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# PH DEPENDENT LEACHING BEHAVIOUR OF Zn, Cd, Pb AND As FROM SLAGS: KINETICS AND MINERALOGICAL CONTROL

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## Abstract

*From the Middle Ages until the beginning of the 20th century, extensive Pb-Zn mining and smelting was carried out in East-Belgium. By lack of waste treatment techniques and sustainable management practices, metal-bearing slags and unprocessed waste were dumped in huge tailings, which still represent an important source of contamination. A chemical and mineralogical characterisation of different types of waste material originating from the former Pb-Zn mining industry was performed in order to gain a better understanding of the slag properties, with special attention to heavy metal release under varying pH conditions, and to bring this in relation to different management scenarios.*

## Introduction

In the mining industry, 3 principal processes can be distinguished, namely mining, mineral processing and mineralogical extraction[1]. Depending on the origin of the minerals and the processing conditions of the minerals, the waste materials of these processes show different properties. Additionally, mining waste generally contains hazardous substances such as heavy metals, radioactive elements, cyanides, *etc*. which can potentially be released under changing environmental conditions, such as changes in pH, (especially when the waste produces acid mine drainage), redox conditions (for example, when (periodical) inundation of the mine waste is possible) or microbial activity. From the Middle Ages until the beginning of the 20th century, extensive Pb-Zn mining and smelting was carried out in East-Belgium. Due to the lack of better waste treatment techniques and of sustainable management practices, metal-bearing slags and unprocessed waste were dumped. Metallurgical processing of these Pb-Zn minerals occurred at several locations, mainly in the northern part of Belgium, also generating important quantities of waste. A chemical and mineralogical characterisation of different types of waste materials related to the former Pb-Zn mining industry was performed in order to gain a better understanding of their properties, with special attention to heavy metal release under varying pH conditions, and to bring this in relation to different management scenarios.

## Methodology

In La Calamine, Plombieres and Angleur (East-Belgium), samples consisting of respectively dredged mine tailing pond sediments, mineral processing waste and waste from the metallurgical process of Zn-production were collected after a preliminary screening and analysis of vertical profiles. In Overpelt (North-Belgium), two waste samples were obtained from a plant for Zn powder manufacturing by air atomisation ("blown zinc") for primary batteries. Total metal concentrations, pH, cation exchange capacity (CEC) and grain size distribution were determined for all the samples and a mineralogical (petrography, XRD, SEM-EDX) investigation was carried out. $pH_{stat}$ leaching tests and geochemical modelling of the pH-dependent leaching behaviour were performed[2].

## Results and discussion

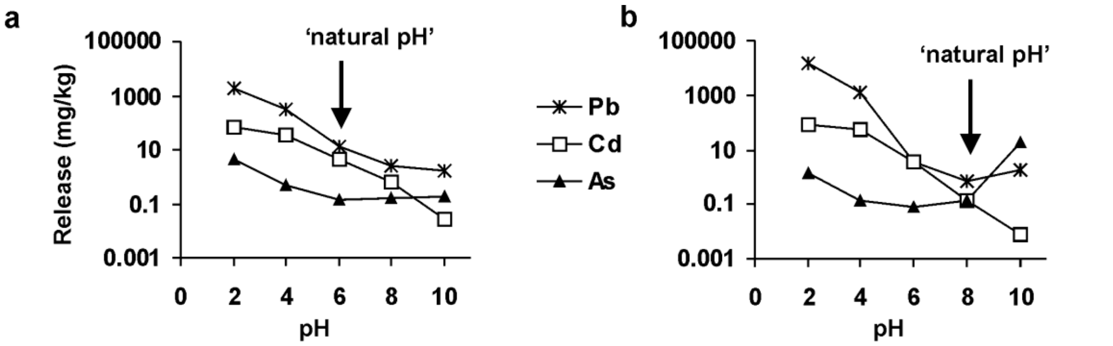
### Mineralogical and physico-chemical characterisation

The waste materials from the four locations were mainly contaminated with Zn, Pb, Cd, Cu and/or As (Table 1). pH was neutral to slightly alkaline for the samples from La Calamine (CA) and Angleur (AN), whereas pH was slightly acidic in the samples from Plombiéres (PB) and Overpelt (OV).

**Table 1:** Total element concentrations, pH and CEC (ND: not determined)

| Sample | Zn % | Cd mg $kg^{-1}$ | Pb % | Cu mg $kg^{-1}$ | As mg $kg^{-1}$ | Ca % | Al % | Fe % | S g $kg^{-1}$ | pH | CEC cmol $kg^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AN | 3.09 | 124 | 1.95 | 1704 | 1928 | 2.22 | 2.45 | 9.48 | ND | 8.0 | ND |
| CA1 | 10.81 | 297 | 2.06 | 60 | 1491 | 4.72 | 3.08 | 11.77 | 12.70 | 6.5 | ND |
| CA2 | 6.77 | 4196 | 0.03 | 29 | 28 | 5.57 | 2.79 | 2.81 | 2.57 | 7.5 | ND |
| PB1 | 1.16 | 63 | 0.52 | 1023 | 474 | 1.9 | 6.21 | 5.87 | 0.22 | 5.3 | 1.33 |
| PB2 | 2.79 | 68 | 0.61 | 6642 | 545 | 1.34 | 2.75 | 7.87 | 0.35 | 5.7 | 1.83 |
| OV1 | 3.56 | 48 | 1.92 | 5383 | 3391 | 1.52 | 2.20 | 19.19 | 2.96 | 5.9 | 19.96 |
| OV2 | 0.47 | 5 | 0.24 | 604 | 141 | 1.66 | 7.92 | 9.09 | 0.38 | 5.8 | 3.35 |

The main minerals in the La Calamine samples were sfalerite, smithsonite, anglesite, cerrusite, galena, pyrite and marcasite in sample CA1 and secondary minerals such as smithsonite, siderite and gypsum in sample CA2. In the slag sample from Angleur, XRD analysis revealed the presence of troilite, arsenopyrite, willemite, and magnesioferrite. SEM-EDX investigation also indicated the occurrence of amorphous silicate phases (glass




Pb: 19.5 g/kg, Cd: 124 mg/kg, As: 1928 mg/kg Pb: 31.5 g/kg, Cd: 305 mg/kg, As: 2294 mg/kg

**Figure 1:** pH-dependent leaching behaviour of Pb, Cd and As in sample CA1 (a) and AN (b). Total Pb-, Cd- and As-concentrations and pH are indicated below the graphs

phases). The slag from Overpelt, sample OV1 is mainly composed of opaque phases (> 80 wt%) and minor amounts of quartz, hematite, goethite, and probably also melilite. Sample OV2 mainly contains Fe-oxides and quartz, fluorite, albite and melilite. The slags from Plombières are composed of iron oxides and quartz, feldspar, fluorite and mullite.

## Combining leaching test results with mineralogical analysis and thermodynamical modelling

For the La Calamine samples, a pH-increase significantly decreases the leachability of Zn, Cd and Pb, whereas the solubility of As is not affected and remains very low (Figure 1a). The results from the $pH_{stat}$ leaching tests, combined with solid-phase characterisation (XRD, SEM-EDX) and thermodynamical modelling (MINTEQA2) confirmed that the solubility of Zn, Pb and Cd is mainly controlled by Pb-Zn minerals (*e.g.* smithsonite). The slag sample from Angleur contains arsenopyrite, a mineral that normally decomposes in oxidising conditions. However, during $pH_{stat}$ leaching under oxidising conditions almost no As was released in the pH range 2–8 (Figure 1a). This can be attributed to the occurrence of this mineral as minute phases occluded in glass phases, protecting the mineral from acid dissolution (Figure 1b). In the samples from Overpelt and Plombières, the release of Zn, Pb and Cd was not controlled by Pb-Zn minerals, but by the reactivity of glass phases and Fe-(hydr) oxides in which these heavy metals are occluded.

## Kinetics of element release during $pH_{stat}$ leaching

Even when similar amounts of heavy metals are released at the end of a $pH_{stat}$ leaching test, the kinetics of heavy metal release can greatly differ, which also provides information on their reactivity in the mining waste samples. For example, in the Angleur sample (AN), the release of Pb was constant with time (related to the slow dissolution of glass phases), whereas in other samples (CA2 and PB2) the release of Pb was initially fast, followed by a decrease in release rate (Figure 2).

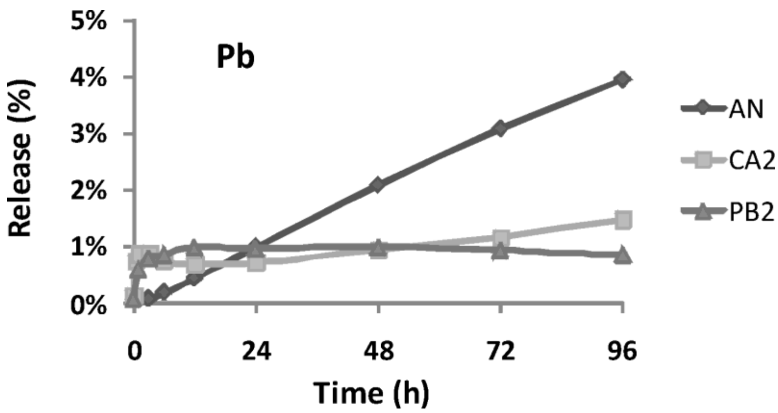


**Figure 2:** Release of Pb (% of total content) during $pH_{stat}$ leaching at pH4

## Conclusion

A high variability in physico-chemical and mineralogical properties of mining waste exists, even at one specific location or in mining waste related to the exploitation and processing of the same ore body. This variability in composition is also reflected in a very diverse heavy metal release behaviour that cannot simply be related to the properties (elemental composition, mineralogy, pH, *etc*.) of the waste materials, but asks for a thorough characterisation of heavy metal release behaviour when the environmental impact and management options for the mining waste are assessed**.** With respect to the waste materials analysed in this study, liming will not be an effective remediation option for the tailing in Angleur, because of the mobilisation of As and Pb when pH increases (Figure 1). In La Calamine, Plombières and Overpelt, liming would contribute to a reduction of the release of Pb, Zn and Cd into the environment. However, at all locations, wind erosion and runoff can cause the spreading of fine-grained dust, especially when the waste material is not covered, making surface stabilisation necessary. The characterisation of waste materials performed in this study can be helpful to evaluate other management scenarios such as the reuse of the slags in building materials, or the application of flotation techniques[3] or bioleaching[4] to remove contaminants from the tailings.

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