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Mineralogical, geochemical, and leaching study of historical Cu-slags issued from processing of the Zechstein formation (Old Copper Basin, southwestern Poland)

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ABSTRACT

Historical Cu-Slags located at former industrial sites in Poland are exposed to weathering that may trigger release of metallic contaminants to the surrounding soils. However, the extent to which different metals are leached depends on the mineral composition of the slags and the conditions of their deposition. Historical slags are often crystalline and composed of phases with a variable response to weathering. Also, weathering of crystalline slags (CS) is different from that of amorphous slags (AS). To understand how the slag phase composition triggers weathering and the ultimate release of metallic elements, we studied the leaching of historical crystalline and amorphous slag. A combined geochemical and mineralogical approach determined the weathering sequence(s) of slag components subjected to different conditions of specific slag disposal. In detail, experiments under: i) various pH conditions in the range of 2–13 in a batch mode simulated slag deposition within a deep soil profile, whereas ii) exposure to solutions of artificial root exudates (ARE) in a dynamic experimental system simulated slag deposition within topsoil. The results demonstrated that crystalline phases in the order Leucite > Plagioclase > Pyroxene are preferentially dissolved in inorganic conditions of a pH ≤ 7, in contrast to glass, which is preferentially dissolved in alkaline conditions (pH > 7). Also, inorganic conditions better promote the dissolution of metal-bearing phases (sulphides and metals) when compared to silicates. In contrast, artificial root exudates do not show preferential dissolution of any phase and cause the strongest leaching in all of the analyzed conditions. We show that reconstructing the susceptibility of complex crystalline slags to weathering requires a specific approach including analyses and interpretation of all major components such as Ca, Mg and K, not merely a focus on Si and metals.

1. Introduction

Slags are byproducts of mining and processing of ore minerals (Ettler et al., 2009; Piatak et al., 2015; Potysz et al., 2015). These metallurgical byproducts are significant in volume; for example, it is estimated that in order to produce a given amount of copper (e.g. 1 ton) the process generates twice the equivalent volume of slag (e.g. 2 tons) (Gorai et al., 2003).

Numerous recent studies (see Piatak et al., 2015 and Piatak, 2018 for review) report that slag based products are widely used for construction purposes. However, several studies (for example Sobanska et al., 2016, Tyszka et al., 2018) show that base metal slags (including copper slags) are not always inert and that their leaching potential could be high, especially in some specific conditions *e.g.*, when exposed to seawater (Schmukat et al., 2012). On the other hand, the study of Lidelöw et al. (2017) shows that despite elevated concentrations of Cu, Ni and Zn in fayalitic copper slags used as road construction materials, the environmental risk associated with these slags is low. Furthermore, the risk can be reduced through appropriate technological measures during road construction. Therefore, it is obvious that before the use of any slag material for any purpose, a detailed use-specific and site-specific study is necessary (Piatak, 2018). Such a study should be multi-approach and include detailed mineralogical and geochemical characterization of the material coupled with leaching tests, as such it should reflect the real situation related either to the use of the slag or to the determination of its impact on the environment (Grosbois et al., 2011, Jarosikova et al., 2017, 2018).

Historical metallurgical slags are often disposed of in the vicinity of former industrial centers and are there subjected to weathering. In particular, they are in direct contact with soils (Kierczak et al., 2013;

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Potysz et al., 2016) and, therefore, it is informative to understand the slag-soil interactions that take place on the surface, within the topsoil layer, and in deeper soil horizons. Different soil depths are characterized by a range of disposal conditions. Deep soils are characterized by various pH conditions that change not only from one dumping site to another, but also vary within the soil depth. According to literature reports, recorded pH conditions can range between: i) 3.7–4.9, 7.2–8.4 and 5.8–8.5 in the soils with admixtures of slags (Kierczak et al., 2008, 2013; Sobanska et al., 2000), ii) 5.1–6.9 in smelter-impacted soils (Ettler, 2016), iii) 4.7–8.4 in smelter impacted topsoil and rhizosphere leachate (Kríbek et al., 2016), and iv) 4.8–6.6 in mining soils (Komárek et al., 2007). Furthermore, extremely low pH conditions (as low as pH = 2) may be encountered in the areas impacted by sulfide-bearing mining wastes (Lottermoser, 2005). Therefore, an experimental leaching study focused on slag exposure to various pH conditions is relevant for estimating potential element release that may occur in soil profiles containing slag fragments. However, it is important to note that pH values in the topsoil rhizospheric horizons are usually lower when compared to those observed in deeper soil horizons, mainly due to root exudation and promoted microbial activity (Nye, 1981; Jones, 1998; Baetz and Martinoia, 2014). Therefore, studies devoted to ongoing interactions at organic-rich rhizosphere interfaces where root exudates come into contact with slag surface are also highly important for assessing potential environmental risks at dumping sites (Potysz et al. 2017, 2018a; Agnello et al., 2018).

One of the areas associated with former copper processing is located in the vicinity of Leszczyna (SW Poland; Fig. 1A and B). As a result of this industrial activity, significant quantities of wastes – pyrometallurgical slags - were produced and deposited as unconstrained slag heaps in the vicinity of the smelters. Interestingly, these slags were also once used as a construction material. The slags were formed into blocks from which both outbuildings and residential buildings were erected (Fig. 2).

The slags selected for study were disposed of without any concern for the environment and they now form irregular accumulations often covered with, or mixed with soil (Fig. 2). Therefore, we decided to use a site-specific approach to better understand the relationships between slag weathering and the release of metallic elements under various conditions. For this reason, we use a combined geochemical and mineralogical approach aimed at determining the weathering sequence(s) of slag components subjected to different conditions of slag disposal. In detail, experiments under: i) various pH conditions in the range of 2–13 in a batch mode simulated slag deposition within deeper parts of the soil profile, whereas ii) exposure to solutions of artificial root exudates (ARE) in a dynamic experimental system simulated slag deposition within topsoil. We believe that such an approach adds valuable information, which is necessary to fully understand the behavior of metal (loid)s in the environment and helps to illuminate new potential applications for slag and/or better slag disposal techniques.

2. Site description

Copper ores that have historically been exploited in Poland typically belong to a strata-bound type of deposit (Kaczmarek and Rożek, 2006). They are located in Lower Silesia within two geological units: the Fore-Sudetic Monocline and the North Sudetic Basin and are related to the Zechstein formation (Fig. 1). The most economically important Polish Cu-ores are situated in the Fore-Sudetic Monocline. These deposits were first documented in the 1950s and their extraction has continued to the present day (Kaczmarek and Rożek, 2006). The first written references about the exploitation and smelting of Zechstein Cu ores in the North Sudetic Basin (in the vicinity of Leszczyna) come from the 16th century (CDS, 1990, 1901XX-XXI). However, the history of the extraction of Cu ores in this area dates back to the Middle Ages (Stolarczyk, 2012). Copper ores in the Leszczyna region are associated with the Lower Permian marls (slate marls, Fig. 1). These deposits were of relatively poor grade, containing 0.5–1.8% Cu. However, their occurrence in the form of relatively regular strata of approximately 2.8 m thick, facilitated their exploitation (Stolarczyk, 2012). The major Cu-bearing minerals of these deposits included: bornite (Cu_5FeS_4), chalcocite (Cu_2S), and chalcopyrite ($CuFeS_2$) accompanied by minor covellite, native Cu, malachite and azurite (Stolarczyk, 2012).

3. Materials and methods

3.1. Sampling and general slag characteristics

More than thirty samples of slags with a total weight of over 20 kg from two sampling sites were collected during fieldwork (Fig. 1c). Even at the stage of macroscopic observations we noticed that the samples from both locations were visually different from each other. Those from Site 1 are most often found as individual, highly porous blocks, which have a maximum diameter of 50 cm (Fig. 2b), whereas those from Site 2 are generally smaller (up to 20 cm in diameter) and characterized by lower porosity compared to slag from Site 1 (Fig. 2c). Slags from both localities occur on the ground surface and/or within soil horizons. On the basis of macroscopic and microscopic observations as well as chemical composition we selected two representative samples (one representing the crystalline slag group and the other representing the amorphous slag group) for the detailed mineralogical and leaching study. Sample HL-1 (Crystalline Slag - CS) comes from the area of the former Cu smelter in Leszczyna (Site 1; Fig. 1c). It has an aphanitic and porous texture and contains a variety of crystalline phases (Table S3, Supplementary materials). Sample HK-1 (Amorphous Slag - AS) was taken approximately five kilometers south of Site 1 near Kondratów (Site 2; Fig. 1c) it is massive and entirely glassy in appearance. We also analyzed secondary phases occurring on the slag fragments (Fig. 2d), i.e. those phases formed after the solidification of the slag melt and also phases that could have formed as the result of both deuteric alteration and weathering.

3.2. Bulk chemical analyses

Slag samples were crushed and pulverized to obtain homogeneous and representative sub-samples for bulk chemical analyses. The chemical compositions of the slags were analyzed by a combination of inductively coupled plasma emission spectrometry (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS) for major, minor, and trace elements. Sample digestion was performed using $LiBO_2/Li_2B_4O_7$ fusion and further dissolution with nitric acid (Bureau Veritas Group Company, formerly ACME Labs). The analytical reproducibility (2σ), as estimated from a replicate analysis of sample HL (Site 1) and two analyses of standards SO-18, and ranges from 0.1% (SiO_2) to 4% (Zn) at 95% confidence limits. Analytical accuracy (2σ), as estimated from 3 measurements of standard (SO-18 and OREAS45EA) is from 0.3% (SiO_2) to 30% (Ag) at 95% confidence limits.

3.3. Mineralogical analyses

The phase composition of the studied slags was identified using a combination of methods including Optical Microscopy, Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (SEM-EDS), X-ray Powder Diffraction (XRD) and electron microprobe analyses (EMPA). Microscopic observations of thin, polished sections of slags were carried out using a petrographic microscope (Leica DM2500P) in transmitted and reflected light. More detailed observations of the slags were carried out using a Scanning Electron Microscope (SEM, JEOL JSM-IT100) coupled with an Energy Dispersive Spectrometer (EDS, Oxford) at high vacuum and using 15–20 kV working mode. Scanning electron microscope observations were also conducted in order to document the weathering features of slag grains subjected to the 30 day leaching tests. The XRD patterns of studied slags

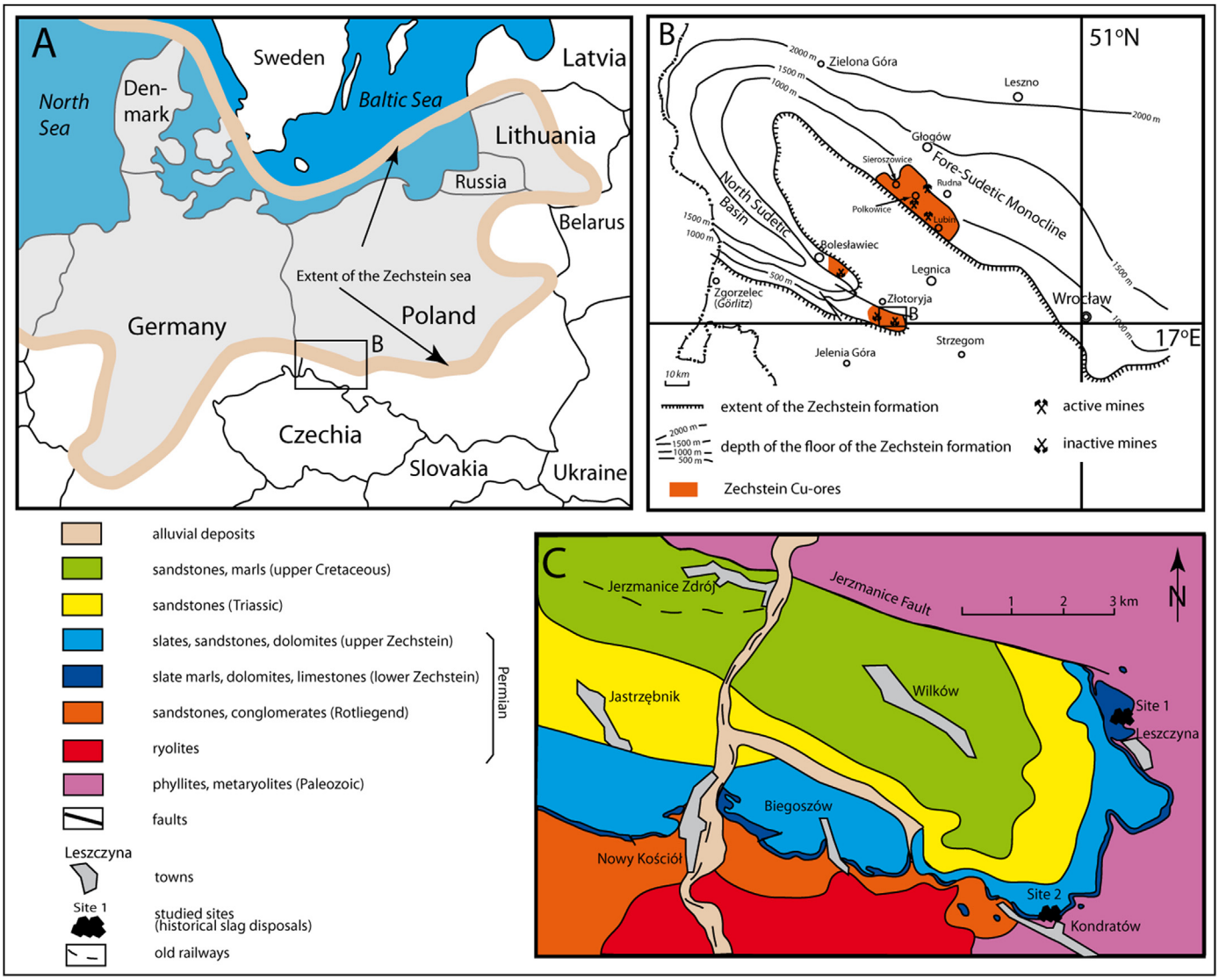


Fig. 1. Location and context of the study: A) Extent of the Zechstein Sea in central Europe (after Garcia-Veigas et al., 2011), B) Zechstein Cu-ores in Poland (after Wyżykowski, 1979), C) Geological map of the studied area showing sampling location (modified after KGHM ZG "Lena" files, sign. 24 page 8).

and their associated secondary phases were recorded using a WAXS/SAXS – EMPYREAN, (PANalytical) diffractometer equipped with a 4 kW high voltage generator of CuKα (1.54060 Å) radiation. The diffraction patterns were recorded in the range of 2-theta angles from 10° to 90° (30 min/analysis). The indexation of the XRD patterns was performed using X'Pert HighScore software based on the PDF-2 ICDD (International Centre for Diffraction Data) database. The chemical composition of the individual slag phases was determined using an electron microprobe analyzer (Cameca SX 100) operated at an accelerating voltage of 15 kV and a beam current of 20 nA. Two analytical programs were used for these analyses. The following standards were applied for the first program (for silicates and oxides): albite (Na), diopside (Mg, Si, Ca), orthoclase (Al, K), apatite (P), barite (S), galena (Pb), rhodonite (Mn) hematite (Fe), chalcopyrite (Cu), sphalerite (Zn), rutile (Ti). The second program was intended for analyses of sulfides and metallic phases and used the following standards (elements analyzed in brackets): chalcopyrite (Cu), apatite (P), sphalerite (Zn), galena (Pb), GaAs (As), hematite (Fe), CoO (Co), NiO (Ni), Ag_2Te (Ag).

3.4. Leaching test

Conditions of the leaching tests used in this study were set to mimic slag weathering processes in the field (larger slag blocks in the uppermost soil horizons and more disintegrated slag particles in the lower horizons). Therefore the grain size was smaller in the pH dependent leaching test, which was designed to mimic slag behavior in deeper soil horizons, than in the test using artificial root exudates, which was designed to simulate rhizospheric conditions.

3.4.1. pH-dependent leaching test

The slags were subjected to leaching tests at pH-static conditions according to US EPA 1313, 2012 protocol. The slag blocks were crushed to obtain a grain size below 0.3 mm. The reason for the choice of such small slag grains was to represent a so-called "worst-case scenario" related to contaminant release (Piatak et al., 2015). Such prepared slags are considered to be representative in terms of mineralogical and chemical composition since whole slag blocks are crushed, leaving no portion of the sample untested after crushing. The pH values fixed in the separate batches were in the range of 2–13. The experiments were carried out at a liquid to solid ratio of 10 L kg^{-1} and agitated on an orbital shaker at a rotation speed of 150 rpm for 24 h. The required pH value in each flask was maintained through the addition of appropriate amounts of 2 M nitric acid (HNO_3) or 1 M potassium hydroxide (KOH). Leaching at pH 9 was carried out with demineralized water (i.e. natural



Fig. 2. Photographs showing studied slags: A) Slag wall of the housing of a mining excavation (Site 1 – Leszczyna), B) Large slag blocks located at site 1, C) Slag fragments occurring at Site 2 (Kondratów), D) Secondary phases commonly present on slag surfaces (Site 1) and associated X-Ray powder diffraction (XRD) pattern corresponding to that of secondary phase brochantite ($Cu_4SO_4(OH)_6$).

samples pH is 9). The approximate volume of the acid/base was initially selected based on a pre-experiment titration curve. The maintenance of a controlled pH value during the experiment was achieved by the manual addition of acid or base via micro pipette. The final pH oscillated ± 0.2 pH from the targeted pH value. An extraction with distilled water was carried out in order to demonstrate each slag's behavior under its natural pH conditions. The leaching experiments were performed in duplicate and accompanied by procedural blanks. After finishing the experiment, the leachates were subjected to a pre-filtration step aimed at eliminating most of the suspended slag particles using nitrocellulose funnel filters. Then, the leachate was filtered using PTFE syringe filters of 0.45 µm pore size. The filtered supernatants were split into two portion aliquots: i) aliquot acidified using 1% vol. concentrated (65%) HNO_3 for elemental analysis and ii) non-acidified aliquot for anion analysis. All the samples were stored at 4 °C until the measurements. Leachate elemental content was determined through the measurements performed using flame and graphite atomic absorption spectroscopy (GBC Avanta instrument).

3.4.2. Leaching test simulating a rhizospheric environment

The second leaching test was aimed at the simulation of slag weathering under rhizospheric conditions. It was carried out in a dynamic experimental system (with solution renewal every 5 days spanning 30 total days) with the use of four different solutions: i) artificial root exudates (ARE) at pH t_0 = 3.5 (ARE 3.5), ii) demineralized water at pH t_0 = 3.5 (DW 3.5), iii) ARE at pH t_0 = 6.7 (ARE 6.7), and iv) demineralized water at pH t_0 = 6.7 (DW 6.7). A synthetic solution of ARE (43.7 mM) was modified after Baudoin et al. (2003) and contained in 1 L: glucose (9.2 mM), fructose (9.2 mM), sucrose (4.6 mM), citric acid (4.6 mM), lactic acid (9.2 mM), and succinic acid (6.9 mM). The sterilized slag grains (1–2 mm) were placed into a perforated polypropylene column tube (0.5 mm pore size) and immersed in a respective sterile weathering solution. All the solid materials were autoclaved (120 °C, 20 min) prior to use, while solutions were sterilized using polyethersulfone (PES) 0.45 µm pore size sterile filters. The experiments lasted 30 days with a regular sampling interval of 5 days after which each slag sample was moved to corresponding fresh leaching solution. The leachate resulting from the previous experimental period was filtered (0.45 µm PTFE filers) and analyzed for its elemental composition. The elemental composition of solutions resulting from each sampling round was measured by inductively coupled plasma atomic mass spectrometry (ICP-MS Nexion 300D Perkin Elmer) in a certified commercial laboratory. Detection limits were typically 0.1 µg/L and 1 µg/L for minor and major elements respectively. Relative standard deviation (RSD) of each measurement was below or equal to 2%. For the measurements with RSD higher than 2%, a standard solution was analyzed and sample analysis repeated in order to ensure high quality and reliability of the data. In addition, each sampling time, the pH and Eh values were measured in the reactors (Figure S1 and S2; Supplementary materials).

4. Results

4.1. Chemical and phase composition of slags

The chemical composition of the studied slags from both sites is different (Table 1), although both contain silica, alumina, calcium, and iron as major oxide components. However, amorphous slag (AS) from Site 2 (HK-1) contains higher amounts of iron and lower of alumina compared to the crystalline slag (CS) from Site 1 (HL-1). Slags from both locations contain similar amounts of potassium, calcium and magnesia as minor components. In terms of metallic element concentrations, both slag groups contain elevated concentrations of Cu. However, in the CS the Cu concentration reaches approximately

Table 1
Chemical composition of studied slags.

Sample ID	CS (HL 1)	AS (HK 1)
Major and minor elements (wt. %)		
SiO_2	46.5	48.3
TiO_2	0.80	0.57
Al_2O_3	17.6	11.8
$Fe_2O_3^{tot.}$	4.76	13.5
MnO	0.21	0.49
MgO	2.73	2.10
CaO	18.1	17.5
Na_2O	0.19	0.21
K_2O	5.97	4.59
Minor and trace elements (mg kg^{-1})		
Cu	4060	19724
Pb	59	53
Zn	164	587

CS – crystalline slag, AS – amorphous slag, $^{tot.}$ – total Fe expressed as Fe_2O_3.

4000 mg kg^{-1}, whereas the AS contains up to 20000 mg kg^{-1} Cu (Table 1).

In terms of mineral composition, the studied samples also clearly differ from each other (Fig. 3). Crystalline slag (CS) contains leucite, clinopyroxene, plagioclase and silicate glass as major constituents with other minor components like wollastonite and melilite (Fig. 3a). Sulfides and intermetallic compounds are common accessory phases in the CS. They are represented by: chalcocite, bornite, pyrrhotite, metallic Cu and unknown intermetallic compounds of Pb, As, Cu, Fe and Ni. The amorphous slag (AS) is composed of silicate glass and minor metallic phases represented by copper and chalcocite (Fig. 3b, SM 1). Sulfides and metallic phases are volumetrically minor components of both the studied material samples, but they constitute the most important metal carriers (particularly for Cu).

In our leaching experiments we focus on the elements which enable the tracking of the dissolution fingerprint of individual phases present in CS and AS slags. Copper was selected to track the dissolution of sulfides and metallic phases, whereas Mg and Ca were chosen to track: i) dissolution of pyroxene and plagioclase in CS and ii) silicate glass in AS.

4.2. Leaching as a function of pH

The slags subjected to the pH-stat leaching test revealed similar general trends in terms of element release. They showed enhanced leaching along with a decrease in pH value in more acidic conditions (Fig. 4). Conversely, as pH levels increased from neutral towards more alkaline conditions, the leaching of the elements (Si, Fe, Al, Mg, Ca, Cu and Zn) was similarly enhanced (Fig. 4). However, the amounts of metals extracted under alkaline conditions were generally lower when compared to the extraction yields achieved when slags were leached in acidic solutions (Fig. 4). The amorphous slag leaching at pH 2 resulted in the highest release of Cu (62.4% of total Cu measured in bulk sample – approximately 12,300 mg kg^{-1}) and Zn (98.8%, 160 mg kg^{-1}), whereas the proportions of other analyzed elements did not exceed 27% (e.g. Si 62,400 mg kg^{-1}). Likewise, crystalline slag leaching with a low pH solution resulted in the maximal release of Cu (52.4% of total Cu – 2100 mg kg^{-1}) (Fig. 4). An extraction of Cu under alkaline conditions reached up to 0.2% (48 mg kg^{-1}) and 0.8% (34 mg kg^{-1}), for the

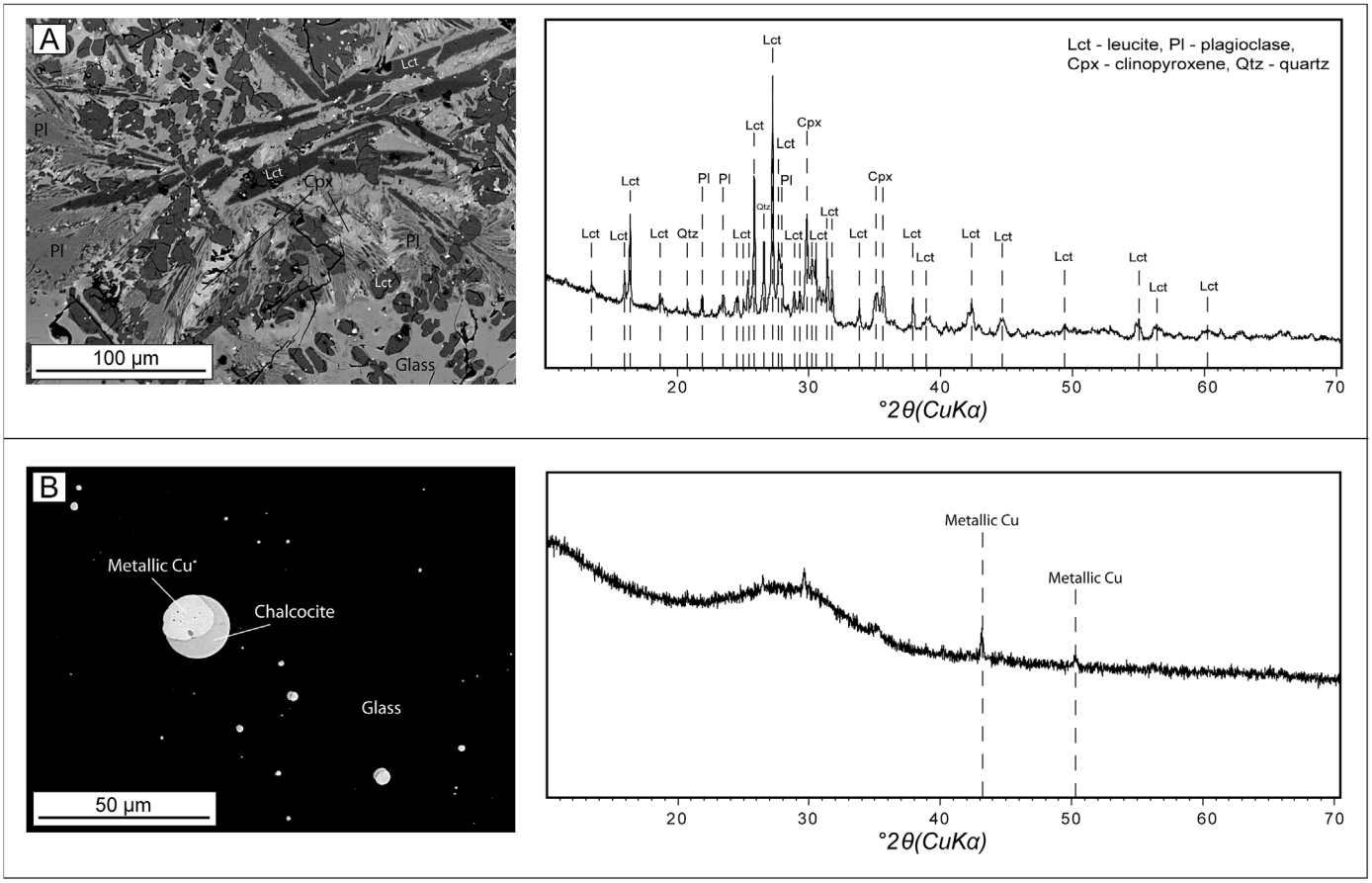


Fig. 3. Microphotograph (BSE images) of the Studied Slags, A) Crystalline Slag (CS) from Site 1 and Associated XRD Patterns, B) Amorphous Slag (AS) from Site 2 and Associated XRD Patterns.

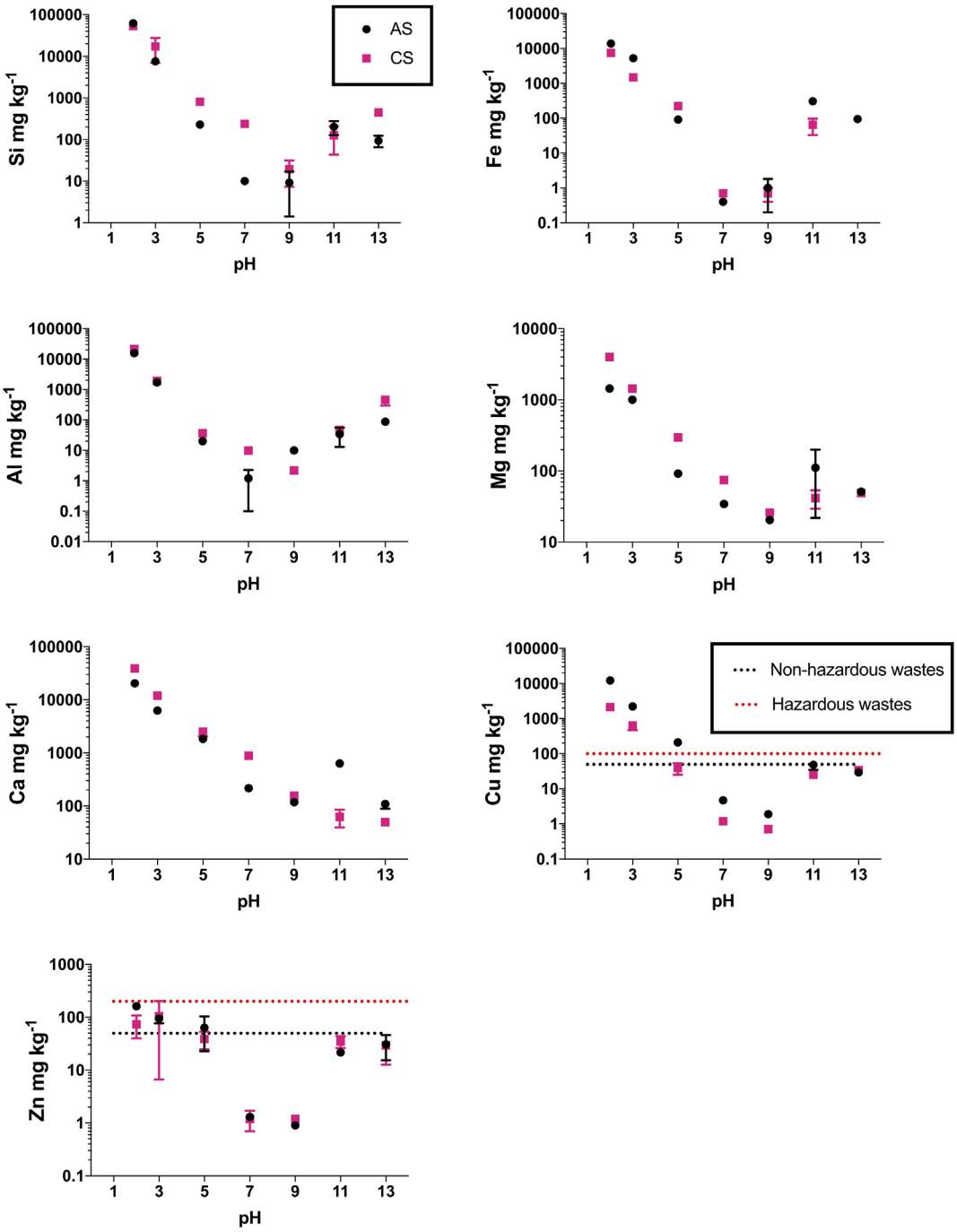


Fig. 4. The Release of the Elements as a Function of pH and Assessment of Metallic Contaminants (Cu and Zn) with Respect to Threshold Limits Specified in EU Regulation.
(pH =
9 natural sample pH).

amorphous and crystalline slags respectively. Furthermore, the release of Ca under acidic conditions was higher in the case of CS and reached up to 30% of total Ca measured in the slag (39,000 mg kg^{-1}), whereas extraction achieved in the case of AS was 16.4% (20,500 mg kg^{-1}). In contrast, Ca extraction rates under alkaline conditions were higher for the amorphous slag (*i.e.* up to 0.5% - 640 mg kg^{-1}) as compared to crystalline slag 0.05% (62 mg kg^{-1}). Similar observations apply to Mg which was released in a higher quantity from crystalline slag under acidic conditions (up to 24.4% - 4000 mg kg^{-1}) as compared to amorphous slag (up to 11.4% - 1400 mg kg^{-1}). In contrast, the slags' exposure to alkaline solution resulted in the release of nearly 1% of Mg from amorphous slag (110 mg kg^{-1}), whereas Mg liberation from crystalline slag did not exceed 0.3% (49 mg kg^{-1}). A complete set of results for the pH-stat leaching test is presented in Table S1 (Supplementary materials).

4.3. Leaching in a simulated rhizosphere environment

The extraction yield achieved under ARE 3.5 and DW 3.5 conditions was lower when compared to the yield obtained following slag exposure to pH-stat conditions. It is believed that the difference can be explained by the small fraction size used in the pH-stat testing as well as

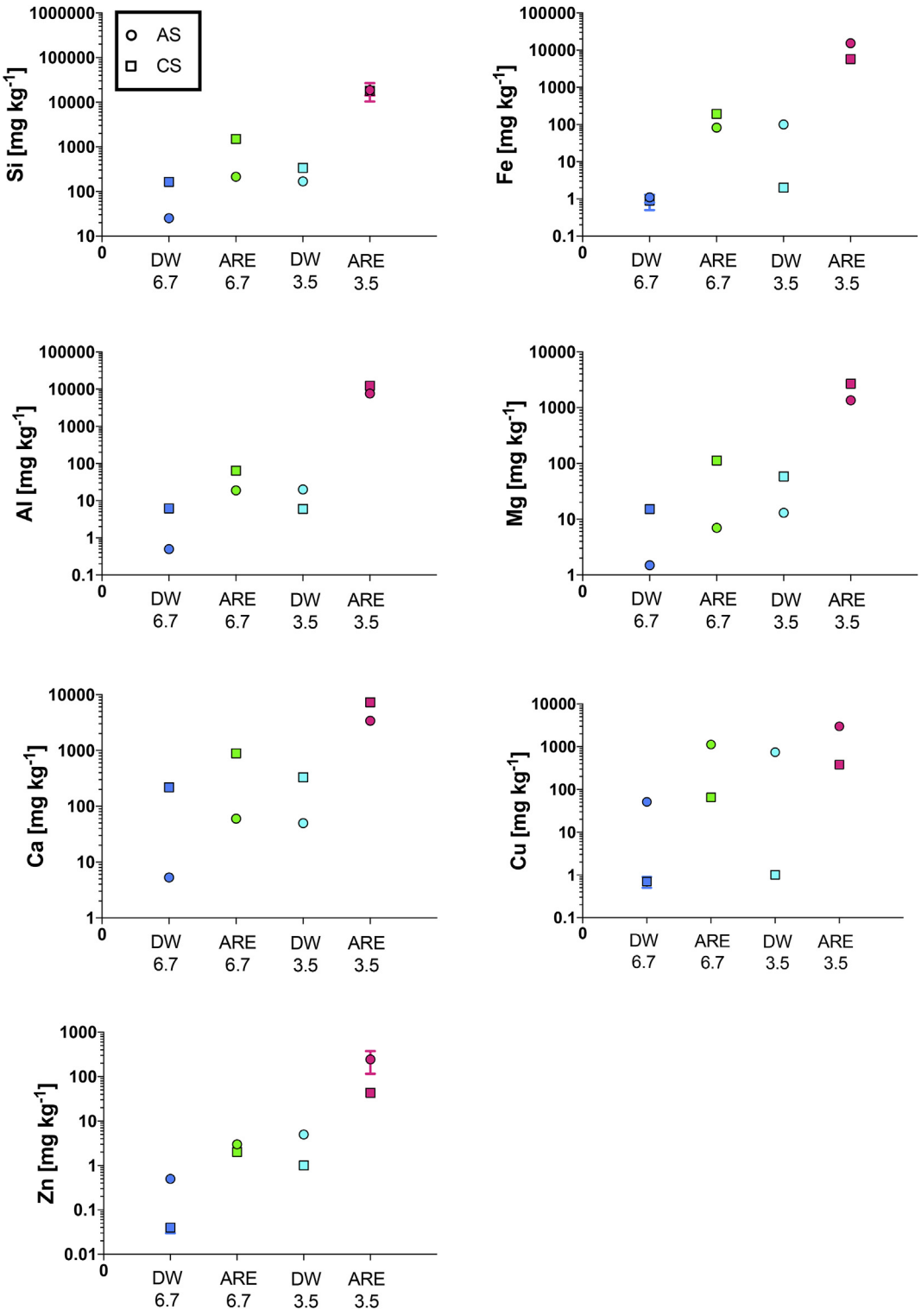


Fig. 5. Cumulative (30 days) release of major and metallic elements upon slag exposure to weathering solutions.

the free pH drift when left under ARE 3.5 and DW 3.5 conditions, which resulted in a pH shift towards less acidic conditions and reached values oscillating: i) in ARE 3.5 between 4.44-4.78 (AS) and 4.85–5.54 (CS) and ii) in DW 3.5 between 5.26-6.22 (AS) and 6.11–7.98 (CS) (Figure S1; Supplementary materials). Therefore, if a comparison between ARE and pH-stat experiments is attempted, then conditions at pH-stat 5 should be considered. However, due to the different slag particles used in both tests, only a quantitative comparison between crystalline and amorphous slags can be made, treating pH-stat and rhizosphere-like conditions as two independent sets of data.

The result of the leaching test simulating slag exposure to rhizospheric conditions demonstrated that artificial root exudates (ARE) enhance the release of the elements relative to corresponding inorganic conditions regardless of the initially fixed pH value (Fig. 5, Table S2; Supplementary materials). Acidic ARE 3.5 had the highest impact on slag dissolution and accounted for the release of up to 16.3% (15,400 mg kg^{-1}) and 12.2% (5800 mg kg^{-1}) of Fe within 30 days of incubation for AS and CS, respectively. Likewise, the release of Cu

reached similarly high values of 15.3% (3000 mg kg^{-1}) and 9.4% (380 mg kg^{-1}) for AS and CS, respectively. This release was 470 times higher when compared to Cu release under organic-free DW 3.5 conditions. The release of Ca from the slags incubated in ARE 3.5 medium was 2.7% (3400 mg kg^{-1}) and 4.0% (7300 mg kg-1) in the case of AS and CS, respectively. The release of Mg under ARE 3.5 conditions was similar for both slag samples and reached up to 10.7% (1400 mg kg^{-1}) for AS and 9.8% (2700 mg kg^{-1}) for CS. The release of Ca and Mg with slag exposure to DW 3.5 was between 50 and 100 times lower than extraction rates achieved under ARE 3.5 conditions (Fig. 5). Furthermore, the 30 day long slag incubation in near-neutral ARE 6.7 conditions extracted 5.7% (1100 mg kg^{-1}) and 1.6% (65 mg kg^{-1}) of Cu for AS and CS, respectively. Among the major elements, the release recorded for Ca in ARE 6.7 solution was 0.05% (60 mg kg^{-1}) and 0.5% (890 mg kg^{-1}) for AS and CS, respectively. Likewise, the release of Mg in ARE 6.7 was 0.05% (7 mg kg^{-1}) and 0.4% (110 mg kg^{-1}) for AS and CS, respectively. A comparison made between ARE 6.7 and DW 6.7 conditions shows that the release rates in the latter solution were between 70 and 200 times lower when compared to those achieved by ARE 6.7 (Fig. 5).

4.4. Scanning electron microscopic observations: weathering features and secondary phases

Scanning electron microscopic observations were done for the experiment simulating rhizosphere conditions. Larger grain size in this experiments allowed for detailed observations of phase alteration and the direct comparison between the experimental products.

4.4.1. Amorphous slag

After leaching with a DW 3.5 solution, AS grains displayed visible alteration features such as: (i) glass exfoliation (Fig. 6 A), (ii) dissolution and removal of Cu droplets (Fig. 6 B) and (iii) formation of weathering crusts coating these droplets (Fig. 6 C). The reaction of the AS with ARE 3.5 solution was more intense and resulted in grain perforation (Fig. 6 D), disintegration of the slag surface with separation of numerous glass layers (Fig. 6 E), as well as the formation of secondary phases frequently found as weathering rinds after Cu-sulfides dissolution (Fig. 6 F). SEM-EDS shows these secondary phases of Cu and Fe trapped in the weathering rinds.

Weathering features of AS grains exposed to near-neutral conditions are presented in Figure S3 (Supplementary materials).

4.4.2. Crystalline slag

The immersion of CS grains in a DW 3.5 solution resulted in several alteration features. The most common was preferential dissolution of leucite compared to glass (Fig. 7 A). Furthermore, sulfides were partially dissolved (Fig. 7 B) and secondary phases entrapping Fe and coating sulfide phases occurred (Fig. 7 C). The CS crystalline phases resulting from ARE 3.5 treatment were weathered to a greater degree as compared to DW 3.5 weathering. These phases had crust coatings (Fig. 7 D - 7 E). Also, the sulfide phases were markedly weathered (Fig. 7 D), however, in some cases the dissolution process was just initiated (i.e. very few signs of weathering were observed) (Fig. 7 G). Furthermore, some grains were highly deteriorated (Fig. 7 F).

Weathering features of the CS grains exposed to near-neutral conditions are presented in Figure S4 (Supplementary materials).

5. Discussion

Metallurgical slags displaying different chemical, phase, and textural properties were subjected to two weathering experiments, approximating conditions encountered in the field, i.e. leaching in acidic organic solutions to simulate weathering in topsoil (where root exudation and subsequent acid production are continuous processes) and leaching in variable pH solutions to simulate weathering deeper within the soil profile. Experiments were designed so that a comparison of crystalline and amorphous slags behavior could be made under exposure to soil-like conditions and the weathering sequence of individual slag phases could be ranked. Due to the differing sizes of slag particles used in both tests, as well as different experimental methodologies, no quantitative comparison between pH-stat and dynamic root exudates weathering experiments can be made. However, our approach was to mimic relationships in the field, where deeper soil horizons usually contain more disintegrated slag, whereas larger slag particles occur in the uppermost horizons.

5.1. Mineralogical control on slag stability - primary phase dissolution

Pyrometallurgical slags, especially these resulting from the smelting of base metal deposits are heterogeneous in terms of texture, chemical, and phase compositions (see Piatak el al. 2015 and Potysz et al., 2015 for an overview). This is mainly caused by the variable characteristics of the smelted ores, and localized differences in the technological processes and cooling rates of the individual slag melts (Piatak et al., 2015; Kierczak and Pietranik, 2011). The latter results in either crystalline or amorphous structures (Fig. 3).

The susceptibility of slags to weathering is closely related to their compositional and structural diversity. Numerous studies dealing with the mineralogy and overall stability of slags proposed possible weathering sequences dependent on the slag type and its phase composition. For instance, the study of Kierczak et al. (2013) showed that the textural characteristics of historical Cu slags are among the most important factors controlling slag weathering rates. Lanteigne et al. (2012) pointed out that the decomposition of slag begins with glass dissolution which in turn leads to the exposure of sulfides and their subsequent weathering, and promotes the formation of secondary phases. Two slag samples chosen for this study were texturally different, therefore we might expect to observe different behaviors between the samples when exposed to weathering forces. On the basis of the leaching tests supplemented by direct observation of the slag, we determined a weathering scheme under a wide range of conditions for these two samples.

The results of the pH-stat leaching tests reveal that under acidic pH conditions Ca, Mg and Si are more easily leached from CS than from AS. It indicates that Ca and Mg crystalline phases (predominately pyroxene and anorthite) are less resistant to weathering under such conditions than glass. Furthermore, at pH 3 this difference was more pronounced for Ca than Mg. This suggests therefore that plagioclase and wollastonite (major Ca bearing phases) are more susceptible to dissolution than pyroxene (major Mg bearing phase). A higher dissolution of crystalline phases than glass under acidic conditions has already been reported in the literature (Ettler et al., 2002; Vítková et al., 2010). Under alkaline conditions, greater volumes of Ca and Mg were leached from the AS than from the CS indicating a lower stability of glass than crystalline phases. These findings are also in agreement with the previous study of Ettler et al. (2002) indicating that a preferential dissolution of glass is observed in neutral (deionized water) and alkaline environments. However, the general complexity of slag phase composition may result in different weathering sequences. For example, in the simple leaching study of Bril et al. (2008) the authors presented a weathering sequence of Zn-bearing phases and ranked them in order from least to most soluble in the following way: spinel, melilite, willemite, and zincite. Surprisingly, another study of Zn-Pb slags by Vanaecker et al. (2014) identified willemite as being more stable than melilite (hardystonite). The above mentioned examples demonstrate that discrepancies can arise when interpreting slag's susceptibility to weathering. This may be caused by a variety of conditions addressed in the different studies, but also by innate differences in the slags' characteristics. Therefore, despite it is generally accepted that silicate glass is less stable than crystalline phases (except under highly acidic conditions; Ettler et al., 2002), some crystalline phases (e.g. leucite reported in Cu-Co slags, Vítková et al., 2010) could be more sensitive to dissolution than glass Similar behavior

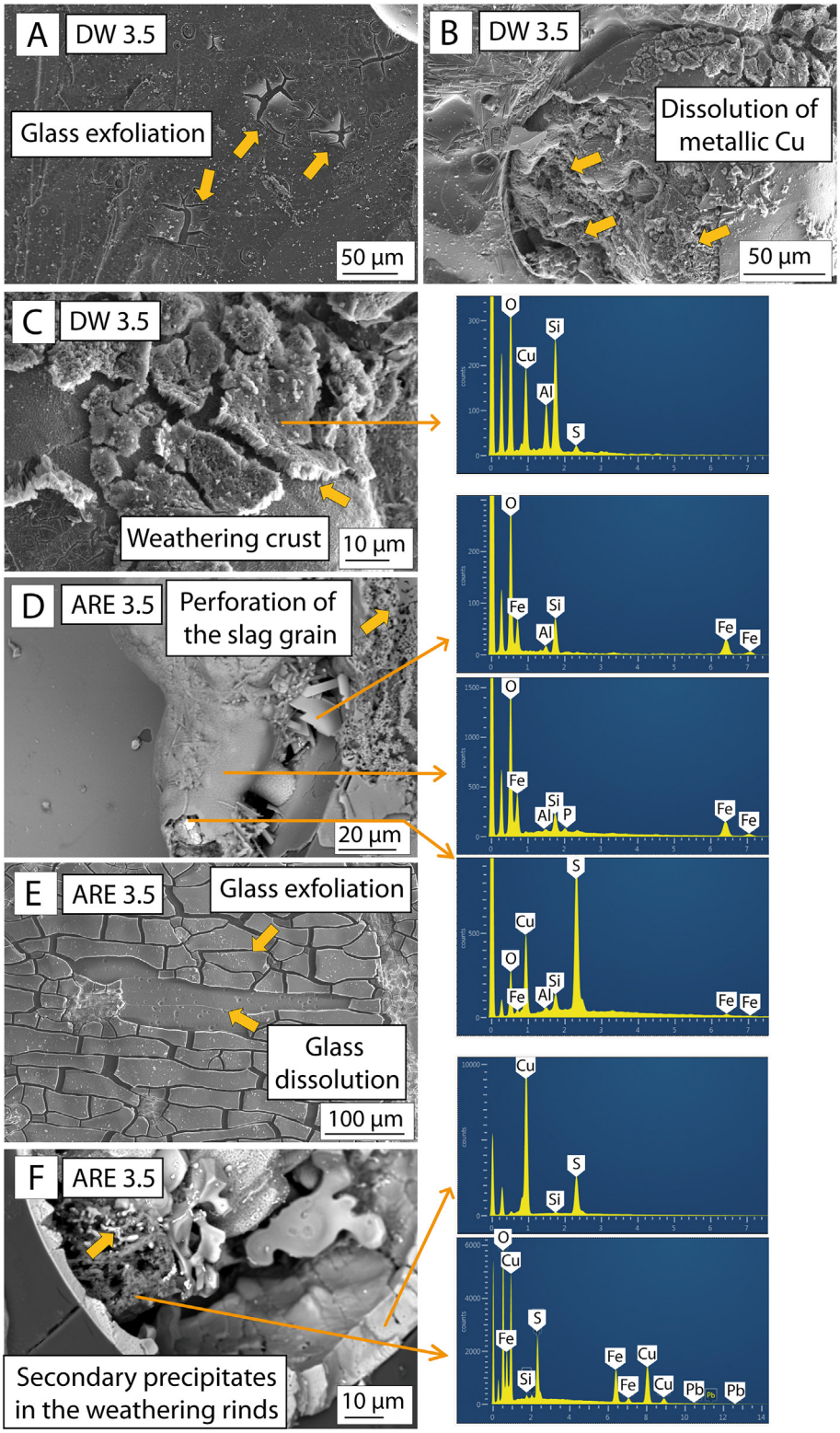


Fig. 6. Scanning electron microscopic images and associated EDS spectra of amorphous slag weathered in demineralized water with initial pH 3.5 (DW 3.5) and artificial root exudates with initial pH 3.5 (ARE 3.5).

of leucite was indeed confirmed by the direct mineralogical observations of CS submitted to an acid leaching solution. These observations allowed us to determine that leucite dissolution precedes the dissolution of glass (Fig. 7 A and B). The low overall stability of leucite is also observed in natural magmatic rocks, where leucite is altered as a result of interaction with a river water (see Gupta, 2015 for the review).

When we take into account more aggressive weathering conditions, simulated in this study by the leaching in an artificial root exudates solution, the behavior of the studied material is less complex and less depended on phase composition. When subjected to an ARE 3.5 solution, simulating the upper layer of soil, the behavior of Ca, Mg and Cu was similar in both types of slag indicating that different crystalline

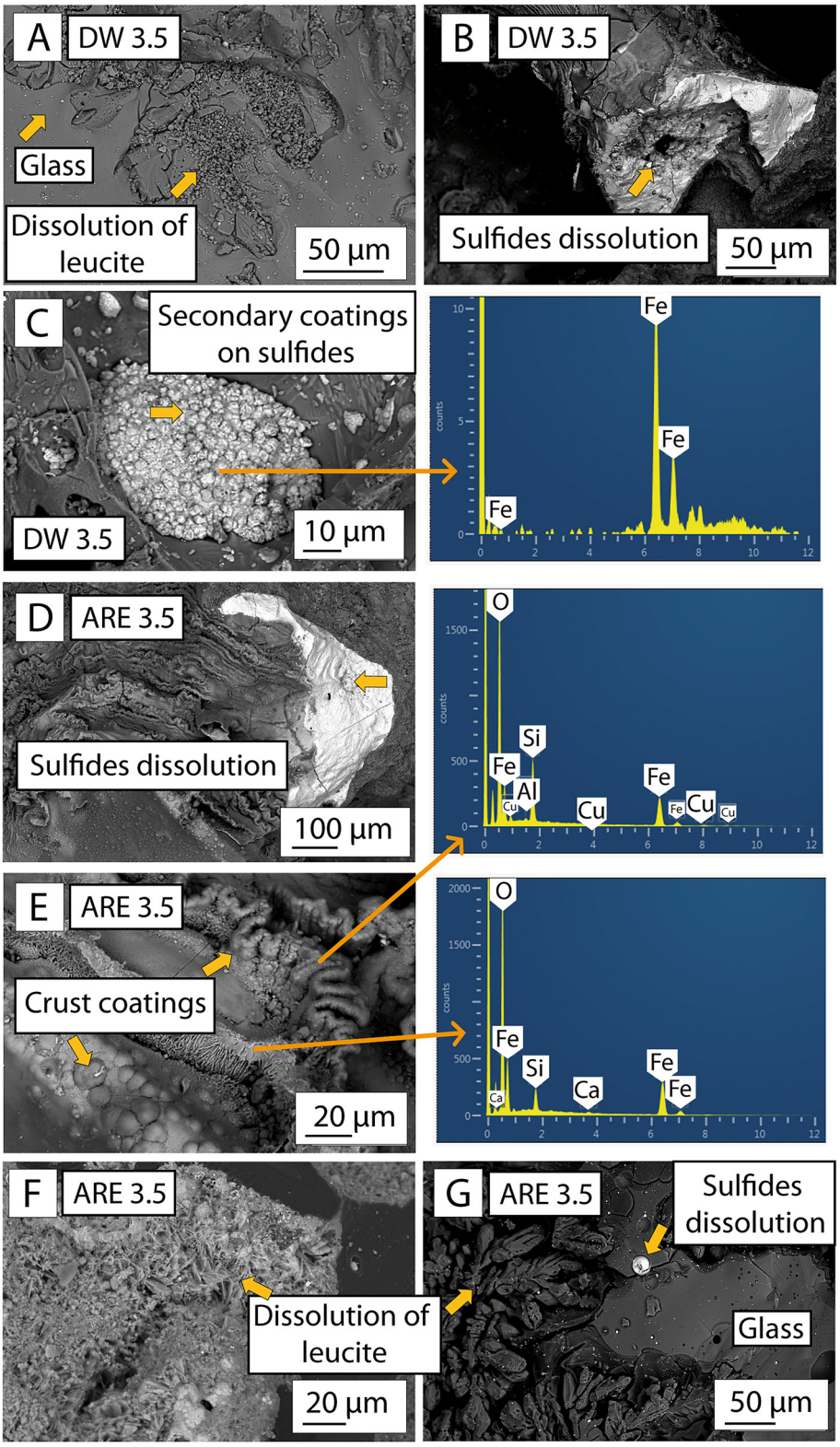


Fig. 7. Scanning electron microscope images and associated EDS spectra of crystalline slag weathered in demineralized water with initial pH 3.5 (DW 3.5) and artificial root exudates with initial pH 3.5 (ARE 3.5).

phases and glass were leached at the same rate. Dissolution of both crystalline phases and glass was observed in SEM images for the ARE 3.5 experiment. Glass was partly dissolved and formed layers that were gradually detached from the glass surface as shown in the exfoliation features presented in Fig. 6 E, similar glass dissolution process was reported by Papadopoulos and Drosou (2012). Furthermore, crystalline phases such as leucite have also suffered from dissolution reaction (Fig. 7 F and G). At this point it is noteworthy to mention the dissolution mechanisms occurring in amorphous and crystalline silicate phases. Amorphous glassy slag dissolution may be restricted to the surface reaction (Fig. 6 E), whereas in crystalline samples dissolution penetrates the sample interior (Horgan et al., 2017; Smith et al., 2017).

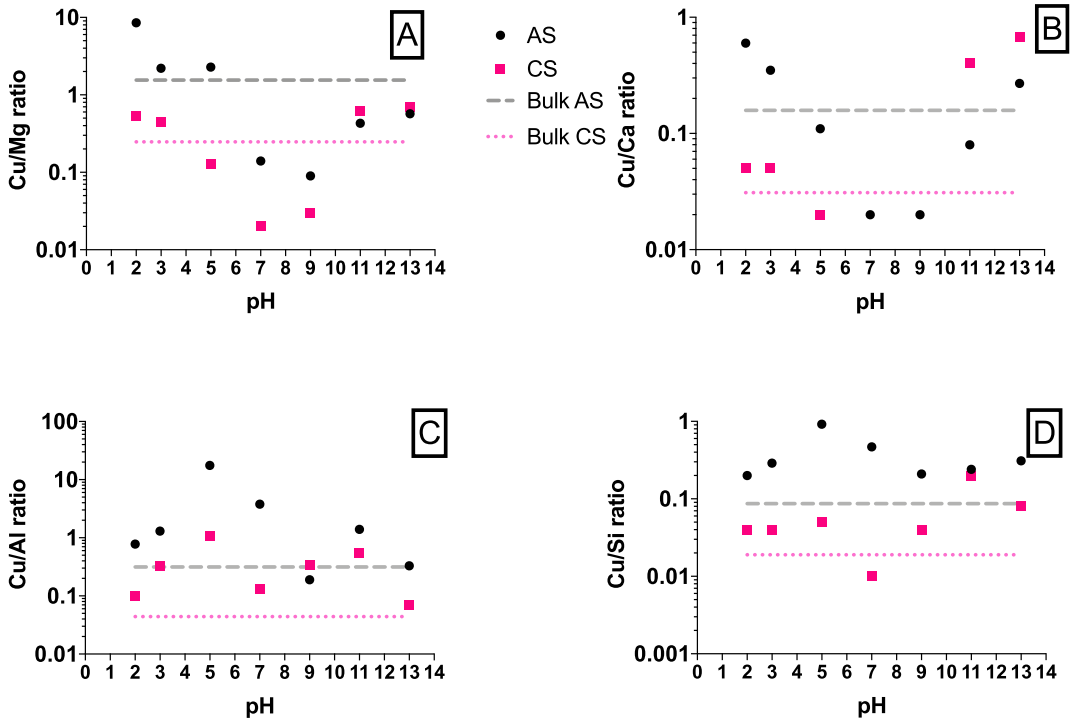


Fig. 8. Theoretical and experimentally achieved element ratios with respect to Cu – effect of pH. *(AS: Amorphous slag, CS: crystalline slag)*
* Cu/Ca ratio between pH 6 and 10 is below 0.01 (not shown in Figure).

This is shown by the weathering features which can be seen in Fig. 7 F and G exhibiting deeper (i.e. towards slag interior) slag penetration.

5.2. Dissolution of metal bearing phases in environmental regulation context

Of particular importance to the analysis of slag stability is the mobility of metallic contaminants. The studied slags contained significant amounts of Cu and this element was present in a variety of phases, mainly sulfides and metallic compounds. In AS it was principally found in the form of metallic Cu and/or chalcocite, whereas in CS Cu was mainly associated with sulfides (Table S3; supplementary materials). The pH-stat leaching test showed that the proportions of Cu released from slags were higher in comparison to other major elements (e.g., Si, Fe, Al, Mg, Ca, Fig. 8) for most of the leaching conditions, which clearly shows that Cu-bearing phases are the highly soluble components of the slags. This is in agreement with the observations of Ettler et al. (2002) who found that sulfides and metallic compounds are the least stable phases regardless of conditions. Furthermore we observe that under acidic conditions Cu is mobilized in similar proportions from both types of slags. In turn, under alkaline conditions we observed higher Cu release rates for CS which indicates that sulfides are less stable than metallic Cu in these conditions.

Mobilization of Cu when compared to threshold limits specified by EU regulations (EU, 1999; EU, 2002), shows that under exposure to natural sample pH 9 both slag types should be classified as non-hazardous materials. However, it has to be emphasized that above mentioned EU legislation is used for the landfill context, while it does not take into account conditions to which the wastes are exposed in natural soil environment (e.g. lower pH conditions). The slags exposure to pH 2–3 led to release of important quantities of toxic elements (Fig. 4). Likewise, exposing the slags to a solution of pH 5 suggests that AS is environmentally more risky than CS. In contrast, the release of Zn at pH levels ranging from 2 to 3 had lower environmental impact than that observed in the case of Cu (Fig. 4). The release rate of Cu and Zn under alkaline conditions was generally low. This is in accordance with the study of Jarošíková et al. (2017) which demonstrated non-hazardous features of various slags in terms of Cu and Zn release at pH levels ranging from neutral towards alkaline, mirroring the results found by Vítková et al. (2011). It is concluded, therefore, that under pH-neutral conditions both slag types are relatively stable materials. However, from an environmental viewpoint acidic conditions are in fact more relevant since these more accurately represent the disposal situation encountered onsite (discussed in detail in section 5.3).

Different behavior of Cu is observed in the ARE 3.5 solution where Cu and major elements were leached in similar proportion as that observed in the bulk slag composition for both AS and CS (Fig. 9). In aggressive solution, silicates and metallic phases are weathered at similar rates with a slight preference for metallic Cu weathering in AS. The fact that metallic phases are the most susceptible slag component to weathering was confirmed by direct analyses. Observations coupled with mineralogical analyses (XRD, SEM-EDS) revealed the presence of secondary phases naturally occurring on the slag surface (e.g., brochantite, Fig. 2D) or formed as a result of leaching experimentation (Fig. 6 C, D, F and Fig. 7 C, E). It also showed that metallic elements were mobilized from the slag and subsequently trapped within newly formed phases, such as those with composition resembling Cu-sulfates and Fe-oxides (Figs. 6 and 7). Secondary phase formation has an important environmental implication, because the process inhibits the mobility of leached elements. The presence of Fe-oxides in particular is responsible for metal stabilization through their adsorption (Michálková et al., 2014). Likewise, Séguin et al. (2005) reported that rhizosphere-driven weathering promotes the formation of oxides that in turn leads to metal retention. Furthermore, a 30-day leaching compared with EU regulations indicates that Cu release exceeded the requirements under ARE 3.5 and DW 3.5 conditions in the case of AS, whereas with CS only in the case of ARE 3.5 are the requirements exceeded (Fig. 8). In contrast, the release of Zn was found to pose a lower environmental concern since concentration levels were at the threshold limit only in the case of AS.

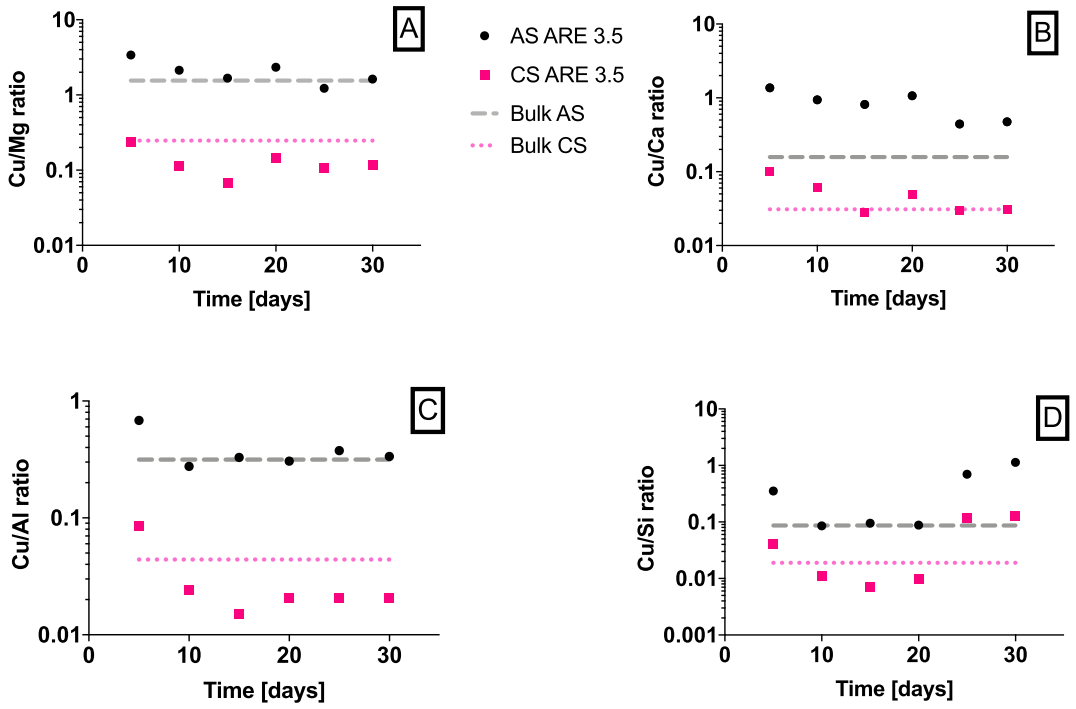


Fig. 9. Theoretical and experimentally achieved element ratios with respect to Cu – effect of different weathering situations (artificial root exudates and acidified demineralized water). *(AS: Amorphous slag, CS: crystalline slag)*.

5.3. Geochemical approach to study element mobility in crystalline slags

Estimating the environmental risk posed by slags is of concern during remediation of slag sites (Bunzl et al., 2001; Houben et al., 2013). As shown in this study, historical slag dumping sites contain diverse slag types composed of multiple phases (Table S3; Supplementary materials). The calculation of the molar ratios of the major elements versus the most easily released element is a useful geochemical tool for deciphering which phase is being dissolved preferentially under specific weathering conditions. For glassy slags, simple molar ratios of silica versus metal concentrations show if metallic or silicate phases are preferentially dissolved. However, a similar simple ratio is not useful to distinguish between preferential weathering of different silicate phases and glass in complex crystalline slags. This study shows that molar ratios should be calculated using major constituents of different phases. In our case, Mg tracked the preferential dissolution of pyroxene whereas, variations in Ca indicated preferential dissolution of plagioclase and/or wollastonite. For example, ratios of Cu/Mg and Cu/Ca showed that at close to neutral conditions, major Ca and Mg bearing phases were less stable than metal bearing phases (Fig. 8). Also the leaching proportions of these two elements showed that pyroxene and plagioclase are preferentially weathered in acidic pH-leaching tests, whereas glass is more weathered in alkaline conditions. A dissolution of pyroxenes and plagioclase at low pH (i.e. $< 3 \sim 4$) has already been reported (McAdam et al., 2008). In contrast, glass dissolution at pH > 9 leads to Si-network breakdown and this could explain the high susceptibility of the glass to dissolving under alkaline conditions (Gin et al., 2015). In fact, looking only at Si and Al leaching behavior, this weathering sequence would not have been reconstructed due to (1) similar Si concentrations in glass and crystalline phases, especially in silica-deficient slags like those in this study and (2) high susceptibility to weathering of leucite – a major Al bearing phase in crystalline slags. Therefore, we have shown that by examining all of the major constituents of crystalline phases we are able to reconstruct a weathering sequence across a range of conditions and by examining the range of metal/major component molar ratios related to bulk slag composition (such as in Figs. 8 and 9) we are able to more fully understand slag dissolution and the accompanying release of metals such as Cu and Zn.

5.4. Environmental and practical implications for the management of studied slags

The results of this study demonstrate enhanced metal (Cu and Zn) leachabilities from slags exposed to organic-free and organic-rich acidic conditions, with the latter being the most impactful. Taking into account the near-neutral character of the soils surrounding the deposits of studied slags, it is expected that the release of contaminants is represented by near-neutral experimental conditions, in which the threshold limits specified by EU regulations were not exceeded. However, a close association of the studied slags with rhizosphere soil necessitates considering the environmental impact in an organic-rich and acidic context. Copper revealed the highest environmental risk. This finding is in accordance with the study of Vaněk et al. (2014) which found Cu as the one of the most mobilized in the rhizosphere. The organic matter (including rhizospheric organic acids) displays a high affinity towards copper that also implies a high mobility sideways as well as downward throughout the soil profile. Furthermore, according to short term leaching test results, dissolution of slags is strongly pH related, with the pH range from neutral towards alkaline being the least impactful as far as contaminant mobilization is concerned. This finding is in accordance with numerous studies addressing the release of metals as a function of pH from a variety of waste materials (e.g. Jarošíková et al., 2017; Vítková et al., 2009; Vítková et al., 2011). Therefore, our findings on copper slag behavior denote two alternative management directions. A relatively poor metal leachability under near-neutral and alkaline conditions implied the potential use of these slags as mineralizing components or additives to engineering products which are alkaline in character (Shi et al., 2008). However, the general optimism in using any slag as a building material has been diminished by later studies showing a high metal mobility out of the slag and was confirmed by the dissolution of metal bearing phases (Schmukat et al., 2012). In contrast, a high leachability of metals under acidic conditions encourages waste management practices which use these slags as secondary metal resources (Potysz et al., 2018b).

6. Conclusions

Our study simulated weathering conditions typical for the sites of historical slag disposal, in particular we examined a range of pH conditions occurring typically at different soil depths during slag-soil interaction. Historical slags are often complex and composed of several crystalline phases with different weathering potential. We showed that for such slags a special approach is required including analyses of all major elements in major phases. As an example, in our study Ca tracked the weathering of plagioclase and Mg tracked that of pyroxene. Silicon was less useful as it could not be easily distinguished between input from various silicates and the glass. Our study showed that different rates of weathering are expected in organic and inorganic conditions, with the former promoting severe dissolution of bulk slag, with the latter being dominated by preferential dissolution of Cu-bearing phases. Also, the different slags (crystalline and amorphous) dissolve at different rates, with crystalline slags being more susceptible to weathering in acidic and neutral conditions whereas amorphous slags are more susceptible in alkaline conditions. Altogether, our study shows strong control of phase composition over the leaching of major slag components and underlines the importance of an extended analytical approach when the weathering potential of such slags is estimated. Based on our geochemical study, the weathering sequence of the slag components can be ranked as follows: i) under ARE conditions: bulk slag, ii) under inorganic acidic conditions: Cu-bearing phases > crystalline phases (leucite > plagioclase, wollastonite > pyroxene) > glass, iii) under alkaline conditions: Cu-bearing phases (sulfides > metallic Cu) > glass > crystalline phases.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.apgeochem.2018.08.027.

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