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Waste Materials in Construction: Putting Theory into Practice

Application of computer modelling to predict the leaching behaviour of heavy metals from MSWI fly ash and comparison with a sequential extraction method

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Abstract:

Combustion residues in general and MSWI fly ashes in particular form a major environmental problem as they are polluted with heavy metals. The heavy metals can be removed from the fly ash by leaching with e.g. the acid waste water obtained in the wet scrubber of the air pollution control system. The remaining fly ash can be landfilled or valorised e.g a. a construction material.
An understanding of the leaching reactions and of the factors that influence leaching is very important for the treatment of fly ash. Therefore the compositionof the fly ash was determined and the influence of pH was examined. Also a sequential extraction procedure was performed on the fly ash. In this paper, the results of experimental leaching tests of fly ash are compared with computer calculations of the thermodynamic equilibrium of the leaching solution - fly ash system. The computer program MINTEQA2, used for this purpose, allows to predict the metal concentrations in the leaching solution, the minerals that precipitate, and the pH of the leaching solution at equilibrium. Comparison of the experimental and calculated leaching data with the results from the sequential extraction procedure allowed to verify the accuracy of the sequential extraction procedure.

1. Introduction

Yearly around 2.8 million tonnes of municipal waste is generated in Flanders, Belgium. From this total amount of MSWI 30% is selectively collected; 43% of the rest fraction is processed in incinerators and 57% is landfilled (*1*). Incineration of one tonne of municipal waste leads to the formation of 10 to 50 kg of fly ash depending on the type of incinerator. The Combustion residues in general, and fly ash in particular, form a major environmental problem. Due to the fact that the legal standards for the emission of contaminants are getting more stringent the air pollution control system of incinerators must be improved, resulting in an increase of the amount of residues. The fly ash is contaminated with heavy metals and PCDD/PCDF. It must be considered as hazardous according to the Flemish environmental legislation (*2*).

Generally, dust particles are removed from the incinerator flue gas by means of an electrostatic precipitator. Wet scrubbers remove in a first stage HCl and HF from the flue gas and in a second stage SO_2. The first stage produces an acid waste water mainly containing HCl and to a lesser extent HF. This acid solution can be used to leach the fly ash, in order to remove part of the heavy metals, as in the 3R process developed in the Karlsruhe Nuclear Research Centre (*3*).

Part of the research in this paper is along similar lines as the work of Comans et al. (*6*) and Eighmy et al. (*7*). In the latter work, the emphasis was, however, on the spectroscopic characterisation of fly ashes, whereas one of the main subjects of the present paper concerns computer predictions and calculations that will be compared with experimental results in order to gain a better understanding of the leaching process. Theoretical calculations were performed using the simulation program MINTEQA2. These results were also compared with the results of a sequential extraction method in order to test the accuracy of this method.

2. Materials and methods

2.1 Definitions

The leachability of the fly ash can be influenced by several parameters. Two of these parameters are acid dose (mol/kg) and L/S-ratio (l/kg).
The parameter AD, the acid dose, is defined as:

$$AD = \frac{amount\ of\ H^+ - ions\ added}{mass\ of\ fly\ ash} \quad (\frac{mol}{kg})$$

The L/S-ratio is defined as:

$$L/S = \frac{volume\ of\ leaching\ solution}{mass\ of\ fly\ ash} \quad (\frac{l}{kg})$$

2.2 Material and characterisation

The fly ash was obtained from the 'Houthalen Waste Incineration Facility" (Houthalen, Belgium), a municipal solid waste facility with an annual capacity of 98 000 ton. The fly ash was collected by a classical electrofilter.
The fly ash was totally dissolved and the concentrations were measured by ICP-MS (Inductively Coupled Plasma Mass Spectrometry). This method gives the total composition of the fly ash. To obtain an approximation of the leachable fraction of the fly ash, a leaching test was conducted in a highly acid environment (18 mole HCl per kg of fly ash), and the metal concentrations in the leachate were measured.
The total amount of CO_3^{2-} bound in the fly ash was determined by leaching the fly ash in an acid environment (1M HCl-solution), whereby the carbonate is converted into CO_2. Nitrogen was blown through the leaching solution to remove the CO_2, which was trapped and neutralised in a 1 M NaOH solution. The carbonate concentration was then determined by titration.
The phosphate concentration in the leaching solution was determined using the *Molybdene-blue* spectrofotometric method (*8*).
The total amount of chloride (the sum of the amount of chloride ions from the HCl leaching solution, and the amount that is leached from the fly ash) was determined by titration with $AgNO_3$.
The particle size distribution was determined with a system of sieves with variable sieve size (0, 45, 63, 100, 200, 300, 400 and 500 µm diameter).
With a sequential extraction procedure the total amount of a metal in the fly ash is divided in different fractions. To this end the fly ash is sequentially leached with different solutions, each selective for a given fraction. The procedure is based upon that of Kirby and Rimstidt *(11)*. *Table 1* gives the different fractions with their specific leaching solutions. In each fraction a L/S-ratio of 200 l/kg is used.

	Fraction	Leaching solution
1	water soluble	distilled water
2	acid soluble	0.5M CH_3COOH
3	oxidizable	0.1M $Na_4P_2O_7$
4	easily reducible	0.175M $(NH_3)_2C_2O_4$ + 0.1M $H_2C_2O_4$
5	moderately reducible	0.1M Na_2EDTA + 0.3M $NH_2OH.HCl$
6	residue	disolution with $HClO_4$ and HF

Table 1: Sequential extraction procedure (11)

The oxidizable fraction is the fraction of metals that is organically bound or occurs as sulfide salt. The reducible fractions consist mainly of Fe- and Mn-oxides which may contain other metals. The easily reducible fraction consists of amorphous oxides and the moderately reducible fraction mainly of crystalline oxides. The metals in the residue are encapsulated in the silicate matrix of the fly ash.

2.3 Leaching experiments

The acid waste water from the wet scrubber may in practice be used as leaching solution. The solution contains mainly HCl and to a lesser extent HF and has a pH around 0.5. During the research pure HCl solutions with different concentrations were used *(4,5)*.
The fly ash and the leaching solution were brought in contact by mechanical shaking for a period of 3 hours. Then, the final pH was measured and the solution was filtered over a glass microfibre filter. Metal concentrations in solution were measured by ICP-MS.
The influence of AD was investigated by using different acid concentrations, resulting in an AD ranging from -2 mol/kg to 18 mol/kg, giving a good view of the evolution of pH and metal concentrations as a function of AD. Negative values of AD were obtained by replacing the HCl-solution with a NaOH-solution.
The leaching experiments were performed with a L/S of 10 l/kg.

2.4 The computer program MINTEQA2

MINTEQA2 version 3.11 (*9*, *10*) is a geochemical model capable of calculating equilibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation states, and precipitation-dissolution of metals. MINTEQA2 was used to determine the equilibrium concentrations in the leaching solution as a function of pH. In a second stage, the influence of certain components of the fly ash on the equilibrium pH of the solution was examined.
Input concentrations for each component were based on determined values for the mass fraction of every component in the leachable fraction of the fly ash, as presented in the Results section (with L/S = 10 l/kg). Contrary to the work of Eighmy et al. (*7*), components were not entered as finite solids but as components in solution.

3. Results

3.1 Characterisation of the fly ash

The total composition and the composition of the leachable fraction of the fly is presented in *table 2*. Major constituents of the fly ash are Al, Ca, Na and K. The other metals have lower concentrations. The rest fraction (about 30 %) consists mainly of silicate compounds (*7*, *11*, *12*).

Component	g/kg fly ash leachable fraction	g/kg fly ash total dissolution	Component	g/kg fly ash leachable fraction	g/kg fly ash total dissolution
Ag	< 0.1	< 0.1	Hg	< 0.1	0.3
Al	73.0	107.0	K	38.7	65.0
Ca	204.2	229.0	Mg	7.9	16.7
Cd	0.3	0.3	Mn	0.7	1.2
Cl		54.0	Na	46.4	54.0
Co	< 0.1		Ni	0.1	0.2
CO_3		22.1	Pb	2.9	3.4
Cr	0.1	0.6	PO_4		27.0
Cu	0.5	0.8	Sn	0.1	0.9
F		0.6	SO_4		58.0
Fe	6.3	16.9	Zn	9.4	12.0

Table 2: Composition of the fly ash

The particle size distribution indicates that the particles are mostly smaller than 200 µm in diameter. Only 7 % is larger than 200 µm. The largest fraction is retained on the sieve corresponding to the 45-63 µm fraction. This particle size distribution is similar to that of other fly ashes (*13*).

3.2 Sequential extraction

Table 3 gives the results for the sequential extraction procedure for the metals Al, Ca, Cu, Zn, Cd and Pb. The results are given as the fraction of the total amount of the metal (%) found in each step.

Fraction	Al	Ca	Cd	Cu	Pb	Zn
water soluble	5.5	21.4	7.2	4.7	6.3	3.7
acid soluble	48.5	61.7	90.2	80.2	78.8	83.2
oxidizable	3.4	2.2	0	1.7	7.2	1.3
easily reducible	18.2	1.3	0	5.4	1.9	2.9
moderately reducible	0.6	7.8	0.7	1.0	3.2	0.2
residue	23.9	5.6	1.8	7.1	2.7	8.6

Table 3: Results of the sequential extraction procedure: fraction (%) of the metals in each step

The leaching solution in the "water soluble" step reaches a pH of 9.9. Only Ca exhibits a high solubility in water. Cd, Cu, Pb and Zn have a high acid solubility. The pH in this step reaches 3.4 after 3hrs. The other steps show a low leachability for all the metals exept for Al. The fraction of Al in the "easily reducible" step is large and a considerable amount stays in the residue. This points out that the residue consists mainly of alumino-silicates.

3.3 pH of the leaching solution

The final pH of the leaching solution is higher than the original pH because of the alkalinity of the fly ash. *Figure 1* shows the evolution of the final pH after extraction as a function of AD. Between acid dose 0 and 4 mol/kg, the pH decreases rapidly. Here, only small amounts of basic metal salts dissolve, so that the added acid is not neutralised. Between acid dose 4 and 12 mol/kg, the pH decreases more slowly and becomes nearly constant. The added acid is consumed to neutralise the dissolving basic metal salts (buffering capacity of the fly ash). When using an AD > 12 mol/kg, the amount of basic salts is insufficient to neutralise the added acid giving a logarithmic decrease in the pH.

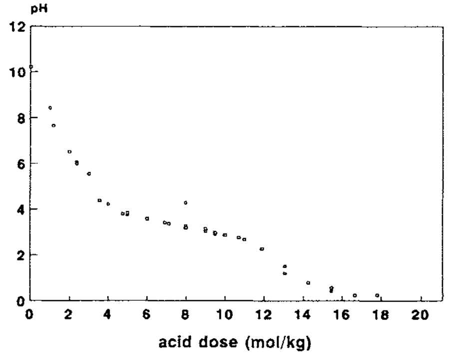

Figure 1: Final pH as a function of the acid dose (L/S=10 l/kg, extraction time=3hrs)

3.4 Simulation

3.4.1 Theoretical solubility

In *figure 2*, the *leaching diagram* for zinc is presented. In the figure the experimental data are presented along with the calculated concentrations (mg/g fly ash) as a function of the pH of the solution after leaching. The leaching diagram represents the quantitative partitioning between the different phases *(15)*. The indicated minerals are the controlling solids at the specific pH value. At pH 6, for example, about one third of the total zinc concentration remains in solution (*figure 2*), whereas one third is precipitated as smithsonite and one third as $ZnO.SiO_2$.

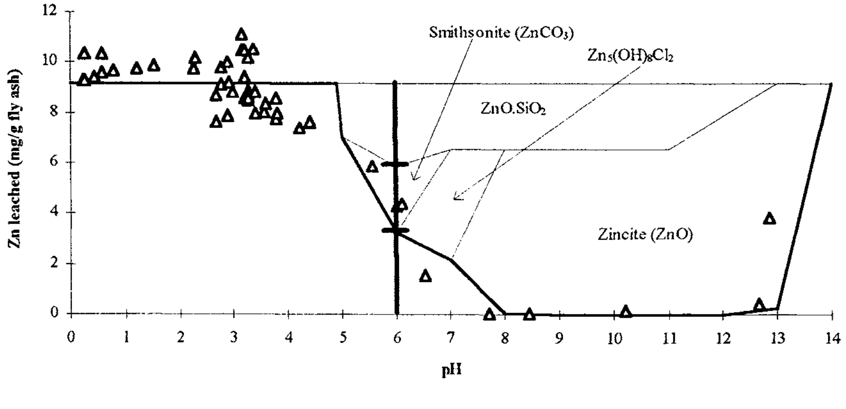

Figure 2: Leaching diagram of zinc (Δ Experimental values; — calculated)

Other solubility controlling solids are $Zn_5(OH)_8Cl_2$ (pH 6 to 8) and ZnO (pH 7 to 13).
At low pH the equilibrium concentration is restricted only by the available amount of Zn in the fly ash. At higher pH values, the concentration at equilibrium is determined by solubility

restrictions. At pH 8, different zinc minerals occur and no more zinc remains in solution. At pH > 13, zinc solubility increases again, due to the formation of hydroxide complexes.
The theoretical predictions are in excellent agreement with the experimental data.
When using the sequential extraction method the results of the first two steps can be compared with these calculated results. In the water soluble step zinc shows a very low leachability at a pH of 9.9 which is reflected by the low values in the leaching diagram. At a pH of 3.4 of the acid soluble step in the sequential extraction method the leaching of Zn is already completed. Thus the water and acid soluble steps give accurately water and acid soluble fraction.

The simulation results for aluminium are given in *figure 3 (15)*. Between a pH of 4 and 13, aluminium is precipitated as diaspore (AlOOH). The leaching diagram is in very good agreement with the experimental values. However, considering the high concentration of aluminium on the fly ashes, aluminium might also exist as an alumino-silicate compound. This was proven by the sequential extraction procedure where a high residue fraction for Al was found. The small water soluble fraction is in good agreement with the low solubility at the pH of 9.9. At pH 3.4 the leaching for Al is not yet completed. Thus the fraction of Al and Ca in the acid soluble step is too low. It is also possible that if in the sequential procedure the pH slightly shifts, different results can be obtained. A final pH in this step of 1.5 would be more appropriate.

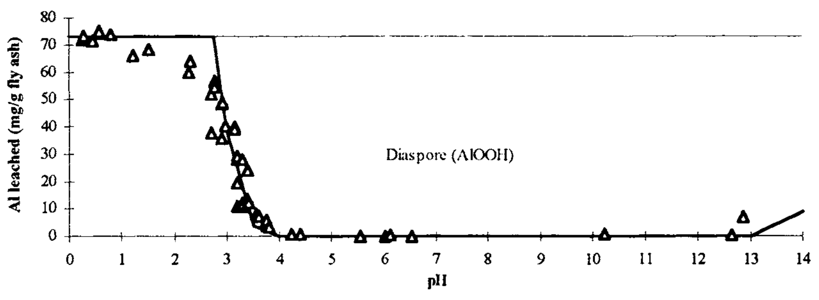

Figure 3: Leaching diagram of aluminium

The leaching diagram for calcium is given in *figure 4 (15)*.

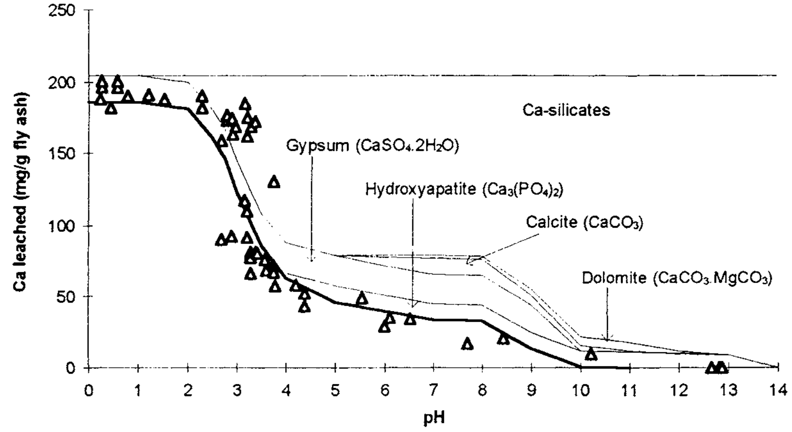

Figure 4: Leaching diagram of calcium

Gypsum was found to be a controlling solid over the whole pH range; at high pH values hydroxyapatite, calcite and dolomite appear as controlling solids.
The higher soluble fraction found for Ca compared to other metals can be explained by the observed leachability at pH 9.9. At pH 3.4 the leaching for Ca is not yet completed. Thus the fraction Ca in the acid soluble step is too low. And again a final pH of 1.5 in this step would be more appropriate.

The leaching diagram for lead is given in *figure 5 (15)*. Only one controlling solid occurs: chloropyromorphite at a pH lower than 9, and $Pb(OH)_2$ at high pH values. When the fly ash is leached with water the fly ash shows a low leachability for lead as can be seen in the leaching diagram. The water soluble step in the sequential extraction method gives also a low leachability. At pH 3.4 the leachability according to this diagram is 0 %. According to the acid soluble fraction in the sequential extraction method it should be almost 100%. This difference can be explained by the absence of a high Cl^--concentration in the acid soluble step where CH_3COOH is used. Thus chloropyromorphite can not be formed and the leachability is higher.

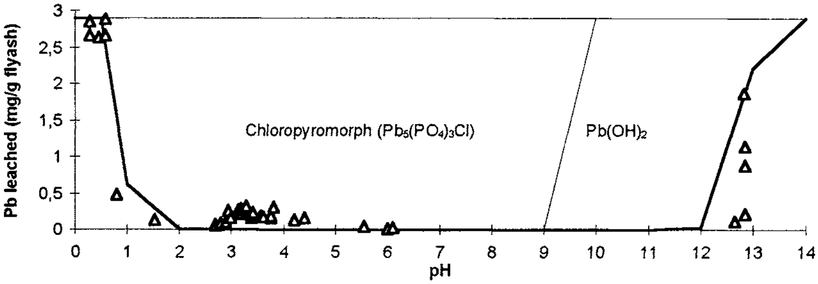

Figure 5: Leaching diagram of lead

Theoretical calculations and experimental determination of the cadmium equilibrium are in good agreement (*figure 6*) *(15)*. Under very basic conditions, $Cd(OH)_2$ occurs. At a pH of 3.4 of the acid soluble step in the sequential extraction method the leaching of Cd is already completed. Thus the acid soluble step gives an exact view of the acid soluble fraction. The water soluble step gives a fraction of 7.2%. This step has a pH of 9.9 and at that moment the leaching of Cd already starts.

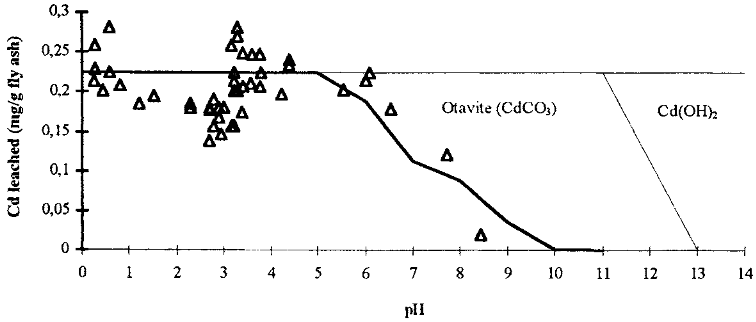

Figure 6: Leaching diagram of cadmium

3.4.2 Equilibrium pH

It is clear that the final pH of the leaching solution is very important for the leaching of the metals and is therefor important for the sequential extraction procedure. The pH is determined by the acid dose and the dissolution of matrix elements. Therefore modelling was also applied to predict the equilibrium pH of fly ash leached with an acid solution of given AD. When the fly ash is brought in contact with the acid solution, basic oxides will dissolve causing an increase of the pH, giving the fly ash a certain buffering capacity. The equilibrium pH after dissolution of basic oxides was calculated by MINTEQA2 for various values of AD. It was found that the variation of pH is mainly related to the AD and the dissolution of aluminium and calcium ($CaCO_3$, CaO and Al_2O_3).

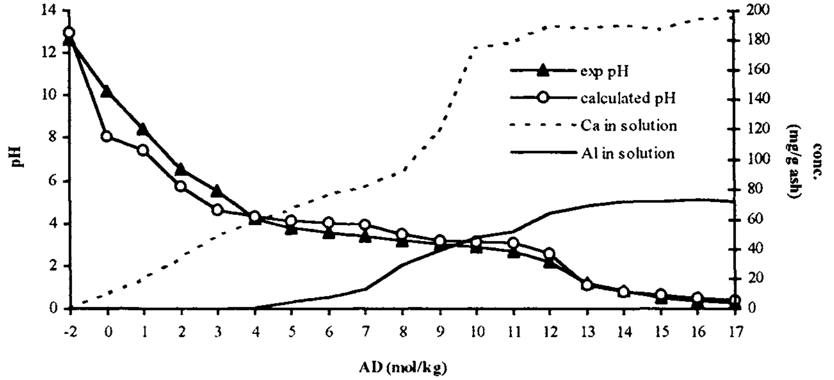

Figure 7: Experimental and calculated pH, calcium and aluminium concentration as a function of the AD

Figure 7 compares experimental and calculated pH values that are in good agreement. The experimentally determined concentrations of calcium and aluminium are also shown. Up to a AD of 4 mol/kg, aluminium oxides do not dissolve and CaO is the main neutralising basic oxide. At a AD higher than 10 mol/kg, calcium is nearly completely dissolved and Al_2O_3 is the main neutralising basic oxide. Once the soluble amount of aluminium is in solution, the buffering capacity of the fly ash is consumed and increasing the AD leads to a logarithmic decrease of the pH.

When the sequential extraction procedure is used for a fly ash with a different Al or Ca composition the pH of the acid soluble step changes, leading to a different result. So the composition of the fly ash has an influence on the results of the sequential extraction procedure.

4. Conclusion

The main elements of the leaching process are solubility and precipitation of heavy metals. Leaching diagrams obtained by simulation calculations are a useful means to obtain a clear picture of the precipitation equilibria for different metals. At a given equilibrium pH of the leaching solution, the leaching diagrams indicate which metals are in solution, and which minerals are precipitated. By comparison with experimental data, the simulation program has proven to give reliable results. Because the results obtained by calculation are in good agreement with experimental results, it may be assumed that the simulation of the leaching behaviour can be extended to fly ashes with different compositions, or to other leaching conditions.

The leaching diagrams can be used to verify the accuracy of the sequential extraction procedure. By comparing the results of the water and acid soluble step of the sequential extraction procedure with the leaching diagrams, it is clear that the acid soluble step should be performed with a more concentrated acid in order to obtain a pH of 1.5. At this pH the leaching process of all of the investigated metals is finished. Otherwise it would be possible to obtain different resutls when the pH of the leaching solution in the acid soluble step shifts slightly. Also the choice of acid can be important for evaluating the leachability of the fly ash. Lead precipitates when HCl is used, but with acetic acid lead has a high leachability. The other metals show no influence of the choice of acid. The results of the water soluble step gives a good agreement with the leaching diagrams.
During the leaching process, the pH of the leaching solution increases as basic metal salts dissolve. The equilibrium pH is determined by the AD, and the amount of $CaCO_3$, CaO and Al_2O_3 on the fly ash. Thus the composition of the fly ash can influence the results of the acid soluble step because the pH changes.

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