

**LANDFILLED FINE GRAINED MIXED INDUSTRIAL WASTE: METAL RECOVERY**

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**Abstract**

This study describes the recovery and removal of heavy metals through washing from fine grained materials, recovered from mixed industrial waste (IW) from a landfill site. During this first screening, solutions of different concentrations of three inorganic acids (H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub>) were tested as possible lixivants. It has been shown that the extraction of most heavy metals should take place at a well defined pH range in order to avoid dissolution of the matrix material (consisting mainly of Si, Fe, Al, Ca). Furthermore, the buffering effect of the studied material was shown to be stronger for smaller particle sizes, due to larger specific contact surfaces with the lixivants and differences in composition.

**Keywords:** recovery, enhanced landfill mining, hydrometallurgy, waste material fines

**1 Introduction**

„Enhanced Landfill Mining” (ELFM) aims to valorise waste materials excavated from landfills as both materials (Waste – to – Material, WtM) and energy (Waste – to – Energy, WtE), while respecting stringent ecological and social criteria [1]. Thus, the treatment plant should be able to recover high quality waste fuel and materials (*e.g.* ferrous and non-ferrous metals) [2]. Furthermore, particle size is a key factor for optimal separation of materials and below a certain cut off size conventional waste separation techniques cannot be applied. Generally, landfill sites contain considerable amounts of fines material, and in the specific case of the landfill site studied here, stored municipal solid waste (MSW) contains on average 43 wt. % fines < 10 mm and industrial waste (IW) 62 wt. % fines < 10 mm [3,4]. Moreover, the reuse of such fines fraction as a replacement for soil or as a construction sand outside the landfill site is limited due to its heterogeneous nature and elevated levels of organic and inorganic contaminants [3]. Therefore, further physicochemical treatment of the generated fines is essential within the ELFM concept. So far, few reports exist on the treatment of the fines fraction [5]. Fines of landfilled IW can contain high metal concentrations [4]. The presence of such metals poses an environmental hazard if not stored under controlled conditions whereby leaching of these contaminants to soil and groundwater is avoided. In some cases, the concentrations of metals, which are also a commodity, can be at similar levels than those in natural ores (**Table 1**). Therefore, hydrometallurgical treatment to remove metal contaminants and potentially recover metals is a possibility that needs to be studied.

**Table 1** Commodity metal content of IW fines, recovered from a landfill site, with respect to their primary ore grading (in mass %)

Element composition	Average ore grade <sup>a</sup>	Average IW fines <sup>b</sup>
Chromium	5.0 %	0.02 – 1.1 %
Copper	0.5 – 2.8 %	0.04 – 1.0 %
Lead	5.0 %	0.05 – 0.56 %
Zinc	2.9 – 9.2 %	0.14 – 1.7 %

<sup>a</sup> USGS Minerals year book, <http://minerals.usgs.gov/minerals/pubs/myb.html>;

<sup>b</sup> Internal VITO information

Hydrometallurgical processes are generally considered to be more ecofriendly and to produce residues suitable for safe disposal as desired metals can be selectively dissolved in suitable lixiviants leaving other impurities in the residue. Several studies report on the leaching of waste materials with the aim to remove and/or recover heavy metals. Nagib et al. investigated the recovery of lead and zinc from fly ash generated from municipal waste incineration plants [6]. The removal of these heavy metals was carried out by acid leaching using different acids such as sulfuric, hydrochloric and acetic acid or by alkaline leaching. It was found that sulfuric acid leaching is effective where most of Zn was dissolved and also hydrochloric or acetic acid leaching effectively dissolved most of Pb and Zn. Jha et al. reviewed the hydrometallurgical recovery of Zn from several zinc containing industrial wastes, such as zinc ash, zinc dross, flue dusts of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge etc. [7]. Different lixiviants such as sulfuric acid, hydrochloric acid, ammoniacal solution, sodium hydroxide and organic acids have been used on a bench scale or indeed on pilot or commercial scale. Similar leaching studies were performed on thermal power plant solid wastes [8], in order to remove several elements such as Al, Fe, V, Ni, Pb and Zn. Such recovery can save metal resources and simultaneously protect the environment by allowing for the utilization of the washed thermal power plant solid wastes. Since, after metal recovery, the residue could be a raw material for new or traditional composites suitable for the building industry or road constructions. Meawad et al. found that recovery of metals with mineral acids is the most promising way for treatment of the thermal power plant residues and transforming them to alternative raw materials [8]. Here, the main driving parameters for efficient metal recovery are the concentration and the liquid to solid ratio (L/S) of the acid used, but other parameters also have to be taken into account.

In the present study, the leaching behavior of fines from mixed industrial waste from a landfill site is described, using different acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl). Part of the challenge in this study is to take account of the very heterogeneous composition that landfilled mixed industrial wastes can have with regard to single industrial waste materials. Therefore, a robust hydrometallurgical treatment is needed, which can selectively recover contaminants and valuable metals and produce a residue with improved environmental properties, so that it can be re-used as a secondary raw material. Here, a first screening of the metal leaching behavior of different lixiviants on a mixed industrial waste fines (< 10 mm) sample recovered from a landfill site has been examined.

## 2 Experimental materials and methods

### 2.1 Samples and materials

Representative samples from municipal solid waste and industrial waste from a landfill site were fully characterized and studied, these results are presented elsewhere [2, 4]. For this study, a

representative sample from mixed industrial waste (IW), containing high contamination levels of heavy metals, was selected and collected by excavation. The sample was consecutively dried and sieved at 10 mm to obtain the fines fraction. This fines sample was further sieved in separate particle size fractions (**Table 2**) of which the fractions 125 – 500  $\mu\text{m}$  and < 125  $\mu\text{m}$  were selected to perform leaching experiments.

**Table 2** Particle size distribution of a fines fraction (< 10 mm) from a landfilled mixed IW

Particle size	4 – 10 mm	2 – 4 mm	0.5 – 2 mm	125 – 500 $\mu\text{m}$	< 125 $\mu\text{m}$
Fraction	18 %	10 %	27 %	35 %	10 %

## 2.2 Leaching experiments

All two particle size fractions of the IW fines sample were subjected to a leaching experiment. Several solutions with different concentrations of hydrochloric, sulfuric and nitric acid were used as lixiviant (**Table 3**). Therefore, each sample was brought in contact with various lixiviants at a liquid to solid ratio (L/S) of 10 and the suspension was stirred for 3 hours at room temperature. After measuring the pH, the solids were filtered off and the eluate was collected.

**Table 3** Concentrations of the used lixiviants

Leaching liquor	Tested concentrations
HCl	0.01 N, 0.1 N, 0.24 N, 0.97 N, 1 N, 6.13 N
HNO <sub>3</sub>	0.01 N, 0.1 N, 0.29 N, 1 N, 1.15 N
H <sub>2</sub> SO <sub>4</sub>	0.01 N, 0.1 N, 0.72 N, 1 N, 2.88 N, 5.63 N

## 2.3 Quantitative analyses

In order to determine the total concentration of the solid materials, each particle size fraction was subjected to a total microwave digestion conform the Flemish method CMA/2/II/A.3 from the compendium for sampling and analyses (CMA) [9].

Total concentrations of the digestion liquid of the particle size fractions; as well as those of the eluates were determined by ICP – AES conform the Flemish CMA/2/I/B.1 [9].

To determine the extracted amount of each element, the concentration of the element in the eluate was compared with the concentration in the original material. These extraction levels, expressed in %, are reported.

## 3 Results and discussion

The investigated starting material for the leaching experiments was characterized. The total concentration of the two particle size fractions of the IW fines sample, as determined by ICP – AES, is shown in **Table 4**. The concentrations are compared with the total concentration non – binding limit (guide) values for use as a construction material of the Flemish “Materials Decree” legislation VLAREMA [10].

The investigated fines sample is mainly composed of Al, Ca, Fe and Si. Some differences in composition are observed depending on the particle size. The larger particle size fraction contains more Si; while Fe, Ca and Al are more abundant in the smaller particle size fraction. The IW fines sample holds a large amount of heavy metals, of which many exceed the guide values of the VLAREMA legislation for use in or as a construction material [10]. The fraction with particle size < 125  $\mu\text{m}$  contains the largest amounts of the heavy metals Zn, Ni, Pb, Cr and

Cu. It is noteworthy that the samples contain a significant amount of organic matter, expressed by the total organic carbon concentration, which lies above 2 wt. % for both samples (**Table 4**).

**Table 4** Total concentration of the investigated particle size fractions of the IW fines sample

Elemental composition (mg/kg)	125 – 500 µm	< 125 µm	VLAREMA Appendix 2.3.2.B
Bromide	< 20	34	
Chloride	770	2100	
Fluoride	> 1300	> 4700	
Al	22000	39800	
Sb	30	<b>59</b>	(50)*
As	12	25	250
Ba	948	1090	(7500)*
Cd	<b>13</b>	<b>48</b>	10
Ca	21900	72500	
Cr	1140	<b>3590</b>	1250
Co	101	303	
Fe	47100	117000	
K	8910	8820	
Cu	<b>512</b>	<b>1640</b>	375
Hg	2.2	0.95	5
Pb	<b>1390</b>	<b>3700</b>	1250
Mg	3110	7120	
Mn	499	1280	
Mo	63	<b>192</b>	(125)*
Na	3930	6610	
Ni	<b>879</b>	<b>2740</b>	250
Se	< 5	< 5	(50)*
Si	148000	89600	
Sn	47	203	
Ti	1670	3330	
V	27	62	
Zn	<b>4130</b>	<b>12100</b>	1250
TOC (wt%)	2.1	5.8	

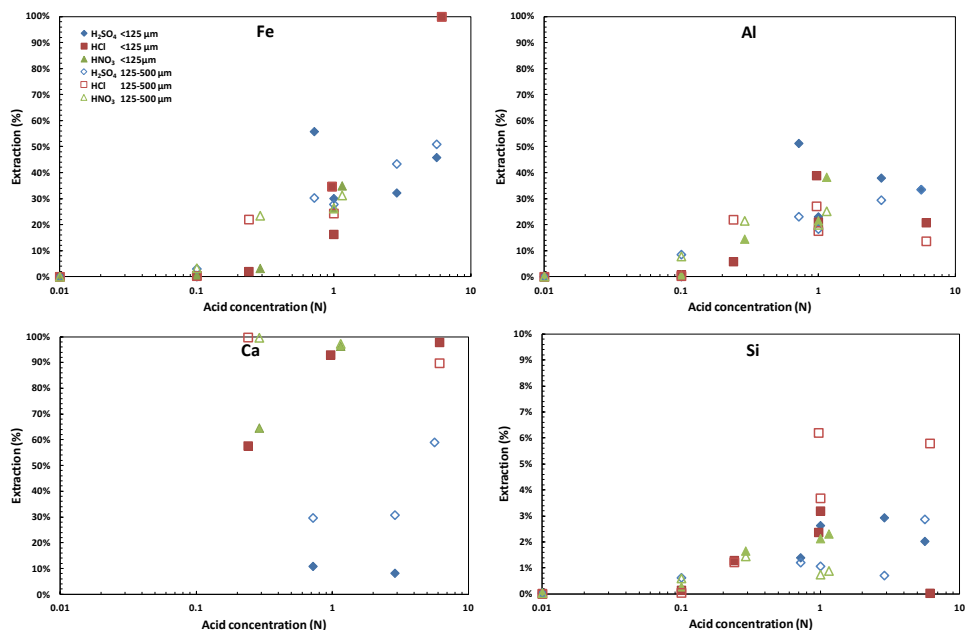
Figures in bold exceed the VLAREMA guide values for use in or as a construction material

\*The values between parentheses are not required in the VLAREMA legislation, but are considered accordingly. Therefore, these values are “test values”.

In order to investigate the (selective) removal of the contaminants present in the IW fines sample, leaching experiments were performed. Strong inorganic acids in varying concentrations were used as leaching liquors in order to screen their efficiency to leach mixed IW fines from a landfill site.

The matrix elements of the fines Al, Ca, Fe and Si, should ideally not dissolve in the leaching solution, in order to selectively recover/remove contaminants. Thereby it becomes possible to potentially reuse the matrix material and to recover the metals in solution more easily. The leaching results of Fe, Al, Ca and Si for the particle size fractions < 125 µm and 125 – 500 µm are shown in **Fig. 1**. The solubility of Fe increases with higher acid concentrations with no clear

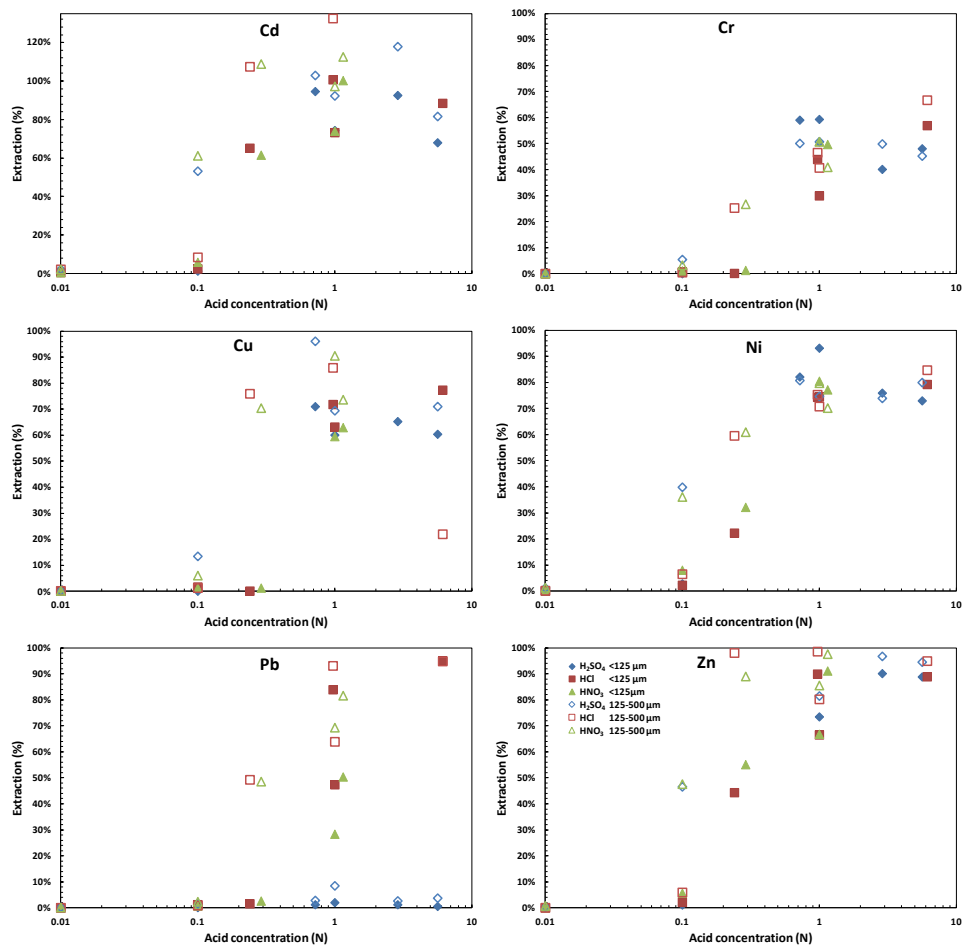
preference for any of the investigated inorganic acids. Low acid concentrations do not dissolve Fe. Similar results are obtained for Al. Ca is almost completely dissolved in HCl and HNO<sub>3</sub>, while (low) concentrations of H<sub>2</sub>SO<sub>4</sub> only dissolve around 10 – 30 % of the Ca due to the low solubility of CaSO<sub>4</sub>. The solubility of silica and silicates is known to be low in most acid environments and less than 10 % of Si is dissolved from the solid into solution. For the elements shown, small variations in leachability can be observed depending on the particle size fraction. The leaching of Fe is mostly larger for the fractions with a larger particle size, while Al leaches the most for the smallest particle size fraction. For Ca, the leaching of the particle size fractions is comparable, except when using H<sub>2</sub>SO<sub>4</sub> as lixiviant some variations can be seen.



**Fig. 1** The leaching results of Fe, Al, Ca and Si for the particle size fractions < 125 μm and 125 – 500 μm with the acids H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub>

**Fig. 2** shows the leaching results for the particle size fractions < 125 μm and 125 – 500 μm of Cd, Cr, Cu, Ni, Pb and Zn; the most abundant heavy metals present in the IW fines sample. The leaching of Cd, Ni and Zn is very high with all acids and almost independent of the acid concentration, except for low acid concentrations which do not dissolve these elements. The leaching of Pb increases with higher concentrations of HNO<sub>3</sub> or HCl, while H<sub>2</sub>SO<sub>4</sub> does not dissolve Pb but forms the insoluble PbSO<sub>4</sub>. Cu is leached by all acids, with no clear preference for any acid. High concentrations of H<sub>2</sub>SO<sub>4</sub> and HCl however slightly diminish the solubility. The leaching of Cr is generally lower compared to the other metals and reaches a maximum solubility of around 60 %.

Based on the results mentioned above, it can be concluded that, for most elements, the solubility is independent on the type of acid used. However, it is known that the leaching behaviour of heavy metals, and elements in general, is strongly influenced by the pH of the eluate [11, 12]. Therefore, the leaching results are displayed as a function of the measured pH of the leachates at the end of each leaching experiment. These end pHs are displayed in **Table 5**.

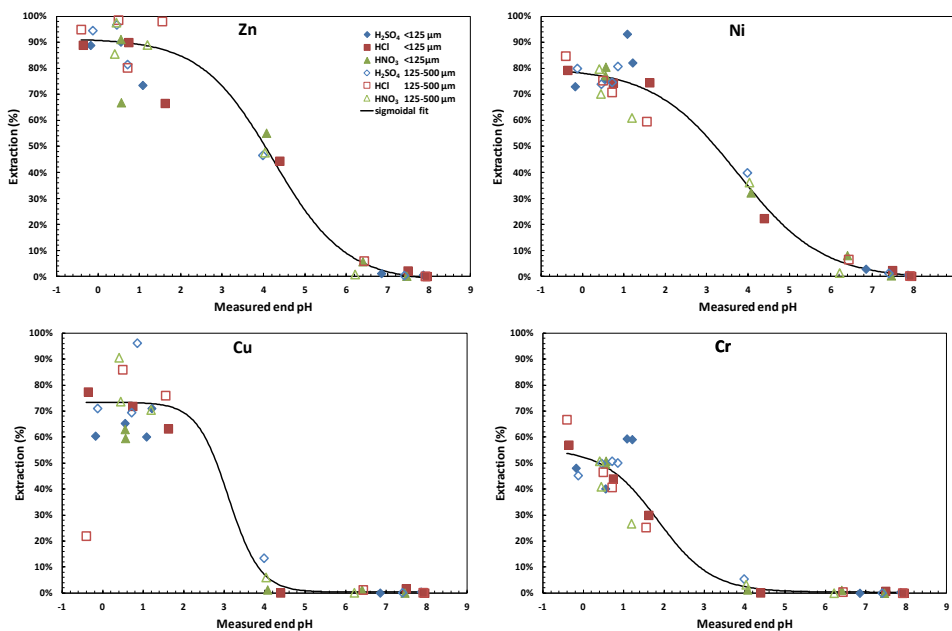


**Fig. 2** The leaching results of Cd, Cr, Cu, Ni, Pb and Zn for the particle size fractions 125 – 500  $\mu\text{m}$  and 125 – 500  $\mu\text{m}$  with the acids

In **Fig. 3** the leaching results of Zn, Ni, Cu and Cr are shown as a function of the measured end pH. A clear trend can be seen for all elements: a lower pH results in a much higher solubility, regardless of the acid used, with an exception for lead and calcium. As a guide for the eye, a sigmoidal curve (Boltzmann) fits well to the observed leaching behaviour as function of the measured end pH. This figure demonstrates that the solubility of the heavy metals is, in most cases, not determined by the specific acid, but mainly depends on the pH. **Fig. 4** shows the sigmoidal curves which were fitted to the measured data for the matrix elements Fe, Al and Si, as well as for the heavy metals which exceeded in most cases the VLAREMA guide value for total concentration (see **Table 4**). The leaching behaviour for each element in the investigated pHs of the eluates measured at the end of each leaching experiment IW fines as a function of end pH is slightly, or significantly, different. Such differences could allow to chose an optimal pH (or acid concentration) for selective metal recovery or removal at which the matrix material dissolves minimally. In fact, in the pH range 4 – 5 most heavy metals leach apparently at a higher rate than Si, Al and Fe, which scarcely dissolve. While the Ca leachability can be kept low by using sulphuric acid as leachate. Furthermore, clearly the heavy metals dissolve

**Table 5** The end pHs of the eluates for the different particle size fractions

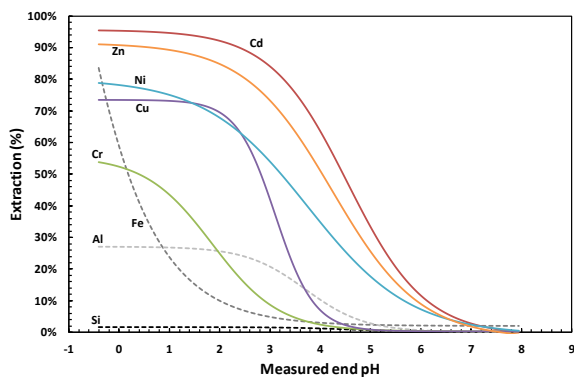
Acid	Acid concentration (N)	pH (at end of reaction)	
		< 125 $\mu\text{m}$	125 – 500 $\mu\text{m}$
$\text{H}_2\text{SO}_4$	0.01	7.86	7.4
	0.10	6.85	3.98
	0.72	1.21	0.85
	1.00	1.08	0.71
	2.88	0.55	0.45
	5.63	-0.18	-0.13
$\text{HCl}$	0.01	7.95	7.91
	0.10	7.49	6.43
	0.24	4.39	1.55
	0.97	0.74	0.49
	1.00	1.62	0.71
	6.13	-0.36	-0.41
$\text{HNO}_3$	0.01	7.46	6.21
	0.10	6.4	4.03
	0.29	4.07	1.19
	1.15	0.55	0.44

**Fig. 3** The leaching results of Zn, Ni, Cu and Cr as a function of the measured end pH

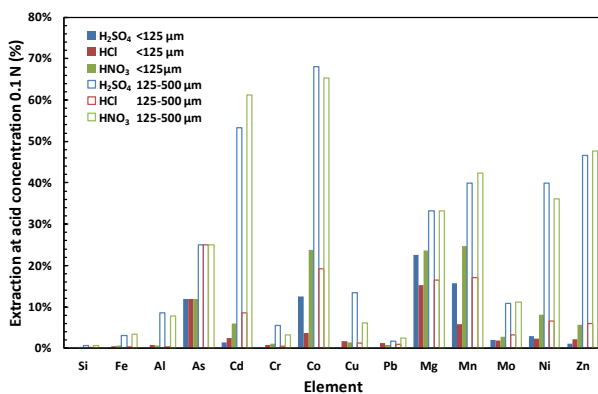
independently of the matrix elements as a function of pH. Such behaviour indicates that heavy metals are probably not embedded in the matrix' crystal lattice, but are adsorbed or weakly associated to the surface of the matrix or are present in or as separate crystal phases.

The leaching tests at an acid concentration of 0.1 N give an end pH which is close to such pH region of interest. To this regard, **Fig. 5** illustrates the extraction of several elements in the acidic

leaching solutions with a concentration of 0.1 N. At this concentration, the matrix elements (Fe, Al, Si) show very low solubilities, while some heavy metals, including Zn but also Cd, Co, Mn and Ni, still dissolve quite well.



**Fig. 4** The fitted sigmoidal (Boltzmann) curves of investigated elements expressing the extraction of the elements as a function of measured end pH



**Fig. 5** The total extraction of investigated elements from IW fines fraction 125 – 500 µm and < 125 µm by means of 0.1 N acid solutions

The figure also displays the above mentioned pH effects. For most elements, the solubility in 0.1 N HCl is much lower compared to the other leaching solutions. This decrease in solubility is caused by the higher (end) pH of the HCl solution compared to the other acidic solutions. Additionally, the figure shows a remarkable difference in solubility between the two particle size fractions. The particle size fraction 125 – 500 µm gives rise to much higher solubilities for all elements, up to ten times higher. Again, this can be explained by a difference in end pH of the leachates. **Table 5** shows the end pHs of the eluates for the different particle size fractions. For the smallest particle size fraction (< 125 µm), the highest end pHs are measured and consequently the lowest solubilities are observed. These higher pHs can probably be caused by two effects: (i) the fact that the specific exposed area of the smaller particles is much larger, and (ii) the difference in chemical composition between the two tested samples. The Al, Ca and Fe concentration of fraction < 125 µm is considerably higher than fraction 125 – 500 µm, where the



SiO<sub>2</sub> fraction is more dominant. Both properties influence the buffering capacity of the materials, which is highest for the fraction < 125 µm.

#### 4 Conclusion

A mixed IW fines sample was recovered from a landfill site and subjected to leaching experiments with three inorganic acids (H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub>). The aim of this study was a first screening for efficient leachate solutions to remove heavy metal contaminants from these fines.

It can be concluded that all types of acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl) are able to extract the most abundant heavy metals (Cd, Cr, Cu, Ni, Pb, Zn), reaching extraction rates of up to 100% for Zn, Pb and Cu at high acid concentration. Furthermore, the matrix elements, Al, Ca and Fe also dissolve considerably at high acid concentrations, which is unwanted. It has been shown that in most cases the solubility of elements is almost, with the exception of Ca and Pb, independent of the type of acid used. However, a connection between the extraction and the pH reached upon contacting the acid solution with the material can be observed. In fact, for the IW fines in a pH region of 4 – 5 most heavy metals will dissolve significantly, while the matrix materials Fe, Si and Al remain in the residue. If need be, the dissolution of Ca can be highly reduced by using H<sub>2</sub>SO<sub>4</sub> solutions. Furthermore, it was observed that the end pH of leaching experiments of particle size fraction 125 – 500 µm was lower than that of fraction <125 µm. It is believed that the buffering effect of the material on the solution is enhanced by the higher specific surface of the smaller particle sizes and a different chemical composition of the matrix materials in the fractions. Hence, these parameters influence the extraction of elements.

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