, residual ions derived from processing reagents may lead to further contamination (Demi, 2003). In most sites the water from tailing dams and impoundments directly enters the local streams (i.e. at Rreshen and Reps), thus carrying contaminants as either stream sediments, suspended matter, or solutes (ENVSEC, 2005). Recent studies (Kumanova et al, 2015) have documented high concentrations of potential contaminants such as $SO_4$, Cr, Pb, Ni, Fe, Cu, Mn, Zn (especially as suspended and colloidal phases) in the river waters within 10km from point sources (tailing and mine sites). Even though ore and metal extraction was conducted with similar methods in all the facilities, the contaminant characters and mobility are site-specific features that depend on numerous parameters. For instance, the ore processed at Rreshen and Gjegjan was particularly rich of arsenopyrites, thus high concentrations of arsenic have been detected into the effluent waters, that may contaminate the local agricultural fields. Physical hazards are documented at several sites mainly due to erosion and failure of the retaining and water- diversion structures. Several damages to the tailing facilities are reported and have also been noticed during sites overviews related to the present work. The most evident damages are seepages in dam and diversion (pipes, channels) structures, washouts on the dump slopes and sinkholes on the top of tailing dams (Fig. 6 C). At Fushe Arrez a loss of 0.5 to 1 million t of materials from the tailing dam into the Fan I Madh stream is documented. Again, variations in the water table heights into the tailing facilities can cause further damages. At Rreshen, for example, a high phreatic surface in the tailing impoundment has been detected (ENVSEC, 2005). Finally, a matter of concern is the actual wind transport of tailings, as reported, for instance, in the nearby of Rreshen (Demi, 2003; ENVSEC, 2005).

**FIGURE 6: A** - TAILING DUMP SHOWING MASSIVE SECONDARY PRECIPITATION AT FUSHE ARREZ (APR. 2015); **B** – WASHOUT IN R2 TAILING DUMP, REPS (NOV. 203); **C** –SINKHOLE IN THE ROOFTOP OF A TAILING DUMP AT KURBNESH (AUG. 2012)

**CHAPTER 3**

# Effects of pyrite separation on the environmental impact of Cu-processing tailings: a case-study at Reps, Mirdita District, Albania

## 3.1 Quantitative Flowsheet approach to the tailing management

Tailing dumps often show assorted features with respect to mineralogy, grain size and geochemistry. Such differences may complicate the quantitative prediction of potential contamination (production of acid drainage and release of toxic elements to the local environment). The variable characters can be due to either various origins of the mined ore, or from the evolution of the processing techniques. The disposal of discards deriving from distinct processing chains into the same facility may also create heterogeneous tailing dumps. A key for the comprehension of heterogeneity is the quantitative flowsheet. The latter is a diagram of the operation sequence, in which quantification of the input and output of each processing stage is provided. The reconstruction of the processing scheme allows to better quantify the actual classes of tailings thus opening a perspective on rationale remediation planning.

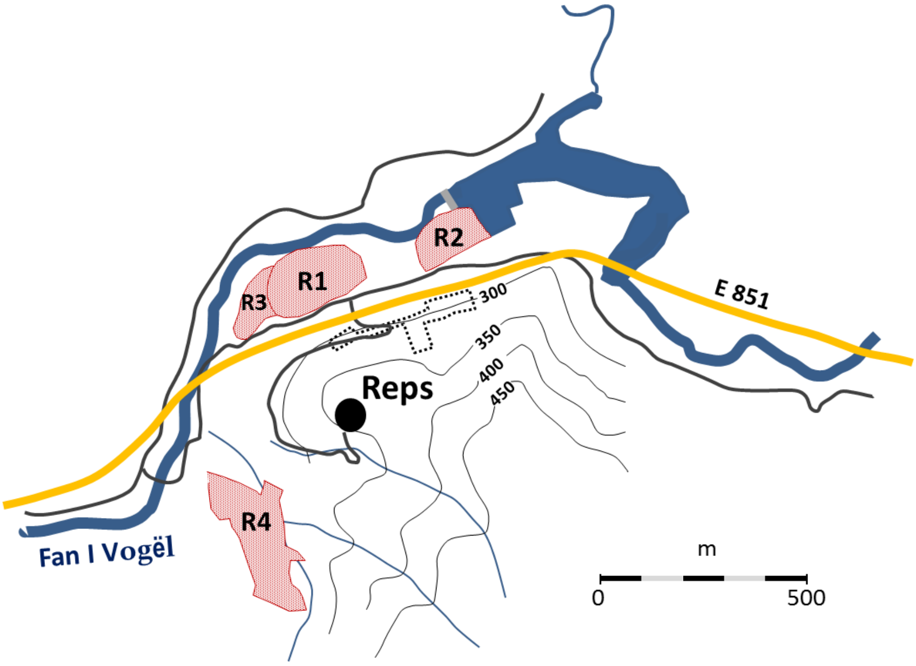

**FIGURE 7:** SCHEMATIC DESCRIPTION OF THE REPS SITE. THE POSITION OF THE FOUR TAILING DUMPS IS INDICATED

## 3.2 Reps site

The Reps site used to be a processing and mining complex. At the present time, it comprises the ruined structures of the processing plant, few former facilities for workers and four tailing dumps (Fig. 7) that are currently under the responsibility of the Albanian State. The abandoned processing facilities and three tailing hips lie on the northern side of the Reps hill, that slopes down to the Fan I Vögel river. The R1, R2 and R3 dumps have been stored just beside the river bank. The R3 tailing pile, in particular is under the high water level. A valley-fill tailing impoundment (R4) is located on the western side of the hill, just downhill to the village of Reps. A risk evaluation of this tailing dam was recently performed and an intervention plan was proposed (ENVSEC, 2005) that has never come into effect. The proposed measures were ment to reduce losses of water and solid materials downstream. The impoundment and water diversion structures, in fact, are seriously damaged and an overtopping event was reported in 2004 (ENVSEC, 2005). In between the processing ruins and the tailing dumps R1, 2,3 the highway E851 to Kosovo passes. The construction camp for the motorway was set on the top and next to the R2 dump and the processing buildings were destroyed. Between 2013 and 2015 an artificial hydrologic basin was excavated. At the present time the R2 dump lies in the lee of the concrete south-western side of the dam (Fig. 7, 8). In April 2015 losses of water on the dump side were noticed (Fig. 8). The R1 and R2 tailings have been dry-stacked horizontally side-hill. The dumps have flat tops and bench - slope geometries grading downward in N-NW direction. In particular, the R1 dump shows five slopes on an overall height of about 30m and is capped by a later, 40-50 cm thick, sand and clay covering. The R2 dump is about 40m high and exhibits three 10-15m high slopes. A 90 cm thick red-brown coarse-grained backfill overtops the tailings in the easternmost part of the dump. Elongated concave washouts (Fig. 4B) on the N slopes expose the underneath finely layered tailings (Fig. 9A). Such washouts denote a considerable loss of material downhill.

**FIGURE 8:** THE WATER DAM BUILT NEXT TO THE R2 TAILING HIP( APRIL 2015). THE PICTURE ON THE LEFT SHOWS WATER SEEPAGES.

**FIGURE 9** TAILING GEOMETRIES OBSERVED IN THE R2 DUMP

A) FINELY LAYERED TAILINGS UNDERNEATH THE BACKFILL COVER

B) LAYERS OF LS TAILING (SEE TEXT)

C) HS TAILING (SEE TEXT) HORIZON

*Processing methods*

Little information is available on the processing activity at Reps. Most of it has been collected by Demi (2003) Daci et al. (2007) Daci and Sinojmeri (2011) and Daci (2013).The milling and concentration facilities operated from 1971 to 1996. The dressing plant was initially fed by the massive sulfide ore of Spaç, and the plant capacity was 120 000tons/year. In 1983 it was enlarged in order to process higher amounts of ore, coming from various mines of the area (Kaçinari, Thirrës, Tuçit, Majës - Madhe and Laj Reps). In 1984 a working line was set exclusively for processing the mineral from the Gurth Spaç mine. By 1996 4.43 M tons of Cu mineral had been processed. Therefore it is possible to infer that the plant capacity must have almost doubled after 1984, exceeding 239 000 tons/year. The average Cu recovery was 85-88%, the concentration of Cu in the output being 18-20%. A pyrite concentrate with 35% S in average was also obtained through a secondary flotation process (Fig. 10). The crushing operations consisted in two size-reduction stages. The run-of-mine ore lumps (below 300 mm in size) passed through a jaw crusher and, after screening, into a cone crusher. The crusher product was screened at 15mm and the over-sized material was recirculated. The ≤15mm ore was sent to two ball mills where the ore was wet-milled in a closed circuit. The overflow was carried to a spiral classifier and the oversize particles were returned to the mills for regrinding. The pulp was treated with reagents (ethyl xanthate, lime, turpentine, sulfuric acid) and sent to the froth flotation cells. Separation of copper was run at pH 11-11.5. A further flotation was run to concentrate pyrite from the discard of the first flotation. The second flotation was thus performed at pH 5 - 5.5, after bathing in opportune reagents (butyl xanthate, turpentine, sulfuric acid).

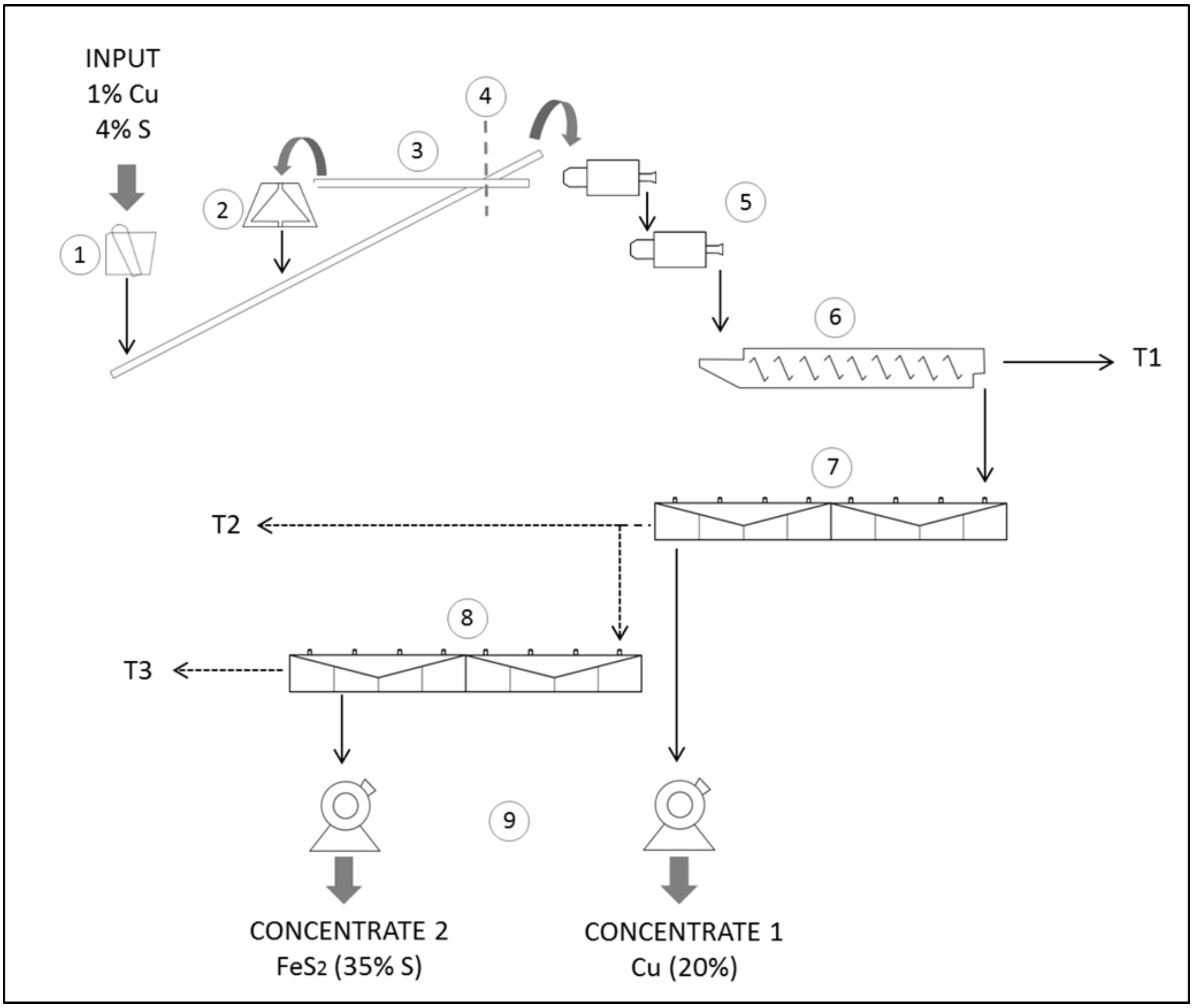

FIGURE 10: FLOWSHEET OF THE REPS DRESSING PLANT. (1) JAW CRUSHER; (2) CONE CRUSHER; (3) RICIRCULATION OF OVER SIZE; (4) SCREEN; (5) BALL MILLS; (6) HYDROCLASSIFICATOR; (7) PRIMARY FLOTATION; (8) SECONDARY FLOTATION; (9) FILTERS.

## 3.3 Materials and methods

*Sample collection*

At Reps 36 solid samples (Appendix B) from two dump bodies (R1 and R2), and 23 superficial water samples (Appendix C) were collected. The tailings were sampled transversally to the horizontal layers, along slope-oriented lines. Sampling lines of R1 are named A, B, C, respectively, whereas sample lines of the R2 dump are named D, E, F, respectively. Given the mineralogical and geochemical preliminary results, water samples were collected to assess acidity and metal content of drainage waters flowing through the most sensitive spot of the Reps site, namely the R2 dump.

The water samples are representative of the upstream flow, pools on the dump roof, runoff (sampled along the R2 dump slopes and at the dump foot ) and downstream delivery (to the Fani river). River water samples were collected both before (November 2013) and after (April 2015) the construction of the artificial impoundment.

*Analytical methods*

Particle size distribution was obtained by dry sieving (from >2mm to <0.063mm) following the standard ASTM size classes. The pH of tailing samples was measured by a pH-meter, after suspending the solid in distilled water (solid:water= 1:2.5). The mineralogical study was conducted by means of optic (reflected and transmitted-light) microscopy, electron microscopy and X-ray powder diffraction (XRPD) analyses. Optical (transmitted- and reflected-light) microscopy was performed on granular samples embedded in epoxy resin and then prepared as polished thin sections. Qualitative XRPD analyses were performed using a high resolution Panalytical X'pert Pro diffractometer, equipped with an incident beam monochromator., hosted at the Earth Science Department of the University of Milan. Scanning electron microscopy (SEM) analyses were performed with a Tescan VEGA TS Univac 5136XM instrument, hosted by the Department of Earth and Environmental Sciences of Milano-Bicocca University, Italy. The electron microscope is equipped with an energy- dispersive (EDS) electron microprobe EDAX Genesis 4000 XMS Imaging 60. Bulk concentration data of major and trace elements were acquired at Actlabs Laboratories (Ancaster, Ontario, Canada) using a Varian Inductively Coupled Plasma (ICP-MS). The powdered samples (<2mm) were previously treated through aqua regia partial extraction. Samples showing concentration over the detection limits were diluted and re- analyzed. Furthermore, electron microprobe spot analyses (EMPA) were performed on single grains of pyrite, chalcopyrite, sphalerite and micro-inclusions. EMP data were collected by a JEOL JXA-8200 microprobe, housed at the Earth Science Department of the University of Milano, Italy. The electron microprobe also allowed to collect images and atomic maps. A series of natural minerals (fayalite for Fe, niccolite for Ni and As, sphalerite for S) and pure elements (Co, Cu) were used as standards. PH, Eh and conductivity of all the water samples were measured in laboratory, after void - filtering. Representative samples were then analysed by multi-elemental ICP-OES Spectro Cirros (Actlabs Laboratories, Ancaster, Canada) after acidification at pH<2.

*Evaluation of acid production*

The AD of solid samples was evaluated according to the AMIRA (IWRI and EGI 2002) revision to the Sobek procedure (Sobek et al. 1978). The Acid–Base Account involves static laboratory procedures to evaluate the balance between acid generating and acid neutralizing processes. The output values are referred to as the maximum potential acidity (MPA) and the acid neutralizing capacity (ANC), respectively. MPA is an estimate of the amount of acid that the sample can release by complete oxidation of sulfides and is expressed as kg$H_2SO_4$/t. The evaluation of MPA is based on the sulfide content and on the conservative assumption that all S is present as pyrite. The procedure for determining the acid neutralizing capacity includes a fizz test, followed by a titration. A negative value of ANC represents a lack of neutralization effects and it is reported in as 0.00. The difference between MPA and ANC is referred to as the net acid-producing potential (NAPP). A negative NAPP (kg $H_2SO_4$/t) value indicates that a sample may prevent acid generation. Conversely, a positive value of NAPP indicates that the sample has an acid production potential.

## 3.4 Results

*hS and lS tailings*

The S concentration data outline two sample populations (Fig. 11) on the basis of sulfide content. These respectively represent high-sulfur materials (hS), characterized by sulfur concentration values of 10.40 – 35.5 wt% and low-sulfur materials (lS), with sulfide ranging between 0.09 and 2.86 wt% (Appendix A). All the hS samples come from the R2 dump. They were collected along the D alignment and on the westernmost side of the dump (sample F7). The in situ materials are dark-grey colored horizons (Fig 9C.), bounded by centimetric, pale yellow-colored and weathering zones. On the other hand, lS samples were collected in both dumps, along A,B,C,E,F alignments (tab.) and represent 87 wt% of the sampled material. These samples present colors varying between reddish- yellow and red (Fig 9B).

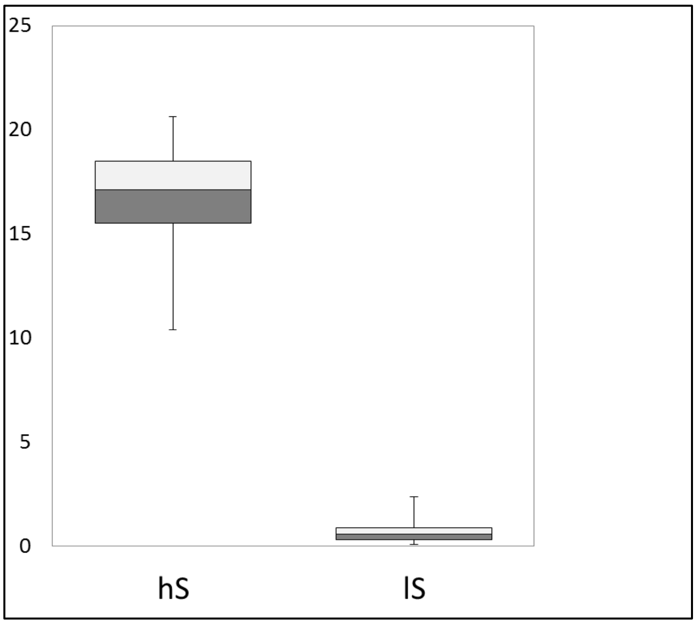

**FIGURE 11:** BLOCK DIAGRAM SHOWING THE HS AND LS CLASSES OF TAILING MATERIALS AT REPS, BASED ON THE S (WT%) DATA DISTRIBUTION

*Mineralogy and mineral chemistry*

Pyrite is the main phase in all the hS samples. It is associated to minor marcasite, chalcopyrite, sphalerite and a Cu-As sulfosalt. Rare galena micro-inclusions were detected into pyrite granules. On the contrary, in the lS class the sulfides are minor phases. Quartz is ubiquitous, while plagioclase has been detected in 80% of samples and chlorite in 70% of samples. Gypsum was detected in all the hS samples and in 30% of the lS. Fe-oxides, Fe-sulfates and rare pyroxenes have been observed by electron microscopy in all the hS samples (Fig. 12). Pyroxenes are in some cases residual (chloritized). Barite forms small (<50µm) discrete granules and inclusions in pyrite. Rare Ti-rich phases have been detected. Heterogeneous concretions of sulfates and silicates cover up both silicate and sulfide phases (Fig. 12). Nevertheless, most of the granule boundaries are sharp and show no alteration. XRD patterns of the of the R1 dump samples indicate the presence of micas, jarosite-group phases, pyroxenes, garnets, clay minerals, hydroxides, talc, amphibole, serpentine, oxides (most probably Mn-bearing oxides, following the geochemical data), that are absent in the R2 dump tailings. The samples are loosed, mainly constituted by isolated grains and sub-millimetric aggregates. Pyrite forms micrometric to millimetric, anhedral, fractured granules. Rare framboidal textures were also noticed (Fig. 13A). Under reflected light pyrite appears to be anomalously anisotropic, probably due to the presence of trace elements in solid solution (mainly As), as shown by mineral chemistry data (Appendix D) and atomic maps (Fig.13B). Chalcopyrite is the main Cu-bearing mineral, the only other Cu phase being a Cu-As sulfosalt (Fig.13C,D). The latter contains the highest concentration (> 20%) of As, that enters as a trace element in all the analyzed phases, as well as Zn. Traces (<1wt%) of Co, and Ni occur in pyrite and chalcopyrite. Co is enriched in pyrite (up to 5'910ppm) relative to the other phases.

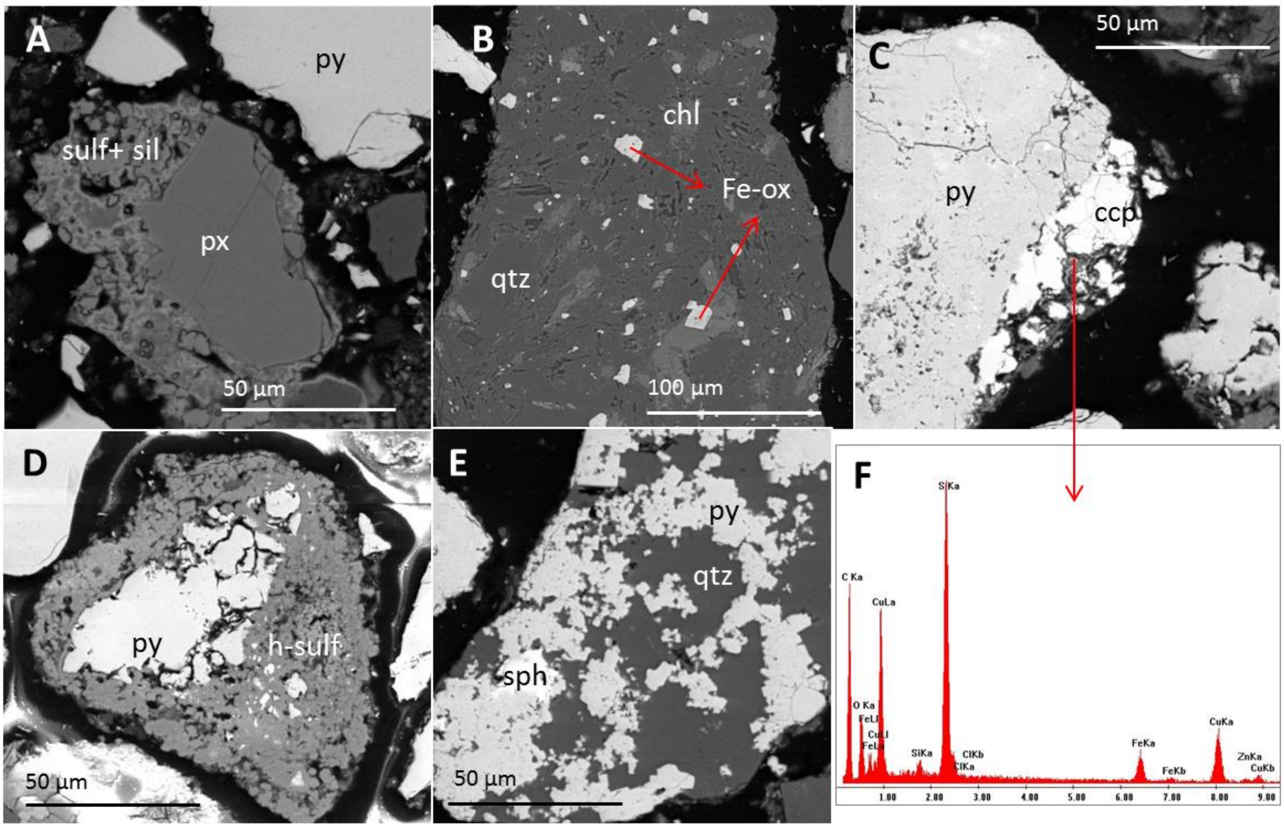

**FIGURE 12:** SEM IMAGES SHOWING SOME PRIMARY AND SECONDARY PHASES OF THE REPS TAILINGS. THE EDS PATTERN (F) SHOWS THE QUALITATIVE COMPOSITION OF A MIXED CONCRETION FORMED BY ALTERATION OF CHALCOPYRITE. PY=PYRITE; PX= PYROXENE; SULF+SIL = CONCRETION OF SULFATES AND SILICATES; H-SULF = HUDROXIDE SULFATE

### *Acid Base Account*

The static test results (tab.) show that the acid generation potential is positive for all our samples. NAPP values in fact are positive and coincide with the corresponding MPAs (ANC=0). The higher sulfide content (10.40 – 35.5%) of the hS samples with respect to the lS ones, leads to a larger amount of $H_2SO_4$ potentially produced, thus to a higher NAPP.

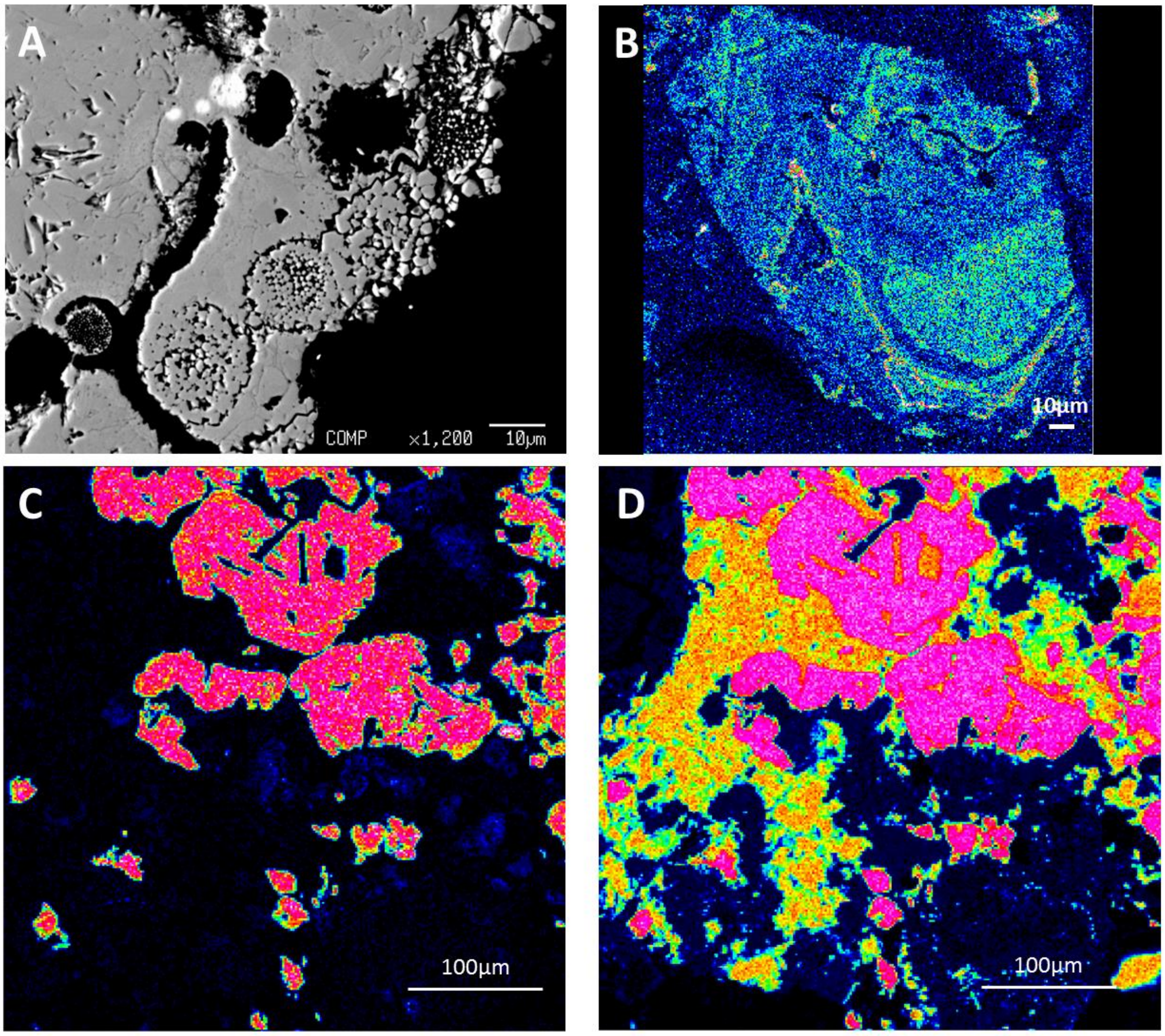

**FIGURE 13:** EMP IMAGES SHOWING
- A) PYIRITE GRANULE WITH MICROMETRIC FRAMBOIDAL TEXTURES
- B) AS ATOMIC MAP OF A PYRITE GRANULE
- C) AS ATOMIC MAP OF CU-AS SULFOSALT PHASES
- D) CU ATOMIC MAP OF CU-AS SULFOSALT PHASES

### *Bulk chemistry*

The major and trace element distribution pattern of, of hS and lS is similar with few exceptions, as shown by Fig. 14. Yet, the two groups differ for the concentration of Cu, Zn, As, Pb, Ag. that is consistently higher in hS samples than in lS samples (Appendix A). S (sulfide) concentration data show a good correlation with Cu, Pb, Zn, As, Ag. Fe, Co, Mo concentration values (Fig. 15A). On the contrary Ti, V, Cr, Ni, Mg, Al and Mn concentration values are higher in the lS samples. Moreover, a lack of correlation exists between the concentration of these element and S wt% as shown, for example, by the Ni (ppm) vs S (wt%) plot in Fig. 15B.

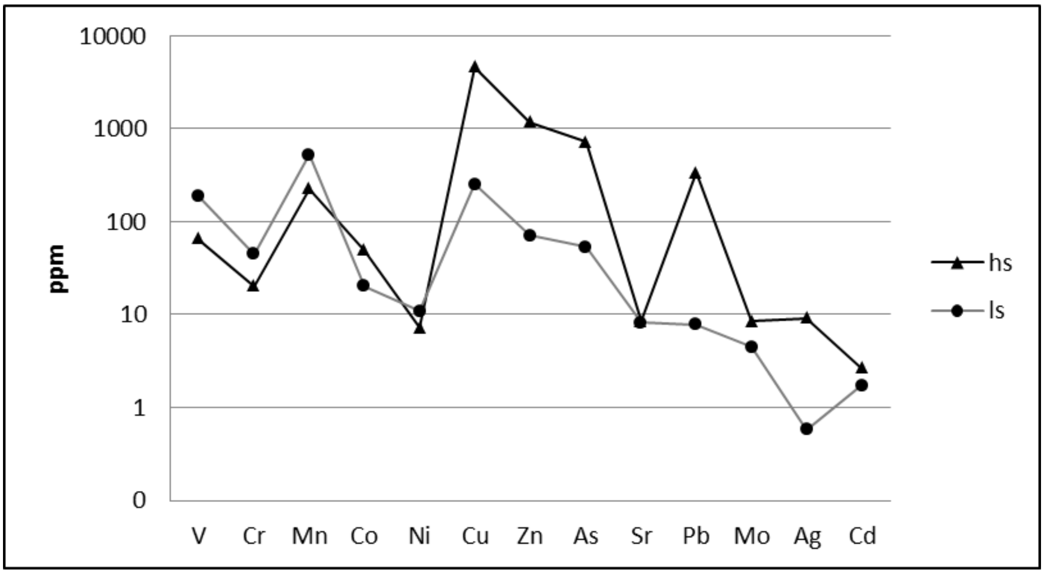

**FIGURE 14:** COMPOSITION (PPM) OF *HS* AND *LS* CLASSES OF SAMPLES FOR SELECTED POTENTIALLY HAZARDOUS ELEMENTS

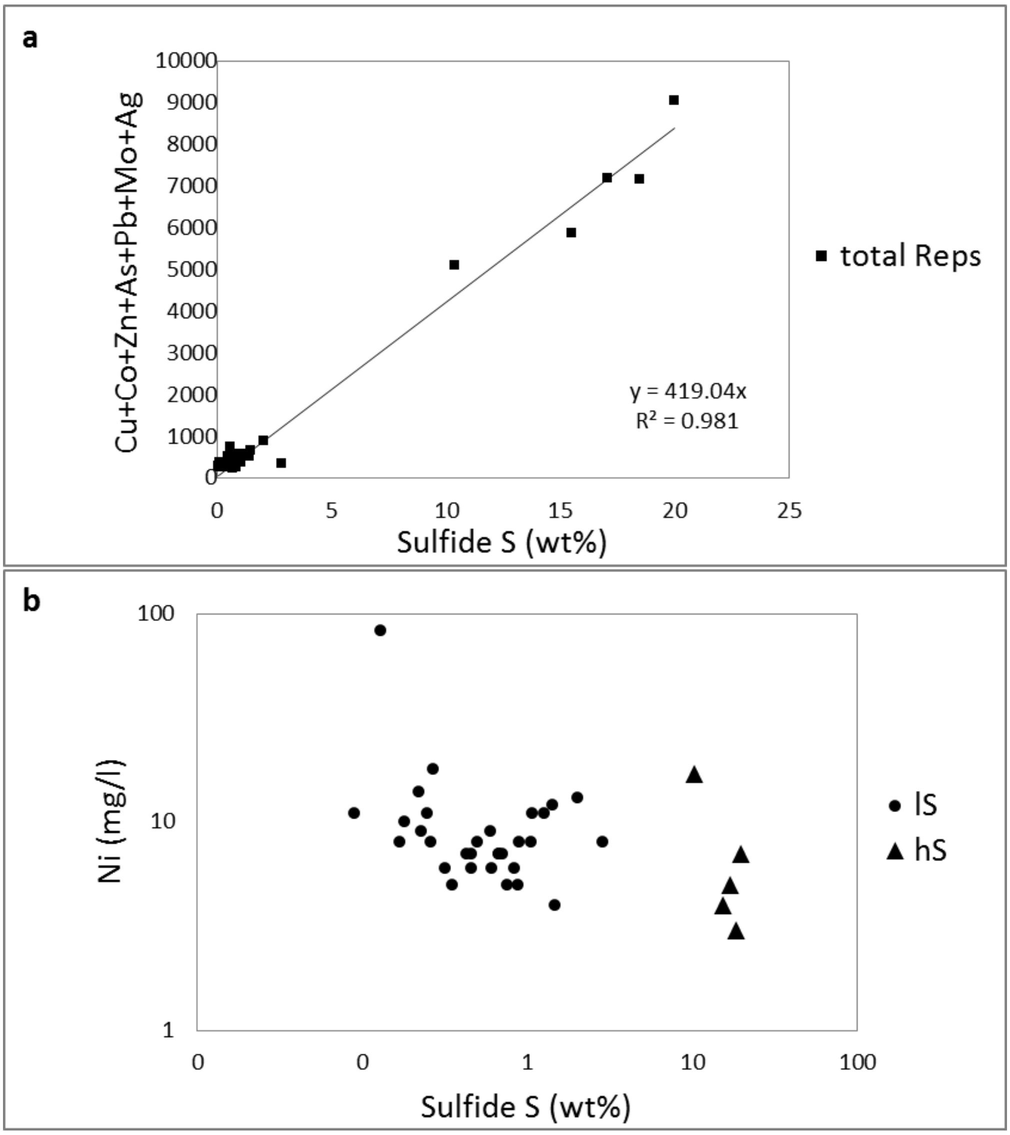

**FIGURE 15:** : BINARY PLOT OF METALS (PPM) VS S (WT%) CONCENTRATION FOR THE REPS SAMPLES

*Particle size distribution*

The grain size of the Reps tailing materials ranges from very fine gravel to very fine silt (based on Udden 1914 and Wentworth 1922), but most samples show the features of sands, from very fine to medium, with variable fractions of silt and fine or very fine gravel. In all samples the distribution is poorly sorted. In R1 dump the fine fraction prevails and the grain size distribution is unimodal in the 90% of the samples. On the contrary, 68% of the R2 samples show a bimodal distribution, with peaks in the fields of the very fine (around 100µm) and coarse sand (above 1000µm). The calculated parameters are given in Appendix C. The central tendency ($D_{50}$) ranges between 78.56 and 826.38µm in the R1 samples and from 104.08 to 2076.11 µm in the R2. The distribution width, expressed by the D90/D10 coefficient varies from 3.77 and 41.37 in the R1 samples while in the R2 samples the range varies between 9.49 and 149.61. As a whole, the R1 samples are more fine grained than the R2 samples (namely, in the R1 samples 52.1% avg. passes through 125µm openings, versus 30.4% avg. in the R2 samples) and less heterogeneous. Among the R2 materials, the hS group appears to be more fine grained than the lS one.

*Waters*

Water chemistry data (Appendix B) show a significant seasonal variation of most element concentrations. In particular, all the runoff waters sampled in November 2013 display higher concentration values than the water sampled in April, 2015, with the exception of k, Cd, Co, Cr, Cu, Zn. Yet, the runoff data (except the values referred to sample R2A19) show high content (> 100 mg/l) of S, Fe, Ca, Al, Mg, followed by Mn and Si. Among sulfide- related metals, Zn shows the highest concentration values. Cu, Co, Cd Pb, and Ag follow in order of abundance. Ni and Cr are also concentrated in drainage waters relative to the upstream waters. S-related metals are in a very good (inverse) correlation with pH values Most runoff waters show in fact an acid pH (3.56 in average), in contrast with the nearly neutral upstream waters. The lowest pH values were detected in November 2013. Furthermore, a chemical-physical zoning exists among runoff waters, in both the sampling periods.

## 3.5 Heterogeneous features and Acid Drainage

The sulfide concentration data highlight that at least two different types of tailing materials have been stacked into the Reps dumps. In particular, we distinguish high sulfide concentration (hS) from low sulfide concentration (lS) tailings. Such a pattern is supported by mineralogical evidences. In fact, sulfide minerals (namely pyrite) are abundant into hS samples, while they constitute minor phases of lS samples. Moreover, the ore-related metals (Cu, Zn, Pb, As, Ag, Mo, Co) concentration in the lS samples is significantly lower than in the hS samples (Fig. 15). Considering the whole data set, a high, positive correlation ($R^2$=0.98) exists, in fact, between sulfide S (wt%) and ore-related metals. These elements are therefore mainly contained in sulfide phases, and the secondary minerals do not represent a significant sink of metals, neither in their low crystallinity, nor in more stable forms (i.e. hematite). SEM analyses, besides, show that most of the sulfide mineral boundaries are sharp and clean, with few traces of reaction, nor secondary precipitation (Fig. 12). Therefore, the low sulfide content of the lS samples is unlikely to represent a mature stage of the AD processes, with massive substitution of the sulfide phases by secondary aggregates. Besides, at the present stage of the process the secondary authigenic phases do not provide any shield against further sulfide reaction (Marescotti et al., 2008). Yet, chemical and physical features of solid and water samples (Appendixes A, B) describe an active acid-drainage process that lowers the pH and contextually increases the concentration of dissolved ions in waters. The dataset referred to water samples, in fact, shows that the waters flowing at the R2 dump foot are more acidic ($pH<4$) and have a higher concentration of metals, with respect to the upstream waters. Moreover, the presence of secondary phases (i.e. gypsum, jarosite, Fe- hydroxides), in the solid samples, even though non-pervasive, indicates that some grade of dissolution-precipitation of S-phases has taken place. The development of AD processes at Reps is mainly controlled by: (i) the presence of highly reactive phases, namely sulfides, in an open-air environment; (ii) textural features that affect the reactivity of the single grains and hence the reaction speed (Akcil and Koldas 2006; Marescotti et al. 2007). Reps tailings, in fact, are small grain sized and have high liberation degree, due to the sequence of dressing stages that led to their final discard (Fig. 10); (iii) low neutralizing capacity of the gangue, as shown by the ANC results. All our samples present a positive acid potential. The MPA is in fact proportional to the S concentration, that exceeds 0.09% in the overall data set. Besides, the pH data referred to the solid materials range between 2.8 and 5.9 (Appendix A) and there is no neutralizing capacity, due to the lack of effective buffering phases such as carbonates. Consequently, the AD process is likely to be persistent in time (Soregaroli and Lawrence 1997), with the strongest effects produced by hS material. The latter in fact yields about 82% of the total evaluated $H_2SO_4$. Therefore, the R2 dump is the most sensitive spot for acid production. Nevertheless, it is worth noting that all the river water samples collected downstream to the R2 dump have a high pH (≥ 6.92). Besides dilution and instantaneous precipitation, a good buffering capacity of the bedrock may be invoked among the causes, despite the local geology is dominated by basalts.

### *Persistence of AD*

Following Servida et al. (2007) we evaluated the persistence (*p*) in time of the AD process for the R2 dump, namely the time required for the R2 tailings to completely drain the $H_2SO_4$. We calculated *p* as the ratio between the total $H_2SO_4$ potential release (TPR) and the annual potential release (APR). The calculation was performed by taking into account the number ($H^+_{2.58}$) of $H^+$ moles required to keep the percolating water at pH= 3.56 (average pH value of the R2 runoff waters, Appendix B). An exhaustive list of the parameters applied to this calculation is given in Table 4. The resulting persistence of the AD phenomenon in the R2 dump is $4*10^3$ years.

| Abbreviation | Value | U.m. | Description |
|---|---|---|---|
| d | 1.89 | $g/cm^3$ | weighed density of tailings |
| M | 705 000 | t | total evaluated mass of the R2 dump |
| A R2 | 140000.00 | $m^2$ | R2 measured area |
| p | 1785 | mm | annual precipitations |
| pH | 3.56 | | |
| MPA avg | 204.48 | kg $H_2SO_4/t$ | total potential release from R2 |
| Vd | 24.99*10^7 | l | drainaga water through R2 |
| APR | 33725.8 | kg $H_2SO_4$ | annual potential release from R2 |
| TPR | 144.16* 10^6 | kg $H_2SO_4$ | total acid potential release from R2 |

**TABLE 4:** MEASURED, INFERRED AND CALCULATED INPUT PARAMETERS FOR CALCULATING THE AD PERSISTENCE AT R2.

A comparison between the time lapse from the plant closure, (about 20 years) and the calculated persistence highlights that the AD process at Reps has just been set up and therefore it cannot yet have significantly altered the primary composition of tailing materials. Chemical data on solid and water samples show that the composition of the runoff water at R2 derives from leaching of sulfides and other phases either. In particular, Ca, Al, Mg, Mn and Si concentrations, deriving from silicates leaching, strongly increase from upstream to runoff waters. Ni and Cr concentration values also increase with drainage, suggesting oxides and silicates leaching. Ni is in fact partially contained in pyrite, but mainly in oxides and silicates, together with Cr, V, and Ti. The runoff water data also reflect the non-homogeneous distribution of hS materials into the R2 dump. The highest metal content and lowest pH values were in fact detected in surficial waters sampled downstream to the D sampling line. The hS materials are expected to be strictly localized in few areas of the dump, namely centrally to the N slope of the R2 dump and in the westernmost edge, where the sample F7 was collected.

## 3.6 Quantitative Flowsheet: effects of single and double flotation

Among the lS class, the R1 and R2 materials differ for grain size and for some mineralogical and bulk chemical features. In general, the R2 samples are coarser grained and more heterogeneous than the R1 samples. Moreover, the silicate and oxide content of R1 tailing samples is higher and affects the bulk chemistry data. In fact, Al and Mn average concentration values in R1 samples are significantly higher. Ti, Cr, Ca and Mg are also slightly enriched in R1 with respect to the R2 lS.

A possible key for understanding the mineralogical and geochemical data presented above is the evolution of the former ore processing methods with time, in particular the transition from a double-flotation to a single-flotation processing stream. An insight of the problem is provided by the Fushe Arrez dumps. Samples of tailing dumps produced during two distinct periods and by different flotation streams were in fact collected at Fushe Arrez (April 2015) and analyzed for sulfide S, major and minor elements. The older tailing dump, produced before 2000 as a by-product of a double flotation, contains less than one half sulfide S than the more recent, single flotation tailing dump (tab. 5). Sulfide-delated trace elements are depleted in FA 4 as well, with the only exception of As and Cu.

| **Sample** | Sulfide S | Fe | Ag | Cu | Cd | Mo | Pb | Ni | Zn | As |
|---|---|---|---|---|---|---|---|---|---|---|
| | %<br>d.l. 0.01 | %<br>0.01 | ppm<br>0.3 | ppm<br>1 | ppm<br>0.3 | ppm<br>1 | ppm<br>3 | ppm<br>1 | ppm<br>1 | ppm<br>0.5 |
| **FA3** | 36.8 | 33.4 | 2.4 | 1560 | 1 | 14 | 61 | 12 | 206 | 890 |
| **FA4** | 15.9 | 19.8 | 0.7 | 2070 | 0.7 | 4 | 15 | 40 | 121 | 276 |

**TABLE 5:** SELECTED ELEMENTS ARE GIVEN FOR TWO TAILING SAMPLES COLLECTED AD FUSHE ARREZ. DATA COLLECTED BY TD ICP AND INAA, AT ACTLABS LABORATORIES (ANCASTER, ONTARIO). SULFIDE S WAS CALCULATED BY DIFFERENCE STOT - SULFATE S . FA3= SINGLE FLOTATION DISCARD; FA4= DOUBLE FLOTATION DISCARD

### *Reconstruction of a processing flowsheet*

In the present work a quantitative flowsheet is provided that integrates information from literature (Demi 2003; Daci et al. 2007; Daci and Sinojmeri 2011; Daci 2013), inferred and computational data. From the available literature we infer that three different discards (T1, T2, T3) must have been produced by the dressing plant activity (Fig. 10), namely by the hydroclassificator and by two different flotation chains. Our mineralogical, grain size and geochemical data, as discussed above, support the presence of at least two different types of tailings (hS and lS) into the R1 and R2 dumps. The quantitative flow-sheet takes shape from the following assumptions.

1) The hS tailing is discarded after chalcopyrite separation (T2), while lS is interpreted as a mixture of T1 and T3.
2) Given an average composition of 1 wt%Cu and 4 wt% S for the unprocessed ore and taking into account the chalcopyrite stoichiometry, we infer that the distribution of S (wt%) in the main sulfide phases ($S_{pyrite}/S_{chalcopyrite}$) of the processing input is 3:1.
3) As we cannot clearly distinguish between the lS tailings (T1 and T3) we assume that the average composition of lS is representative of either T1 or T3. As a matter of fact, as the average S (wt%) value is lower than 1% (Appendix A), the validity of this assumption is not crucial to the following mass balance.

Based on the available data on processing (Demi, 2003; Daci et al., 2007; Daci and Sinojmeri, 2011 and Daci, 2013), the processing is contained a pyrite-chalcopyrite assemblage, 1% Cu ($Cu_{ore}$) and 4% S ($S_{ore}$) in average. The milling and classification stage produced a first tailing ($T_1$) that represented 75% of the input and contained 0.7%S in average ($S_{ls}$). Given the percentage (25%) of the hydro-classification output that was sent to flotation ($F_{feed}$), we used a weighted average in order to calculate the S weight percentage of the flotation input ($S_{feed}$).

$$\textbf{(1)}\ \ (S_{feed} * F_{feed}) + (S_{ls} * T_1) = S_{ore}$$

The resultant $S_{feed}$ is 13.9 wt%. The computational percentage of sulfides in the flotation input is 29.4, based on the $S_{pyrite}/S_{chalcopyrite}$ ratio. The remaining 70.6% represents the non-sulfide gangue minerals. The Cu concentrate ($F_{Cu}$) was 17.8% of the flotation output. The latter was calculated a weighted average, as follows.

$$\textbf{(2)}\ \ F_{Cu} * (Cu_{out}) + (1 - F_{Cu}) * (Cu_{hS}) = Cu_{conc}$$

As the Cu average concentration value of the output ($Cu_{out}$) is 3.92%, the Cu concentration into the final concentrate is 19% and the average Cu concentration in hS ($Cu_{hS}$) is 0.45%, the resulting $F_{Cu}$ is 17.84. Based on $Cu_{hS}$ the second discard (T2) comprised 1.3% chalcopyrite, 29.7% pyrite (given the stoichiometry of pyrite and the $S_{hS}$-$S_{ccp}$ value) and, by difference, 69% gangue. Depending on the processing period, T2 was either discarded (as hS tailings) or sent to the secondary flotation.

$$\textbf{(3)}\ \ (F_{py} * S_{conc}) + (1 - F_{py}) * (S_{lS}) = S_{feed}$$

The secondary flotation produced a 35% S pyrite concentrate ($S_{conc}$) starting from a 19.8% S input ($S_{feed}$), that corresponds to the average $S_{hs}$. As calculated with the (3), the weight fraction of the pyrite concentrate ($F_{py}$) with respect to the secondary flotation feed is 54%, whereas the the remaining 46% corresponds to the flotation discard ($T_3$). $T_3$. The latter is assumed to have the same average S content as the lS tailings ($S_{lS}$) and is almost entirely constituted by gangue minerals.

In summary, the adoption of either a single or a double flotation flow-sheet yelded to different outputs. The output of the single flotation process was constituted by 4.6% Cu concentrate (19 wt% Cu) and two discards: T1 (lS) and T2 (hS), that respectively represented 75% and 20.4% of the initial input. On the other hand, the double flotation process led to produce two valuable concentrates and two discards. T1 (lS) and the Cu concentrate were in the same proportions of the previous case, whereas the secondary flotation produced 9% of pyrite concentrate (35 wt% S) and 11.5% of T3 (lS) tailing. The hydroclassificator tailing T1 is therefore expected to be, by far, the most abundant discard in the Reps dumps. It was produced upstream to the flotation, all over the entire activity of the processing plant. On the contrary, T2 and T3 were produced alternately by processes that operated in different periods of time. In such a frame, the R2 dump represents a mixture of T1 (lS) and T2 (hS), that is the tailings produced by a single-flotation chain. On the contrary, R1 hosts a mixture of T1 and T3, or rather the tailings produced by a double-flotation activity. Despite the hS is a minor fraction (≤ 20.5%) of the whole R2 dump, it represents most of the concern regarding the Reps dump site. This material is localized in irregular non-horizontal patterns, leading to configure massive discharges from the single-flotation stream. The double flotation stream led to a significant reduction of the sulfide content in the tailings. Furthermore, the flotation discard was reduced by 43%.

## 3.7 Conclusions

At Reps AD processes are active, as indicated by low pH values and high metal load in the waters draining the R2 dump. These effects are mainly due to the presence of reactive sulfides and to the lack of buffering phases, in small grain sized materials. More than 80% of the material piled in R1 and R2 dumps has a sulfide content <3% (lS). The tailing material with S>10% (hS) is only localized in certain areas of the R2 dump. Notwithstanding it represents less than one fifth of the Reps tailings, the hS material has a high acid generating capacity and it yields about 82% of the total evaluated $H_2SO_4$ production. Therefore, most of the concern regarding the site of Reps is due to the R2 dump, where the AD process is persistent on a time span of thousands years. A separate management of the hS material would have reduced by over 40% the tailing mass and furthermore it would have prevented most of the acid drainage production.

CHAPTER 4

# Evaluation of heterogeneous sulfide – rich tailings as secondary raw materials. Reps case-study

## 4.1 Pyrite market and potential tailing recycling market

The main industrial application of pyrite in most countries worldwide used to be the production of sulfuric acid (Ober 2000), but since the recovery of sulfur from oil and sulfide processing was introduced as a diffuse practice, the pyrite market has become quite limited. However, pyrite is highly available and very economic and its mineral properties are useful to some minor industrial applications. For instance, pyrite is widely used as a re-sulfurizing agent for steels, in order to increase its machinability. Another common application is in grinding and abrasive tools, due to the mineral hardness. The capacity to absorb ultra-violet radiation make it useful as a glass pigment, i.e. for the production of brown bottles (Schellenbach and Krekeler, 2012). The roasting of pyrite (as well as of other sulfide ores) releases sulfur dioxide. The latter has several applications like in the paper production and in the food industry, where it is used as preservative. Pyrite is also a semiconductor and it has become interesting for the production of low cost solar panels (Wadia et al. 2009) and as a cathode material in non-rechargeable lithium batteries. Nevertheless, such technological applications require high purity and homogeneous grain size of the raw material, hence synthetic iron disulfide is normally preferred (Zhang et al., 2011; 2012). The presence of impurities, in fact, affect the semiconductor properties (Abraitis et al. 2004; Savage, 2008). Fine pyrite mineral particles have been successfully applied to the treatment of waste waters derived from industrial sources of As, Cu, Cr, thus avoiding the use of chemical reagents. For instance, pyrite is an efficient reductant of Cr(VI), as well as an adsorbent and coagulant for Cr(III) hydroxo-complexes (Zouboulis et al., 1995). Such applications do not exclude the problem of waste management, as the resulting metal-rich, fine pyritic discards require an opportune, safe storage. The use of pyritic mine and processing discards as soil amendment has been evaluated in the past years. Pyritic tailings, in fact, can increase the availability of micronutrients to calcareous or deficient soils. However, it is necessary to characterize precisely the bulk chemistry of the amendment and carefully monitor the concentration of trace elements, in order to avoid soil contamination (Tozsin and Arol, 2015). A large market for pyrite does not exist. Yet, the removal of high tonnages of hazardous (and costly) discards, coupled with the possibility to sell them as industrial minerals may be in several cases a main driver for pyrite recycling. The reuse and recycling of tailings, in particular, may be convenient for major processing costs have already been encountered.

| | SULFEX 600 * | SULFEX 06 * | SULFEX 520* | PY CONC ** | PY POW ** | PY LUMPS ** | PY GRAN ** |
|---|---|---|---|---|---|---|---|
| **Fe (%)** | min 38 | min 40 | min 40 | 44-45 | | 41-43 | 41-43 |
| **S (%)** | min 44 | min 45 | min 45 | min 50 | 50 - 48 | min 48 | min 48 |
| **$SiO_2$ (%)** | | | max 8 | 1-2 | | 1-3 | 1-3 |
| **Grain size requirements** | $d_{50}$ = max 10%<br>$d_{90}$ = max 15% | > 6mm = max 10% | 5-20 mm = min 90% | | 50-150µm | 10-50mm | 1-5mm |

**TABLE 6: SAIL PARAMETERS FOR SOME REAL PYRITIC PRODUCTS.**
*** COURTESY OF VENETA MINERARIA; ** COURTESY OF AGAMMYA INTERNATIONAL (HTTP://WWW.SULPHURPYRITES.COM)**

## 4.2 Gravity separation applied to recycling

When the contained value of the ores is low, it is essential to reduce the operational costs. Energy consumption is a key parameter for assessing the processing viability. In general, the physical methods are low-energy consumers, if compared to the chemical methods and the gravity separation equipment has a lower cost per tonne than other technologies. Furthermore, such methods require the use of little or any reagent, thus minimizing the environmental impact as well. Gravity concentration is the separation of minerals based on differential movement of particles characterized by different specific weight and hydraulic properties. (O Burt, 2002; Willis and Napier-Munn, 2006). Some gravity methods are often selected for dealing with low-grade. low-tonnage and small-scale streams, also in completion to other techniques, in order to improve the efficiency and reduce the use of reagents (Sousa et al., 2010). Gravity separation is widely used for tailing reprocessing, for instance to recover residual heavy or precious metals from flotation/leaching discards (Willis and Napier-Munn, 2006; Sousa et al., 2010). Shaking tables, in particular, can provide a high recovery/enrichment ratio and still constitute a suitable method for low tonnage streams. The operativeness of shaking tables is based on physical mechanisms like stratification under water riffles, separation through a flowing film and application of a horizontal force (O Burt, 2002; Willis and Napier-Munn, 2006). This kind of technology requires low installation capital and operating costs, any use of reagents and moreover it can be applied to a wide range of grain size (Vieira, 2006). Therefore, a shaking table method, coupled with an upstream sieve and a downstream filter appears as a suitable option for both (i) reducing energy consumption and (ii) reducing the loss of material.

## 4.3 Materials and methods

Gravity separation tests were performed by the use of a *Gemini* water shaking table (Fig. 16), hosted at the Department of Earth and Environmental Sciences of Milano-Bicocca University, Italy. The *Gemini* has a fiberglass, trapezoidal deck. The latter is longitudinally split in two symmetrical sides by a pipe that delivers water along the entire deck length through a series of taps. The deck is supported by a steel frame. The table has a longitudinal adjustable tilt and shakes in the same direction, with variable speed. The table is fed through a conic vibrating feeder. The input rate can be regulated, as well as water supply. The granules are driven ahead and enter the channels on the deck depending on their relative response to the acting forces.

The output of each run included a concentrate, a mix and a tailing, based on the specific weight of the materials. The output products were poured into plastic containers by the use of a funnel and oven-dried at 60 °C.

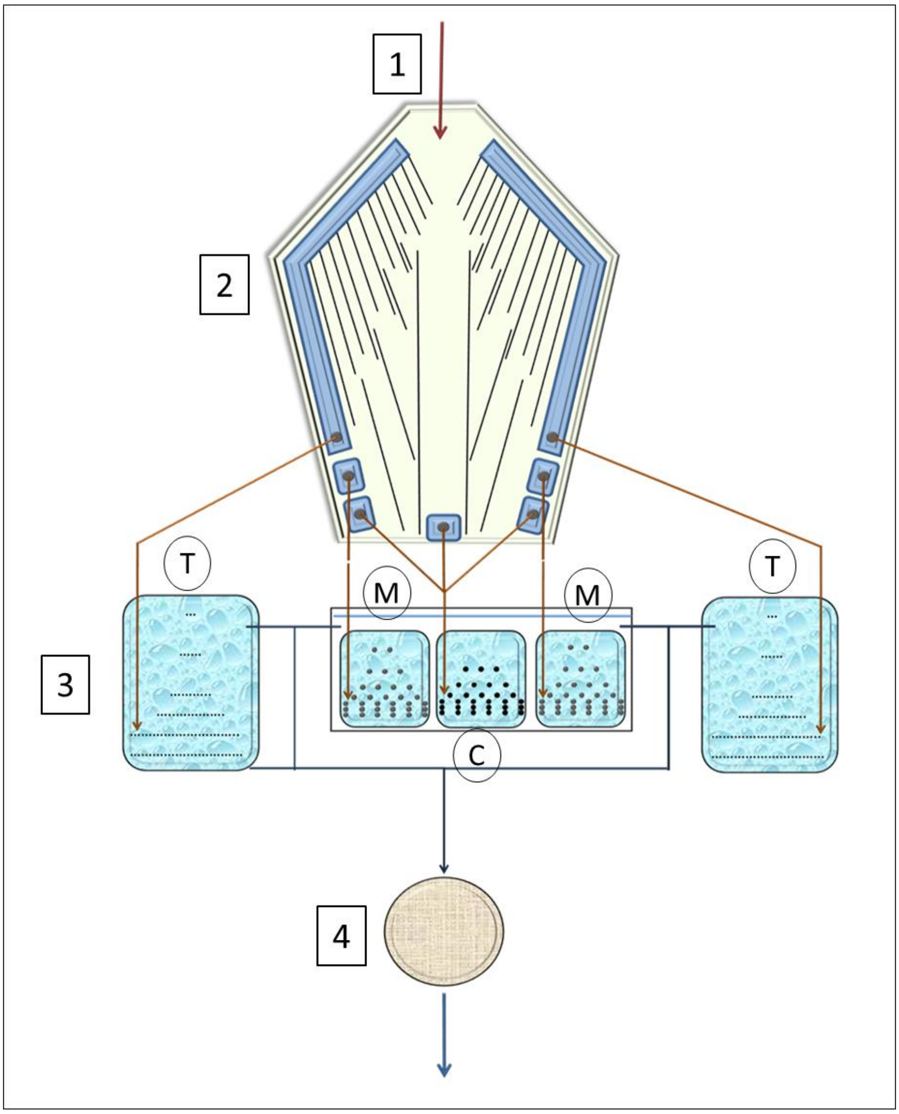

**FIGURE 16:** SCHEMATIC REPRESENTAION OF THE *GEMINI* SHAKING TABLE. (1) FEEDER; (2) SEPARATION DECK; (3) SETTLING BUCKETS (C=CONCENTRATE; M=MIX; T=TAILING); (4) FILTER

Grain size analyses were performed by dry-sieving, using standard ASTM size classes. Adopted screen light dimensions were: 1mm, 0.5mm, 0.25mm, 0.125mm, 0.063mm. The >1mm grain fraction was discarded. XRD analysis were performed on the concentrate, the mix and tailing outputs and compared with those obtained from each corresponding feed. Bulk concentration data were acquired at Bureau Veritas Laboratories (Ancaster, Ontario, Canada). Sulfide S was calculated as difference of total sulfur and sulfate S. Au concentration was detected by INAA fire assay, at the Aclabs Laboratories. The set of major and minor elements was analysed by lithium fusion ICP.

Four mixed samples were prepared, starting from R tailing samples (D, E, F lines). In preparing these samples we took into consideration two main variables. (1) the pyrite content (from mineralogical analyses, supported by geochemistry) and (2) the grain size.

- $Feed_1$: mix of hS (D1-4, F7) samples (120g each. All the grain fractions are proportionally represented. The mix passed through a 500µm screening and the coarser fraction went through a closed circuit regrind in order to obtain a <500 µm fine grained sample.
- $Feed_2$: mix of hS (D1-4, F7) samples (150g each). The mix passed through a 500µm, screening and the coarser fraction was discarded. The finer grain fractions are proportionally represented.
- $Feed_{3:}$ mix of hS and lS (D1-4, E1-5, F1-7) samples. All the grain fractions are proportionally represented. The mix passed through a 500µm, screening and the coarser fraction went through a closed circuit regrind in order to obtain a <500 µm fine grained sample.
- $Feed_4$: mix of hS and lS (D1-4, E1-5, F1-7) samples. The mix passed through a 500µm, screening and the coarser fraction was discarded. The finer grain fractions are proportionally represented.

A further test ($R2_1$) sample was collected along the D line, specifically in correspondence of a pyrite-rich horizon. The test was performed with introduction of a filter downstream to the shaking table. Moreover, the settling of particles was improved by lengthening the delivering pipes to the button of the settling buckets (Fig. 16) and by introducing a longer settling time after the end of the separation test. Two feed samples were created by parting.

- R211 was delivered to the shaking table without preliminary screening.
- $R21_{63\text{-}500}$ was prepared by sieving, in order to obtain a 63-500µm feed. The finer and coarser grain fractions were discarded.

The separation tests were performed with an average water flux of 0.18 l/s.

## 4.4. Results

All the concentrate ($C_{1\text{-}4}$) and the mix ($M_{1\text{-}4}$) outputs of the shaking table tests are relatively enriched in pyrite, as shown by the XRD patterns and by the concentration data (Appendix E). Furthermore, the tailings ($T_{1\text{-}4}$) are relatively enriched in silicates and Al-silicates. A high inverse correlation in fact exists between S and either $SiO_2$ (R2=0.98) or $Al_2O_3$ (R2=0.97) data in the outputs of the first run of tests. CaO shows the lowest correlation ($R^2$=0.12) with the distribution of silicates, mainly due to the abundant presence of gypsum into the concentrates (Fig. 17). The concentrates obtained from the sulfide-rich feeds ($C_1$ and $C_2$), show a more effective relative reduction of gangue. Moreover, $C_1$ and $C_2$ constitute the 32.54-36.54% of the shaking table output, whereas the concentrates deriving from heterogeneous-samples ($C_1$ and $C_2$) are 15.92-16.48% of the output, the major fraction being the tailings (59.34-63.09%). The mixes ($M_{1\text{-}4}$) constitute the lowest weight fraction of all the outputs (4-14%) but are always relatively enriched in pyrite (Appendix E.). The feeds prepared by screening ($Feed_2$, $Feed_4$) show a higher enrichment ratio, with respect to the re-grinded products ($Feed_1$, $Feed_3$), either in case of a heterogeneous (lS+hS) or a sulfide-rich (hS) feed.

During the first set of tests a percentage between 15 and 18 of fine-grained materials was lost to the drainage. Therefore, for the second set of tests (R21, $R21_{63\text{-}500}$ feeds) a filter was introduced downstream to the drain and the settling of particles was improved, which allowed to reduce losses to 7-12%.

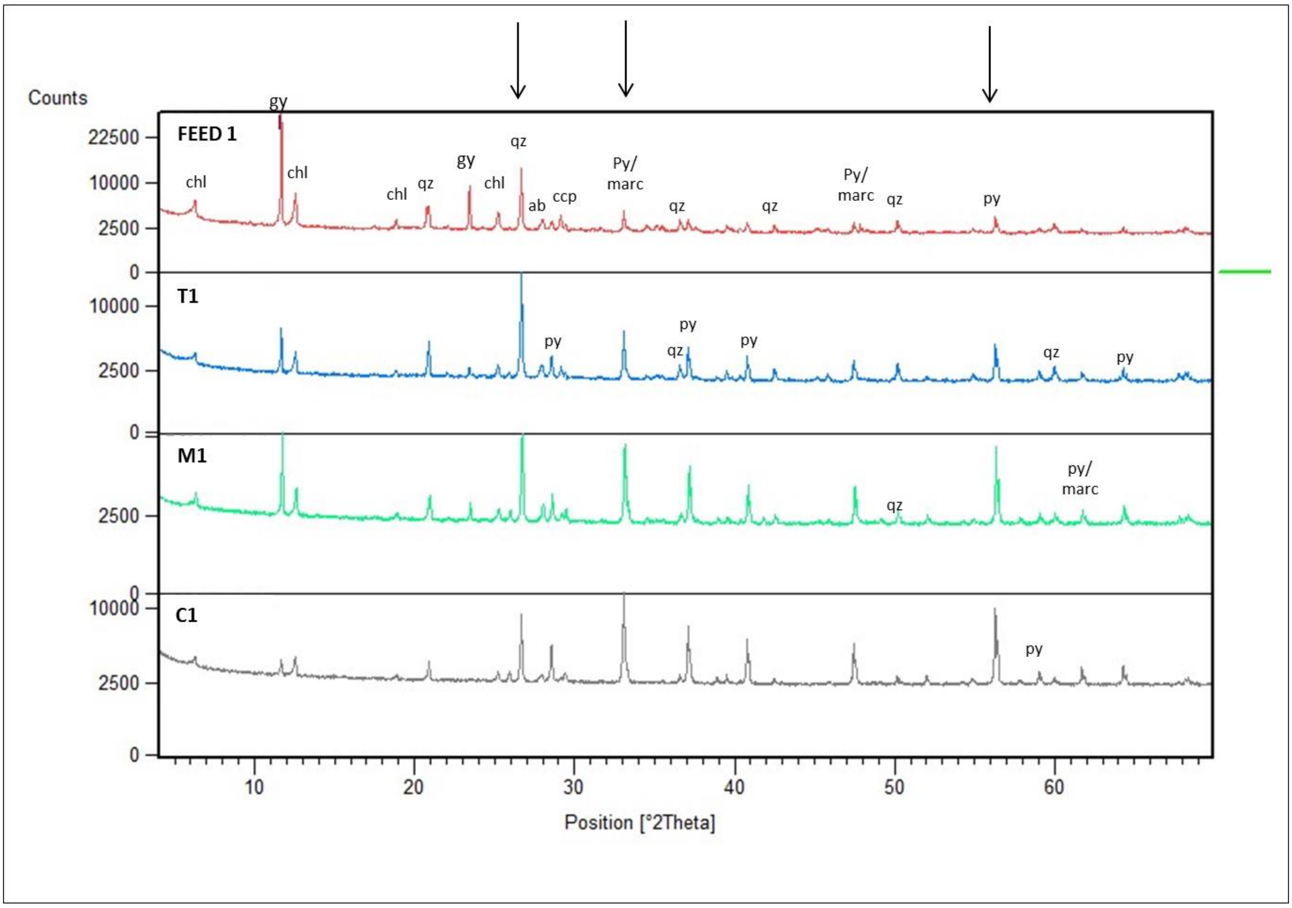

**FIGURE 17:** XRD PATTERNS OF THE FEED 1 INPUT AND THE SEPARATION OUTPUTS. THE ARROWS INDICATE REPRESENTATIVE PEAKS FOR COMPARISON. MAJOR PEAKS ARE LABELED: CHL= CHLORITE; GY=GYPSUM; QZ= QUARTZ; AB= ALBITE; CCP= CHALCOPYRITE; PY= PYRITE; MARC= MARCASITE.

## 4.5 Discussion

The diffractogram peaks (Fig. 17), the positive enrichment ratio ([S] concentrate/ [S] feed) values and the correlation data between major elements show that the *Gemini* table is an effective separation method for R2 tailings. The gravity separation, in fact, produces concentrates that are relatively enriched in pyrite (Fig. 17, 18), starting from feeds that are either sulfide-rich (hS) or heterogeneous (hS+lS). A closed circuit regrind upstream to the separation produces a more sulfide -rich feed with respect to a 500µm screening, either in case of a heterogeneous or a hS starting material. Nonetheless, the $C_4$ concentrate is more sulfide-rich than the $C_3$ and the S concentration is equal in $C_1$and $C_{2.}$ The >500µm rejected fraction is to be considered within the recovery calculation, in order to compare properly the results obtained from the different feeds (Tab. 7). The actual concentration ratio (ar) was thus calculated by taking into account the fraction that was eliminated from the hS (16.82%) and from the heterogeneous (29.36% ) mix to create respectively $Feed_2$ and $Feed_4$. The actual recovery (ar) was then evaluated with respect to the composition of the starting materials (sm), represented by the $Feed_1$ and the $Feed_3$. The actual recovery is hence calculated as $\mathbf{ar = S_C * ac / S_{sm}}$ , being $S_C$ and $S_{sm}$ the concentration of S into the concentrate and in the starting material, respectively.

The total recovery ($r_{tot}$) is the recovery of sulfide S with respect to the overall R2 dump. Since the hS materials constitute 20% of the R2 tailings and contain about 80% of the total sulfide, the total recovery of the $C_1$ and $C_2$ concentrates is to be corrected for these data (Tab. 7).

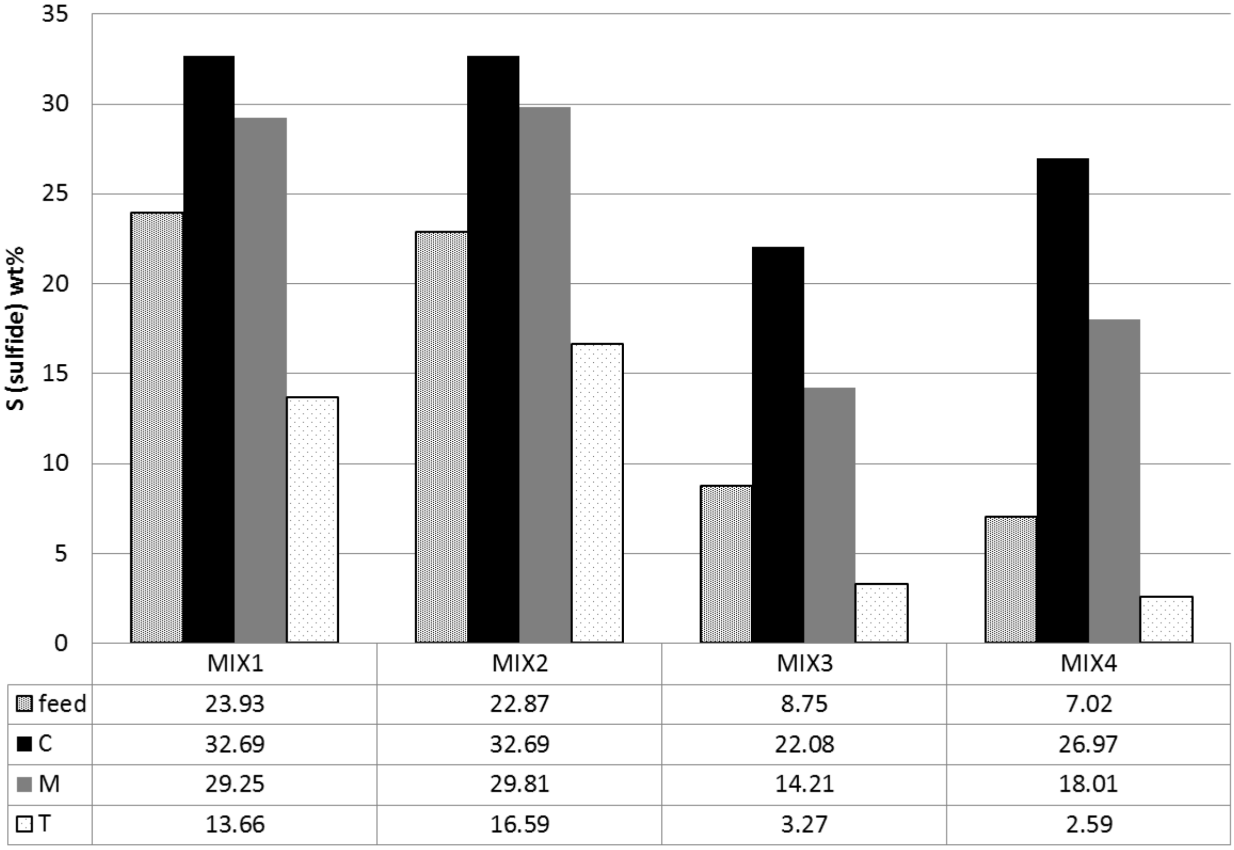

**FIGURE 18:** DIAGRAM SHOWING THE SULFIDE CONCENTRATION (WT%) AND THE RELATIVE ENRICHMENT RELATIONSHIPS BETWEEN THE FEEDS 1-4 AND THE SHAKING TABLE OUTPUTS.

| | Enrichment ratio ([S] concentrate/ [S] feed) | Conc. Ratio (C wt/feed wt) | actual r | r feed | r tot |
|---|---|---|---|---|---|
| C1 | 1.37 | 0.33 | 0.33 | 0.44 | 0.36 |
| C2 | 1.43 | 0.37 | 0.30 | 0.43 | 0.29 |
| C3 | 2.52 | 0.16 | 0.16 | 0.42 | 0.42 |
| C4 | 3.84 | 0.16 | 0.11 | 0.43 | 0.43 |
| M1 | 1.22 | 0.15 | 0.15 | 0.18 | 0.15 |
| M2 | 1.30 | 0.13 | 0.11 | 0.14 | 0.11 |
| M3 | 1.62 | 0.07 | 0.07 | 0.11 | 0.11 |
| M4 | 2.57 | 0.05 | 0.03 | 0.08 | 0.08 |

**TABLE 7:** CONCENTRATION PARAMATERS FOR THE C AND M OUTPUT OF THE FIRST ROUND OF GRAVITY SEPARATION TESTS (SEE TEXT)

The results on enrichment and concentration ratio, combined with the grain size data outline a series of possible recovery scenarios for the R2 tailing dump (Fig. 19).

- Reprocessing the hS materials with a closed-circuit regrind upstream would require to re-work 20% of the R2 tailing dump. The separation would lead to a S recovery of 44%. The overall S recovery from the dump would be 36%.
- Reprocessing the hS materials via upstream screening and exclusion of the <500 µm grain fraction would feed the gravity separation with 17% of the R2 tailing dump. The separation would provide an actual recovery of 42%. The overall S recovery from the dump would be 29%.
- Reprocessing the entire R2 dump with a closed-circuit regrind would lead to recover 42% S in total.
- Reprocessing the entire R2 dump by applying an upstream screening and exclusion of the <500 µm grain fraction would feed the gravity separation with 71% of the R2 tailing dump. The separation would lead to recover 35% S in total.

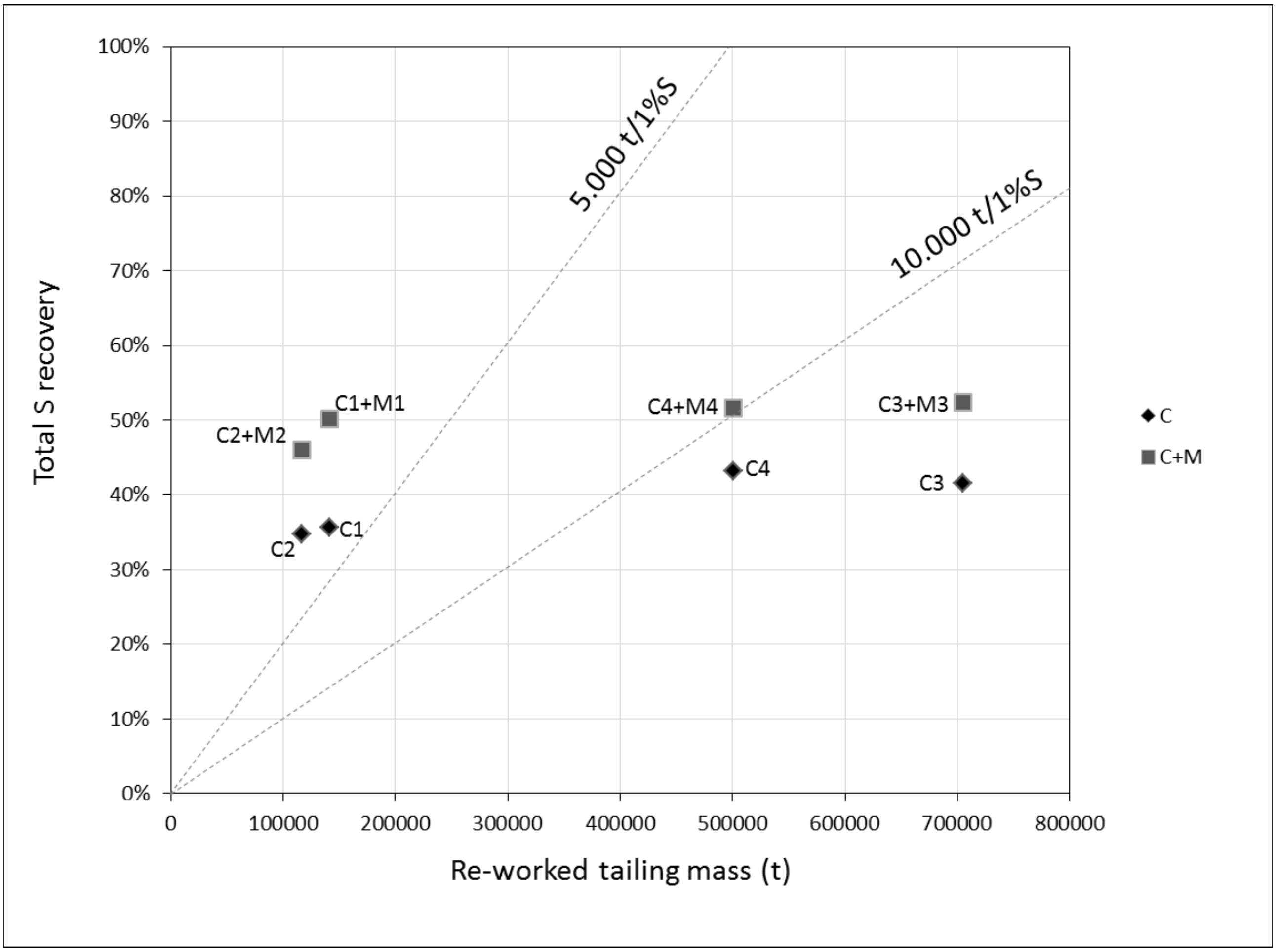

**FIGURE 19:** TOTAL S (WT% ) RECOVERY VS THE HYPOTETICAL RE-PROCESS MASS. C=CONCENTRATES ; C+M= BLENDING OF MIX AND CONCENTRATE OUTPUTS

The predicted results of recovery are graphically shown in Fig. 19. The diagram shows the amount of R2 tailings that must be reworked as a function of the desired S recovery. As for processing in general the working costs are almost proportional to tonnages (O Burt, 2002; Willis and Napier-Munn, 2006), the ideal goal is to recover as much valuable as possible, by processing the lowest amount of material. For instance, the 5 000t/1%S line defines an economically advantageous field. The results of S concentration and recovery for the samples $C_3$ and $C_4$ depict a scenario of effective separation, but do not fill the economic requirements for a sealable product (Tab. 6). In order to increase the recovery and gain value an option would be to blend the concentrate and mix (C+M) of each output. As the input samples show a high liberation degree (SEM, MP images), such a solution would not require regrinding and gravity reprocessing of the mixes. Moreover, the enrichment ratio in the M samples is positive, with S concentration values closer to those of C samples than to the T sulfide content. Therefore, blending is expected to increase the total recovery (Fig. 19), without requiring further processing. Nevertheless obtaining a $M_1$+$C_1$ product appears to be an ideal solution for R2 reprocessing, it is necessary to consider the high costs the re-grinding. Thus, a careful costs/benefits analysis is required, in the light of the potential product value.

The results obtained from samples Feed $_{1\text{-}4}$ are highly affected by loss of ultra-light tailings downstream. The effective recovery of the finest fractions (<50µm) is a major problem of gravity concentration. Furthermore, the presence of slimes (ultra-fine particles) can change the viscosity and hence reduce the effectiveness of separation. Very fine particles (<10µm) are hence commonly removed by the use of hydrociclones (O Burt, 2002). The second run of tests was performed with minor losses of ultrafine particles to the drainage, due to the prolonged settling time and to the introduction of a filter downstream. Yet, the particle size must have greatly affected these tests. In fact, despite the input samples (R21, R21$_{63\text{-}500}$) have the highest S concentration values, the recoveries do not improve significantly, with respect to the results of the first run (Appendix E). The R21 sample, in particular, was directly fed to the shaking table, without preliminary size-control. The resulting concentrate (R21$C_1$) shows the lowest enrichment ratio and a weak concentrate ratio, compared to the other tests. On the other hand, the exclusion of coarser and finer grain sizes in the preparation of R21$_{63\text{-}500}$ decreased the S concentration of the feed sample. One possible solution for reducing the size effect would be to feed the shaking table with different grain size classes separately.

Ideally, the alternatives for tailing separation at Reps are the following:

- To extract single hS horizons and lenses from the dump, hence gaining a very low- tonnage and high grade product.
- To reprocess the hS tailings and create a C+M sealable product, with an overall extraction of S comprised between 40% (screening upstream) and 50% (regrinding upstream). Yet, such an option would require an efficient selective removal, which could be difficult to achieve.
- To reprocess the entire R2 tailing dump with upstream screening and set the shaking table in order to obtain a C+M final concentrate. Such an option would require higher working costs than the previous, but a S extraction over 50% could be obtained
- Reprocessing the overall dump with regrinding appears to be a cost-prohibitive option (concentrates below the 5 000t/1%S curve, Fig. 19) and moreover it does not assure a more effective recovery return.

The selective extraction and processing of hS horizons, with a (M+C) table setting is likely to produce satisfactory S concentration values, being 48% the minimum for a fine-grained sealable pyritic product, (i.e, *Sulfex 06*, or *Py pow*, Tab. 6). The applications for such products would be either in the glass, paper or abrasive industry. In fact, the presence of impurities, namely As, Co, Ba, Ni, Zn, Cu in pyrite (Appendix E; Fig.13B) make it unsuitable for technical applications such as in the semiconductor industry. For the same reason, the use of these materials is not recommended in soil-amendment or other environmental applications. Moreover, the grain size of the tailings is out of range for the steel resulfurization.

On the other hand, gravity separation is a viable and advisable option for extracting sulfide-rich materials from tailing dumps and hence to reduce their environmental footprint. In fact, even if not recycled, lower volumes of hS tailings could be managed separately, with increased environmental benefits and contained costs. For instance, a C1-like (32%S) tailing would account for about 6% of the present R2 mass, hence it would both extract a significant amount of sulfide S and constitute a relatively easy-to manage dump. On the other hand, a C3-like (22%S) tailing dup would account for about 15% of R2. The latter would be therefore a less preferable option.

*Comments on Au separation and metal recycling*

One widespread application for the reprocessing of tailings is metal recovery, in particular precious metal recovery (Willis and Napier-Munn, 2006; Zhang et al., 2006; Antonijevic et al., 2008; Valderrama and Rubio, 2008; Dehghani et al., 2009; Sousa et al., 2010; Hudson et al., 2011; Lottermoser, 2011). Among the processing discards of the Mirdita and Puka mining districts are some high metal - containing materials, with features that would favor the concentration of either Cu (ENVSEC, 2005), or Au (Kastrati et al., 2014). Preliminary concentration tests have also been performed by the use of the *Gemini* shaking table, in order to separate gold from various tailings. The results indicate that the Au concentration in tailings at some sites (namely Prosek, Fushe Arrez and, to minor extent, Reps) may justify re-processing. The highest Au concentration values were detected in the <38µm grain fractions (Tab. 8). Preliminary concentration tests were performed with feeds created by opportune blending of tailing samples. A 250 - 38µm grain fraction range was chosen for the separation tests. The obtained recoveries may be improved by mixing the finest fractions and the concentrates and by adding a closed circuit regrind upstream to the gravity separation (Kastrati et al., 2014)

| **Samples** | **Au**<br>**ppm**<br>**d.l 0.005** |
|---|---|
| **R2** | 352-684 |
| **R2 - F** | 577 |
| **Rr** | 42-52 |
| **Sp** | 155 |
| **Pr** | 1260 |
| **Pr - F** | 6070 |
| **Ku** | 301 |
| **Fa (avg)** | 1350 |
| **R2C1** | 1.000 |
| **R2M1** | 1.017 |
| **R2C** | 759 |
| **PRC** | 3730 |

**TABLE 8:** REPRESENTATIVE GOLD CONCENTRATION DATA ON TAILING SAMPLES FROM FARIOUS DUMP SITES IN NORTHER ALBANIA. R2= REPS 2; RR= RRESHEN; SP= SPAC; PR= PROSEK; KU= KURBNESH; FA= FUSHE ARREZ. THE “F” LABLE INDICATES A <38µM FINE FRACTION. OUTPUT OF THE GRAVITY SEPARATION ARE INDICATED AS EITHER C (= CONCENTRATE), OR M (= MIX)

## 4.6 Conclusions

The water shaking table method is effective in separating valuables from the R2 tailings. In particular, the concentration of pyrite may lead to recover 29-52% of the total sulfide S of the R2 dump. The highest S recovery (52%) would be acquired by reworking the overall R2 dump and blending the mix and the concentrate outputs (M+C) of the gravity separation. A more cost-effective solution would be to localize and reprocess only the hS tailings with a closed circuit regrind upstream to separation, which would yield a 50% S recovery. The size-effect due to the presence both ultrafine particle a relatively wide size range ( >500 µm - < 38 µm) can be reduced by feeding the shaking table with different grain size classes separately.

The final concentrate may also become a sealable product and the gold content may increase the value of pyritic concentrates, given a measured selection of the separation input and parameters. Separation can therefore be used to both confer value to wastes and create smaller sulfide-rich dumps, with lower reclamation costs.

## CHAPTER 5

# General conclusions

In the abandoned mining and processing site of Reps two tailing dumps (R2 and R2) have been studied. The site is subject to Acid Drainage processes, as indicated by the ABA results and by low pH values combined with high metal load in the waters draining the R2 dump. The AD effects are likely to last over a time span of $10^3$ years. Two different types of tailings (hS, lS) have been recognized based on the sulfide S content. These are interpreted as by-products of two different mineral processing chain. In particular, the R1 dump hosts two tailings (T1 and T3) deriving from hydroclassification and from a double flotation stream, respectively. The primary flotation was dedicated to Cu concentration and produced a pyrite-rich tailing that went through the secondary flotation in order to obtain a pyrite concentrate. Therefore, all the resulting tailing materials are sulfide-poor (lS). On the other hand, the R2 dump hosts tailings deriving from a single flotation stream, which led to obtain a Cu concentrate, a sulfide-poor (lS) tailing from hydroclassification and a sulfide-rich (hS) tailing from flotation. As a consequence, more than 80% of the material piled in R1 and R2 dumps has a sulfide content <3% (lS). The hS tailing (S>10%) is only localized in certain areas of the R2 dump and accounts for about 82% of the total evaluated $H_2SO_4$ production. It is stressed that a separate management of the hS tailing would have prevented most of the acid drainage effects. When the double flotation stream was active, in fact, the discard was reduced by 54% and moreover it was entirely constituted by lS (T1 and T3) tailings. In other words, a double flotation stream led to a much lower environmental imprint of the discarded materials and gained some value by selling the more contaminating fraction. Multiple waste streams in processing chains are widespread (Geise et al., 2011; Schellenbach, 2011) and features similar to those observed in Reps dumps are likely to be common, as well. As a matter of facts, the alternation of single and double flotation processing chains may produce small amounts of high sulfide content tailings, yet largely responsible for the majority of the acid drainage effects. Therefore, in inactive sites the environmental management should take start, when possible, from the knowledge of the former processing methods and from a site-specific characterization of each dump, in order to assess the presence and distribution of both high-sulfide and low-sulfide content materials. On the other hand, the separation of pyrite in active plants (for instance downstream to Cu-flotation) whether the value of the obtained pyrite concentrate is economic or not, could be useful to reduce both the costs waste management and the environmental impact.

Re-processing is advisable as a way to reduce the environmental footprint of tailing dump, either at active or closed sites. In particular, the water shaking table separation is a cost-effective and low-impact method that can be successfully applied to the processing discards. At Reps the effectiveness of pyrite separation is mainly linked to the respective distribution and amount of the hS and lS materials. In fact, the total reprocessing of the Reps tailings (R1 + R2) would lead to high working costs (proportionally to the amount of processed material), against a very poor recovery. On the other hand, the knowledge of the amount and distribution of the hS tailings can lead to a >50% total

S recovery, with reduced operational costs. In general, tailing re-processing requires a good characterization of the waste materials, in order to assess correctly the ore grade, the liberation degree and the possible heterogeneities. Based on such information, the conception of the correct processing flow-sheet can constitute a cost-effective solution to the environmental impact of the dump site. The concentrate, in fact, may be either valuable product, or a special low-volume discard to be managed separately.

Metal recovery from tailings has become a common economic solution, due to the evolution of the technological recovery. The concentration of metals, on the other hand, commonly requires the use of reactants (i.e. for Cu flotation, or for Au leaching) and moreover it leaves behind pyritic discards. Therefore, such a solution alone does not constitute a tool for environmental management of tailings. Still, metal concentration may increase the value of the pyritic discard and may also contribute to mass reduction. Therefore, whether the ore grades are sufficiently high, a suitable option would be to associate a metal-concentration stream to a pyrite separation stream.

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# APPENDIX A

## Representative geochemical data of the Reps tailing samples

The sample group (hS, lS) based on sulfide S content (see text) is labelled for each sample.

| Sample | S group | S | Fe | Ti | Al | Ca | Mg | Na | V | Cr | Mn | Co | Ni | Cu | Zn | As | Sr | Pb | Mo | Ag | Cd | pH | NAPP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | % | % | % | % | % | % | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | | kg $H_2SO_4$/t |
| | d.l. | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.001 | 1 | 1 | 5 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 1.00 | 0.1 | 0.5 | | |
| **A1** | lS | 0.27 | 10.20 | 0.11 | 4.25 | 0.2 | 2.15 | 0.032 | 190 | 56 | 100 | 115 | 130 | 145 | 160 | 176 | 190 | 3 | 3 | 0.3 | b.d.l. | 4.05 | |
| **A2** | lS | 0.09 | 9.70 | 0.09 | 5.05 | 0.18 | 2.92 | 0.025 | 202 | 40 | 95 | 112 | 126 | 140 | 154 | 170 | 184 | b.d.l. | 3 | 0.2 | b.d.l. | 4.33 | |
| **A3** | lS | 0.17 | 11.90 | 0.12 | 4.41 | 0.16 | 2.45 | 0.022 | 213 | 35 | 100 | 113 | 127 | 142 | 156 | 170 | 185 | b.d.l. | 3 | 0.2 | b.d.l. | 4.19 | |
| **A4** | lS | 0.35 | 7.39 | 0.11 | 2.43 | 0.12 | 1.45 | 0.030 | 131 | 34 | 65 | 77 | 87 | 97 | 106 | 116 | 126 | 24 | 6 | 0.8 | b.d.l. | 3.32 | 10.71 |
| **A5** | lS | 0.25 | 11.40 | 0.10 | 4.29 | 0.14 | 2.56 | 0.025 | 187 | 50 | 95 | 110 | 124 | 139 | 152 | 168 | 181 | b.d.l. | 5 | 0.3 | b.d.l. | 3.73 | 7.65 |
| **A6** | lS | 0.23 | 10.10 | 0.14 | 4.52 | 0.21 | 2.66 | 0.025 | 204 | 34 | 95 | 109 | 123 | 137 | 150 | 164 | 179 | b.d.l. | 4 | 0.2 | b.d.l. | 4.21 | |
| **A7** | lS | 0.46 | 11.10 | 0.10 | 4.32 | 0.35 | 2.51 | 0.024 | 212 | 32 | 95 | 111 | 125 | 140 | 154 | 168 | 182 | 5 | 3 | 0.3 | b.d.l. | 3.78 | 14.08 |
| **B1** | lS | 1.43 | 10.10 | 0.09 | 4.58 | 0.3 | 2.64 | 0.026 | 188 | 38 | 90 | 104 | 117 | 131 | 144 | 158 | 171 | b.d.l. | 3 | 0.2 | b.d.l. | 4.02 | 43.76 |
| **B2** | lS | 2.86 | 16.10 | 0.09 | 2.47 | 0.15 | 1.42 | 0.031 | 155 | 26 | 70 | 80 | 90 | 100 | 110 | 120 | 130 | 3 | 3 | 0.4 | b.d.l. | 3.26 | 87.52 |
| **B3** | lS | 0.67 | 11.00 | 0.09 | 3.33 | 0.32 | 1.91 | 0.040 | 178 | 36 | 85 | 98 | 111 | 123 | 136 | 148 | 161 | b.d.l. | 3 | 0.3 | b.d.l. | 3.43 | |
| **B4** | lS | 0.67 | 11.10 | 0.11 | 2.56 | 0.13 | 1.56 | 0.029 | 167 | 44 | 85 | 98 | 110 | 123 | 136 | 148 | 161 | 3 | 4 | 0.4 | b.d.l. | 3.57 | |
| **B5** | lS | 0.26 | 11.50 | 0.13 | 4.03 | 0.13 | 2.31 | 0.024 | 211 | 31 | 95 | 110 | 124 | 138 | 152 | 166 | 180 | b.d.l. | 4 | 0.3 | b.d.l. | 4.16 | |
| **B6** | lS | 0.71 | 9.84 | 0.11 | 4.25 | 0.72 | 2.46 | 0.033 | 200 | 36 | 95 | 108 | 122 | 136 | 150 | 164 | 178 | b.d.l. | 4 | 0.3 | b.d.l. | 3.8 | 21.73 |
| **B7** | lS | 0.83 | 14.20 | 0.11 | 2.98 | 0.2 | 1.67 | 0.026 | 197 | 32 | 90 | 103 | 116 | 129 | 142 | 156 | 169 | 4 | 3 | 0.4 | b.d.l. | 3.21 | |
| **C1** | lS | 1.07 | 11.60 | 0.09 | 4.01 | 0.82 | 2.49 | 0.033 | 183 | 51 | 95 | 109 | 123 | 137 | 152 | 166 | 179 | 6 | 6 | 0.4 | b.d.l. | 3.47 | 32.74 |
| **C2** | lS | 0.22 | 10.90 | 0.10 | 4.51 | 0.17 | 2.84 | 0.036 | 191 | 70 | 110 | 124 | 140 | 156 | 172 | 188 | 205 | b.d.l. | 3 | 0.2 | b.d.l. | 3.96 | |
| **C3** | lS | 1.05 | 10.20 | 0.11 | 2.97 | 0.32 | 1.75 | 0.032 | 152 | 44 | 80 | 91 | 103 | 115 | 126 | 138 | 150 | 5 | 5 | 0.4 | b.d.l. | 3.46 | 32.13 |
| **C4** | lS | 0.32 | 11.30 | 0.10 | 3.52 | 0.19 | 2.01 | 0.027 | 183 | 28 | 85 | 95 | 108 | 120 | 132 | 144 | 156 | b.d.l. | 4 | 0.4 | b.d.l. | 3.92 | 9.79 |
| **C5** | lS | 0.18 | 9.70 | 0.06 | 4.73 | 0.16 | 2.8 | 0.023 | 197 | 30 | 90 | 104 | 117 | 130 | 144 | 156 | 170 | b.d.l. | 3 | 0.2 | b.d.l. | 3.78 | |
| **C6** | lS | 0.13 | 7.15 | 0.15 | 6.56 | 0.6 | 1.93 | 0.034 | 199 | 183 | 170 | 194 | 221 | 247 | 274 | 300 | 326 | 11 | 1 | 0.2 | b.d.l. | 3.85 | |
| **D1** | hS | 15.50 | 14.10 | 0.08 | 0.7 | 1.13 | 0.29 | 0.050 | 40 | 8 | 15 | 18 | 20 | 22 | 24 | 26 | 27 | 400 | 11 | 11.3 | b.d.l. | 2.48 | 474.30 |
| **D2** | hS | 18.50 | 16.00 | 0.06 | 0.31 | 0.88 | 0.09 | 0.030 | 25 | 6 | 10 | 10 | 10 | 11 | 12 | 12 | 13 | 512 | 9 | 11.2 | b.d.l. | 2.56 | 566.10 |
| **D3** | hS | 35.50 | 20.40 | 0.07 | 1.13 | 0.21 | 0.63 | 0.027 | 61 | 19 | 30 | 32 | 35 | 39 | 42 | 46 | 49 | 278 | 8 | 8.7 | 1.5 | 3.26 | 1124.02 |
| | | | | | | | | | | | | | | | | | | | | | | | |

| Sample | S group | S | Fe | Ti | Al | Ca | Mg | Na | V | Cr | Mn | Co | Ni | Cu | Zn | As | Sr | Pb | Mo | Ag | Cd | pH | NAPP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | % | % | % | % | % | % | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | | kg $H_2SO_4$/t |
| | **d.l.** | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.001 | 1 | 1 | 5 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 1.00 | 0.1 | 0.5 | | |
| **D4** | hS | 10.40 | 15.70 | 0.07 | 4.21 | 0.6 | 2.26 | 0.039 | 158 | 58 | 85 | 100 | 113 | 126 | 138 | 152 | 164 | 155 | 6 | 3.1 | 2.0 | 3.74 | 318.24 |
| **E1** | lS | 0.76 | 13.10 | 0.08 | 2.19 | 0.11 | 1.26 | 0.049 | 201 | 40 | 95 | 110 | 124 | 138 | 152 | 166 | 181 | 8 | 5 | 0.7 | 2.5 | 3.85 | 23.26 |
| **E2** | lS | 1.27 | 17.70 | 0.08 | 0.46 | 0.21 | 0.17 | 0.071 | 200 | 29 | 90 | 102 | 114 | 127 | 140 | 152 | 166 | 20 | 13 | 2.0 | 2.0 | 2.98 | 38.86 |
| **E3** | lS | 1.47 | 16.20 | 0.08 | 0.6 | 0.05 | 0.29 | 0.107 | 194 | 36 | 90 | 103 | 117 | 130 | 142 | 156 | 169 | 62 | 7 | 2.4 | b.d.l. | 2.62 | 44.98 |
| **E4** | lS | 0.43 | 8.73 | 0.07 | 2.73 | 0.08 | 1.63 | 0.044 | 173 | 31 | 80 | 94 | 106 | 118 | 130 | 142 | 154 | 7 | 4 | 0.4 | b.d.l. | 4.05 | 13.16 |
| **E5** | lS | 0.90 | 13.60 | 0.10 | 1.9 | 0.1 | 1.1 | 0.060 | 195 | 44 | 95 | 109 | 124 | 138 | 152 | 166 | 180 | 9 | 7 | 1.0 | b.d.l. | 3.8 | 27.54 |
| **F1** | lS | 0.50 | 10.40 | 0.09 | 2.75 | 0.18 | 1.65 | 0.042 | 189 | 34 | 90 | 102 | 115 | 128 | 142 | 154 | 168 | 7 | 5 | 1.0 | b.d.l. | 5.9 | 15.30 |
| **F2** | lS | 0.61 | 12.40 | 0.06 | 1.81 | 0.12 | 1.01 | 0.041 | 191 | 51 | 100 | 112 | 127 | 141 | 156 | 170 | 185 | 5 | 4 | 0.5 | b.d.l. | 4.13 | 18.67 |
| **F3** | lS | 0.46 | 12.70 | 0.08 | 2.04 | 0.19 | 1.13 | 0.052 | 191 | 44 | 95 | 108 | 122 | 136 | 150 | 164 | 177 | 8 | 6 | 0.9 | b.d.l. | 4.81 | 14.08 |
| **F4** | lS | 2.04 | 13.80 | 0.10 | 2.9 | 0.47 | 1.8 | 0.054 | 189 | 66 | 105 | 120 | 135 | 151 | 166 | 182 | 197 | 7 | 6 | 1.0 | b.d.l. | 4.1 | 62.42 |
| **F5** | lS | 0.88 | 16.00 | 0.10 | 1 | 0.11 | 0.5 | 0.053 | 198 | 30 | 90 | 102 | 115 | 128 | 140 | 154 | 166 | 15 | 6 | 1.1 | b.d.l. | 3.92 | 26.93 |
| **F6** | lS | 0.60 | 13.40 | 0.09 | 2.35 | 0.3 | 1.42 | 0.057 | 205 | 47 | 100 | 116 | 131 | 146 | 160 | 176 | 190 | 6 | 4 | 0.6 | 0.5 | 5.16 | 18.36 |
| **F7** | hS | 17.10 | 13.80 | 0.05 | 0.56 | 0.96 | 0.21 | 0.035 | 40 | 10 | 15 | 19 | 21 | 23 | 26 | 28 | 30 | 325 | 8 | 11.4 | 4.5 | 2.85 | 523.26 |
| | | | | | | | | | | | | | | | | | | | | | | | |
| | **MAX hS** | 35.50 | 20.40 | 0.08 | 4.21 | 1.13 | 2.26 | 0.05 | 158.00 | 58.00 | 85.00 | 100.24 | 113.04 | 125.83 | 138.00 | 152.00 | 164.22 | 512.00 | 11.00 | 11.40 | 4.50 | 3.74 | |
| | **MIN hS** | 10.40 | 13.80 | 0.05 | 0.31 | 0.21 | 0.09 | 0.03 | 25.00 | 6.00 | 10.00 | 9.52 | 10.15 | 10.78 | 12.00 | 12.05 | 12.68 | 155.00 | 6.00 | 3.10 | 1.50 | 2.48 | |
| | **AVG hS** | 19.40 | 16.00 | 0.07 | 1.38 | 0.76 | 0.70 | 0.04 | 64.80 | 20.20 | 31.00 | 35.84 | 40.00 | 44.15 | 48.40 | 52.68 | 56.61 | 334.00 | 8.40 | 9.14 | 1.60 | 2.98 | |
| | **ST. DEV. hS** | 8.50 | 2.36 | 0.01 | 1.44 | 0.32 | 0.80 | 0.01 | 47.99 | 19.42 | 27.82 | 32.98 | 37.40 | 41.81 | 45.84 | 50.81 | 55.05 | 119.41 | 1.62 | 3.18 | 1.31 | 0.47 | |
| | | | | | | | | | | | | | | | | | | | | | | | |
| | **MAX lS** | 2.86 | 17.70 | 0.15 | 6.56 | 0.82 | 2.92 | 0.11 | 213.00 | 183.00 | 170.00 | 194.31 | 220.58 | 246.85 | 274.00 | 300.00 | 325.67 | 62.00 | 13.00 | 2.40 | 2.50 | 5.90 | |
| | **MIN lS** | 0.09 | 7.15 | 0.06 | 0.46 | 0.05 | 0.17 | 0.02 | 131.00 | 26.00 | 65.00 | 76.73 | 86.67 | 96.61 | 106.00 | 116.48 | 126.42 | 3.00 | 0.50 | 0.20 | 0.50 | 2.62 | |
| | **AVG lS** | 0.71 | 11.76 | 0.10 | 3.24 | 0.24 | 1.82 | 0.04 | 189.23 | 44.58 | 94.08 | 107.81 | 121.71 | 135.60 | 149.44 | 163.41 | 177.30 | 10.90 | 4.50 | 0.58 | 1.67 | 3.90 | |
| | **ST. DEV. lS** | 0.60 | 2.46 | 0.02 | 1.37 | 0.18 | 0.73 | 0.02 | 17.81 | 27.37 | 16.52 | 18.70 | 21.33 | 23.95 | 26.73 | 29.33 | 31.84 | 12.91 | 2.11 | 0.51 | 0.85 | 0.61 | |

# APPENDIX B

## Representative analytical data of Reps water samples

The sample types are labelled: Ra= rain water; Ri= river water; Ro= pools at the dump rooftop; Ru= runoff at the dump food; Up= upstream (to R2 tailin) stream water

| | | | | | **Ba** | **Al** | **K** | **Mg** | **Mn** | **Si** | **Ag** | **As** | **Ca** | **Cd** | **Co** | **Cr** | **Fe** | **Cu** | **Na** | **Ni** | **Pb** | **S** | **Sr** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | µg/l | mg/l | mg/l | mg/l | mg/l | mg/l | µg/l | µg/l | mg/l | µg/l | µg/l | µg/l | mg/l | µg/l | mg/l | µg/l | µg/l | mg/l | µg/l | µg/l |
| **Samples** | **Type of samples** | **Sampling period** | **pH** | d.l. | 20 | 0.1 | 0.1 | 0.1 | 0.01 | 0.1 | 5 | 30 | 0.1 | 2 | 2 | 20 | 0.01 | 2 | 0.1 | 5 | 10 | 1 | 10 | 5 |
| R2 A1 | **Ru** | Nov. 2013 | 2.44 | | 200 | 281 | 1 | 275 | 15.8 | 79.2 | 50 | < 300 | 453 | 216 | 0.875 | 0.2 | 1170 | 15.5 | 75.7 | 333 | 200 | 2530 | 530 | 101 |
| R2 A2 | **Ru** | Nov. 2013 | 2.34 | | 200 | 485 | 1 | 321 | 20.6 | 85.8 | 50 | < 300 | 427 | 157 | 1.29 | 0.2 | 778 | 6.63 | 34.1 | 504 | 110 | 2660 | 500 | 97.4 |
| R2 A3 | **Ru** | Nov. 2013 | 2.91 | | 20 | 45 | 1.7 | 50.1 | 2.63 | 34.9 | 5 | < 30 | 219 | 18 | 0.143 | 0.02 | 114 | 1.08 | 15.5 | 61 | 30 | 481 | 210 | 12.9 |
| R2 A4 | **Ru** | Nov. 2013 | 2.64 | | 20 | 38.2 | 0.9 | 42.7 | 1.67 | 60.5 | 5 | < 30 | 232 | 4 | 0.125 | 0.02 | 8.79 | 1.19 | 11.2 | 49 | 10 | 403 | 200 | 5.21 |
| R2 A5 | **Up** | Nov. 2013 | 7.2 | | | | | | | | | | | | | | | | | | | | | |
| R2 A6 | **Up** | Nov. 2013 | 7.01 | | | | | | | | | | | | | | | | | | | | | |
| R2 A7 | **Ro** | Nov. 2013 | 7.28 | | 130 | 0.1 | 2.8 | 17 | 0.01 | 9.6 | 5 | < 30 | 48.6 | 2 | 0.002 | 0.02 | 0.05 | 0.016 | 11.8 | 5 | < 10 | 32 | 140 | 0.047 |
| R2 A8a | **Ro** | Nov. 2013 | 7.33 | | | | | | | | | | | | | | | | | | | | | |
| R2 A8b | **Ro** | Nov. 2013 | 7.24 | | | | | | | | | | | | | | | | | | | | | |
| R2 A9 | **Ri** | Nov. 2013 | 7.79 | | 20 | 0.1 | 2.5 | 11.5 | 0.01 | 14.5 | 5 | < 30 | 18.9 | 2 | 0.002 | 0.02 | 0.01 | 0.007 | 7.8 | 5 | 10 | 10 | 70 | 0.016 |
| R2 A10 | **Ri** | Nov. 2013 | 7.67 | | 20 | 0.1 | 1.3 | 14.1 | 0.01 | 12.5 | 5 | < 30 | 34.2 | 2 | 0.002 | 0.02 | 0.01 | 0.004 | 8.1 | 5 | 10 | 21 | 70 | 0.006 |
| R2 A11 | **Ra** | Nov. 2013 | 6.77 | | 30 | 0.1 | 1.5 | 0.5 | 0.01 | 1.9 | 14 | < 30 | 5.7 | 2 | 0.002 | 0.02 | 0.01 | 0.015 | 3.5 | 5 | 10 | 3 | 20 | 0.189 |
| R2 A12 | **Up** | Apr. 2015 | 7.44 | | | | | | | | | | | | | | | | | | | | | |
| RA 13 | **Ro** | Apr. 2015 | 7.81 | | < 20 | < 0.1 | 19.2 | 1.4 | < 0.01 | 1.2 | < 5 | < 30 | 33.4 | < 2 | < 2 | < 20 | < 0.01 | 15 | 3.2 | < 5 | < 10 | 13 | 30 | < 5 |
| RA 14 | **Ro** | Apr. 2015 | 8.2 | | < 20 | < 0.1 | 3.9 | 7.5 | < 0.01 | 6.5 | < 5 | < 30 | 41.8 | < 2 | < 2 | < 20 | 0.01 | 4 | 3.9 | < 5 | < 10 | 8 | 40 | < 5 |
| RA 15 | **Up** | Apr. 2015 | 7.73 | | < 20 | < 0.1 | 3.8 | 16.5 | < 0.01 | 9.8 | < 5 | < 30 | 38 | < 2 | < 2 | < 20 | < 0.01 | 6 | 5.3 | < 5 | < 10 | 28 | 40 | 18 |
| RA 16 | **Ri** | Apr. 2015 | 7.36 | | < 20 | < 0.1 | 9.5 | 5.9 | < 0.01 | 5.6 | < 5 | < 30 | 35.7 | < 2 | < 2 | < 20 | < 0.01 | 7 | 3.3 | < 5 | < 10 | 6 | 50 | 37 |
| RA 17 | **Ru** | Apr. 2015 | 4.12 | | < 20 | 35.5 | 9.1 | 34.6 | 2.55 | 12.9 | < 5 | < 30 | 95.7 | 20 | 144 | < 20 | 7.22 | 3740 | 6.8 | 56 | 10 | 264 | 90 | 7920 |
| RA 18 | **Ru** | Apr. 2015 | 3.34 | | < 20 | 348 | < 0.1 | 234 | 15.1 | 38.8 | < 5 | 60 | 420 | 573 | 828 | 60 | 1000 | 36200 | 40.1 | 248 | 110 | 2340 | 390 | 97100 |
| RA 19 | **Ru** | Apr. 2015 | 6.87 | | < 20 | < 0.1 | 8.1 | 8.3 | < 0.01 | 6.5 | < 5 | < 30 | 54.2 | < 2 | < 2 | < 20 | 0.19 | 7 | 4.5 | < 5 | < 10 | 24 | 50 | 10 |
| RA 20 | **Ru** | Apr. 2015 | 3.85 | | < 20 | 51.4 | 15.2 | 54.8 | 4.13 | 35.7 | < 5 | < 30 | 176 | 6 | 170 | < 20 | 2.05 | 1370 | 15.9 | 60 | < 10 | 351 | 230 | 6360 |
| RA 21 | **Ru** | Apr. 2015 | 3.55 | | < 20 | 49.7 | 9.9 | 60 | 3.45 | 39.3 | < 5 | < 30 | 135 | 8 | 196 | < 20 | 1.43 | 1440 | 8.4 | 84 | < 10 | 316 | 150 | 7810 |
| RA 22 | **Ri** | Apr. 2015 | 6.92 | | < 20 | < 0.1 | 7 | 6.5 | < 0.01 | 5.4 | < 5 | < 30 | 34.3 | < 2 | < 2 | < 20 | 0.03 | 3 | 3.3 | < 5 | < 10 | 8 | 40 | 9 |
| RA 23 | **Ri** | Apr. 2015 | 7.97 | | < 20 | < 0.1 | 3.4 | 6.1 | < 0.01 | 5.6 | < 5 | < 30 | 32 | < 2 | < 2 | < 20 | < 0.01 | 3 | 3.3 | < 5 | < 10 | 5 | 30 | < 5 |

# APPENDIX C

## Grain size statistical data

Table C1: grain size statistics of R1 samples

| Sample id. | < 125 µm (%) | $D_{50}$ (mm): | ($D_{90}$ / $D_{10}$) |
|---|---|---|---|
| **A1** | 44 | 136 | 6 |
| **A2** | 77 | 83 | 31 |
| **A3** | 55 | 112 | 24 |
| **A4** | 59 | 108 | 15 |
| **A5** | 70 | 79 | 42 |
| **A6** | 37 | 148 | 7 |
| **A7** | 69 | 89 | 32 |
| **B1** | 54 | 116 | 14 |
| **B2** | 41 | 161 | 26 |
| **B3** | 37 | 158 | 21 |
| **B4** | 53 | 120 | 6 |
| **B5** | 50 | 125 | 17 |
| **B6** | 56 | 113 | 11 |
| **B7** | 66 | 92 | 32 |
| **C1** | 49 | 127 | 18 |
| **C2** | 46 | 134 | 13 |
| **C3** | 46 | 133 | 4 |
| **C4** | 48 | 129 | 13 |
| **C5** | 66 | 97 | 23 |
| **C6** | 17 | 826 | 32 |
| **min** | 17 | 79 | 4 |
| **max** | 77 | 826 | 42 |
| **avg** | 52 | 154 | 19 |

Table C2: grain size statistics of R2 samples. hS and lS samples are labelled

| Sample id. | | < 125 µm (%) | $D_{50}$ (mm): | ($D_{90}$ / $D_{10}$) |
|---|---|---|---|---|
| **D1** | hS | 35 | 181 | 11 |
| **D2** | hS | 52 | 121 | 14 |
| **D3** | hS | 35 | 174 | 9 |
| **D4** | hS | 35 | 215 | 85 |
| **E1** | lS | 24 | 232 | 42 |
| **E2** | lS | 23 | 283 | 79 |
| **E3** | lS | 17 | 343 | 36 |
| **E4** | lS | 16 | 254 | 33 |
| **E5** | lS | 31 | 173 | 17 |
| **F1** | lS | 21 | 202 | 21 |
| **F2** | lS | 14 | 2076 | 40 |
| **F3** | lS | 35 | 195 | 96 |
| **F4** | lS | 32 | 237 | 100 |
| **F5** | lS | 30 | 208 | 150 |
| **F6** | lS | 26 | 215 | 53 |
| **F7** | hS | 61 | 104 | 66 |
| **min** | | 14 | 104 | 9 |
| **max** | | 61 | 2076 | 150 |
| **avg** | | 30 | 326 | 53 |

| Sample id | < 63 µm (%) | >500µm (%) | D50 (mm): | (D90 / D10) |
|---|---|---|---|---|
| **FEED 1** | 13 | 17 | 149 | 5 |
| **FEED 3** | 11 | 29 | 205 | 3 |
| **R2 C1** | 4 | 1 | 164 | 5 |
| **R2C2** | 6 | 0 | 148 | 5 |
| **R2C3** | 2 | 1 | 174 | 4 |
| **R2C4** | 4 | 1 | 147 | 3 |
| **R2 M1** | 14 | 1 | 128 | 13 |
| **R2M2** | 10 | 1 | 128 | 6 |
| **R2M3** | 1 | 2 | 156 | 4 |
| **R2M4** | 16 | 3 | 128 | 15 |
| **R2 T1** | 40 | 0 | 102 | 68 |
| **R2T2** | 18 | 1 | 80 | 70 |
| **R2T3** | 14 | 0 | 142 | 29 |
| **R2T4** | 12 | 0 | 141 | 15 |
| **R21** |  |  | 89 | 5 |
| **min** | 1 | 0 | 80 | 3 |
| **max** | 40 | 3 | 174 | 70 |
| **avg** | 12 | 1 | 137 | 20 |

Table C3: grain size statistics of representative shaking table samples. Feed, concentrate (C), mix (M) and tailing (T) samples are labelled.

# APPENDIX D

## Mineral chemistry (MP) data

Table D1: minerals detected by point analyses are labelled: py= pyrite; ccp= chalcopyrite; ba=barite; sph=sphalerite

| | **S** | **Fe** | **As (ppm)** | **Co (ppm)** | **Ba (ppm)** | **Ni (ppm)** | **Zn (ppm)** | **Cu (ppm)** | **Min. phases** |
|---|---|---|---|---|---|---|---|---|---|
| **D1 - 1** | 54.35 | 46.74 | 1000 | 400 | 370 | 10 | 10 | 2700 | py |
| **D1 - 2** | 54.18 | 47.59 | 2010 | 390 | 60 | 260 | 10 | 1890 | py |
| **D1 - 3** | 54.04 | 47.76 | 1180 | 180 | 70 | 10 | 10 | 330 | py |
| **D1 - 4** | 53.4 | 47.58 | 670 | 370 | 10 | 10 | 630 | 190 | py |
| **D1 - 5** | 53.76 | 47.4 | 1650 | 1200 | 10 | 10 | 400 | 2110 | py |
| **D1 - 6** | 53.69 | 47.18 | 1590 | 1040 | 270 | 40 | 500 | 1590 | py |
| **D1 - 7** | 53.96 | 46.63 | 1250 | 680 | 10 | 220 | 930 | 2610 | py |
| **D1 - 8** | 53.54 | 47.01 | 1580 | 700 | 10 | 40 | 380 | 1850 | py |
| **D1 - 9** | 53.77 | 46.73 | 1720 | 670 | 830 | 10 | 10 | 2710 | py |
| **D1 - 10** | 54.44 | 47.03 | 1410 | 170 | 530 | 10 | 290 | 2470 | py |
| **D1 - 11** | 53.59 | 46.58 | 1630 | 530 | 450 | 130 | 160 | 3160 | py |
| **D1 - 12** | 53.46 | 46.67 | 1340 | 760 | 10 | 10 | 1000 | 2660 | py |
| **D1 - 13** | 53.28 | 46.85 | 1430 | 930 | 320 | 10 | 390 | 3140 | py |
| **D1 - 14** | 53.45 | 46.96 | 1360 | 880 | 300 | 220 | 130 | 2740 | py |
| **D1 - 15** | 53.44 | 47.16 | 1250 | 650 | 190 | 10 | 180 | 2830 | py |
| **D1 - 16** | 53.98 | 47.02 | 1730 | 1090 | 10 | 10 | 850 | 2330 | py |
| **D1 - 17** | 53.43 | 46.81 | 2030 | 940 | 10 | 110 | 770 | 3410 | py |
| **D1 - 18** | 53.7 | 47.08 | 1660 | 490 | 10 | 10 | 10 | 3100 | py |
| **D1 - 19** | 53.59 | 46.73 | 1270 | 450 | 610 | 10 | 700 | 2170 | py |
| **D1 - 20** | 53.28 | 46.52 | 2240 | 740 | 10 | 10 | 10 | 3080 | py |
| **D1 - 21** | 53.45 | 46.42 | 1790 | 280 | 10 | 10 | 10 | 2410 | py |
| **D1 - 22** | 53.41 | 46.87 | 1350 | 690 | 30 | 370 | 60 | 2820 | py |
| **D1 - 23** | 54.87 | 47.14 | 10 | 5910 | 10 | 10 | 20 | 70 | py |
| **D1 - 24** | 54.42 | 47.11 | 250 | 4360 | 10 | 230 | 680 | 10 | py |
| **D1 - 25** | 54.45 | 46.99 | 310 | 2700 | 10 | 400 | 10 | 10 | py |
| **D1 - 26** | 54.03 | 47.11 | 10 | 4670 | 850 | 10 | 1240 | 120 | py |
| **D1 - 27** | 54.73 | 47.28 | 10 | 3850 | 10 | 430 | 730 | 10 | py |
| **D1 - 28** | 35.83 | 31.3 | 10 | 380 | 10 | 10 | 1180 | 347800 | ccp |
| **D1 - 29** | 54.77 | 47.68 | 650 | 1060 | 410 | 800 | 630 | 600 | py |
| **D1 - 30** | 54.55 | 47.11 | 730 | 730 | 1050 | 10 | 640 | 10 | py |
| **D1 - 31** | 54.9 | 48.13 | 1070 | 470 | 10 | 10 | 10 | 620 | py |
| **D1 - 32** | 36.08 | 30.79 | 10 | 790 | 140 | 10 | 10 | 346600 | ccp |
| **D1 - 33** | 35.73 | 31.13 | 550 | 660 | 610 | 160 | 110 | 346100 | ccp |
| **D1 - 34** | 54.83 | 47.96 | 220 | 120 | 300 | 10 | 1450 | 10 | py |
| **D1 - 35** | 54.01 | 48.21 | 20 | 2080 | 330 | 100 | 10 | 90 | py |
| **D1 - 36** | 54.36 | 47.71 | 1400 | 2200 | 1430 | 10 | 10 | 400 | py |
| **D1 - 37** | 54.69 | 47.72 | 10 | 250 | 10 | 10 | 10 | 310 | py |
| **D1 - 38** | 54.52 | 47.65 | 370 | 1030 | 1170 | 10 | 10 | 10 | py |
| **D1 - 39** | 54.82 | 47.67 | 270 | 640 | 10 | 10 | 910 | 60 | py |
| **D2 - 1** | 54.03 | 47.23 | 5110 | 400 | 140 | 40 | 20 | 10 | py |
| **D2 - 2** | 54.73 | 47.74 | 620 | 1050 | 440 | 450 | 10 | 540 | py |
| **D2 - 3** | 53.57 | 47.6 | 2430 | 150 | 80 | 10 | 710 | 10 | py |

| | S | Fe | As (ppm) | Co (ppm) | Ba (ppm) | Ni (ppm) | Zn (ppm) | Cu (ppm) | Comment |
|---|---|---|---|---|---|---|---|---|---|
| **D2 - 4** | 53.64 | 47.41 | 640 | 250 | 1040 | 100 | 10 | 10 | py |
| **D2 - 5** | 53.62 | 46.98 | 4410 | 410 | 630 | 10 | 10 | 1210 | py |
| **D2 - 6** | 54.58 | 47.9 | 1540 | 510 | 520 | 10 | 10 | 10 | py |
| **D2 - 7** | 53.36 | 47.11 | 1940 | 560 | 10 | 10 | 310 | 560 | py |
| **D2 - 8** | 54.44 | 47.02 | 1220 | 490 | 250 | 10 | 10 | 220 | py |
| **D2 - 9** | 53.83 | 47.15 | 1170 | 1190 | 760 | 10 | 120 | 1580 | py |
| **D2 - 10** | 53.19 | 46.96 | 4070 | 80 | 150 | 100 | 140 | 860 | py |
| **D2 - 11** | 54.08 | 47.96 | 1270 | 530 | 70 | 10 | 10 | 10 | py |
| **D2 - 12** | 53.75 | 47.38 | 2440 | 770 | 10 | 10 | 10 | 1230 | py |
| **D2 - 13** | 54.52 | 47.28 | 1460 | 710 | 10 | 510 | 490 | 480 | py |
| **D2 - 14** | 54.73 | 47.62 | 130 | 1020 | 10 | 10 | 10 | 240 | py |
| **D2 - 15** | 35.85 | 31.4 | 890 | 450 | 1570 | 610 | 10 | 346800 | ccp |
| **D2 - 16** | 53.63 | 46.91 | 5820 | 640 | 10 | 10 | 960 | 750 | py |
| **D2 - 17** | 54.55 | 48.08 | 10 | 1540 | 10 | 10 | 10 | 170 | py |
| **D2 - 18** | 53.95 | 47.68 | 260 | 1090 | 1150 | 10 | 480 | 30 | py |
| **D2 - 19** | 53.63 | 47.39 | 4010 | 940 | 10 | 290 | 100 | 310 | py |
| **D2 - 20** | 53.22 | 47.5 | 3090 | 390 | 10 | 10 | 10 | 50 | py |
| **D2 - 21** | 54.51 | 47.51 | 1300 | 860 | 10 | 10 | 10 | 10 | py |
| **D2 - 22** | 8.39 | 0.2421 | 410 | 10 | 602200 | 550 | 10 | 10 | ba |
| **D2 - 23** | 8.02 | 0.286 | 740 | 120 | 601000 | 730 | 310 | 1220 | ba |
| **D2 - 24** | 8.21 | 0.3294 | 10 | 260 | 597800 | 10 | 10 | 10 | ba |
| **D3 - 1** | 29.64 | 1.02 | 207700 | 150 | 80 | 10 | 83600 | 440600 | en |
| **D3 - 2** | 35.6 | 30.97 | 940 | 240 | 1700 | 210 | 1060 | 345900 | ccp |
| **D3 - 3** | 54.34 | 47.62 | 2340 | 10 | 1220 | 10 | 1410 | 3330 | py |
| **D3 - 4** | 53.26 | 44.96 | 470 | 370 | 710 | 230 | 2260 | 1190 | py |
| **D3 - 5** | 52.71 | 44.82 | 340 | 810 | 10 | 440 | 560 | 10 | py |
| **D3 - 6** | 53.01 | 44.86 | 670 | 500 | 220 | 220 | 890 | 270 | py |
| **D3 - 7** | 52.82 | 43.87 | 1090 | 480 | 30 | 10 | 920 | 2110 | py |
| **D3 - 8** | 53.18 | 44.68 | 100 | 10 | 10 | 310 | 10 | 240 | py |
| **D3 - 9** | 53.18 | 44.36 | 260 | 290 | 10 | 240 | 1320 | 650 | py |
| **D3 - 10** | 53.51 | 44.51 | 420 | 750 | 420 | 460 | 290 | 10 | py |
| **D3 - 11** | 53 | 45.03 | 10 | 1060 | 140 | 570 | 1880 | 1000 | py |
| **D3 - 12** | 52.47 | 42.89 | 2080 | 440 | 10 | 100 | 2230 | 7560 | py |
| **D3 - 13** | 49.24 | 41.84 | 1630 | 640 | 750 | 10 | 3300 | 52600 | py |
| **D3 - 14** | 52.87 | 43.66 | 10 | 840 | 290 | 10 | 5900 | 3220 | py |
| **D3 - 15** | 52.97 | 44.08 | 580 | 850 | 10 | 440 | 4200 | 820 | py |
| **D3 - 16** | 53.17 | 43.77 | 10 | 540 | 10 | 10 | 2200 | 190 | py |
| **D3 - 17** | 53.55 | 43.87 | 260 | 920 | 320 | 380 | 2570 | 1110 | py |
| **D3 - 18** | 53.22 | 43.95 | 10 | 590 | 990 | 10 | 840 | 10 | py |
| **D3 - 19** | 53.64 | 44.15 | 10 | 200 | 90 | 330 | 1260 | 10 | py |
| **D3 - 20** | 52.43 | 43.95 | 3560 | 800 | 10 | 10 | 10 | 1180 | py |
| **D3 - 21** | 38.8 | 35.82 | 10 | 170 | 10 | 400 | 3200 | 1890 | ccp |
| **D3 - 22** | 53.48 | 44.67 | 10 | 940 | 370 | 10 | 10 | 600 | py |
| **D3 - 23** | 52.89 | 44.28 | 130 | 620 | 490 | 320 | 10 | 110 | py |
| **D3 - 24** | 36.73 | 31.18 | 300 | 760 | 1140 | 10 | 500 | 336100 | ccp |
| **D3 - 25** | 54.74 | 47.52 | 540 | 590 | 10 | 10 | 10 | 4890 | py |
| **D3 - 26** | 55.55 | 47.98 | 610 | 910 | 910 | 10 | 590 | 4830 | py |
| **D3 - 27** | 54.68 | 47.75 | 10 | 950 | 280 | 10 | 2060 | 3220 | py |
| **D3 - 28** | 53.88 | 47.59 | 290 | 1410 | 10 | 10 | 10 | 4290 | py |
| **D3 - 29** | 54.82 | 47.83 | 400 | 610 | 370 | 130 | 720 | 1370 | py |
| **D3 - 30** | 54.56 | 47.97 | 620 | 620 | 570 | 90 | 820 | 880 | py |
| **D3 - 31** | 54.61 | 47.82 | 740 | 670 | 10 | 130 | 580 | 1760 | py |

| | S | Fe | As (ppm) | Co (ppm) | Ba (ppm) | Ni (ppm) | Zn (ppm) | Cu (ppm) | Comment |
|---|---|---|---|---|---|---|---|---|---|
| **D3 - 32** | 53.74 | 47.65 | 840 | 1140 | 10 | 10 | 580 | 3560 | py |
| **D3 - 33** | 54.29 | 47.62 | 900 | 600 | 280 | 500 | 1340 | 1520 | py |
| **D3 - 34** | 55.15 | 47.77 | 1410 | 680 | 470 | 330 | 830 | 1040 | py |
| **D3 - 35** | 54.27 | 47.01 | 760 | 10 | 10 | 70 | 10 | 4290 | py |
| **D3 - 36** | 54.36 | 47.16 | 1540 | 1240 | 1150 | 10 | 10 | 3450 | py |
| **D3 - 37** | 54.21 | 47.67 | 940 | 500 | 590 | 10 | 10 | 1540 | py |
| **D3 - 38** | 54.32 | 47.45 | 590 | 910 | 10 | 510 | 380 | 930 | py |
| **D3 - 39** | 54.59 | 47.51 | 960 | 420 | 610 | 250 | 170 | 1750 | py |
| **D3 - 40** | 54.18 | 47.42 | 640 | 1100 | 10 | 10 | 850 | 6510 | py |
| **D3 - 41** | 53.66 | 46.89 | 190 | 680 | 10 | 600 | 220 | 12100 | py |
| **D3 - 42** | 54.77 | 47.7 | 340 | 1250 | 10 | 820 | 10 | 1630 | py |
| **D3 - 43** | 52.54 | 44.18 | 11000 | 520 | 100 | 10 | 5190 | 45800 | py |
| **D3 - 44** | 54.38 | 46.8 | 850 | 270 | 10 | 10 | 230 | 1340 | py |
| **D3 - 45** | 54.16 | 47.22 | 140 | 980 | 10 | 90 | 10 | 390 | py |
| **D3 - 46** | 8.89 | 0.7268 | 120 | 110 | 598200 | 10 | 620 | 100 | ba |
| **D3 - 47** | 9.4 | 0.0996 | 150 | 10 | 583400 | 510 | 10800 | 190 | ba |
| **D3 - 48** | 54.41 | 46.63 | 2540 | 40 | 120 | 10 | 17500 | 1490 | py |
| **D3 - 49** | 34.27 | 3.27 | 80 | 10 | 10 | 10 | 628800 | 1480 | sph |
| **D3 - 50** | 9.14 | 0.2777 | 220 | 10 | 597500 | 10 | 370 | 10 | ba |
| **D3 - 51** | 54.56 | 46.68 | 690 | 830 | 1610 | 10 | 60 | 15800 | py |
| **D3 - 52** | 36.56 | 31.5 | 620 | 10 | 1710 | 10 | 730 | 343300 | ccp |
| **D4 - 1** | 53.09 | 46.41 | 1210 | 860 | 850 | 10 | 1940 | 6520 | py |
| **D4 - 2** | 53.33 | 46.32 | 2200 | 1250 | 10 | 10 | 260 | 3810 | py |
| **D4 - 3** | 53.75 | 46.33 | 3670 | 380 | 10 | 10 | 580 | 5490 | py |
| **D4 - 4** | 54.9 | 46.84 | 1590 | 440 | 10 | 10 | 420 | 1280 | py |
| **D4 - 5** | 54.28 | 47.07 | 1810 | 10 | 730 | 10 | 1280 | 10 | py |
| **D4 - 6** | 54.06 | 46.55 | 2780 | 670 | 380 | 10 | 430 | 2090 | py |
| **D4 - 7** | 54.99 | 46.79 | 830 | 1150 | 10 | 10 | 810 | 1450 | py |
| **D4 - 8** | 55.13 | 46.86 | 20 | 270 | 490 | 120 | 1120 | 1910 | py |
| **D4 - 9** | 55.12 | 46.88 | 40 | 10 | 10 | 10 | 140 | 100 | py |
| **D4 - 10** | 54.28 | 46.47 | 60 | 760 | 630 | 10 | 10 | 1470 | py |
| **D4 - 11** | 52.63 | 43 | 12100 | 340 | 70 | 380 | 10 | 15300 | py |
| **D4 - 12** | 55.06 | 47.64 | 400 | 1090 | 830 | 350 | 1300 | 160 | py |
| **D4 - 13** | 54.52 | 47.53 | 1070 | 660 | 10 | 10 | 10 | 390 | py |
| **D4 - 14** | 33.94 | 4.52 | 890 | 10 | 10 | 10 | 560600 | 46200 | sph |
| **D4 - 15** | 54.09 | 46.86 | 2620 | 470 | 10 | 10 | 13000 | 1330 | py |
| **D4 - 16** | 10.11 | 0.4008 | 450 | 60 | 594700 | 10 | 110 | 350 | ba |
| **D4 - 17** | 54.57 | 47.84 | 280 | 340 | 10 | 200 | 10 | 300 | py |
| **D4 - 18** | 55.23 | 47.51 | 10 | 730 | 10 | 10 | 10 | 30 | py |
| **D4 - 19** | 54.88 | 47.35 | 10 | 950 | 410 | 10 | 220 | 880 | py |
| **D5 - 1** | 55.35 | 47.67 | 470 | 1040 | 160 | 10 | 450 | 10 | py |
| **D5 - 2** | 54.29 | 47.21 | 1650 | 1050 | 140 | 890 | 240 | 440 | py |
| **D5 - 3** | 54.35 | 47.25 | 4060 | 770 | 40 | 10 | 1280 | 610 | py |
| **D5 - 4** | 9.57 | 0.4266 | 170 | 20 | 592500 | 10 | 10 | 10 | ba |
| **D5 - 5** | 54.73 | 47.46 | 590 | 930 | 10 | 10 | 630 | 10 | py |
| **D5 - 6** | 54.74 | 47.38 | 290 | 590 | 10 | 10 | 10 | 1110 | py |
| **D5 - 7** | 54.99 | 47.58 | 10 | 510 | 250 | 30 | 350 | 280 | py |
| **D5 - 8** | 55.08 | 47.77 | 10 | 1290 | 10 | 380 | 440 | 540 | py |
| **D5 - 9** | 55.23 | 47.66 | 190 | 1030 | 80 | 10 | 310 | 10 | py |
| **D5 - 10** | 55.37 | 47.58 | 220 | 590 | 730 | 110 | 730 | 10 | py |
| **D5 - 11** | 54.98 | 47.58 | 120 | 590 | 810 | 10 | 1120 | 10 | py |
| **D5 - 12** | 54.35 | 47.86 | 1540 | 630 | 70 | 10 | 920 | 20 | py |

Table D2: average EMP data (wt%) for pyrite (py), chalcopyrite (ccp), sphalerite (sph) and barite (ba)

| | | S | Fe | As | Co | Ba | Ni | Zn | Cu |
|---|---|---|---|---|---|---|---|---|---|
| Py | MAX | 55.55 | 48.21 | 1.21 | 0.59 | 0.14 | 0.09 | 0.59 | 4.58 |
| | MIN | 52.43 | 42.89 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | AVG | 51.47 | 43.91 | 0.12 | 0.08 | 1.92 | 0.01 | 1.00 | 1.58 |
| | ST. DEV. | 10.31 | 10.91 | 0.17 | 0.08 | 12.73 | 0.02 | 4.99 | 6.74 |
| | | | | | | | | | |
| Ccp | MAX | 38.80 | 35.82 | 0.09 | 0.08 | 0.17 | 0.06 | 0.32 | 34.78 |
| | MIN | 35.60 | 30.79 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.19 |
| | AVG | 36.40 | 31.76 | 0.04 | 0.04 | 0.09 | 0.02 | 0.08 | 30.18 |
| | ST. DEV. | 1.05 | 1.66 | 0.04 | 0.03 | 0.08 | 0.02 | 0.11 | 12.12 |
| | | | | | | | | | |
| Sph | MAX | 34.27 | 4.52 | 0.09 | n.d. | n.d. | n.d. | 62.88 | 4.62 |
| | MIN | 33.94 | 3.27 | 0.01 | n.d. | n.d. | n.d. | 56.06 | 0.15 |
| | AVG | 34.11 | 3.90 | 0.05 | - | - | - | 59.47 | 2.38 |
| | ST. DEV. | 0.23 | 0.88 | 0.06 | - | - | - | 4.82 | 3.16 |
| | | | | | | | | | |
| Ba | MAX | 10.11 | 0.73 | 0.07 | 0.03 | 60.22 | 0.07 | 1.08 | 0.12 |
| | MIN | 8.02 | 0.10 | n.d. | n.d. | 58.34 | n.d. | n.d. | n.d. |
| | AVG | 8.97 | 0.35 | 0.03 | 0.01 | 59.59 | 0.02 | 0.15 | 0.02 |

# APPENDIX E

## Pyrite gravity separation data (C= concentrate; M=mix; T=tailing)

| | S/S- | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | MnO | $Cr_2O_3$ | Ba | Ni | Sr | Zr | Y | Nb | Sc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample id.** | % | % | % | % | % | % | % | % | % | % | % | % | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| | 0.02 | 0.01 | 0.01 | 0.04 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.002 | 5 | 20 | 2 | 5 | 3 | 5 | 1 |
| FEED1 | 23.93 | 30.42 | 4.33 | 38.25 | 1.38 | 1.34 | 0.57 | 0.27 | 0.32 | <0.01 | 0.04 | 0.013 | 2497 | <20 | 38 | 15 | 6 | <5 | 11 |
| FEED2 | 22.87 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| FEED3 | 8.75 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| FEED4 | 7.02 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| C1 | 32.69 | 17.39 | 2.42 | 50.04 | 0.78 | 0.84 | 0.34 | 0.13 | 0.18 | <0.01 | 0.02 | 0.022 | 1720 | <20 | 24 | 7 | 3 | <5 | 6 |
| C2 | 32.69 | 15.07 | 2.03 | 52.23 | 0.65 | 0.63 | 0.27 | 0.11 | 0.15 | <0.01 | 0.02 | 0.015 | 1670 | <20 | 22 | 6 | 3 | <5 | 6 |
| C3 | 22.08 | 33.09 | 4.17 | 39.21 | 1.33 | 0.55 | 0.53 | 0.25 | 0.31 | <0.01 | 0.03 | 0.015 | 1034 | <20 | 23 | 15 | 6 | <5 | 11 |
| C4 | 26.97 | 25.04 | 3.22 | 45.86 | 1.05 | 0.41 | 0.38 | 0.19 | 0.26 | <0.01 | 0.03 | 0.022 | 1273 | <20 | 21 | 11 | 5 | <5 | 9 |
| M1 | 29.25 | 22.71 | 3.30 | 45.66 | 1.13 | 1.03 | 0.41 | 0.17 | 0.23 | <0.01 | 0.03 | 0.019 | 2193 | <20 | 31 | 10 | 5 | <5 | 9 |
| M2 | 29.81 | 21.96 | 2.97 | 46.26 | 0.98 | 0.83 | 0.40 | 0.17 | 0.22 | <0.01 | 0.03 | 0.018 | 2089 | <20 | 28 | 10 | 5 | <5 | 8 |
| M3 | 14.21 | 42.82 | 5.33 | 32.06 | 1.68 | 0.65 | 0.70 | 0.33 | 0.41 | <0.01 | 0.04 | 0.013 | 1041 | <20 | 28 | 19 | 8 | <5 | 14 |
| M4 | 18.01 | 37.39 | 4.70 | 36.13 | 1.54 | 0.63 | 0.58 | 0.28 | 0.38 | <0.01 | 0.04 | 0.018 | 1344 | <20 | 30 | 16 | 7 | <5 | 13 |
| T1 | 13.66 | 44.43 | 6.01 | 26.37 | 1.82 | 2.06 | 0.85 | 0.41 | 0.46 | <0.01 | 0.04 | 0.010 | 2699 | <20 | 52 | 22 | 8 | <5 | 16 |
| T2 | 16.59 | 41.63 | 5.12 | 29.24 | 1.44 | 1.67 | 0.80 | 0.37 | 0.43 | <0.01 | 0.04 | 0.010 | 3121 | <20 | 52 | 21 | 7 | <5 | 13 |
| T3 | 3.27 | 52.84 | 7.01 | 23.50 | 2.09 | 1.03 | 0.89 | 0.52 | 0.64 | 0.03 | 0.04 | 0.011 | 644 | <20 | 33 | 30 | 9 | <5 | 18 |
| T4 | 2.59 | 56.97 | 7.15 | 20.31 | 2.10 | 0.90 | 0.98 | 0.50 | 0.64 | 0.02 | 0.04 | 0.009 | 532 | <20 | 33 | 30 | 10 | <5 | 19 |
| R21 | 47.6 | | | | | | | | | | | | | | | | | | |
| R21C1 | 49.6 | | | | | | | | | | | | | | | | | | |
| R21 63-500 | 34.5 | | | | | | | | | | | | | | | | | | |
| R21C4 | 48.5 | | | | | | | | | | | | | | | | | | |

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