

LEACHING AND GEOCHEMICAL MODELLING OF A METALLURGICAL SLAG HEAP

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Introduction

Europe is full of metallurgical waste heaps which have been deposited in the past. Such heaps represent, on the one hand, a loss of valuable land and a potential threat to the environment, especially to underground water, but, on the other hand, they are a mixture of valuable resources which could be returned to the metallurgy sector, as well as to other sectors, predominantly the building sector. One of the main factors which hinder the use of these heaps for resource recovery purposes is insufficient knowledge about their environmental properties.

In this study, the metallurgical slag heap in the Javornik area, which is situated just outside the steelmaking town of Jesenice, in north-west Slovenia, was investigated. Approximately 400 000 tons of metallurgical wastes have been deposited there. They consist mainly of slags from carbon and stainless steel production (72.8% of the disposed material), EAF and VOD dust (18.8% of the disposed material), refractory materials (8% of the disposed material), and other metallurgical wastes. The model approach was used, in which a chemical speciation fingerprint (CSF) is developed from pH dependent leaching data, and is then used as a basis for the subsequent reactive transport modelling of laboratory tests and the evaluation of field measurements in the groundwater.

Materials

Sampling of samples from the heap

Sampling was carried out on 11 locations on the metallurgical heap, 5 samples sampled at a depth of around 6 m and 6 samples sampled at a depth of around 20-30 cm below the landfill surface. A composite sample, consisting of a mixture of 10 individual samples, was subjected to a laboratory characterisation leaching test (SIST EN

14429:2015; d < 1 mm), whereas the individual samples were subjected to single step batch leaching tests (SIST EN 12457-4, 2002; d < 10 mm).

Groundwater monitoring (years 2011-2015)

GW monitoring was carried out twice annually (in spring and autumn), starting in year 2011, on 7 piezometers (P1-P7). The piezometers P1 and P2 were located outside the area covered by the metallurgical heap, and thus represented reference piezometers.

Data comparison and geochemical modelling

The database/expert system LeachXS™ was used for the management of data, *i.e.* the pH dependent leaching data, the batch data, the GW data, and data for the visualisation of the calculated and measured results¹. Chemical speciation of the pH dependent data was performed using the ORCHESTRA modelling framework² embedded in LeachXS™. The results of the modelling were based on multi-element modelling, taking into the account all (33) measured elements. Detailed information about the geochemical modelling is given in van der Sloot and Kosson³ and Loncnar *et al.*⁴

Results and Discussion

The total chemical composition of the composite sample is given in Table 1.

Table 1: Total chemical composition of the composite sample

wt%	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe _{tot}	Cr ₂ O ₃	MnO	TiO ₂	S	C	F
	26.59	14.68	6.93	8.39	16.0	2.20	3.67	0.409	0.26	1.84	0.49

In Figure 1, the model results for the composite landfill sample (just selected elements) are given in comparison with the original pH dependence data. In all cases, the test data are given for comparison with the modelling results at both L/S = 10 mL/g and L/S = 0.3 mL/g (all the other parameters remaining the same) in order to estimate the accuracy of the model by means of the given minerals and the sorption parameter selection for both a wide pH range as well as a wide L/S range³⁻⁵. In the case of many elements (Ca, Si, Al, Mg, Fe, Mn, Ni, Pb, Zn) the measured concentrations at L/S = 10 mL/g corresponded well with the model simulations. Overall the results of the modelling indicate that the solubility control of solution concentrations as described by the assemblage of minerals and sorptive phases provides a reasonable description of the metallurgical heap over a wide pH range under mildly reducing conditions, which are the conditions for the laboratory handled landfill samples.

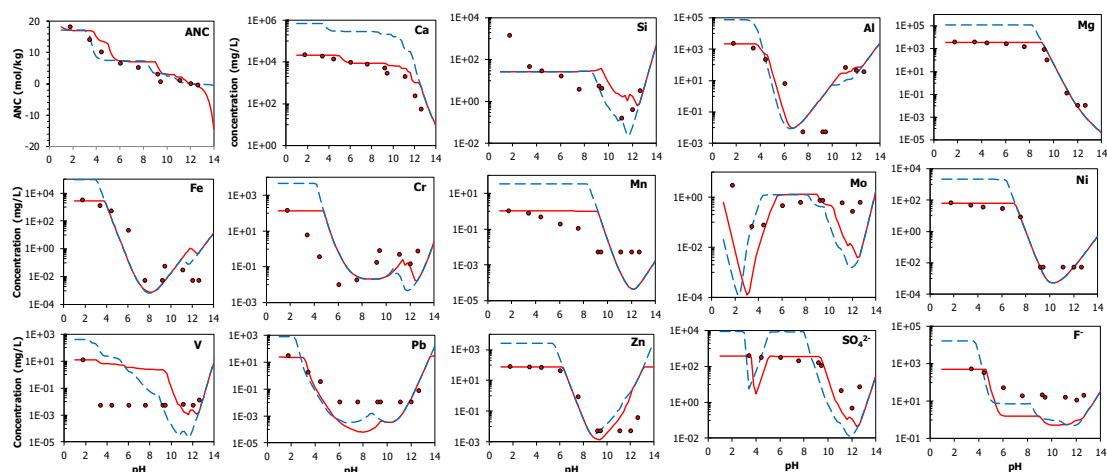


Figure 1: Measured and predicted leaching behaviour of major, minor and trace elements as a function of pH. Solid circles: the pH dependence test; lines: prediction at L/S = 10 mL/g (red/full line), prediction at L/S = 0.3 mL/g (blue/dashed)

The leaching curves as described earlier are the product of complex chemical processes in both the leachate solution and the solid phase of the waste material³⁻⁵. In Figure 2, the partitioning of Ca and Cr in the liquid and solid phases is highlighted (presented as a function of pH). This figure illustrates that different processes control the Ca and Cr leaching at different pH values.

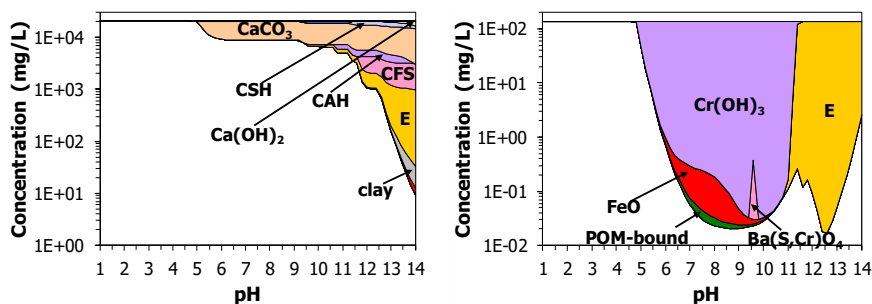


Figure 2: Partitioning of the Ca and Cr over different chemical phases as obtained from the modelling (Key: E = ettringite, CFS = $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, CAH = $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, CSH = jennite)

In Figure 3, the results of the batch tests of the individual samples and the GW monitoring data are placed in context with the pH dependent leaching data of the composite landfill sample. In the case of the majority of the investigated elements, the results of the batch test plot are along with the pH dependent leaching curve for the composite sample, which indicates that the same solubility controlling phases control leachability. In the case of Ca, a slightly lower Ca concentration of some individual samples was measured, which indicates carbonation of some spot samples more than others. The main differences between the results of the batch tests and those based on pH dependence tests, on the one hand, and the GW data, on the other hand, is the contact with the landfill material, which is absent in the case of the GW monitoring. In the case of some elements (Ca, Mg, Mo) the GW data show lower measured concentrations. However, in the case of some elements (Ni, Pb, partly Zn and Mn) the

GW data fall right on the pH dependent curve of the composite sample. As can be seen from Figure 3, there was not a big difference in the measured concentrations between the reference piezometers (marked by blue circles) and the piezometers (marked by black squares) on the landfill area, indicating limited influence of the landfill area on the quality of the GW.

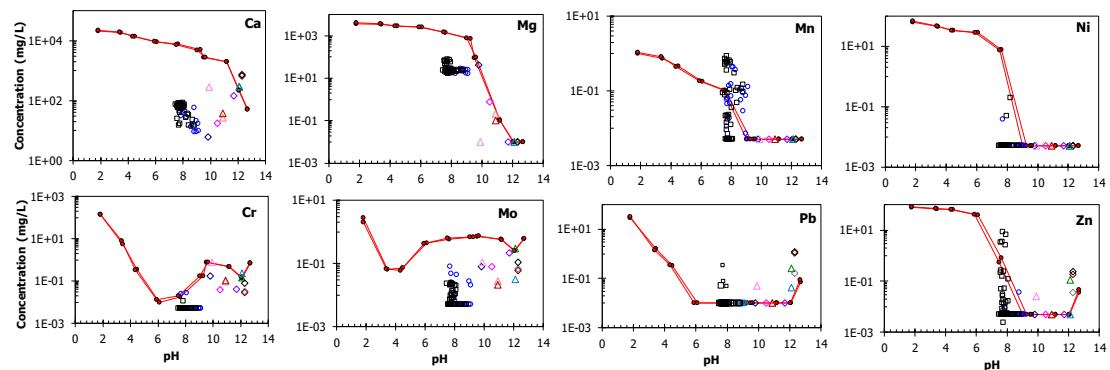


Figure 3: Comparison of the pH dependent leaching of the landfill sample (marked by dots) with the GW monitoring (blue circles = reference piezometers; black squares = P3-P7) and the individual samples from the metallurgical heap (various symbols; batch at L/S = 10 mL/g)

Conclusions

In this study characterisation leaching tests were combined with chemical speciation modelling. This approach provides benefits for understanding the observed leaching behaviour, which is needed for decision about future management of waste heap. It can thus form the basis for the projection of the long-term leachate quality of the landfill under changing exposure conditions such as carbonation and oxidation. Bringing together data from various laboratory leaching tests, field data, and modelling results, provides a much more complete picture of the release controlling factors in landfill than can be provided by any single one of these data sources.

References

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