Weathering of metallurgical slag heaps: multi-experimental approach of the chemical behaviours of lead and zinc

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Abstract

The production of lead and zinc in the Lead Blast Furnaces of metallurgical factories produces a huge amount of slags. These slags are a Pb-Zn-rich vitreous material with a CaO-SiO_2-FeO-rich glass matrix containing metallic lead droplets and Fe oxides. The resulting slag heap is exposed to weathering and can be a source of chemical pollution. In this study, different experiments allow the study of the behaviour of Zn and Pb during the weathering of slags. First, a Teflon leaching column (ascending flux) equipped with samplers in order to collect the fluid inside and at the outlet of the column was used. The second experiment was a pure water flow on a polished section of slag. The third system was an outdoor experiment where the slag was exposed to natural weathering comparable to the heap. ICP-AES and ESEM-EDS have been used to follow the evolution of the water chemistry and the slag compositions and textures during the experiments. Two episodes of Pb and Zn releases were noticed at the column outlet. A first brief episode might be caused by some colloids or slag dust releases. The second episode essentially results from glass and metallic lead dissolution. Hydrocerusite locally appeared in the column. Investigations carried out on the polished sections show complex alteration patterns. They suggest that the behaviour of the glass and of minor phases is closely linked to the local structure and composition at the slag surface. Outdoor experiments show slower kinetics than in the other experiments, but the alteration type is similar despite some differences.
Keywords: metallurgical slag, iron-silica-lime glass, waste leaching, lead and zinc releases.

1   Introduction

In the industrial basin of the Nord-Pas-de-Calais (France), blast and smelting furnaces have been used to produce lead and zinc during the last century. The Noyelles-Godault factory has generated a huge amount of waste. In its Lead Blast Furnace production unit, the production of 1 ton of metal generated approximately 1 ton of metallurgical slags [1]. These slags contain several percents of Pb and Zn [1–3] and others pollutants as Cr, Cd, As [2]. They were not reused as raw materials. Four million tons of such primary smelting slags were then stored in a slag heap spread on 1 km² next to the factory [2].

The pollutant releasing abilities of various lead-zinc metallurgical slags have already been discussed in numerous previous works. Indeed, contaminant mobility has been tested in different environments in order to evaluate the ways slags can be reused as raw materials or just to evaluate the stabilization abilities of their storage conditions. The studies concerning the leachability in concrete-like conditions [3, 4], when used as road materials [5], in pure or acidic water [2, 4, 6, 7] or in contact with organic solutions [8] are more or less common. More specific studies on glass leaching abilities have also shown that the glass composition [9–12], the local environment of iron [13, 14] and the pH and temperature [10] are very important parameters concerning the leaching resistivity in lime-silica glasses. Secondary phase formations [2, 6, 7, 8, 15] and sorption phenomena on glass or crystalline phases [16–20] can also play an important role on the pollutant mobility/immobility.

Slag heaps are generally not protected from rainfalls. Slags are thus exposed to weathering conditions. The most accessible part of the heap for the water may be governed by flow conditions. Yet, most of previous studies were made in batch conditions. To our knowledge, no study using the present Lead Blast Furnace slags in open flow system using pure water has been performed.

This work proposes to follow Zn and Pb mobility in two original laboratory leaching experiments in pure water flow conditions and to compare the laboratory results with slag alteration under natural weathering conditions in draining and non-draining conditions.

2   Materials and methods

2.1 Slag characterization

Slags are generally smaller than 2 mm. The size distribution is lognormal with a 500 μm dominant class [1]. The phase arrangements in the slags have already been described at micrometric scale by Deneele [2] estimated the waste is composed at 80% (in volume) of a FeO-SiO$_2$-CaO glass with few percents of Pb and Zn. Slags also contain 19% of crystallized iron oxides and 1% of plurimicrometric droplets of metallic lead. Automorphous spinels are spread into the iron-lime-silica glass matrix. This glass also contains few mass percents of others elements like Al, Mg, Na and K. Spinels have a chromium rich centre (MgCr$_2$O$_4$) while the composition evolves to franklinite (ZnFe$_2$O$_4$) or sometimes

in magnetite ($Fe^{2+}Fe^{3+}_2O_4$) to the borders [2]. Plurimicrometric and dendritically shaped oxides have also been described as Zn substituted wüstite ($Fe_{0.85-x}Zn_xO$) [1, 2]. Metallic lead droplets which sizes range between 1 μm and 400 μm [1, 2] have also been identified.

2.2 Column test

The LBF slags used here come from Noyelles-Godault (France). A significant volume of 300 kg of slags has been sampled at the end of the metallurgical process during 1 month (frequency: 2 or 3 samplings for a week) [2]. The diameters (d) of the slag used for this test range between 2 and 2.5 mm. The slag surfaces have been cleaned from most of dust by three successive ultra-sonic baths in alcohol.

   The column is a 220 mm high PTFE cylinder with an internal diameter (D) of 25 mm. The D/d ratio of 10 and the column height must create a homogeneous flux. Teflon is used to avoid sorption phenomena on the column wall. At three levels of the column, openings filled with septa allow to do in-situ leachate samplings with specific needles [15]. In front of these openings, PTFE cylinders called samplers are placed (Figure 1). Hydrodynamic tests using tracer have shown, they do not create any notable disturbance on the ascending flux. At the column inlet, a Teflon piece is placed to homogenize the flux. The column contains about 150 g of slags. The column is connected to a pump (Figure 2) and a pure water reservoir (pH = 5.6). The pump provides a constant flow at 60 ml.h^{-1}. At the column outlet, a fraction collector driven by a computer allows to sample the leachate with a high frequency (for example, 1 sample by hour).
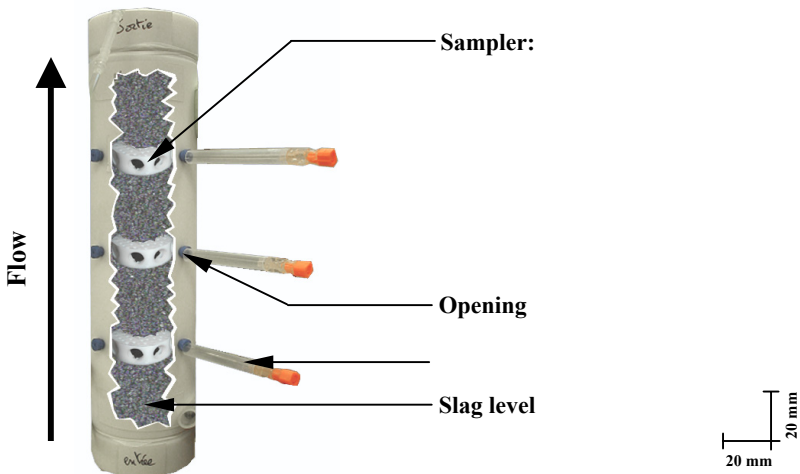

Figure 1:   Photomontage showing the column interior and exterior.

A Thermo ICP-AES has been used to estimate the concentration of the following elements: Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Ti, Zn. The detection level is approximately about 20 ppb for the majority of the analysed elements. Cu detection level is a little higher: 50 ppb.
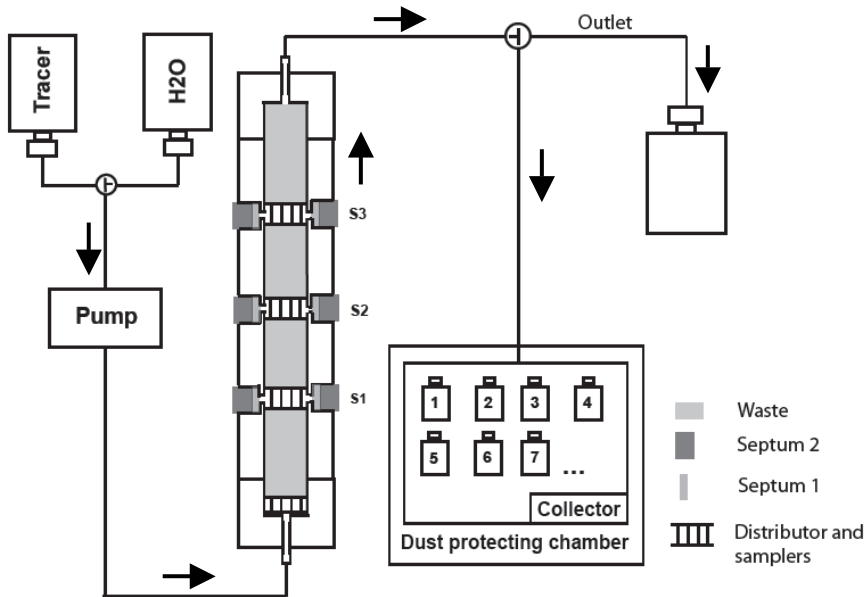

Figure 2:   Scheme of the experimental device.

2.3 Polished section test

This leaching experiment is very close to the one described before. The column is replaced by a polished section container. The container is supplied with pure water connected to a peristaltic pump which provides a constant flow of $60ml.h^{-1}$. The sections are 60 mm long and 20 mm wide. To make these polished sections, slag grains are included in an epoxy resin and are polished in order to expose slag surfaces (40% of the total upper face). There are approximately 3 mm between the section surface and the upper side of the container. Then, the Darcy velocity in the container is about $1m.h^{-1}$. The sections were observed by ESEM 15 and 26 days after the beginning of the experiment. The chemical analyses have been obtained at 26 days with ESEM-EDS.

2.4 Outdoor weathering

In this experiment, draining and non-draining conditions which may occur in the heap are simply reproduced with the help of specific jars. In each sort of experiments polished sections were exposed to climatic conditions. The evolution of the slag aspect was followed by ESEM.

2.5 Electron microscopy

The morphology and composition of slag sections before and after alteration was studied using a FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM). The tungsten electron source is used at 20 kVolt. The spatial resolution of its X-ray Energy Dispersive System (EDS) probe is about 1 μm^3. The accuracy of the analyses can reach 0.5% (in weight) in high vacuum. In order to be reused, the polished sections were not carbon coated as usual and were inserted in the ESEM chamber in low vacuum mode. The relatively low pressure in ESEM chamber (≤ 0.45 Torr) reduces the analysis accuracy. Then, only the global trend has been considered.

3 Results and discussion

3.1 Column test

3.1.1 Leachate chemistry

During the first hours of experiment, the pH value at the column outlet is enhanced to 7 and increases to 7.8. The pH (Figure 3 A) rapidly decreases to reach a value near to 6 (*i.e.* near pure water pH). Concerning ICP-AES analyses, only four elements (Ca, Si, Pb and Zn) were detected in relatively high amount in the leachates. No iron was detected. In the first hours, Pb, Zn and Ca releases (Figure 3 B, C, D) may be linked to the pH variations.

Indeed, the concentrations of Pb and Ca in the first samples were the highest measured during the test. This can be connected to dust cleaning at the slag surfaces. Indeed, tests have shown that dust is very difficult to keep out before the experiments. After the pH stabilization at 6, Ca, Pb and Zn progressively reached an approximately constant releasing level at 0.5, 0.15 and 0.15 ppm respectively. Si releasing slowly increases during the experiments (Figure 3 E) to reach 0.45 ppm at $t_{1400 h}$.

The Ca and Si loss indicate the glass matrix alteration was persistent throughout the experiment. Considering the electron microscopy observations, Ca and Si may not be fixed in secondary phases. The Ca releasing rate is around 30 $\mu g.h^{-1}$ in the second part of the experiment and the Si releasing rate ranges between 10 and 30 $\mu g.h^{-1}$. The Pb and Zn releasing rate is around 10 $\mu g.h^{-1}$ in the second part of the experiments

3.1.2 Waste observations at t_{end}

ESEM-EDS analyses show leaching evidences on the glass and, particularly, near the column inlet. Some glass fields are highly fractured (Figure 4 A), however it may be due to desiccation of hydrolysed glass in the ESEM chamber. Traces of glass alteration are less important when slags are situated further from the column inlet. EDS analyses have shown the further from the inlet the glass is, the less important the Si and Ca loss is. Then, glass alteration essentially occurs at the bottom of the column (Table. 1) Leachate compositions are closely linked to this phenomenon. Indeed, the in-situ samplings show that the leachate chemistry does not really change between the three samplers and the outlet.

Conversely, superficial lead droplets often react in the entire column. Punctually, big lead droplets are not totally dissolved and plurimicrometric carbonates have been formed near (Figure 4 B). The iron oxides seem to be relatively stable. Thus, Zn may not be released from the dendritical wüstite spread in the glass. Its source may be only the glass.
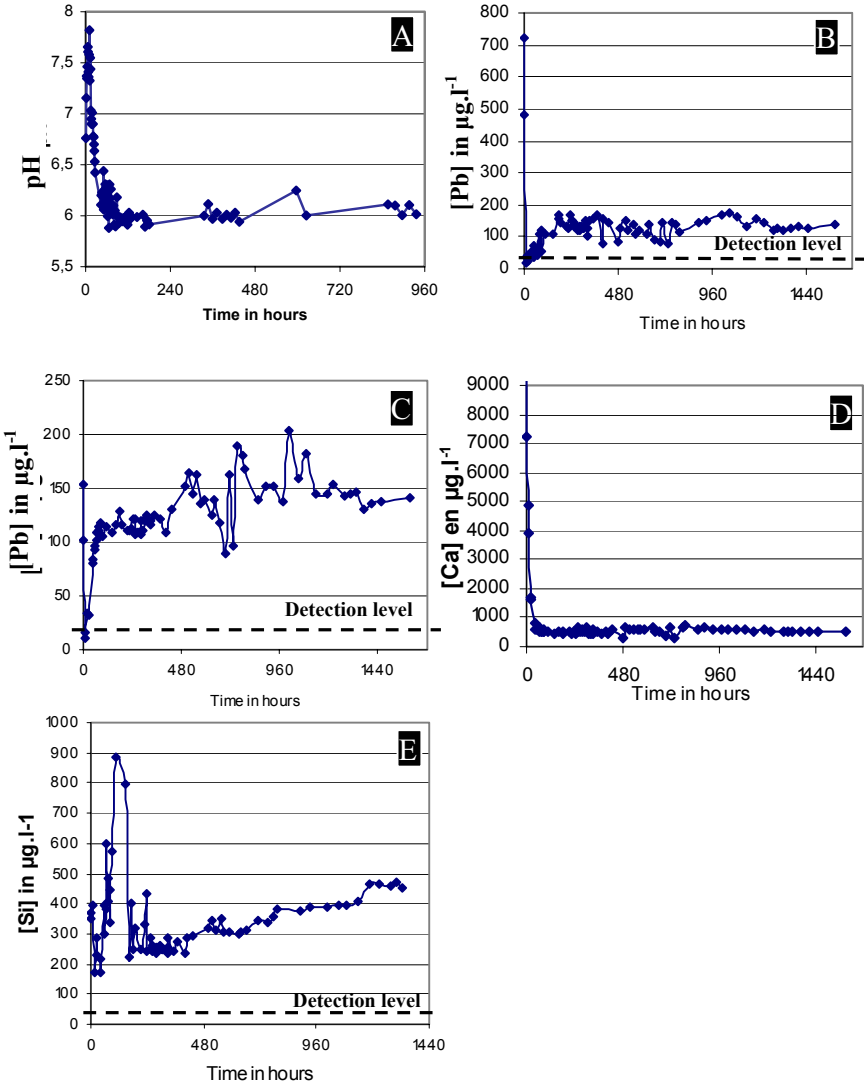

Figure 3: Graphs showing the pH evolution at the column outlet (A). Graphs (B), (C), (D) and (E) respectively show Pb, Zn, Ca and Si releasing during the experiment.

3.2 Polished section tests

ESEM showed the same type of glass alteration (Figure 4 C) and lead carbonate formations as in the column test. Laminar flux encountered in this test enhanced micro-canyon formation (by glass alteration) less observed in column test. Glass can be kept fresh in some saved regions. Nevertheless, Ca and Si losses correspond to altered glass regions similar to these observed in the column (Table 1). Highly fractured and lightening zones often correspond to regions downstream dissoluting big lead droplets (Figure 4 D).
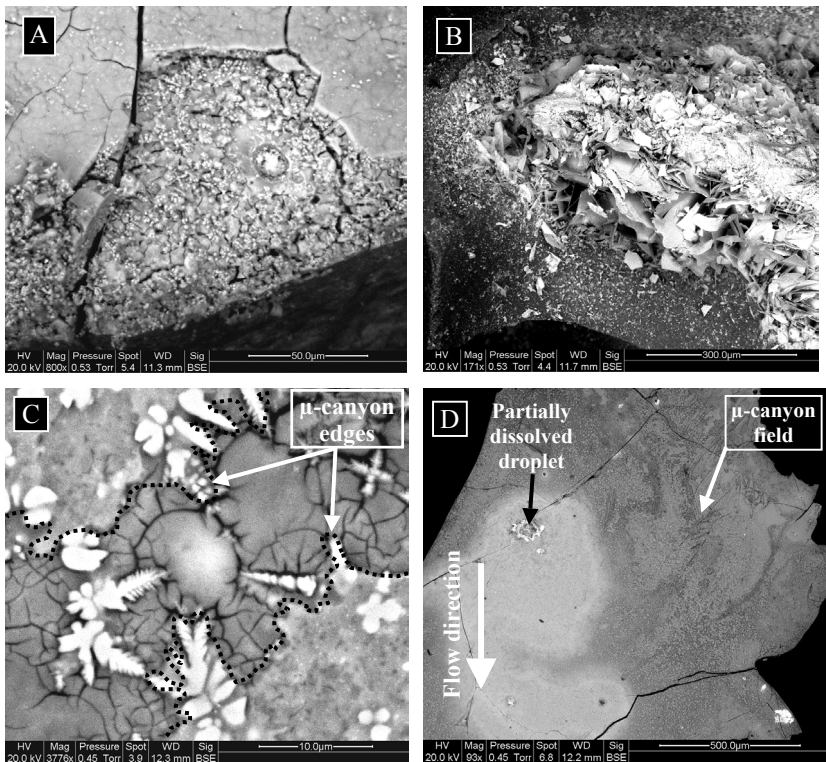

Figure 4:   SEM images of waste surfaces altered in the different experiments: (A) and (B) in column, (C) and (D) in the polished section experiments.

Some ESEM images might be consistent with [16,18] results showing lead sorption are supposed to happen in conditions similar to such influenced zones. Nevertheless no such evidence has been found with EDS punctual analyses. In altered zones, preliminary EDS analyses treatment may indicate that Ca is

generally highly released conversely to Si, which releasing rate may be assumed to be lower. In these zones, there is a relative Fe enrichment.

Table 1:   Statistics of EDS analyses of fresh and altered glass (% in weight).

		SiO_2	CaO	FeO
Fresh glass (**167 analyses**)	mean	34.35	28.92	36.72
	min	24.54	24.61	26.30
	max	40.13	34.98	47.55
First slag level of the column (**24 analyses**)	mean	13.78	3.12	83.10
	min	7.70	0.87	44.10
	max	36.02	36.02	91.44
Glass leached in container (**21 analyses**)	mean	30.41	11.06	58.53
	min	10.39	4.63	45.01
	max	42.37	23.04	84.99

3.3 Outdoor weathering

The results of this experiment are highly comparable to the polished section ones. During the glass alteration, there also is a Ca loss. However, the Si loss is more difficult to observe. Glass is also highly fractured and sometime lightens (Figure 5 A). Some micro-canyons can be observed in the altered glass. Lead carbonates are smaller (Figure 5 B) and apparently amorphous lead deposits which have not been observed in the laboratory experiments are here visible. Suspicion of sorption phenomena might be rarely observed on iron oxides near lead droplets. Thus, slags altered in weathering conditions may have a globally similar behaviour than in laboratory experiments.
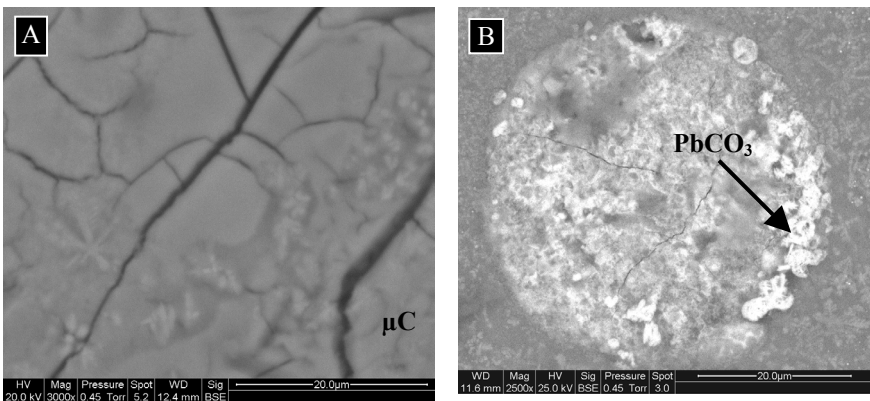

Figure 5:   (A) altered glass matrix with fractures and micro-canyons (μC) both induced by leaching, (B) altered lead droplets and lead carbonates.

4   Conclusion

The laboratory experiments proposed here are useful to study the behaviour of Pb and Zn during metallurgical slag weathering. Indeed, they globally conduct to a comparable waste evolution than observed when altered in climatic conditions. It appears that when in contact with pure water in open flow conditions, slag releases relatively high and constant amounts of pollutants (Pb, Zn). It is linked to combined dissolution effects affecting glass and lead droplets. The advance of the glass alteration may be doped by big droplet dissolution. Pollutant immobilization may occur by lead carbonate formation but lead sorption on glass might be a minor mechanism. Nevertheless, complementary investigations (FIB, TEM-EDS, XANES…) will be necessary to better describe pollutant releases and glass leaching mechanisms.

Acknowledgements

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