PROCEEDINGS OF THE 7TH INTERNATIONAL

SLAG VALORISATION SYMPOSIUM

SHIFTING GEARS TO A CLIMATE-NEUTRAL & RESOURCE EFFICIENT SOCIETY

KU LEUVEN
MATERIALS ENGINEERING

ENVIRONMENTAL ASSESSMENT AND VALORISATION POTENTIAL OF WASTE FROM HISTORICAL MINING AND ORE PROCESSING

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Introduction

Waste from historical mining and ore processing activities was commonly deposited in on-site dumps, which are still present today. Mine waste typically consists of tailings and waste rock; however, slags and various rubble, such as remaining equipment from the processing plant, have also commonly been disposed of on-site. These waste materials can contain high levels of metal(loid)s which can pose a threat to the environment. At a historical Zn-Pb mine in Plombières, Belgium, many primary slags and fragments of weathered ceramic pipes, which remain from ore processing, are present on-site. While much attention was already paid to the characterisation of mine tailings, slags and ceramics deserve special consideration due to their specific characteristics (e.g., high content of amorphous phases).[1] In the present study, a chemical and mineralogical characterisation is performed, for a preliminary assessment of the environmental impacts and valorisation potential of the slags and ceramic pipe fragments.

Methodology

The environmental impact of the samples was assessed based on a series of different leaching tests, (pseudo) total elemental content and mineralogical analyses. A slag sample (PL_65A) and a ceramic pipe sample (PL_66A) (Table 1) from the historical Zn-Pb mining site in Plombières, Belgium were ground to a powder for analyses. The pH of the samples was measured in a water suspension (liquid/solid ratio: 10 l/kg) (18.30 field pH meter, Eijkelkamp). Additionally, the samples were subjected to aqua regia (AR) digestion, according to the modified ISO 11466 method,[1] determining the pseudo total elemental content. For comparison, the total elemental content and the volatile fraction was determined by X-ray fluorescence (XRF, (Panalytical Axios-Minerals) and loss on ignition (LOI, material heated to 1000°C) (Wienerberger NV - Central Laboratory Beerse (B)). Additionally, the mineralogy was determined by X-ray diffraction (XRD, Philips PW1830 Analytical X-ray BV, CuKα radiation, 45 kV and 30 mA, graphite).

The US EPA's Toxicity Characteristic Leaching Procedure (TCLP)[2] and an EU batch leaching test (EN 12457-2)[3] were performed on the slags and ceramic pipes samples, according to the standardized procedure for initial hazard classification. For a more in-depth investigation of the effect of pH conditions on the release of metal(loid)s, a pH-dependent leaching test was performed according to the EN 14997 (2015) procedure.[4]

Table 1: Plombières mine waste samples and description

Sample Code	Type	pH	Colour (Munsell colour chart)
PL_65A	Slags	6.1	7.5 YR 4/1
PL_66A	Pipes (ceramics)	6.8	10 YR 3/1

Eluates from the leaching tests were filtered through a 0.45 µm membrane filter, acidified (except for alkaline leachates) with HNO_3, and stored at 5-10°C until analysis. Samples were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 730ES) for 23 elements.

Results and Discussion

Mineralogical and chemical characterisation

XRD analysis revealed that both the slag and pipe samples consisted of amorphous phases, quartz, mullite, kaolinite, Fe-oxides, muscovite and feldspars. Additionally, the slag contained barite.

In Table 2, the chemical composition of both samples is presented. AR digestion only yields 'pseudo' total element concentrations. However, when XRF results were below the detection limit (e.g., As, Cu, Cd, Ni, Sb), AR digestion results are also shown. Slags are often utilized in green construction materials, such as ceramics; therefore, (pseudo) total element concentrations are shown in comparison with the VLAREMA Flemish legislative guide values for use in or as a construction material.[5] The results revealed that the slag contained high levels of As (1885 mg/kg), Cu (2205 mg/kg), Pb (11504 mg/kg) Sb (248 mg/kg) and Zn (15479 mg/kg), while the ceramic pipes contained rather high levels of Pb (1490 mg/kg) and Zn (6471 mg/kg). Therefore, these samples cannot be considered for use in or as construction materials in Flanders (see guide values in Table 2).

Mobility of metal(loid)s

The TCLP was performed to simulate the worst-case scenario of co-disposal in landfills, to determine the toxicity of the sample based on the mobility of metal(loid)s. The results from the TCLP are presented in comparison with the US EPA's regulatory thresholds for As, Cd and Pb (Table 3). The leaching of Pb is above the US-EPA regulatory threshold (5 mg/l) for both samples and is thus considered a threat to the environment. Furthermore, the pH-dependent leaching test (Figure 1) revealed that under acidic conditions (pH < 5), As, Cu, Pb and Zn had an increased release in both samples. This can be problematic because acid rain occurs within this pH range and can cause leaching of these metal(loid)s into the environment. Under alkaline conditions, the release of Zn slightly decreased while As, Cu, and Pb have an increased leachability; therefore, co-disposal with lime would not be an adequate management scenario. Under neutral pH conditions (i.e., EN 12457-2 test, Figure 1), a considerable release of As and Pb was still seen for sample PL_65A. Even under extremely acidic (pH <2) or alkaline (pH >12) conditions, the metal(loid)s are not completely leached because they are incorporated in amorphous phases inhibiting the release of the metal(loid)s. However, a micro mineralogical analysis (e.g., SEM-EDX, FEG-EPMA) would be necessary to further assess this.

Table 2: XRF, LOI and AR digestion results of sample PL_65A and PL_66A. ND: not detected. Values in bold are above the VLAREMA guide values for use in or as a construction material.[5]

	XRF (n=1)			AR digestion (n=2)		
mg/kg (unless indicated)	PL_65A	PL_66A		PL_65A	PL_66A	VLAREMA guide values[5]
LOI, wt%	2.3	3.9				
Si	220 383	315 187				
Al	130 635	99 943		5540 ± 146	19 097 ± 72	
As	**582**	ND		**1885 ± 53**	34 ± 5	250
Ba	ND	1102		40.5 ± 0.4	33.6 ±0.2	
Ca	18264	5757		5205 ± 74	1410 ± 116	
Cd	ND	ND		5.0 ± 0.0	8.8 ± 0.0	10
Co	ND	ND		91 ± 3	6.4 ± 0.3	375
Cr	ND	363		19.9 ± 0.6	23.9 ± 0.6	1250
Cu	ND	ND		**2205 ± 89**	75 ± 12	375
Fe	83 961	20 680		103 306 ± 2761	7051 ± 624	
Ni	ND	ND		80 ± 3	12.0 ± 0.1	250
Pb	**11 504**	**1490**		**2948 ± 45**	458 ± 46	1250
S	1181	608		8506 ± 219	284 ± 12	
Sb	ND	ND		**248 ± 4**	13 ± 1	50
Zn	**15 479**	**6471**		**15 526 ± 147**	**3 107 ± 174**	1250

Table 3: Results of the TCLP (in mg/l). NSE: No standard established.

mg/l	As	Cd	Cu	Pb	Zn
PL_65A	0.11 ± 0.02	<0.02	0.71 ± 0.03	**266 ± 81**	5.2 ± 0.1
PL_66A	<0.1	0.34 ± 0.01	0.21 ± 0.02	**10 ± 1**	34.4 ± 0.7
Regulatory Thresholds (US EPA)	5	1	NSE	5	NSE

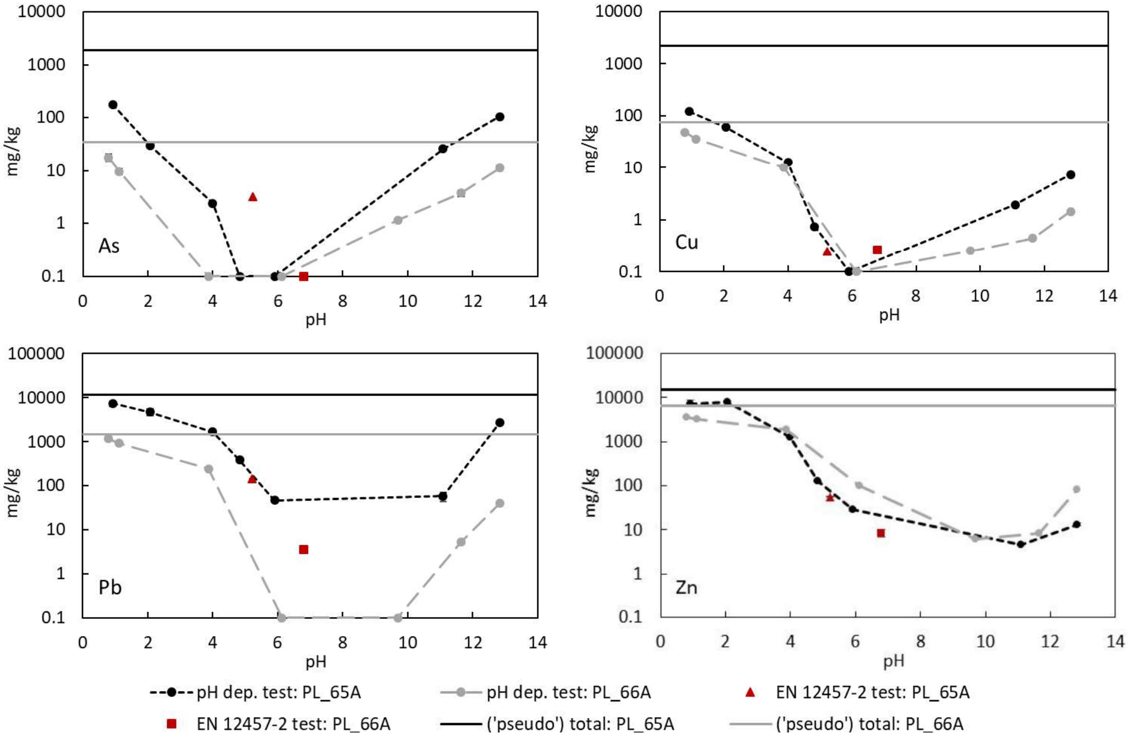

Figure 1: Mobility of As, Cu, Pb and Zn during the pH-dependent and EN 12457-2 leaching tests in comparison with the ('pseudo') total content (XRF for Pb and Zn, AR digestion for As and Cu).

Conclusion

Overall, the slag and pipe samples contained high levels of metal(loid)s (e.g., Pb, Zn) and the mobility of Pb exceeded the TCLP US-EPA threshold. The total content of As, Cu, Sb, Pb and Zn also exceeded the VLAREMA guide values;[5] therefore, it would not be possible to integrate the slag or pipe fragments into construction materials in Flanders. However, this characterisation can aid in the evaluation of other waste management scenarios such as the removal of contaminants through bioleaching.

References

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