

HEAVY METAL RELEASE FROM POROUS INORGANIC POLYMERS MADE FROM Fe-RICH SLAG: EFFECT OF Al CONTENT AND CURING TIME

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Introduction

Significantly increased CO₂ emissions and awareness of the limits of natural resources is driving research in producing traditional materials using alternative resources, developing fundamentally new materials and embracing new approaches. For the production of porous inorganic polymers (IP) using alkali activation, alternative resources are for example Fe-rich metallurgical residues. One of the ways in producing these IP is by mixing the solid precursors with an alkaline solution and a gas-releasing agent.^{1,2} One of these gas releasing agents can be a metal (Al, Si or Zn), which is oxidised and reduces water to produce H₂ gas. These porous IP can be used in various applications like adsorbents, filters, catalysts, acoustic and thermal insulators.¹ One drawback in using secondary resources is the heavy metal content and the possible release of these metals into the environment. In this study the use of a Cu slag was investigated as a potential precursor in producing Fe-rich porous IP. The heavy metal release was studied in function of the amount of foaming agent and sample age. In addition, the release of heavy metals was compared to European limits for landfilled waste.

Materials and methods

A finely milled Cu slag with a Blaine fineness of $5000 \pm 400 \text{ cm}^2/\text{g}$, according to EN 196-6n was used as precursor. The precursor was mixed with an activating solution using a hand mixer (Bosch MFQ4070) for 4 min using a L/S of 0.35. After mixing, 0.1 wt% and 0.2 wt% Al (1-5 μm , AEE) and 0.035 wt% sodium oleate was added and additionally mixed for 30 s. After mixing, these samples were cast in 10 cm wide cubes, sealed and cured for 24 h at 40°C. After curing, the samples were stored for 3 days at 25°C in sealed conditions. For the leaching, the samples were subsequently crushed at a particle size < 4 mm. The dry weight of the crushed samples was

determined at 105°C according to EN 12880.⁴ Leaching was studied by using a one stage batch test at a L/S of 10 L/kg according to BS EN 12457-4:2002.⁵ Samples were split and mixed for 24 h at 7 rpm with demineralised water (< 0.5 mS/m). Afterwards, the leachates were centrifuged for 15 min at 6000 rpm and filtrated through a 0.45 µm syringe filter. After filtration, the leachates were analysed using ICP-OES (Varian 720 ES) for the elements As, Cr, Cu, Mo, Ni, Se and Zn. This procedure was executed using triplicates for samples cured for 5 d and 90 d, denoted by the suffix 5 d and 90 d. The reduction potential (Eh) of the solutions was measured by using a SCE saturated calomel reference electrode (0.241 V). The Ati orion model 162 was used for conductivity measurements (Ec). The chemical composition of the Cu slag was characterised using a Bruker S8 Tiger–X-ray spectrometer (XRF). In addition, porous IP were characterised by means of X-ray computed tomography (CT) using a Bruker Skyscan 1172 in order to calculate the porosity of the samples.

Results and discussion

The chemical composition of the used Cu slag is shown in Table 1. The slag is mainly characterised by a high FeO and SiO₂ content. Metals present as main elements (> 0.1 wt%) are Cr, Zn and Cu, respectively.

Table 1: Chemical composition in wt% of the precursor (estimated relative error is 10%)

wt%	FeO	SiO ₂	Al ₂ O ₃	CaO	P ₂ O ₅	Na ₂ O	Cr ₂ O ₃	ZnO	MgO	CuO	Others
Cu-slag	40.9	32.3	11	3.9	2.2	2.0	1.6	1.5	1.4	0.3	2.8

CT images in Figure 1 show that the porosity increases from 55 to 80% by increasing the Al content from 0.1 to 0.2 wt%. The amount and size of the large pores increase by increasing the amount of foaming agent.

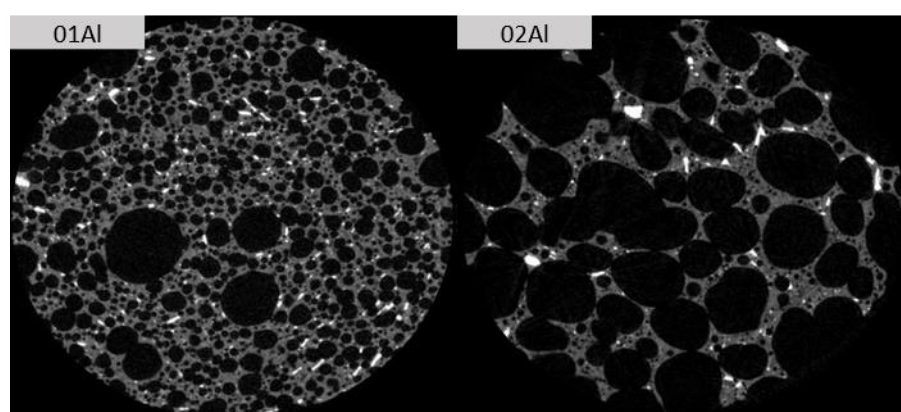


Figure 1: CT images of the 01Al and 02Al samples; the diameter is 8 mm

Table 2 shows the properties of the leachate after centrifugation and filtration. The data show that the leachate pH and Ec (mS/cm) are higher for the 02Al 5 d and 90 d

samples compared to the 01Al5d and 90 d. The higher release of ions in solution can be explained by the significant increase in porosity. It is also apparent that the pH and amount of released ions are reduced after 90 d. Furthermore, it is shown that the Al content does not significantly influence the reduction potential of the leachate. The leachate has a slightly positive oxidation potential, meaning that the chemical species present in the solution are able to oxidise.

Table 2: Properties measured of the material before leaching: Dry weight and the leachate (pH, Ec and Eh)

	pH	EC (mS/cm)	Eh (V)
01Al5d	11.72 ± 0.03	2.57 ± 0	0.283 ± 0.003
02Al5d	11.79 ± 0.01	2.98 ± 0.03	0.279 ± 0.004
01Al90d	11.09 ± 0.08	2.35 ± 0	-
02Al90d	11.13 ± 0.13	2.54 ± 0	-

The measured heavy metals from the leachate normalised on the dry weight (DW) are shown in Figure 2. The high leaching elements (> 10 mg/kg dry DW) are Mo and Zn. The release of Mo and Se exceeded the legislative limits for non-hazardous waste according to the European legislation for landfilled wastes.⁶ In addition, the data show that the release of heavy metals is similar after 90 d for all samples. Although an increased porosity is reflected in an increased release of ions in solution (Table 2), it does not automatically lead to an increase in released heavy metals. In fact, the elements As, Mo, Ni and Se decrease with increasing porosity after 5 d. However, after 90 d these elements (except Mo) are leaching to a similar degree with their low porosity counterpart.

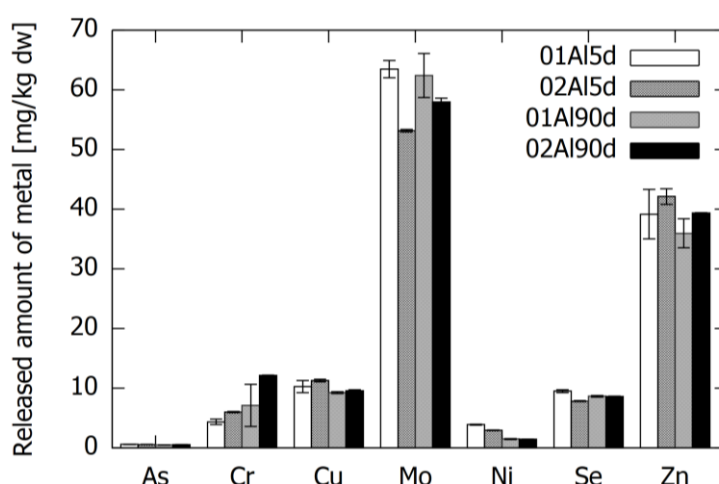


Figure 2: Released concentrations of different metals after leaching; Leachates were analysed using ICP-OES

The element Ni shows a decrease in concentration for 01Al and 02Al from 5 d to 90 d, in Figure 2, which could reveal its speciation. To explore this further for Ni, adsorption

to hydro ferrous oxide and hydroxide precipitation were modelled with Visual MINTEQ. Modelling shows that hydro ferrous oxide did not influence the immobilisation of Ni with pH, although Ni can be 100% adsorbed. However, Table 3 shows the calculated output if Ni is allowed to be present as Ni(OH)₂. If the pH declines during aging, the amount of Ni in solution due to Ni(OH)₂ dissolution decreases. It is hypothesised by these findings that Ni could be present as Ni(OH)₂ in the IP foams.

Table 3: Effect of the reactive Ni concentration and pH on the dissolution of Ni(OH)₂ using Visual MINTEQ; In all possible simulations a lower degree of Ni in solution is calculated

wt% reactive Ni in IP	0.1	0.01	0.001	0.0002
% in solution pH of 11.72	0.6	5.9	46.8	100.0
% in solution pH of 11.09	0.2	2.1	19.1	69.1

Conclusion

In this study, the heavy metal release from porous IP based on a Fe-rich Cu slag was investigated. By increasing the added Al foaming agent, a higher porosity was obtained. The increased porosity of these porous IP leads to an increased release of ions in solution. However, the release of heavy metals in solutions shows a more complex trend. As, Mo, Ni and Se decrease with increasing porosity after 5 d. After 90 days As, Cu, (Mo), Ni, Se and Zn leach at comparable levels regardless of the porosity in the sample. Furthermore, combination of experimental and modelled data suggests that Ni could be present as Ni(OH)₂, resulting in lower release with curing age due to a lower pH.

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