

**Uncertainty in the measurement of toxic metals mobility in mining/mineral wastes by standardized BCR<sup>®</sup>SEP**

Manuel A. Caraballo<sup>1,2\*</sup>, Alexander Serna<sup>1</sup>, Francisco Macías<sup>3</sup>, Rafael Pérez-López<sup>3</sup>, Carlos Ruiz-Cánovas<sup>3</sup>, Pablo Richter<sup>4</sup>, Mercedes Becerra-Herrera<sup>4,5\*</sup>

1 Mining Engineering Department, University of Chile, Avda. Tupper 2069, 8370451 Santiago, Chile

2 Advanced Mining Technology Center, University of Chile, Avda. Tupper 2007, 8370451 Santiago, Chile

3 Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus “El Carmen”, E-21071 Huelva, Spain

4 Department of Inorganic and Analytical Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, P.O. Box 233, Santiago, Chile.

5 Department of Chemistry, Faculty of Science, University of Chile, P.O. Box 653, Santiago, Chile.

## **Abstract**

Mining residues management is one of the greatest challenges for mining companies around the world. The increasing consciousness of the general public and governments about the potential threat that those residues can pose to the environment is demanding consistent and precise methodologies for assessing the potential release of toxic metals. On this regard, the modified BCR<sup>®</sup> sequential extraction procedure (SEP) is frequently the chosen assessing protocol. However, this protocol was designed to study soils and sediments with low to moderate metal pollution, and validation of its applicability to mining residues is missing. The present research covers this gap of knowledge by subjecting selected highly polluted mining residues to the modified BCR<sup>®</sup>SEP. On the light of these results, it was confirmed that most of the metal bearing minerals in the mining residues were not completely dissolved in the corresponding SEP and, therefore, the application of BCR<sup>®</sup>SEP to mining residues systematically leads to an underestimation of metals mobility. The necessary changes to optimize the BCR<sup>®</sup>SEP to study mining residues would set a extraction procedure distinctively different from the original; thus it is strongly recommended to use alternative approaches to assess toxic metals mobility in highly polluted mining residues.

## **Keywords**

Mining residues; mine pollution; BCR sequential extraction; metals mobility; environmental mineralogy

## 1. Introduction

Studies on toxic metals mobility from solid residues are commonly focused on the bulk chemical characterization and the specific determination of certain chemical elements in the leachates generated after subjecting the solid sample to a liquid extraction procedure (e.g., EN 12457-2 [1], US EPA TCLP [2] or Method 1627-EPA [3]). Although this approach may be suitable for a great variety of metal polluted residues, it is inaccurate to characterize accurately mining residues. Those residues commonly comprise complex mineralogical matrixes where major, minor, and trace elements are specifically bound to different crystallographic positions in the minerals [4]. This particularity has been conventionally addressed by the extensive generation of selective mineral dissolution protocols [5-7], aiming to associate the use of a specific liquid chemical reagent with the selective dissolution of a precise mineral phase for the subsequent release of the chemical elements from the crystal lattice.

These digestion schemes typically comprise several independent extraction steps designed to mimic certain environmental conditions, inducing mineral dissolution and the concomitant release of metals into solution. The logic behind sequential extraction procedures (SEP) is of special interest to the environmental sciences, and, more precisely, to the study of mobility and availability of toxic metal pollutants. These procedures would allow to estimate the stability of a residue using several consecutive chemical reagents, which extract operationally defined phases in a sequence that simulates different environmental conditions. However, in order to interpret accurately the mobility of metals from a sample using a sequential extraction, the extraction protocol needs to be optimized to ensure that all metals susceptible to be liberated in each extraction step are indeed

selectively and completely released from the containing matrix. If these considerations are not taken into account, the principle behind a sequential extraction cannot be guaranteed, and misguided or erroneous interpretations about metals mobility might be easily generated.

The Community Bureau of Reference of the European Union, proposed a standardized 3-step SEP in 1993 that was named as the BCR® SEP [8]. Despite the advancement the creation of this protocol represented for the standardized study of toxic metal mobility in polluted soils and sediments, a modified BCR® SEP was proposed by Sahuquillo et al. in 1999 [9] to solve some inconsistencies detected during trace elements extractions. Moreover, a certified reference material (BCR®701) using sediments from Lake Orta Piemonte, Italy, was created in 2001 [10,11]. This reference material is accompanied by certified concentration values for six trace elements (Cd, Cr, Cu, Ni, Pb and Zn) in the three extraction steps comprising the BCR® SEP.

Due to the consistency and versatility of the modified BCR® SEP, it has become one of the most used standardized protocols to study toxic metals mobility in soils and sediments. Sutherland [12] reported that several hundred published works used this protocol (from 2001 to 2010) to study contaminated samples from environments as diverse as: soils (arable, forest, mine-contaminated, roadside, smelter-contaminated), sediments (marine, lacustrine, river mining-impacted, urban river, road-deposited), atmospheric particulate matter, ferromagnesian clays, mining, mineral processing and industrial wastes, and sewage sludge. To update this information, browsing the keyword “BCR sequential extraction” in the Web of Science (last time checked 08/02/2018) 911 publications appear, adding up to

23,456 times cited, 12,062 citing articles. Moreover, it is relevant to notice that the most cited articles on this topic have over 954 cites.

As previously mentioned, the BCR<sup>®</sup>SEP procedure was originally created to assess metals mobility in soils and sediments with low to moderate metal pollution. Although this procedure is gaining great acceptance and use among scientists and engineers studying toxic metals mobility in mining residues [13-18], the application of this standardized procedure to mine residues is leading to ambiguous and deceptive interpretations. If the complete dissolution of a targeted mineral is not achieved in the extraction step designed to that purpose, the remaining mineral fraction may be dissolved in latter extraction steps obtaining false results. For instance, when a residue entirely made of a metal sulfide (e.g., pyrite, FeS<sub>2</sub>) is not completely dissolved in the extraction step designed for the selective dissolution of sulfides (i.e., third step of the BCR<sup>®</sup>SEP), it may release a significant proportion of its metallic content at the final pseudototal digestion. This extraction behavior could be interpreted as the metal in the residue exhibiting two different mobilities, when in fact all the metal in the residue will be equally available (in the long term) and will present the same environmental risk. The scope of the present study is to evaluate this uncertainty in the measurement of toxic metals mobility in mining/mineral wastes using the standardized BCR<sup>®</sup>SEP. Special attention will be placed on the evaluation of the expected complete and selective mineral dissolution by the reagents used in the different steps of the extraction protocol.

## **2. Materials and Methods**

### **2.1. Selected mining residues**

Five samples were selected as representative of the main types of residues from the mining and processing activities in mined massive sulfide deposits from the Iberian Pyrite Belt (IPB; SW Spain and S Portugal). However, to open the results obtained in the present study to broader interpretations (enabling direct extrapolations to mining residues on different metallic mining districts), the following restrictions were considered during the selection of the samples: a) to cover a wide range of mineral phases showing major differences in their stability and dissolution under various relevant environmental conditions, b) to include the most common types of mining residues generally observed in metallic mining districts, and c) to facilitate the assessment of the potential optimization of the BCR<sup>®</sup>SEP for heavily metal polluted mining residues.

The 5 selected residues correspond to: 1) pyrite-rich mine tailings (*Tailings*), 2) crushed extracted gossan (*CEG*), 3) heap leaching residue (*HLR*), 4) mine slag (*Slag*) and 5) metal polluted acid soil (*Soil*). The soil sample is representative of soils developed on sulfide-mining tailings or metal polluted riverbanks. Although not strictly a residue, these soils are acidic, strongly impoverished in nutrients, and contain high concentrations of hazardous chemical elements. A more detailed description of these residues is offered in the Supplementary Materials.

All residues were heated at 40°C during 24h until completely dry and were ground in a tungsten carbide mill for 2 minutes.

## 2.2 Solids and liquids analyses and characterization

Both sequential extraction procedure and *aqua regia* pseudototal digestion employed in the current study are summarized in the Supplementary Materials and full details can be found elsewhere [10,11].

Major cations (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si and Zn) in 212 liquid aliquots from the multiple extractions and digestions were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin-Elmer® Optima 3200 RL). Detection limits were: 0.1 mg/L for As, Ca, Cu, Cr and Mn, Si and Zn; 0.2 mg/L for Al, Co, Fe, Mg, Ni and S; 0.5 mg/L for Cd, K, Na and Pb. These detection limits were calculated considering the main signals and standard deviations of a blank measured ten times. Calibration with sets of standards was performed at the beginning and at the end of each ten-samples analytical sequence. Certified Reference Material SRM-1640NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material (European Commission Institute for Reference Materials and Measurements) were used. The analytical precision error was estimated to be approximately 5% for ICP-AES.

The semi-quantitative mineralogical characterization of the mining residues was conducted by powder X-ray diffraction (XRD) of randomly oriented powder samples using a Bruker D5005 X-ray diffractometer with CuK $\alpha$  radiation. Diffractometer settings were: 40 kV, 30 mA, and a scan range of 2–65° 2 $\theta$ , 0.02° 2 $\theta$  step size, and 5s counting time per step.

### 2.3. Experimental design and Quality Assurance/Quality Control (QA/QC)

The ratio between the amount of solid submitted to the sequential extraction and the amount of liquid extractant used is one of the most common operational parameters that

needs to be optimized when the application of a sequential extraction wants to be broaden to different residues. Consequently, the present study anticipated a possible optimization of this operational parameter by testing three different initial amounts of mining residues (i.e., 1g, 0.5g and 0.25g) to the modified BCR<sup>®</sup>SEP. The resulting experimental design is synthesized in Figure 1. As shown, each sample (studied using duplicates, “x2”) generated a total of 6 sub-samples that were submitted to the complete SEP protocol (3 steps + 1 aqua regia step). This experimental design generated a total of 178 aliquots (including extracts after each step of the BCR<sup>®</sup>SEP, aqua regia digestions and procedural and reagents blanks).

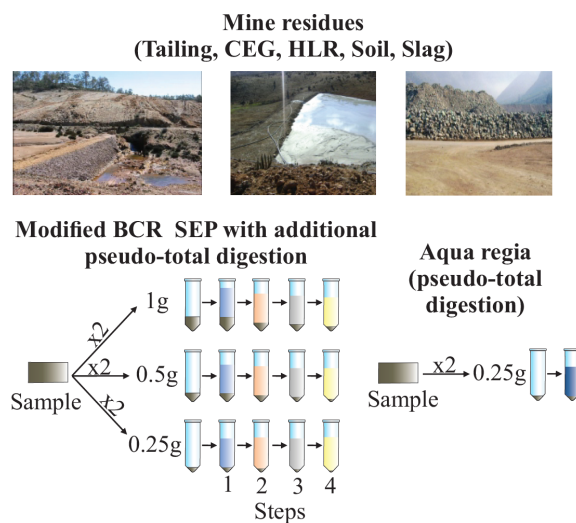


Figure 1. Sketch of the experimental design used in the current research

The QA/QC studies performed in the present research are explained in detail in the Supplementary Materials. The results of these analyses guaranteed (for all the studied elements) the absence of any cross-contamination during the experiments. Additionally,

three decreasing amounts of the BCR<sup>®</sup>701 certified standard (i.e., 1g, 0.5g and 0.25g) were subjected to the modified BCR<sup>®</sup>SEP to verify the reliability of this methodology and to test the possible effect that this decrease may have on the sequential release of the certified metals. Notice that the modified BCR<sup>®</sup>SEP establishes 1g as the initial amount of sample to be studied. The results fairly align with previous studies [11, 12]. However, the present study was able to differentiate two different behaviors among the certified metals (Figure S1 and Table S1): 1) disregarding the original amount of BCR<sup>®</sup>701 used, Cr, Ni and Pb extracted concentrations during the 3 steps perfectly reproduce the certified values; whereas 2) Cu and Zn release shows a slight dependency with the original amount of sample used.

### **3. Results and Discussion**

To assess metals availability and mobility in mining residues, it is advisable to consider a sequenced approach where the mining residues are characterized moving from a bulk to a detailed scale. In accordance with that approach, the following sequence of studies is proposed: 1) bulk chemistry characterization, to confirm the pseudo-total chemical composition; 2) semi-quantitative mineralogical characterization, to identify mineral phases and their relative abundance; and 3) sequential extraction using specific reagents, to mimic mineral weathering under different environmental scenarios.

#### **3.1. Bulk chemistry and mineralogy of the selected mining residues**

In addition to a selection of frequent major elements forming the most abundant minerals in metallic ore deposits and associated residues (i.e., Al, Ca, Cu, Fe, K, Mg, Mn, Na, S and Si), several other elements were considered due to their well known toxicity (i.e., As and

Co) and/or because their concentrations have been certified in the standard BCR<sup>®</sup>701 for the three steps of the BCR<sup>®</sup>SEP (i.e., Cd, Cr, Cu, Ni, Pb and Zn).

As can be observed in Table 1, the selected residues from the IPB have some attributes in common, including very high contents of Fe and, to a lower extent, high concentrations of S, Cu, Pb and Zn. This typical feature is a direct consequence of both the original ore mineralogical and chemical composition, and the mining and metallurgical processes employed. Likewise, these mining residues also show very low concentrations of Cd, Cr or Ni (below the detection limits of the ICP-AES used in this study).

Table 1. Concentration of some selected elements released from the 5 mine residues and the BCR-701 standard after aqua regia digestion

Samples Code	Samples Type	Al	As	Ca	Co	Fe	K	Mg	Mn	Na	S	Cd	Cr	Cu	Ni	Pb	Zn
						(g/Kg)			(mg/Kg)								
Tailing	Pyritic tailing	0.1	1.52	0.6	0.12	390.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	416.6	b.d.l.	b.d.l.	805	b.d.l.	16,819	1,800
CEG	Crushed extracted gossan	0.6	5.17	0.3	b.d.l.	218.0	0.3	b.d.l.	0.1	b.d.l.	4.0	b.d.l.	b.d.l.	207	b.d.l.	14,063	100
HLR	Heap leaching residue	3.4	3.06	12.4	0.07	184.6	0.8	1.1	0.2	0.66	20.7	b.d.l.	b.d.l.	952	b.d.l.	8,537	555
Soil	Metal polluted soil	7.3	0.92	7.3	0.09	202.6	2.6	1.0	0.2	1.18	19.7	b.d.l.	b.d.l.	1,662	b.d.l.	9,315	4,080
Sag	Mine slag	2.5	0.01	6.8	b.d.l.	240.9	0.7	2.9	1.2	0.05	9.0	b.d.l.	b.d.l.	3,432	b.d.l.	1,275	22,545
BCR-701	Analytical standard	15.2	0.03	10.0	b.d.l.	30.0	3.1	7.6	0.5	b.d.l.	2.0	b.d.l.	252	281	105	143	484
	Certified BCR-701											11.7	272	275	103	143	454
Maximum		15.2	5.2	12.4	0.12	390.0	3.1	7.6	1.2	1.2	416.6	b.d.l.	252	3,432	105	16,819	22,545
Minimum		0.1	0.01	0.3	b.d.l.	30.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2.0	b.d.l.	b.d.l.	207	b.d.l.	143	100

b.d.l. = below detection limit

When compared with the BCR<sup>®</sup>701 (Table 1), the selected mining residues characteristically show concentrations of Cu, Fe, Pb, S and Zn between 1 or even 2 orders of higher magnitude (depending on the specific element under comparison). Since the BCR<sup>®</sup>701 standard corresponds to a metal polluted lake sediments with low to moderate metals concentrations, it is reasonable to assume that a similar scenario can be anticipated if most metallic mining residues are compared with this reference material.

Specifically, each singular mine residue was characterized by: 1) *Tailings*, extreme concentrations of Fe and S, very high concentrations of As, Pb and Zn and high concentrations of Cu and Co; 2) *CEG*, extreme concentration of Fe, very high

concentrations of As and Pb, and high concentrations of Cu, S and Zn; 3) *HLR*, extreme concentration of Fe, very high concentrations of As, Pb and S, and high concentrations of Cu, Co, Mn and Zn; 4) *Soil*, extreme concentration of Fe, very high concentrations of Cu, Pb, S and Zn, and high concentrations of Co and Mn; and 5) *Slag*, extreme concentrations of Fe and Zn, very high concentrations of Cu, Mn, and S, and high concentrations of Pb.

Regarding the samples mineralogy, the XRD patterns (Supplementary Materials) confirmed the presence of a great variety of mineral phases (Table 2).

Table 2. Samples semiquantitative mineral composition obtained by XRD

Samples	Sulfates					Oxides			Sulfides	Silicates					
	Jrs	Pb-Jrs	Brt	Szm	Pbt	Gp	Gth	Hem	Mag	Py	Qz	Ab	Cr	Fa	Ill
Tailing			10							73	7	6	4		
CEG	12		4	15	8		29	9			23				
HLR	13					14	9	28			36				
Soil		30				19					43				8
Slag									27		2			71	
BCR-701															

Jrs = jarosite ( $KFe_3(OH)_6(SO_4)_2$ ); Pb-Jrs = plumbojarosite ( $PbFe_6(SO_4)_4(OH)_{12}$ ); Brt = barite ( $BaSO_4$ ); Szm = szomolnokite ( $FeSO_4$ ); Pbt = parabutlerite ( $Fe(SO_4)(OH)$ ); Gp = gypsum ( $CaSO_4 \cdot 5H_2O$ ); Gth = goethite ( $FeO(OH)$ ); Hem = hematite ( $Fe_2O_3$ ); Mag = magnetite ( $Fe_3O_4$ ); Py = pyrite ( $FeS_2$ ); Qz = quartz ( $SiO_2$ ); Ab = albite ( $NaAlSi_3O_8$ ); Cr = clorite ( $(Mg,Fe)_3(S,Al)_4O_{10}(OH)_8$ ); Fa = fayalite ( $Fe_2SiO_4$ ); Ill = Illite ( $K_{0.65}Al_2(Al_{0.65}S_{3.35})O_{10}(OH)_2$ )

The most relevant mineralogical information can be summarized as follows: 1) *Tailings*, essentially comprised of pyrite and minor amounts of silicates and barite; 2) *CEG*, principally formed by Fe oxides (goethite > hematite), Fe sulfates (jarosite, szomolnokite and parabutlerite) and quartz; 3) *HLR*, primarily made of Fe oxides (hematite > goethite), Fe and Ca sulfates (jarosite and gypsum) and quartz; 4) *Soil*, predominantly silicates (quartz > clays) and Fe-Pb and Ca sulfates (plumbojarosite and gypsum); and 5) *Slag*, essentially made of fayalite (iron silicate) and magnetite (iron oxide) and some quartz.

In this regard, it is important to take into account that semi-quantitative analyses generated using XRD information are highly dependent on the presence of unidentified minor mineral phases and amorphous or poorly-crystalline phases as part of the original mining residues (Supplementary Materials). Although this effect can be considered almost negligible in samples like *Tailing*, *CEG* or *HLR* (very crystalline samples where all the relevant diffractions peaks were assigned to specific mineral phases), it can be assumed to have a great impact on the results obtained from the samples *Soil* and *Slag* (samples with important concentrations of amorphous or poorly crystalline mineral phases). Considering this limitation, the use of the semi-quantitative information generated in the present study will be mostly limited to anticipate the extraction behavior of the residues in the BCR<sup>®</sup>SEP (e.g., possible oversaturation problems during mineral dissolution) rather than providing an accurate compositional description of samples.

3.2. Evaluation of mineral dissolution capability during the application of the BCR<sup>®</sup>SEP to mining residues

As previously mentioned, all sequential extraction schemes rely on the selectivity of the chosen chemical reagents to liberate the metals under study from the matrix hosting them. According to that, in order to generate reliable metals mobility interpretations, selective and complete dissolution of the minerals hosting them must be achieved by the sequential extraction step designed to that purpose.

To gain a better understanding of the effects that a possible incomplete dissolution of the minerals in the mining residues may have on the BCR performance (and on the subsequent environmental interpretations), the sequential release of the main mineral-forming elements will be studied (Figure 2).

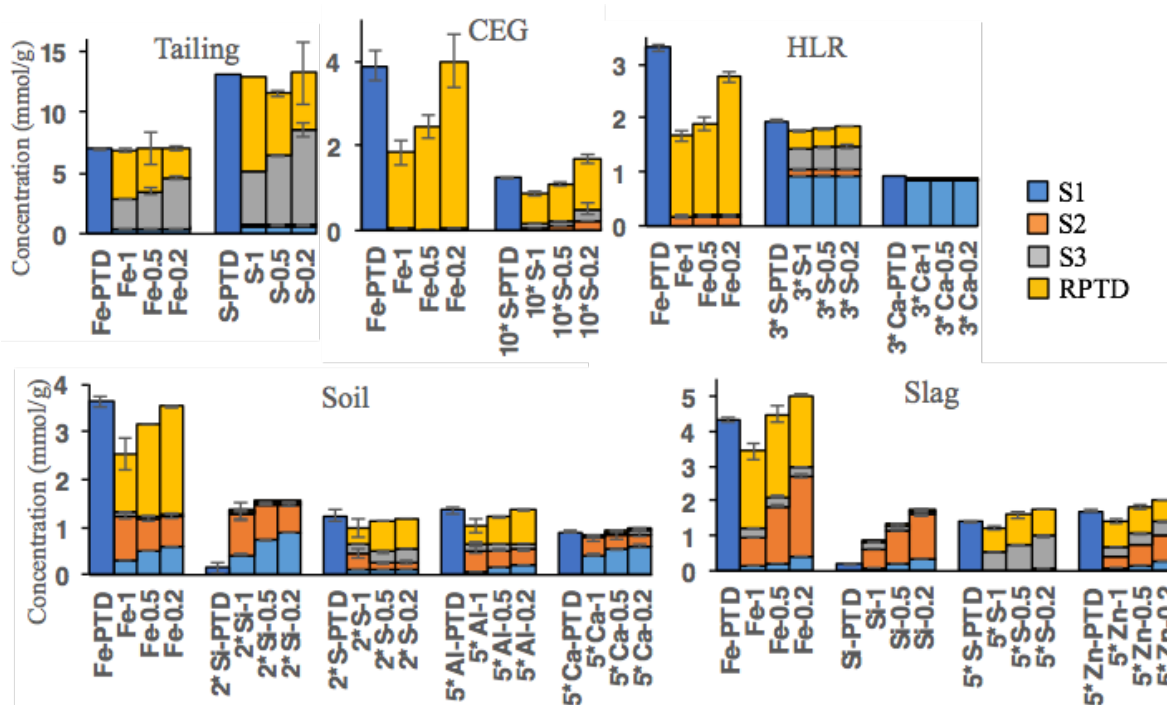


Figure 2. Concentration of the main mineral forming elements released during the 3 sequential extraction steps of the BCR<sup>®</sup>SEP, (i.e., S1, S2 and S3), and the aqua regia pseudo-total digestions of the initial samples (PTD) and the final residues (RPTD). The first blue bar for each element corresponds to the pseudototal digestion performed to each sample (e.g., Fe-PTD). X-n, with X corresponding to each specific element studied (i.e., Fe, S, Ca, Si, Al and Zn) and n from 1 to 0.2, represents the concentration of each element released if a different amount of solid sample is initially submitted to the BCR<sup>®</sup>SEP (e.g., Fe-1, Fe-0.5 and Fe-0.2 = iron released using 1g, 0.5g and 0.2g of sample). Please note that, to facilitate their visualization, some elements are shown with their concentrations multiplied by a whole number (e.g., 10\*S in CEG).

*Tailings* sample is mainly composed by pyrite (FeS<sub>2</sub>, Table 2) that should be easily dissolved under strong oxidizing conditions. Therefore, a complete dissolution of this mineral could be expected in the third step of the BCR<sup>®</sup>SEP. Both Fe and S release in this residue, as well as As, Cu and Zn (impurities in pyrite in substitution of Fe or as other minor sulfides), are mainly controlled by pyrite dissolution and should, theoretically, be also mostly constrained to the BCR<sup>®</sup>SEP third step. As can be noted from Figure 2, those elements are released in both the third and the fourth step, increasing their proportion in S3

with respect to S4 as the amount of solid initially subjected to the sequential extraction decreases (i.e., from Fe-1 to Fe-3). This behavior is typically indicative of incomplete mineral dissolution due to mineral oversaturation in solution [6]. Taking into account these observations, it is evident that the BCR<sup>®</sup>SEP is not able to selectively and completely dissolve pyrite in samples where this mineral is the major phase. Furthermore, it is important to notice that this inability to completely dissolve pyrite is not overcome when the initial amount of sample submitted to the BCR<sup>®</sup>SEP is reduced (See Fe-0.2 and S-0.2 in Tailing, Figure 2). By contrast, despite being a sulfate, the solubility of barite is complex, and optimum conditions for this mineral dissolution have not been completely understood. Several works have been performed in order to understand better barite solubility, specially using organic chelating agents at different concentrations and temperatures [19-21]. Nevertheless, there is not a clear consensus about the optimum conditions for the dissolution of this mineral. Therefore, barite dissolution during the BCR<sup>®</sup>SEP (and consequent Ba and SO<sub>4</sub><sup>2-</sup> release to the extracting reagents) should mostly be achieved during the first step but some barite could easily reach the following steps of the sequential extraction and even the residue. Chlorite amount in the sample can be considered negligible and so it can be considered Fe released during the sequential extraction (compared to Fe released from pyrite).

Both *CEG* and *HLR* are mainly comprised of iron oxides, quartz and, to a lower extent, sulfates (Table 2). Iron oxides solubility is known to be highly dependent on mineral crystallinity [22]. As a consequence, a great variety of sequential extraction schemes have been specifically designed to untangle the information of the different Fe oxide minerals typically present in environmental samples [5, 23]. The second step of the BCR<sup>®</sup>SEP is designed to selectively dissolve poorly crystalline Fe and Mn oxides typically present in

soils or fresh sediments [8,9]. Consequently, it is not surprising that the highly crystalline Fe oxides in samples CEG and HLR remain almost unaltered until the fourth step, and , therefore, almost no Fe is released until the final extraction step (Fig.2). Similarly, jarosite ( $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$ ) and other crystalline Fe sulfates may remain undissolved (or only partially dissolved) until the fourth step of the BCR<sup>®</sup>SEP. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in *HLR* is a highly soluble sulfate and, as expected, its digestion (marked by a 1 to 1 molar release of S and Ca; Fig.2) is completely achieved in the first step of the BCR<sup>®</sup>SEP. It is worth noticing the higher error bars in samples *CEG* and *HLR* caused by the higher heterogeneity of these two samples compared with samples *Tailings*, *Soil* and *Slag* (fine grain homogeneous samples).

*Soil* sample corresponds to an acidic soil comprised by sulfates (Pb-jarosite and gypsum) and silicates (quartz and illite, Table 2). Jarosite is the only detected mineral accountable for Fe release to solution (Fig.2). For that reason, the release of this metal during the first, second and fourth steps of the sequential extraction mark the non-selective dissolution of jarosite during the BCR<sup>®</sup>SEP. On the other hand, Ca release to solution marks gypsum dissolution and, as expected, it is limited to the first step of the sequential extraction. Notice that S/Ca molar ratio is higher to 1 since part of the S released during the first step also corresponds to the partial dissolution of jarosite (Fig.2). Quartz is a very resistant mineral that requires very strong reagents (e.g., HF) to undergo some significant dissolution in the short periods of time typically involved in sequential extraction protocols. Therefore, almost no quartz is expected to be dissolved during the BCR<sup>®</sup>SEP. Conversely, clays have been reported to undergo dissolution when subjected to the BCR<sup>®</sup>SEP as a result of: hydrolysis of relatively weak Mg–O bonds (362 kJ/mol) during all stages, reduction of Fe(III) during hydroxylamine hydrochloride extraction; and, oxidation of Fe(II) during

hydrogen peroxide extraction [24]. As a result, some illite dissolution can be anticipated during all steps of the BCR<sup>®</sup>SEP. Specifically, illite partial dissolution can be traced by the released of Al during the first, second and fourth step of the sequential extraction (Figure 2).

*Slag* is mostly comprised of fayalite ( $\text{Fe}_2\text{SiO}_4$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and a minor amount of quartz (Table 2 and Supplementary Materials), the only phases detected by XRD. However, significant amounts of amorphous or poorly crystalline Fe-silicates and Fe-oxides are typically present in this type of smelting residues [25]. Previous studies have proposed that fayalite is soluble in either dilute HCl or acetate buffered solutions [26]. Hence, as already pointed out for other minerals in the present study, the dissolution of fayalite can be expected throughout the several extraction steps of the BCR<sup>®</sup>SEP due to the lack of selectivity of the reagents used in the extraction protocol. Magnetite dissolution is responsible for a significant amount of the iron released in the second step of the SEP (design to dissolve iron oxides). Nonetheless, tracking Fe and Si release (Fig.2), fayalite dissolution seems to be also achieved in the second extraction step (Fe/Si molar ratio of 2) and in the final residue digestion (fourth step). Notice that the systematic absence of Si in the fourth step of the BCR<sup>®</sup>SEP and in the pseudototal digestion of the initial samples (e.g., samples soil and slag in figure 2) is due to the use of aqua regia. This digestion protocol is known to report anomalously low Si concentrations after the samples digestion [11,13,16] but the exact mechanism (e.g., inefficient mineral dissolution, evaporation or re-precipitation of the dissolved Si) is not completely understood. Finally, a small amount of S (with a concentration more than one order of magnitude lower than Fe) is also released during the third and fourth step of the extraction procedures (Figure 2). This S release could

be attributed to the dissolution of small amounts of sulfides undetected by XRD (because of their low concentration, low crystallinity or both).

Additionally, if the pseudo-total digestion is compared with the sum of the four sequential steps a common tendency might be observed for all samples but *Tailings*. Although all elements present this trend, the discussion will be exemplified using only Fe for the sake of clarity. As shown in Figure 2, the sum of Fe concentrations extracted during the four sequential steps clearly shows an increasing **tendency**, with the minimum value corresponding to Fe-1 (1g of mining residue submitted to the BCR<sup>®</sup>SEP, standardized amount of sample according to the BCR<sup>®</sup>SEP) and the maximum to Fe-0.2 (0.2g of mining residue submitted to the BCR<sup>®</sup>SEP). Besides, the Fe concentration obtained after the pseudo-total digestion typically matches the sum of Fe concentrations obtained if 0.2g of mining residue is used. These behaviors can be explained by the oversaturation of extractant solutions with respect to certain minerals due to the high mineral concentration of the mining residues and/or the small amount of extractant employed in the different steps of the BCR<sup>®</sup>SEP. This hypothesis is supported by the visual observation made during the BCR<sup>®</sup>SEP where almost all the reaction vessels contained some remaining sample after the fourth step (incomplete mineral dissolution). On top of that, the amount of remaining solids in the reaction vessels was lower for the samples with a reduced initial amount of mining residue submitted to the BCR<sup>®</sup>SEP. These tendencies are typically found on optimization studies leading to selective and effective extraction methodologies [5,6]

Summarizing, from the 14 minerals detected in the different mining residues submitted to the BCR<sup>®</sup>SEP, only gypsum showed strong evidences of a complete and selective dissolution restricted to a single sequential extraction step. This inefficient mineral dissolution was observed for the three mineral/extractant ratios tested.

### 3.3. Assessment of the modified BCR<sup>®</sup>SEP applicability to study toxic metals mobility in mining residues

As previously mentioned, the BCR<sup>®</sup>SEP was designed to study metals mobility in soils and sediments, and valid interpretation of the results should be limited to the six trace elements (Cd, Cr, Cu, Ni, Pb and Zn) certified in the reference material BCR<sup>®</sup>701. Toxic metals mobility in the selected mining residues will be evaluated based on the mineral selective dissolution study performed in the previous section. Due to the intrinsic characteristics of the mining residues under study, the discussion will be focused on As, Cu, Pb and Zn.

If the BCR<sup>®</sup>SEP results were to be blindly accepted and directly interpreted (as many studies have done [11, 13-18] and may keep on doing), As, Cu and Zn in the sample *Tailings* would be interpreted as partially mobile under oxidizing environments (released in Step 3) and partially immobile (released after the residue pseudo-total digestion), and, therefore, posing only a partial potential danger to the environment. However, if As, Cu and Zn results (*Tailing* sample, Figure 3) are compared with Fe and S results in Figure 2, similar tendencies for the release of these elements are observed. Thus, a realistic interpretation of these results should consider that most of the sample is comprised of pyrite and this mineral will dissolve completely under natural oxidizing conditions generating acidic metal polluted waters. Lead removal is limited to the second extraction step, and it is probably linked to an unidentified Pb-bearing oxide (Fig. 3).

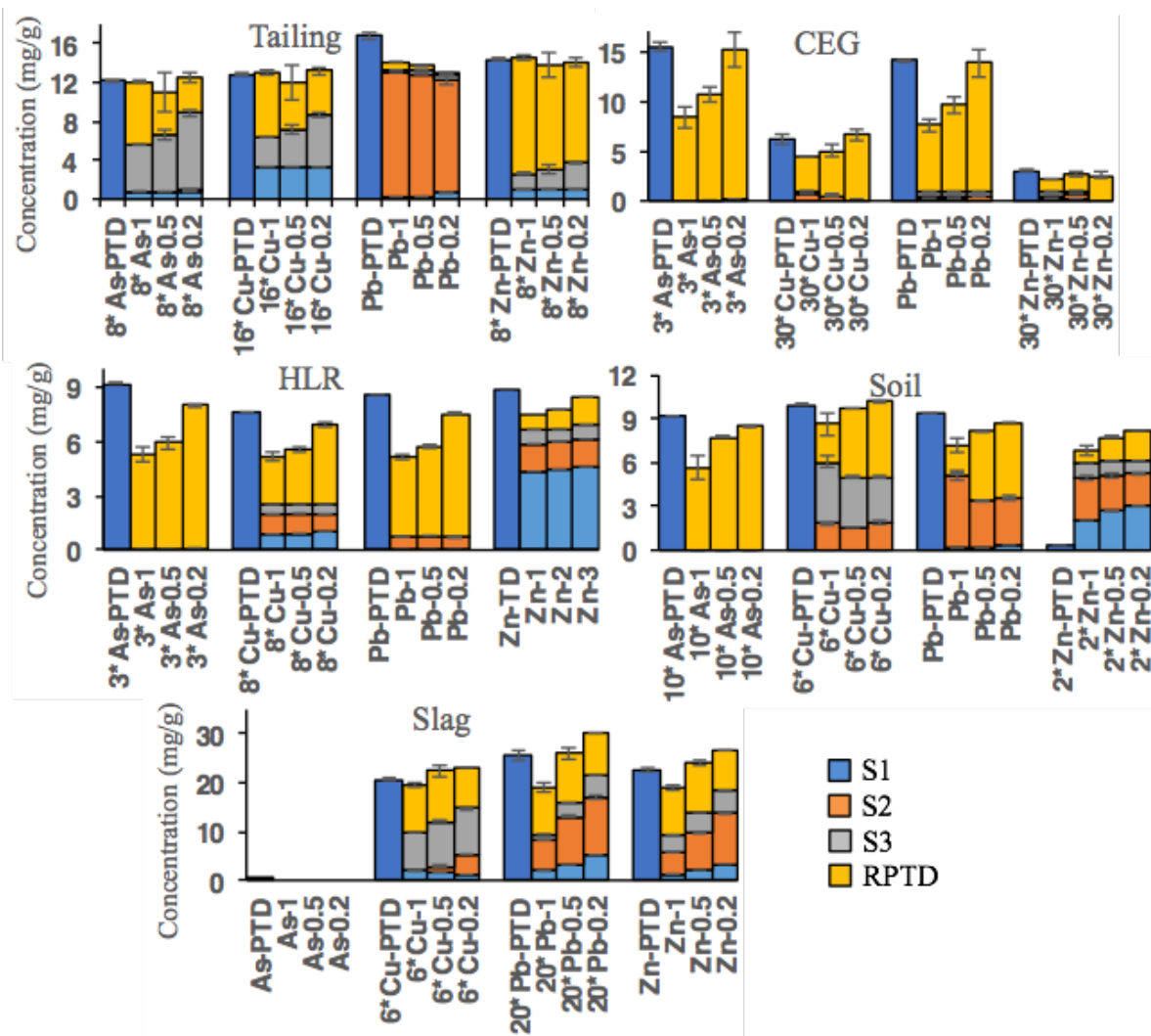


Figure 3 Concentration of the main toxic metals released during the 3 sequential extraction steps of the BCR<sup>®</sup>SEP, (i.e., S1, S2 and S3), and the aqua regia digestions of the initial samples (PTD) and the final residues (RPTD). The first blue bar for each element corresponds to the pseudototal digestion performed to each initial sample (e.g., Pb-PTD). X-n, with X corresponding to each specific element studied (i.e., As, Cu, Pb and Zn) and n from 1 to 0.2, represents the concentration of each element released if a different amount of solid sample is initially submitted to the BCR<sup>®</sup>SEP (e.g., Pb-1, Pb-0.5 and Pb-0.2 = lead released using 1g, 0.5g and 0.2g of sample). Please notice that to facilitate their visualization, some elements are shown with their concentrations multiplied by a whole number (e.g., 30\*Cu in CEG).

As for As, Cu, Pb and Zn in sample CEG, a direct interpretation of the BCR<sup>®</sup>SEP would suggest that all these elements are immobile and do not present any environmental risk.

Nevertheless, the study of the sample mineralogy (mainly Fe-oxides and Fe-sulfates) and the tendencies shown by its main components (i.e., Fe and S) during the extraction procedure (Figure 2) clearly reveal that the BCR<sup>®</sup>SEP does not achieve a complete selective mineral dissolution. It could be argued that as these minerals were not dissolved during the three steps of the BCR<sup>®</sup>SEP they would be very difficult to dissolve in nature. However, there are many reports of these precise minerals dissolving in nature without much effort (if the time and environmental conditions are given) and generating acidic metal polluted waters [27 and references therein].

As expected by their similar mineralogy, As, Cu, Pb and Zn released from sample *HLR* showed a very similar behavior if compared with sample *CEG*. Consequently, the same reasoning applied earlier can be used here. The only relevant difference corresponds to the release of Cu and Zn in *HLR* during the first step of the sequential extraction. These metals could be partially substituting Ca in gypsum or, most probably, forming part of other undetected sulfates. According to that, the BCR<sup>®</sup>SEP is able to suitably predict the mobility of part of the Cu and Zn in *HLR* yet it fails to represent the availability of the remaining Cu and Zn, as well as all the As and Pb in this mine residue.

Lead is by far the most abundant toxic metal in *soil* and its release is linked to the unselective and incomplete dissolution of Pb-jarosite throughout the BCR<sup>®</sup>SEP and the residue pseudototal digestion. Therefore, the mobility of this toxic metal is underestimated since Pb-jarosite at the environment is relatively simple to dissolve [27]. There is not a clear common tendency for As, Cu and Zn, but generally speaking, the results of the BCR<sup>®</sup>SEP suggest a restricted or very limited mobility for most of them; whereas the

mineralogy of the sample advises to consider this type of residue as to prone to generate water metal pollution and acidity.

Finally, Pb and Zn release from *Slag* is clearly associated with the unselective dissolution of fayalite (where those elements substitute Fe) and to a lesser extent to the dissolution of magnetite; whereas Cu is probably included in Fe-Cu alloys, according to previous studies [28]. As a result, once again the mobility of those elements is underestimated because of the inability of the reagents used to selectively dissolve the targeted mineral in each step of the BCR<sup>®</sup>SEP.

#### 3.4. Implications, concluding remarks and the environmental geometallurgical approach

As it was extensively discussed throughout the present work, an accurate prediction of toxic metals mobility can not rely only on chemically based tests such as the BCR<sup>®</sup>SEP. The mineralogy of the mining residues highly controls toxic metals liberation as well as the water chemistry around the residues. Therefore, there is a clear need to create new standardized methods that combine bulk chemistry, sequential extractions and mineralogy; as well as other factors like mineral texture or grain size. On this respect, there are several authors, within the research area of environmental geometallurgy, that are setting the ground for the future generation of standardized chemical and mineralogical protocols. Among others, the studies from Parbahakar [29,30], Dold [31] and Brough [32] highlight the importance of knowledge transfer between different scientific and engineering disciplines to tackle similar problems. Specifically, they recommend using a geochemistry–mineralogy–texture (GMT) approach to predict acid rock drainage generation. Whereas these and other methods to anticipate metals release to the environment from mine residues

are being improved or created, a mineralogical study (e.g., by XRD) of the remaining residue after each BCR extraction step should be included. This additional information will confirm if the selective mineral dissolution was complete or only partial, and if the elemental release in each extraction step is influenced or not by the limitations of the extraction protocol.

On the other hand, managing mining residues is one of the current greatest challenges for mining companies and decision makers. These challenges involve, among others, temporal and final safe disposition, prevention of water metal pollution during and after operation, rehabilitation and/or remediation of old polluted sites, or chemical stabilization of the residues. Because of the gigantic amount of mineral residues generated by the mining companies around the world, and the increasing consciousness of the general public and governments about the potential threat that those residues present to the environment; the annual expenditure on mining residues characterization and metal pollution assessment is becoming of high concern for the mining companies. Taking into account these observations, underestimating toxic metal mobility in mining residues can have a tremendous impact not only in the environment, but also in the economy of the mining companies (payment of environmental penalties, lost of credibility, implementation of remediation plans, etc.).

## **Acknowledgments**

This study was partially financed by the program Fondecyt Iniciación N°11150002 and U-Inicia from the University of Chile. The authors thank M. Cabañas and R. Bartrolí (IDAEA-CSIC) for their analytical assistance, Dr. Gerasimos Lyberatos (editor in chief)

and two anonymous reviewers for their suggestions and comments that significantly improved the quality of the original manuscript.

## References

- [1] EN 12457-2, Characterization of Waste, Compliance Test for Leaching of Granular Wastes Materials and Sludges, Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 l kg<sup>-1</sup> for Materials with Particle Size Below 4 mm (without or with Size Reduction), European Committee of Standardization, CEN/TC 292, 12/02/2002 p. 28.
  
- [2] US EPA (US Environmental Protection Agency), Kinetic Test Method for the Prediction of Mine Drainage Quality, United States Environmental Protection Agency, Washington, DC, December 2011, p. 37.
  
- [3] R.W. Lawrence, Y. Wang, Determination of neutralization potential in the prediction of acid rock drainage(1997). In: Proceedings of the fourth international conference on acid rock drainage, vol.1, Vancouver, BC, pp 451–464.
  
- [4] A. K. Parbhakar-Fox, M. Edraki, D. Bradshaw, S. Walters, Development of a textural index for the prediction of acid rock drainage, *Miner. Eng.* 24 (2011) 1277–1287.
  
- [5] B. Dold, Dissolution kinetics of schwertmannite and ferrihydrite in oxidized mine samples and their detection by differential X-ray diffraction (DXRD), *Appl. Geochem.* 18 (2003) 1531–1540.
  
- [6] M.A. Caraballo, T.S. Rotting, J.M. Nieto, C. Ayora, Sequential extraction and DXRD applicability to poorly crystalline Fe- and Al-phase characterization from an acid mine water passive remediation system, *Am. Mineral.* 94(2009)1029-1038.

- [7] O. Abollino, M. Malandrino, A. Giacomino, E. Mentasti, The role of chemometrics in single and sequential extraction assays: A review: Part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition, *Anal. Chim. Acta* (2011) 688 104-121.
- [8] A.M. Ure, P. Quevauviller, H. Muntau, B. Griepink, Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities, *Int. J. Environ. Anal. Chem.* 51 (1993) 135.
- [9] A. Sahuquillo, J.F. Lopez-Sanchez, R. Rubio, G. Rauret, R.P. Thomas, C.M. Davidson, A.M. Ure, Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure, *Anal. Chim. Acta* 382 (1999) 317.
- [10] G. Rauret, J.F. Lopez-Sanchez, D. Luck, M. Yli-Halla, H. Muntau, Ph. Quevauviller, The certification of the extractable contents (mass fractions) of Cd, Cr, Cu, Ni, Pb and Zn in freshwater sediment following a sequential extraction procedure, BCR-701, European Commission, EUR 19775 EN, Luxembourg, Belgium, 2001.
- [11] M. Pueyo, G. Rauret, D. Luck, M. Yli-Halla, H. Muntau, Ph. Quevauviller, J.F. Lopez-Sanchez, Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure, *J. Environ. Monitor.* 3 (2001) 243.
- [12] R.A. Sutherland, BCR®-701: A review of 10-years of sequential extraction analyses. *Anal. Chim. Acta* 680 (2010) 10-20.

- [13] F. Macías, M.A. Caraballo, J.M. Nieto, Environmental assessment and management of metal-rich wastes generated in acid mine drainage passive remediation systems, *J. Hazard. Mater.* 229-230 (2012) 107-114.
- [14] E. Fernandez-Ondono, G. Bacchetta, A.M. Lallena, F.B. Navarro, I. Ortiz, M.N. Jimenez, Use of BCR sequential extraction procedures for soils and plant metal transfer predictions in contaminated mine tailings in Sardinia, *J. Geochem. Explor.* 172 (2017) 133-141
- [15] M. Sethurajan, D. Huguenot, P.N.L. Lens, H.A. Horn, L.H.A. Figueiredo, E.D. van Hullebusch, Fractionation and leachability of heavy metals from aged and recent Zn metallurgical leach residues from the Trs Marias zinc plant (Minas Gerais, Brazil), *Environ. Sci. Pollut. R.* 23 (2016) 7504-7516.
- [16] E. Margui, V. Salvado, I. Queralt, M. Hidalgo, Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes, *Anal. Chim. Acta* 524 (2004) 151-159.
- [17] J. Shiowatana, R.G. McLaren, N. Chanmekha, A. Samphao, Fractionation of arsenic in soil by a continuous-flow sequential extraction method, *J. Environ. Qual.* 30 (2001) 1940- 1949.
- [18] R. Perez-Lopez, A.M. Alvarez-Valero, J.M. Nieto, R. Sáez, J.X. Matos, Use of sequential extraction procedure for assessing the environmental impact at regional scale of the Sao Domingos Mine (Iberian Pyrite Belt), *Appl. Geochem.* 23 (2008) 3452- 3463.
- [19] C.V. Putnis, M. Kowacz, A. Putnis, The mechanism and kinetics of DTPA-promoted dissolution of barite, *Appl. Geochem.* 23 (2008) 2778–2788.

- [20] B.Y. Zhen-Wu, K. Dideriksen, J. Olsson, P.J. Raahauge, S.L.S. Stipp, E.H. Oelkers, Experimental determination of barite dissolution and precipitation rates as a function of temperature and aqueous fluid composition, *Geochim. Cosmochim. Ac.* 194 (2016) 193-210.
- [21] B.S. Bageri, M.A. Mahmoud, R.A. Shawabkeh, S.H. Al-Mutairi, A. Abdulraheem, Toward a complete removal of barite (barium sulfate BaSO<sub>4</sub>) scale using chelating agents and catalysts *Arabian J. Sci. Eng.* 42 (2017) 1667-1674.
- [22] R.M. Cornell and U. Schwertmann, *The iron oxides: structure, properties, reactions, occurrences and uses*, WILEY-VCH, Weinheim (2003).
- [23] R. Matthies, A.C. Aplin, A.J. Boyce, A.P. Jarvis, Geochemical and stable isotopic constraints on the generation and passive treatment of acidic, Fe–SO<sub>4</sub> rich waters, *Sci. Total Environ.* 420 (2012) 238-249.
- [24] P.C. Ryan, S. Hillier, A.J. Wall, Stepwise effects of the BCR sequential chemical extraction procedure on dissolution and metal release from common ferromagnesian clay minerals: A combined solution chemistry and X-ray powder diffraction study, *Sci. Total Environ.* 407 (2008) 603-614.
- [25] N. M. Piatak, M.B. Parsons, R.R. Seal II, Characteristics and environmental aspects of slag: A review, *App. Geochem.* 57 (2015) 236-266.
- [26] D. Daval, D. Testemale, N. Recham, J.M. Tarascon, J. Siebert, I. Martinez, F. Guyot, Fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) dissolution kinetics determined by X-ray absorption spectroscopy, *Chem. Geol.* 275 (2010) 161-175.
- [27] J.M. Bigham and D.K. Nordstrom, Iron and aluminum hydroxysulfates from acid sulfate waters. In: Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (Eds.), *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance. Reviews*

- in *Mineralogy and Geochemistry*, (2000) Mineralogical Society of America, Chantilly, Virginia, 351–403.
- [28] A.M. Álvarez-Valero, R. Pérez-López, and J.M. Nieto, Prediction of the environmental impact of modern slags: A petrological and chemical comparative study with Roman age slags, *Am. Mineral.* 94 (2009) 1417–1427
- [29] A. Parbhakar-Fox, M. Edraki, D. Bradshaw, S. Walters, Development of a textural index for the prediction of acid rock drainage, *Miner. Eng.* 24 (2011) 1277–1287.
- [30] A. Parbhakar-Fox and B.G. Lottermoser, A critical review of acid rock drainage prediction methods and practices, *Miner. Eng.* 82 (2015) 107-124.
- [31] B. Dold, Acid rock drainage prediction: A critical review. *J. Geochem. Explor.* 172 (2017) 120-132.
- [32] C.P. Brough, R. Warrender, R.J. Bowell, A. Barnes, A. Parbhakar-Fox, The process mineralogy of mine wastes, *Miner. Eng.* 52 (2013) 125-135.