pH Dependent Leaching Behavior of Zn, Cd, Pb, Cu and As from Mining Wastes and Slags: Kinetics and Mineralogical Control

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Abstract From the Middle Ages until the beginning of the twentieth century, extensive Zn–Pb 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 characterization of different types of mining waste 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.

Keywords Environmental impact · Heavy metals · Mining · pH_{stat} · Slag · XRD

Introduction

In the mining industry, 3 principal processes can be distinguished, namely mining, mineral processing and metallurgical extraction [1]. All these processes produce waste, and depending on the origin and the processing conditions of the minerals, the waste materials show different properties. Additionally, mining waste generally contains hazardous substances such as heavy metals, radioactive

elements, cyanides,... which are not always strongly immobilized in the waste materials and can 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. Moreover, the potential release of hazardous elements depends of the distribution between different phases in a waste material, which reflects the blast furnace charge and temperature, as well as the cooling conditions of slags [2].

Despite the long history of mining at many locations, the environmental impact associated with mining activities only became an important issue in the second half of the twentieth century. Surface waters, groundwater, river sediments, overbank sediments, biota and even human beings affected by mining waste have been the subject of many investigations (e.g. [3–5]).

Often, mining waste such as slags find a use as secondary resource. For example, slags from Pb–Zn mining have extensively been used for road construction paving [6]. In the Campine region in Belgium and The Netherlands, zinc slags were used until the 1970s to improve public and private roads. Mining waste contained in landfills, slag heaps, and tailing ponds can be mined and valuable metals can be recovered from the waste. This process is referred to as ‘technospheric mining’ [7] and can contribute in a decrease of the environmental burden caused by mining waste. The recycling potential of mining waste is, from a technical point of view, mainly influenced by the available technologies and the physical, chemical and mineralogical properties of the waste materials. It is not the purpose of the present paper to investigate the possibilities of recycling waste, since this would also require a thorough economic and technological assessment,

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Table 1 Examples of studies dealing with Pb, Zn, Cd and/or Cu leaching from different types of mining waste and slags (in chronological order)

Type of mining waste or slag	Type of leaching test	Results	References
Slag from metallurgical tailings from the Ag/Pb/Zn/Cu mining	Leaching tests with natural rainwater, water rich in humic substances, ammonium nitrate solution	Pollutants are mobilized by seepage water and wind erosion	[8]
Acid slags (silica rich) and basic slags (lime rich) from the recycling of EAF dusts into an impure zinc oxide, called Waelz oxides,	Batch leaching tests at pH 5 and pH 12.5, (5 steps) pH _{stat} test (pH = 4–12).	Alkaline slags are more sensitive to the influence of pH. Silica-rich slags are characterized by a low buffer capacity	[6]
Ore minerals, slags, and tailings from a Pb–Zn mineralization	Batch leaching experiments with deionized water adjusted with HNO ₃ at pH 1 and 5.8, and Water from a moor lake, rich in humic acids	Flotation tailings release the highest amounts of toxic elements into the environment and the absolute amount released is mainly pH controlled	[9]
Spent copper slag	TCLP test pH _{stat} test	Low leaching of heavy metals, making the slag suitable to be used as a fill material for land reclamation	[10]
Mineral processing waste from an abandoned copper mine facility	TCLP, Field Leach Test (FLT), deionized water extraction tests, controlled pH experiments, sequential extractions	Variation in the extracted amounts was attributed to the use of different particle sizes, extraction fluid and contact time	[11]
Slag waste produced during smelting of Pb–Zn ores	In vitro gastric dissolution technique	Almost 100 % of Pb would be bio accessible in the smallest slag particles (<20 µm)	[12]
Piles in a Pb and Zn mining area with sphalerite (ZnS) and galena (PbS) as major mined ores were	Sequential extractions physiologically based extractions	Agreement between metal lability as determined by sequential extractions and SBET results suggests that they can also provide reasonable estimate of oral bioavailability	[13]
Rotary holding furnace (RHF) copper slag	TCLP, multiple extraction (USEPA method 1,320)	Heavy metals present in the slag are stable and are not likely to dissolve significantly even through repetitive leaching	[14]
Mine waste from the production of Au, Ag, Cu, Pb, Zn, and Mn	TCLP, sequential extractions	Low amount of elements extracted by alkaline extractants (NH ₄ Cl and NH ₄ F)	[15]
Slag from former Zn-smelting facility	Synthetic precipitation leaching procedure (USEPA Method 1,312)	Low leachate Zn concentrations for samples with Zn partitioned into spinel, high Zn release from sulphides	[16]
Copper smelting slag	EN 12457-2 batch tests, CEN/TS 14997 pH-static tests	A higher proportion of the fine-grained fraction generally led to greater leaching of Cu, Co and Zn	[17]
Slag heap from a primary lead smelter	TCLP, synthetic precipitation leaching procedure (SPLP) and British Columbia special waste extraction procedure (SWEP)	Lead slag was stable in weak acidic environments for short contact times	[18]
Carbonate wastes produced from the enrichment of lead oxide ores, using gravity separation and flotation techniques	Acid–base-counting (ABA), TCLP, 5 step sequential extraction procedure	ABA test indicated that the generation of acidic waters is not a likely mechanism for the mobilisation of contaminants from this type of waste, due to their high acid neutralizing potential	[19]
Inorganic polymers synthesized from fly ash and primary lead slag	EN12457 leaching test	pH is an important factor as Pb is immobilised in the binding phase, while this is not the case for Zn and As.	[20]
Slag produced through a plasma reactor	Dissolution experiments 6 M and 10 M NaOH, L/S = 40; 4, 8, 24 and 96 h	33 and 54 wt% of Al and Si respectively become available for the highly amorphous slag, while dissolved Al and Si are below 5 wt% when slag pot cooling is applied	[21]
Smelting wastes (pyrometallurgical slags) from Cu mining and smelting	Batch leaching with deionized water, stream solution and 0.02 mol l ⁻¹ citric acid solution	Leachates from a stream water solution and distilled water contain lower concentrations of metal(loid)s compared to leachates from a citric acid solution	[22]

Table 1 continued

Type of mining waste or slag	Type of leaching test	Results	References
Fly ash from a Co smelter	pH _{stat} leaching at pH 5–12	Contaminant release from minor metallic phases and silicate or glassy fraction.	[23]

but the characterization of mining waste applied in this study can be helpful for the evaluation of recycling and metal recovery possibilities.

Heavy Metal Leaching from Mining Waste and Slags

Heavy metal release from mine waste has been studied in many countries. An overview of some selected papers dealing with Zn-, Pb-, Cd-, Cu- and As leaching from mine waste which are relevant for the present study is provided in Table 1.

These results show that the release of Pb and Zn and other elements from the mining wastes is controlled by the pH of the leachates, and that leaching is also mainly affected by grain size and the mineralogical composition of the mining waste and slags glass phases. Nevertheless, the comparison of the results of these different studies is not always straightforward because of the different conditions (reaction time, type of reagent used to simulate acid or alkaline conditions, concentration of the reagents used, etc.). Several types of leaching tests are commonly used to investigate heavy metal release from waste materials. In most of the studies on heavy metal leaching from slags and mining waste, leaching is investigated to check the compliance with environmental standards. When no further characterization of the waste material is carried out, the more detailed interpretation of the reactions and mechanisms responsible for leaching is rather limited.

The most frequently used tests for mining waste are described below. Besides these more or less standardized tests, several batch leaching test with rainwater, diluted acid solutions, water with humic substances are described in literature, but they will not be addressed

TCCLP (Toxicity Characteristic Leaching Procedure) (Method 1311) [24, 25]

Toxicity characteristic leaching procedure is one of the Federal EPA test methods that are used to characterize waste (both organic and inorganic analytes) as either hazardous or non-hazardous for the purpose of disposal. The material is extracted for 18 h (agitation with an end-over end-shaker) with an amount of extraction liquid equal to 20 times the weight of the solid phase. The extraction liquid is chosen on the basis of waste alkalinity (CH_3COOH ,

pH = 4.93 ± 0.05 for sample pH < 5 and: CH_3COOH , pH = 2.88 ± 0.05 for sample pH > 5). The test tries to simulate a worst-case scenario where the waste is co-disposed with municipal solid waste.

SPLP (Synthetic Precipitation Leaching Procedure) (Method 1312) [26]

Synthetic precipitation leaching procedure Method 1312 simulates acid rain precipitation. Considering a worst-case scenario [27] to the waste during the practice of disposal. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For a waste, the extraction fluid employed is a pH 4.2 solution (made by adding a 60/40 wt% mixture of sulphuric and nitric acids (or a suitable dilution) to reagent water until the pH is 4.20 ± 0.05).

Sequential Extractions

Although sequential extraction procedures were originally designed for soils and sediments, they are also commonly used to characterize waste materials. Despite the fact that some of these extraction procedures are standardized (e.g. the SMT sequential extraction procedure), their application for the characterization of waste materials is questionable [28, 29].

Availability Test

Different standards exist, developed in different countries, for this test. The EA NEN 7371 [30] standard is used by the Environment Agency's to determine acceptance at landfill 1. It relates to the determination of the maximum potential for leaching of inorganic components from granular waste materials and is often referred to as the maximum availability test. This EA standard is based on the Dutch waste characterisation standards NEN 7341 [31] and NEN 7371 [32]. "The purpose of this availability test is to indicate the quantity of a particular component that may leach out from a granular waste material exposed to extreme conditions (for example, in the very long term, after disintegration of the material, full oxidation and/or loss of acid neutralising capacity), in an aerobic environment". The test conditions present a worst case leaching scenario rather than the

conditions that might be expected to prevail in a landfill, and thus the test provides an upper limit to the leaching potential in a landfill environment. The results using this test are derived as the (cumulative) leaching of components, in mg per kg dry matter. The acid neutralisation capacity (ANC) values at pH7 and pH4 also can be determined from the test data (EA NEN 7371 [30]).

pH_{stat} Test

In pH_{stat} test which has been standardized by the EU (CEN/TS 14997 [33]), pulverized material is leached for 24 h at eight different pH-values with the same liquid/solid ratio of 10. For a more detailed characterization of element release, longer experiments, with regular sampling of the leachate are sometimes carried out to address the kinetics of elements release during pH_{stat} leaching. An important advantage of pH_{stat} leaching tests compared to most tests mentioned above is that the pH can be more accurately controlled and that the acid neutralizing capacity of the material is also determined, which should be considered a key characteristic of waste materials.

In the present study, a very detailed version of pH_{stat} leaching test was applied, not only analyzing heavy metal and As release at different pH values, but also assessing the kinetics of element release during the complete duration of the test (96–120 h). For a more thorough interpretation of the results, additional parameters, such the release of major elements (Fe, Ca, sulphate) was also monitored and the pH_{stat} leaching tests were combined with a mineralogical and microscopical characterization of the slags.

Pb–Zn Mining and Smelting in Belgium

From the Middle Ages until the beginning of the 20th century, extensive Zn–Pb mining and smelting was carried out in East-Belgium. Approximately 1.1 million tons of Zn and 0.13 million tons of Pb were produced in the Verviers Synclinorium (East-Belgium) during the 19th century and the beginning of the 20th century [34]. The La Calamine deposit was exploited from the fourteenth century up to 1884. The ‘calamine’ ore is a mixture of Zn carbonates and Zn silicates, containing smithsonite (ZnCO₃), hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O) and willemite (Zn₂SiO₄) [35]. It was the largest Zn ore body in Belgium and produced more than 600,000 tonnes of zinc metal [36]. In Plombières, sphalerite and galena were mined and smelted in equal proportions from 1844 to 1882 [37]. After this period, mainly imported ores from Spain and Greece, were smelted in Plombières until the closure of the smelter in 1922.

By lack of waste treatment techniques and of sustainable management practices, metal-bearing slags and unprocessed

Table 2 Overview of the samples with indication of their origin

Sample	Location	Type of waste
AN	Angleur	Metallurgical waste (slag) from pyrometallurgy
CA1	La calamine	Processing waste (mine tailing pond)
CA2		Processing waste (mine tailing pond)
OV1	Overpelt	Metallurgical waste (slag) from powder metallurgy
OV2		Metallurgical waste (slag) from powder metallurgy
PB1	Plombières	Processing waste (mine tailing)
PB2		Processing waste (mine tailing)

waste were dumped. Besides the important amount of waste that is stored in huge mine tailings, the surroundings of the tailings are often contaminated as a consequence of the dispersal of contaminants by wind erosion, runoff or fluvial transport [38].

Processing of these minerals occurred at several locations, such as in Angleur (north-eastern part of Belgium) and Overpelt (northern part of Belgium) (Table 2).

In the present study, waste materials from metallurgical processing and from mineralogical extraction will be investigated. A chemical and mineralogical characterization of different types of slag and mining waste originating from the former Pb–Zn mining industry was performed in order to gain a better understanding of the waste properties, with special attention to heavy metal release under varying pH conditions, and to bring this in relation to different management scenarios.

Methodology

Site Description and Sampling

Samples from different types of mining waste were collected at 4 different locations in the northern and north-eastern part of Belgium (Table 2).

- In La Calamine, samples were taken from a tailing pond containing dredged material from a sedimentation pond, which was used to store wastewaters from the former Pb–Zn mine [39]. In the centre of the tailing pond, a profile was excavated (with a spade) until a depth of 4 m and samples were taken every 10–20 cm, from which two samples were selected after initial screening (at 97 and 210 cm depth).
- The industrial dump site in Angleur, located at 5 km from the city of Liège (eastern Belgium) is composed of waste from the metallurgical process of zinc production between 1837 and 1905 (La Vielle

Montagne/UMICORE). Until 1885, the zinc ore originating from the exploitation of the nearby La Calamine ore body consisted mainly of a mixture of smithsonite (ZnCO_3), hemimorphite ($\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$) and willemite (Zn_2SiO_4) [36]. Between 1885 and 1905, the ore that was used for Zn production was composed of zinc sulphides. Within the dump, a vertical profiles (3 m) deep was sampled every 30 cm and after a first screening of the samples, the sample taken between 150 and 180 cm depth was selected for a more detailed mineralogical and chemical characterization.

- Finally, in Overpelt, two waste samples were obtained from a plant for zinc powder manufacturing by air atomization (“blown zinc”) for primary batteries.

The dump site in Plombières is dominated by stacked retorts, which were used by Zn-smelters in the late eighteenth century for the production of Zn [36]. The slags of Plombières have been the subject of investigations (mainly concerning their mineralogical composition and Pb- and Zn content) in the past because of economic importance (e.g. [40]). The slags are composed of various combinations of alloys and natural minerals e.g. metallic alloys, phosphides, sulphides and carbides of As, Mn, Fe, Pb, Cu and Zn. The main and common primary phases are Fe- and Al-spinels substituted by Zn, V, Cr, Ti and Mg, Ca, Zn-rich fayalite, melilite, corundum and apatite. Also iron silicates, ZnO and ZnS are supposed to be the main Zn containing phase. Pyrite, melnikovite and iron oxides as the weathering productions of Zn- and Pb-ores [40]. Two surface samples were collected from the mine tailing at this site.

For each sample, approximately 2 kg of material was taken. All samples were air-dried. For determination of pH, oxidisable substances and total element concentrations, about 0.5 kg of sample was crushed in a mortar and well mixed, after which the sample was quartered and milled in a tungsten carbide mill.

Physicochemical Analysis

pH was measured in a water suspension (solid/liquid ratio = 1/2.5) (pH Hamilton Single pore electrode). Organic carbon was determined according to the Walkley and Black method [41]; effective cation exchange capacity (CEC) was analyzed applying the ‘silver thiourea method’ [42, 43]. Total element concentrations (Al, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn, Fe, Mg, Mn, K and Ca) were determined after dissolution of the samples with a mixture of 3 concentrated acids (4 mL HCl_{conc} , 2 mL $\text{HNO}_{3\text{conc}}$ and 2 mL HF_{conc}). A certified reference material (GBW07411 Soil) and sample triplicates were used for quality control. Values (in mg kg^{-1}) obtained were for Cd 25.9 (certified value 28.2 ± 1.3), Zn: 3,630 (certified value $3,800 \pm 300$),

Ni: 22.3 (certified value 24.2 ± 2.1), Cu: 62.9 (certified value 65.4 ± 4.7), Pb: 3,010 (certified value $2,700 \pm 100$), Cr: 57.5 (certified value 59.6 ± 5.0) and As: 193 (certified value 205 ± 11). Some measured values for the certified material are out of the certified range because the method used in this study (acid attack followed by ICP-MS measurement) is different from the method used to obtain the certified values (X-ray Fluorescence). All reagents used for analysis were of analytical grade. All glassware was acid rinsed with HNO_3 0.2 mol L^{-1} before usage.

Total S was determined with the Ströhlein Sulfur Analyzer (model S-mat, Carbolite Co. Ltd., Bamford-Sheffield). Grain size was determined by laser diffraction analysis (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK) after removing carbonates (0.1 mol L^{-1} HCl), iron oxides (0.5 % oxalic acid, boiling) and organic carbon (35 % H_2O_2 , 60°C) and applying a peptizing solution (10 g L^{-1} sodium polyphosphate, boiling).

pH_{stat} Leaching

The pH_{stat} experiments were carried out with an automatic multi titration system (Titro-Wico Multititrator, Wittenfeld and Cornelius, Bochum, Germany). 80 g of material (<2 mm fraction) was put in an Erlenmeyer flask together with 800 mL of distilled water and placed on a horizontal shaking device. A pH-electrode and an automatic titration dispenser were attached to each flask. The suspensions were first shaken for 30 min without addition of acid and then the titration was started. Previous experiments performed in our laboratory [44] demonstrated that the rapid addition of acid to the soil–water suspension could lead to an exceeding of the set-point pH. Therefore, the concentration of the titration solution was adapted to the set-point pH (pH 2:2.5 mol L^{-1} HNO_3 , pH 4:1 mol L^{-1} HNO_3 , pH 6:0.25 mol L^{-1} HNO_3 , pH 8:0.5 mol L^{-1} NaOH and pH 10:2.5 mol L^{-1} NaOH). The choice of the concentration of the titration agent was based on a rapid potentiometric titration, which was carried out to deduce the acid neutralizing behaviour of the sample. The interval of pH-acquisition was set to 200 s (instead of 1 s) to give the system enough time to react and eventually neutralise the acid before more acid was added [45].

At regular time intervals (0, 0.5, 1, 3, 6, 12, 24, 48, 72 and 96 h/168 h), a sample of the suspension was taken over a filter (0.45 μm Acrodisc, Pall, East Hills, NY) by means of a syringe attached to a flexible tube (For more details see also [44]). Immediately after sampling, the sample was acidified with a drop of concentrated HNO_3 (ultrapure) to bring the pH < 2. Subsequently the sample was kept in a refrigerator until analysis. For 3 samples, namely samples AN, CA1 and CA2, pH_{stat} leaching behavior was investigated at pH values 2, 4, 6, 8 and 10 and the duration of the

pH_{stat} leaching test was 96 h. For the other samples (OV1, OV2, PB1 and PB2), only pH 4 was investigated, during 168 h.

Analysis of Leachates

The solutions (digests from the 3-acid attack and the pH_{stat} leachates) were analyzed by Flame Atomic Absorption Spectrometry (Thermo Electron Corporation S Series AA) for Ca, Fe, K and Al. For As, Cd, Cr, Cu, Mn, Ni, Pb and Zn a multi element analysis by Induced Coupled Plasma Mass Spectrometry (ICP-MS, HP 4500 series) was carried out. The samples were diluted just before analysis with 5 % HNO₃ (ultrapure). Standard series were made up starting from the '10 ppm Multi-Element Calibration Standard-2A in 5 % HNO₃' (Hewlett Packard, Palo Alto, CA). An Indium (In) internal standard was applied to both samples and standards. The spectroscopic interference of ArCl, which has the same m/z as As (75) was corrected according to the recommendations of the EPA (method 200.8 [46]). Each ICP-MS measurement was carried out with three repetitions holding relative standard deviations below 5 %. Accuracy was also checked by measuring standard solutions as unknown samples. In the final leachates, dissolved organic carbon was measured with a TOC analyser (SkalarFormacsHT TOC analyser, Breda, The Netherlands); sulphate was measured by turbidimetry [47] and chloride and phosphate by colorimetry [48]. Electrical conductivity (18.34 EC-meter, Eijkelkamp, The Netherlands) and redox potential (Mettler Toledo Pt 4805-S7/165 Combination redox electrode, Zaventem, Belgium) were also determined.

Geochemical modelling of the leachate chemistry was performed with the thermodynamical speciation code VisualMinteq [49, 50].

Mineralogical Analysis

A mineralogical sample characterization was conducted by X-ray diffraction (XRD, Philips®, Co-target, $\lambda = 1.79 \text{ \AA}$). The XRD-characterisation was performed on pre-concentrated samples. Diffractometer settings were 30 kV, 30 mA, 10–75° 2 θ , step size 0.04° 2 θ and 2 s counting per step. Pre-concentration was achieved by separating different fractions according to magnetic (Frantz isodynamical separator) and density properties (bromoform [CH₃Br, $\rho = 2.89 \text{ g cm}^{-3}$]). This should facilitate mineralogical identification of particular minerals that otherwise would be untraceable in a bulk sample due to high background counts of the XRD technique [51]. Clay mineralogy was determined on orientated clay preparates. The mineral phases on the XRD patterns were determined by comparison with previously published patterns [52]. The residues of the pH_{stat} leaching test on sample AN at pH 2 and pH 10

were analyzed by scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX; JSM-6400) on imbedded and polished slag fragments.

Results and Discussion

Mineralogical and Physico-Chemical Characterization

The waste materials from the four locations were mainly contaminated with Zn, Pb, Cd, Cu and/or As (Table 3). pH was neutral to slightly alkaline for the samples from La Calamine and Angleur, whereas pH was moderately acid in the samples from Plombières and Overpelt. The main minerals detected in the different samples are mentioned in Table 4.

With respect to the acid neutralizing capacity (ANC) at pH 4 (Table 5), important differences are observed between the different slags. At first sight, the slags with a neutral to slightly alkaline pH (Table 3) tend to be characterized with a higher ANC at pH4 (ANC_{pH4}). However, this cannot be generalized since the two samples from Overpelt (OV1 and OV2), which exhibit a comparable pH (5.9 and 5.8 respectively) show a very different ANC_{pH4} (1,074 and 40 mmol kg⁻¹ respectively). Sample OV1 also displays a cation exchange capacity (CEC) which is much higher than the other samples (Table 3). CEC can also contribute to the ANC of this sample, as the ANC is also much higher compared to samples OV2, PB1 and PB2 (Table 5).

pH-Dependent Leaching Behavior and Acid Neutralizing Capacity

Although some general patterns could be distinguished in the pH-dependent leaching behavior of elements (Fig. 1), differences were also observed, related to the specific (mineralogical) composition of the slags. A more detailed discussion of the relation between the leaching behavior and mineralogical composition is provided under the Sect. "Leaching Test Results Versus Mineralogical Composition and Modeling".

The release of heavy metals (Zn, Cd, Cu, Ni, Pb) increases with decreasing pH due to the dissolution of minerals and the desorption of these elements from reactive surfaces (for example (Fe)-oxides). At pH 10, an increased solubility of Cu, and in some samples also of Zn, Pb and Ni is observed, most likely because the amphoteric character of these elements, favoring the formation of hydroxyl-complexes at alkaline pH values.

Arsenic is a particular element since it is a metalloid, that can occur as oxy-anion (arsenite and arsenate), which explains its release at alkaline pH values in sample AN. However, for sample CA1 the solubility of As was not

Table 3 Total element concentrations, pH and CEC of the investigated samples

Sample	Zn (%)	Cd (mg kg ⁻¹)	Pb (%)	Cu (mg kg ⁻¹)	As (mg kg ⁻¹)	Ca (%)	Al (%)	Fe (%)	S (g kg ⁻¹)	K (%)	Mg (%)	pH	CEC (cmol kg ⁻¹)
AN	3.09	124	1.95	1,704	1,928	2.22	2.45	9.48	ND	ND	ND	8.0	ND
CA1	10.81	297	2.06	60	1,491	4.72	3.08	11.77	12.70	1.06	0.48	6.5	ND
CA2	6.77	4,196	0.03	29	28	5.57	2.79	2.81	2.57	1.53	0.30	7.5	ND
OV1	3.56	48	1.92	5,383	3,391	1.52	2.20	19.19	2.96	0.44	0.61	5.9	19.96
OV2	0.47	5	0.24	604	141	1.66	7.92	9.09	0.38	2.07	0.72	5.8	3.35
PB1	1.16	63	0.52	1,023	474	1.9	6.21	5.87	0.22	1.52	0.78	5.3	1.33
PB2	2.79	68	0.61	6,642	545	1.34	2.75	7.87	0.35	0.69	0.28	5.7	1.83

Table 4 Mineralogical composition of the samples analyzed in this study

Sample	Minerals
AN	Troilite, arsenopyrite, willemite, magnesioferrite, Fe ₁₁ Zn ₄₀ , laihunite, wollastonite, kirschsteinite, amorphous silicate phases (glass phases)
CA1	Sphalerite, anglesite, pyrite, galena and marcasite
CA2	Smithsonite, cerrusite, siderite, calcite and gypsum
OV1	Opaque phases (>80 %), minor amounts of quartz, hematite, goethite, melilite
OV2	Fe-oxides and quartz, fluorite, albite and melilite
PB1	Iron oxides, quartz, feldspar, fluorite and mullite.
PB2	Iron oxides, quartz, feldspar, fluorite and mullite.

affected by a pH increase and remained very low (Fig. 1) and in sample CA2 As was even not released at all in the pH-range 2–10.

The amount of acid or base (ANC or BNC respectively) added to the suspension to reach a certain pH value is also presented in Fig. 1, showing that different slags and waste materials behave very differently upon external addition of H⁺ or OH⁻.

Time Dependent Element Release During pH_{stat} Leaching at pH 4

Monitoring of element release as a function of time (Fig. 2) showed that the time-dependent release pattern was either dependent on the sample composition, either element-specific. In general, most of the elements were rapidly released at the beginning of the experiment (first 24–48 h), afterwards the release slowed down. Arsenic was generally characterized by decrease in concentrations as a function of time, because of re adsorption reactions occurring at pH 4, due to the anionic nature of arsenic (occurring as arsenite or arsenate). The release of Zn, Cd and Ni from sample CA2 fluctuates between 12 and 96 h, most likely because of precipitation reactions. Decreasing Fe concentrations were also observed with time for the slags from Plombières (PB1 and PB2), whereas for sample CA1, a strong increase in the release of Fe was measured after 48 h.

In a study on the pH_{stat} leaching behaviour of major and trace elements from land-disposed dredged sediments, Cappuyns et al. [45] concluded that ANC can be related to the amount of CaCO₃ in the sediments, since sediments with a high CaCO₃ content were also characterized by a high ANC. However these results which are applied to

Table 5 Acid neutralizing capacity (ANC_{pH4}) and mount of elements released and at the end of the pH_{stat} leaching test (96 h for AN, CA1 and CA2; 168 h for OV1, OV2, PB1 and PB2)

	ANC (mmol kg ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	Zn (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cu (mg kg ⁻¹)	As (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Ca (mg kg ⁻¹)
AN	735	<50	1,088	51.6	1,218.6	90.6	0.1	13.7	12.9	2,033
CA1	1,223	6,353	2,913	36.8	304.6	9.7	0.1	0.5	12.8	3,668
CA2	2,368	1,240	37,891	162.3	18.4	1.9	0.0	162.3	60.1	7,650
OV1	1,074	3,944	3,419	41.2	216.7	33.9	1.2	5.8	0.2	771
OV2	40	7,293	3,518	21.3	410.3	1,033	0.2	9.6	0.5	286
PB1	362	5,207	12,737	12.4	1,272.6	0.1	0.2	20.1	2,593	1,892
PB2	423	5,107	763	1.5	53.2	6.3	0.1	10.1	45.2	127

Fig. 1 pH-Dependent release of Zn, Cd, Pb, Cu, As, Ni, Fe and Ca (in mg kg^{-1}) and ANC or BNC (in mmol kg^{-1}) (measured at the end of the pH_{stat} leaching test)

sediments cannot be generalized for slags, as the ANC_{pH4} could not directly be related to the carbonate or even Ca content of the slags.

In anoxic sediments containing sulphides, oxidation of reactive sulphides is generally observed during pH_{stat} leaching, which was an additional source of protons during pH_{stat} leaching [53]. However, sulphides in the slags are much less reactive than sulphides in river sediments and the amount of sulphate released during pH_{stat} leaching is also rather limited and cannot directly be related to the evolution of ANC with time (Fig. 3).

It is also important to address the fact that for some samples, pH_{stat} leaching tests were performed during 96 h, whereas for other samples, a longer experiment time (168 h) was used, which makes that ANC (and release of elements) is not entirely comparable. However, the ANC curves as a function of time often showed an asymptotical trend, allowing to model the long-term ANC. ANC and the cumulative release of elements as a function of time can be described mathematically as the sum of two independent first-order reactions [54] i.e.:

$$H_b(t) = BC_1(1 - \exp(-k_1t)) + BC_2(1 - \exp(-k_2t)) \quad (1)$$

where $H_b(t)$ (mmol kg^{-1}) corresponds to the buffered protons at time t , BC_i (mmol kg^{-1}) is the buffering capacity of system i , k_i (h^{-1}) is the rate coefficient of the buffer system i and t (h) is the time after starting the titration.

Analogously, the cumulative release of an element m at time t is given by:

$$RL_m = RC_1(1 - \exp(-r_1t)) + RC_2(1 - \exp(-r_2t)) \quad (2)$$

With RC_i (mg kg^{-1}) = the release capacity of buffer system i , r_i (h^{-1}) is the rate coefficient of the buffer system i and t is the time after starting the titration. The release capacities of the two buffer systems (RC_1 and RC_2) can be considered as two dominant sinks for heavy metals from which elements are released with a different rate. It has to be noticed that the two 'buffer systems' are only operationally defined and that they are not automatically related to specific components of the slag, for example certain minerals contained in the slags. Theoretically, it is possible

Fig. 2 Time-dependent release of Zn, Cd, Pb, Cu, As, Ni, Fe and Ca (in mg kg^{-1}) and ANC (in mmol kg^{-1}) at pH 4

Fig. 3 ANC, release of Ca and sulphate as a function of time at pH4 (samples OV1, OV2, PB1 and PB2)

to consider more than two buffer systems, for example, by defining a buffer system (RC_i) for each mineral which can dissolve upon titration with acid or base. However, it can be questioned whether this would lead to a more comprehensive interpretation of the results of the leaching test. A mineralogical sample investigation before and after pH_{stat} leaching provided some insight in the reactions (i.e. dissolution of minerals) responsible for the release of certain

elements during pH_{stat} leaching. In sample CA1, anglesite was dissolved during pH_{stat} leaching at pH 10. However, because the amount of anglesite in the sample was not quantified and because Pb reprecipitated as $\text{Pb}(\text{hydr})\text{oxides}$ at pH 10, it was not possible to quantify the amount of Pb released by dissolution of anglesite.

The modeling (Eqs. 1, 2) is also useful to calculate a (theoretical) ANC on long term (by filling in $t = \infty$ in

Table 6 Buffer capacities and rate coefficients calculated by fitting the ANC curves and the release of Zn at pH 4 as a function of time according to respectively equation 1 and 2

	BC ₁ (mmol kg ⁻¹)	BC ₂ (mmol kg ⁻¹)	k ₁	k ₂	ANC _{end} (mmol kg ⁻¹)	ANC _{t=∞} (mmol kg ⁻¹)	RC ₁ (mg kg ⁻¹)	RC ₂ (mg kg ⁻¹)	r ₁	r ₂	Zn _{end} (mg kg ⁻¹)	Zn _{t=∞} (mg kg ⁻¹)
AN	444	280	0.23	0.04	735	724	519	517	0.06	0.04	1,088	1,036
CA1	90	1,223	1.69	0.02	1,223	1,313	411	2,913	1.77	0.02	2,913	3,324
CA2	267	2,368	0.36	0.02	2,368	2,634	—	—	—	—	37,891	—
OV1	73	395	1.41	0.01	362	468	1,484	2,022	1.54	0.02	3,419	3,507
OV2	115	276	2.06	0.03	423	391	2,079	1,295	2.70	0.04	3,518	3,375
PB1	113	942	0.33	0.02	1,074	1,055	685	12,249	0.07	0.02	12,737	12,933
PB2	5	35	1.67	0.14	40	40	198	495	0.95	0.03	763	693

ANC_{end} and Zn_{end} = acid neutralizing capacity and amount of Zn released at the end of the pH_{stat} test; ANC_{t=∞} and Zn_{t=∞} = acid neutralizing capacity and amount of Zn released on long term (t = ∞)

Fig. 4 X-ray diffraction pattern of sample CA1: original sample and sample after pH_{stat} leaching at pH 2, 4 and 10, showing the disappearance of anglesite at pH 10

Eq. 1), allowing a comparison between the different slag samples (Table 6).

Leaching Test Results Versus Mineralogical Composition and Modeling

The results from the pH_{stat} leaching tests, combined with solid-phase characterization (XRD, SEM-EDX) and thermodynamical modelling (VisualMinteq) confirmed that the solubility of Zn, Pb and Cd in the mine pond tailing of La Calamine is mainly controlled by Pb–Zn minerals (sphalerite, smithsonite, anglesite, galena). At low pH-values (pH 2 and 4), no heavy metal containing minerals disappeared from the sample CA1 (La Calamine). At alkaline pH, however, anglesite was removed from the sample (Fig. 4). Modelling the solubility of anglesite as a function of pH showed that anglesite is indeed completely dissolved at pH 10, but Pb reprecipitates as Pb-(hydr)oxides, explaining for the very low Pb-concentration found in the leachate at pH 10 (Fig. 1). Based on VisualMinteq calculations, a partial dissolution of anglesite occurs at pH 2 and 4, but XRD-

analysis indicates that the dissolution of anglesite is not significant at acid pH-values (Fig. 4).

On the contrary, 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. Even in the sample with a very high release of Zn at pH 4 (sample PB1, Table 5) no Zn-containing discrete minerals could be detected with XRD. In sample PB1 (Plombières), XRD analysis indicated that CaF₂ disappeared after pH_{stat} leaching at pH 4, which agreed with the results of geochemical modeling of CaF₂ solubility. These results can also be linked to the important ANC_{pH4} (Table 5) measured in this sample and the high amount of Ca released during pH_{stat} leaching at pH 4 (Fig. 3) compared to the waste samples with a comparable pH (PB2, OV1 and OV2), but with a much lower ANC_{pH4}.

The slag sample from Angleur (AN) contains arsenopyrite, a mineral that normally decomposes in oxidizing conditions. However, during pH_{stat} leaching under oxidizing conditions almost no As was released in the pH range

Fig. 5 SEM-analysis of sample AN after pH_{stat} leaching at pH 2, showing a Si-rich skeleton remaining after acid attack

2–8 (Fig. 1). This may be attributed to the occlusion of this mineral in glass phases, protecting the mineral from acid dissolution. At pH 2, arsenopyrite disappeared from the sample, but readsorption of As on positively charged mineral surfaces most likely explains why no As is found in the pH_{stat} leachate.

The mineralogical composition of the sample after it had been subjected to a pH_{stat} leaching test at pH 2 mainly consisted of willemite, $\text{Fe}_{11}\text{Zn}_{40}$, SiO_2 and $\text{Fe}_{1.6}\text{SiO}_4$. SEM analysis of the residue that remained after pH_{stat} leaching at pH 2 showed that many grains were clearly attacked by the strong acidity, only leaving a Si-rich skeleton behind (Fig. 5). In the original sample, the same grains with abundant Fe and Zn were still intact. At pH 10, the grains were also still intact and traces of precipitated Fe were found. XRD analysis of the residue after pH_{stat} leaching at pH 10 revealed the presence of wollastonite (CaSiO_3), kirschsteinite (CaFeSiO_4), $\text{Fe}_{11}\text{Zn}_{40}$, willemite (Zn_2SiO_4), laihunite ($\text{Fe}_{1.6}\text{SiO}_4$).

The limited leaching of heavy metals at pH 8 (=natural pH of sample AN) is in accordance with the fact that the metals are associated with stable or relative stable oxides, silicates, sulphides and carbonates. The pH-dependent solubility of willemite (a Zn-containing mineral identified in sample AN) was modeled with the speciation code VisualMinteq. The amount of willemite used as input in the model was calculated based on the amount of Zn found in the pH_{stat} leachate at pH 2, assuming that Zn was entirely coming from the dissolution of willemite. The Zn model release agreed well with the observed release of Zn from sample AN as a function of pH, which may indicate that Zn-solubility in this sample is (partly) controlled by the dissolution of willemite. However, XRD analysis of sample before and after pH_{stat} leaching did not show the disappearance of this mineral, indicating that there was only a partial dissolution of willemite.

Most of the samples were characterized by a relatively high Fe-content (Table 3). XRD analysis of the slags allowed to identify some Fe-containing minerals (e.g. hematite, goethite, pyrite, troilite). However, the amount of Fe released during pH_{stat} leaching was generally very low, even at pH 2 (600, 7,123, 438 mg kg^{-1} in sample AN, CA1 and CA2 respectively, Fig. 1), suggesting that the dissolution of Fe-containing minerals was not significant. Moreover, the theoretical dissolution of these minerals was often lower than the dissolution predicted by VisualMinteq, mainly because of kinetic constraints [55].

pH-Dependent Leaching Behavior and Potential Management Scenarios

Metal bearing slag particles can constitute an important environmental problem once they end up in the soil and surface waters surrounding the processing facility or disposal site. Although the focus in this study is mainly the influence of pH and mineralogy the mobility of Pb, Zn, Cd, Cu and As, other factors can influence heavy metal retention and release from slags. The alteration of slag particles in soil, such as the increase in porosity, a modification of their morphology and the partial dissolution of the slag particles result in the release of a hazardous elements [56]. On the other hand, Ettler et al. [57] showed that organic acids (naturally) occurring in soils may result in the precipitation of secondary phases such as amorphous hydrous ferric oxides, amorphous SiO_2 and microcrystalline calcite and may result in the scavenging of heavy metals in and below the soil cover of slag disposal sites. Some mine tailings, especially in sulphidic mine tailings characterized by acid mine drainage, show a highly varied and complex microbial ecology within a very heterogeneous geochemical environment [58]. Some bacteria in Pb–Zn mining environments resist high concentrations of Cd and Zn, and are able to promote the plant growth of metal-accumulating plant species [59]. Moreover, artificial inoculation of mine tailings with bacterial strains can improve plant resistance to heavy metals by reducing the uptake of some toxic elements [60]. The mining wastes and slags studied in the present paper do not generate acid mine drainage and it was also not the purpose to investigate the potential of micro-organisms in phyto stabilisation or phyto remediation applications. Nevertheless, micro-biological interactions could be considered for the full assessment of potential remediation strategies.

For 3 samples, namely from Angleur (AN) and La Calamine (CA1 and CA2), pH_{stat} leaching behaviour was studied in a range of pH values between pH 2 and 10. By combining the results of the pH_{stat} leaching test, solid-phase characterization (XRD, SEM-EDX) and thermodynamical

modelling (VisualMinteq), it could be concluded that the solubility of Zn, Pb and Cd in the mine pond tailing of La Calamine is mainly controlled by Pb–Zn minerals. In Angleur, vitreous phases seem very important in controlling heavy metal mobility since metals that are locked up in a silicate matrix are protected against leaching.

Liming will not be an effective remediation option for the tailing material represented by sample AN, since As and Pb will be mobilised when pH increases (Fig. 1). However, for waste materials from La Calamine (CA1 and CA2), a pH-increase significantly decreases the leachability of Zn, Cd and Pb, whereas the solubility of As is not affected and remains very low (Fig. 1). The application of hydroxyapatite and natural phosphate rock effectively reduce the heavy metal solubility in mining impacted soils [61, 62] and can also be applied as an amendment to mine tailings. Preliminary tests performed on one slag sample from La Calamine (CA1) showed that the addition of phosphates in combination with liming can result in an additional decrease of heavy metal solubility and contribute to a reduction of the release of Pb, Zn and Cd into the environment, whereas the release of As is not affected.

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 which cannot simply be related to the properties (elemental composition, mineralogy, pH,...) 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 mining waste and slags analyzed in this study, liming will not be an effective remediation option for the tailing in Angleur, because of the mobilization of As and Pb when pH increases. In La Calamine, Plombières and Overpelt, liming contributes 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 characterization of waste materials performed in this study can be helpful to evaluate other management scenarios such as the reuse of mining waste in building materials, or the application of flotation techniques [63] or bioleaching [64] to remove contaminants from the tailings.

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