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Study of different assisting agents for the removal of heavy metals from MSW fly ashes

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Abstract

This work presents the results of the extraction of Zn, Pb, Cu, Mn and Cd from Municipal Solid Waste (MSW) incinerator fly ashes. In the present work the following assisting agents were evaluated for their capacity to remove heavy metals from fly ash into solution, in a wide pH range: EDTA, ammonium acetate, ammonium citrate, Na-Gluconate and water.

Results obtained in these extractions indicate that cadmium and lead present the highest removals with 75% and 61% of total concentration, although not obtained with the same extraction agent. Removal for the other metals was up to 49% for Cu, 20% for Zn and only 2% for Mn.

The results indicate that Na-gluconate presents the best removal efficiencies for both zinc and lead, while performing also well for the other metals. Na-gluconate is aprox. 2 times more efficient in extracting lead than EDTA (which is the second best) and 61 times better than ammonium acetate. Ammonium acetate performs best for cadmium and copper. Na-gluconate stands out as a good assisting agent. Besides the good performance observed in the extraction tests it also presents some additional characteristics such as non-toxicity, good performance at high pH values, formation of charged complexes with the metals and reasonable price, that points out the possibility of using it as an assisting agent in the electrodialytic remediation of fly ash.

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1 Introduction

Fly ash resulting from the incineration of municipal solid waste is loaded with leachable heavy metals and other contaminants and is therefore considered hazardous waste. There are two different approaches to solve the problem: either to encapsulate the heavy metals inside, so that they will not come out, and this can be accomplished by techniques such as solidification/stabilization and vitrification or, on the contrary, to remove them from the fly ash.

The treatment of MSW fly ash by an electrodialytic technique is currently under investigation at DTU and reflects the second approach (removal of heavy metals). The electrodialytic remediation, which was originally developed for the remediation of soils [1], is based on the application of an electric field that causes the metal ions to migrate towards the electrode compartments, from where they can be removed, according to their charges. However, in order to electromigrate, the metals or their complexes should be in solution.

Current methods for mobilizing heavy metals from finely divided solid material (such as soil and fly ash) are: water extraction, acid extraction, base extraction and complexation.

Extensive studies have been conducted in the past on the extraction of heavy metals from contaminated soils by washing with water (see the review by Peters [2]). A major difference between these two matrixes is that the pH of MSW fly ash is usually extremely alkaline (10-12). This alkalinity results from the presence of an excess lime added for the flue gas treatment in the incineration plant. At these high pH most of the metals are immobilized as hydroxides or carbonates, and therefore can not be extracted.

Extraction of heavy metals by washing with an acidic solution can dissolve the hydroxides and is a common procedure for soils. However, an effective acidic extraction of heavy metals from MSW fly ash requires pH values lower than 4. Due to the high buffering capacity of fly ash those pH values are only possible if large amounts of acid are added. In addition to this, the acid works by dissolving or destroying the solid structure of the fly ash, and this can lead to further release of contaminants that were previously encapsulated in the matrix [3], which can constitute a problem if fly ash is to be landfilled or reused.

On the other hand, an extraction in alkaline media, which would slightly attack the matrix, would only release very soluble heavy metal salts (such as chlorides) [3] and thus is not effective in removing contaminants.

Due to the particular characteristics of MSW incinerator fly ash the extraction must be achieved by other means than the acidic/alkaline solubilization. The problem with using these extractants with MSW fly ash is, once again, the high pH, and therefore the selection of the right chelants is critical. Each type of metal is extracted to a different degree, depending on the state of the metal, the binding mechanism to the solid matrix, the pH and the type of extracting agent used. Very little is reported on extraction from MSW fly ash, as this problem has only recently been tackled [4].

In the present work four different assisting agents were studied in order to find those most suitable for MSW fly ash. In a first series of experiments

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different assisting agents were evaluated for their capacity to remove heavy metals from fly ash into solution. Since one of the agents appeared to perform better than the others, a new series of experiments was conducted for this agent only, in which the behaviour was evaluated as a function of pH at two different concentrations.

2 Selection of assisting agents to be tested

A complex consists of a central metal cation to which several anions or molecules (called *ligands*) are bonded. Chelates are metal complexes in which the ligand is able to establish two or more bonds with the metal. There is a wide range of commercially available chelants. From these only a few were chosen, according to the following.

Chelates are generally more stable than complexes containing only one bond so the first were favoured in this work. Another issue is the working pH: it is important to choose ligands for which the resulting chelate is stable at alkaline media, since this is the pH of the fly ash. In order to work with the electrodialytic remediation technique it is also required that complexes are electrically charged, so that they can be mobilized by the electric field. One additional condition is the non-toxicity of both the complexes and eventual decomposing products [3]. Finally, it is also important that the fly ash resulting from the process maintains its structural integrity, and this means that the matrix should not be destroyed during the treatment. According to the conditions described the following agents were tested: EDTA, ammonium acetate, ammonium citrate, Na-gluconate and water, at different pH.

EDTA (ethylenediaminetetraacetate) is a strong chelate, very effective in complexing heavy metals. In this study it was used only for comparison purposes, since there are currently health and safety concerns regarding its use.

Ammonium citrate and ammonium acetate form soluble multidentate complexes with various metals and have been used for the extraction of heavy metals from polluted soils [2] and from MSW fly ash [4].

Sodium-gluconate (Na-gluconate) has never been used as assisting agent for the electrodialytic remediation of fly ash. However it has been referred previously [3] as a possible leaching agent for heavy metals from fly ash. The selection for the present work is based on its ability to form stable complexes with heavy metals in alkaline media. Also it is a naturally occurring organic molecule of the sugar acids group, currently used as additive in the food industry, therefore with non-toxic characteristics.

Water is used for comparison purposes.

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3 Experimental procedure

3.1 Batch extraction with different assisting agents

Batch extractions were conducted with EDTA, acetate, citrate, Na-gluconate and distilled water. The procedure consisted in placing 1,00 g of sample into 50 ml plastic containers and adding 25 ml of 4% extractant solution, thus obtaining an L/S ratio of 25. The containers were placed on a shaker table for 24 hours. The pH was measured and the samples were filtered using 45-μm Gelman filter paper. The filtrate's pH was adjusted to 2 (with nitric acid) for conservation purposes and distilled water was added to a final volume of 50 ml. The filtrate was stored in plastic vials and stored at 5°C until analysis by atomic absorption spectrophotometry.

3.2 Extraction with Na-gluconate at different pH

Extractions were conducted using water, 3% Na-gluconate or 6% Na-gluconate at different final pH.

The procedure consisted of putting 0,80 g of sample into 25 ml plastic containers and adding 15 ml of 4% and 8% Na-gluconate solutions. Different volumes of acetic acid and distilled water were added to make up a total volume of 20 ml, resulting in final Na-gluconate concentrations of 3% and 6% (respectively) and an L/S ratio of 25. The containers were placed on a shaker table and after 24 hours the pH was measured and the samples filtered using a 45-μm Gelman filter paper. The filtrate's pH was adjusted to 2 (with nitric acid) for conservation purposes and distilled water was added to a final volume of 50 ml. The filtrate was then stored in plastic vials and stored at 5°C until analysis by atomic absorption spectrophotometry.

Procedure was repeated using distilled water instead of Na-gluconate. In this case acidification was made with nitric acid instead of acetic acid.

4 Results

4.1 Batch Extractions with different assisting agents:

The amount of each metal extracted using different assisting agents was calculated using the concentration of the metal in solution and the mass of fly ash. Results (average of six replicates) are presented in figure 1, as well as the final pH for each agent.

Comparison between the mass of metal extracted and the mass originally present in fly ash (determined by acid digestion) is shown in figure 2. Additionally, it is also shown in the first column of figure 2 the percentage of readily soluble metal (determined by sequential extraction).

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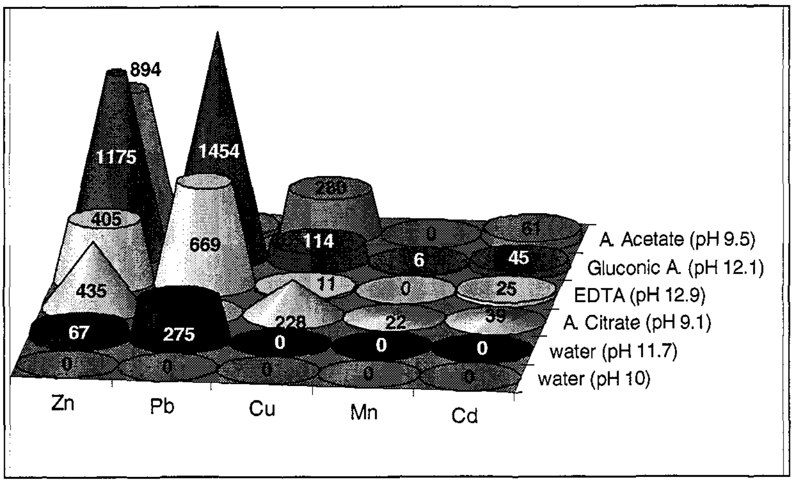

Figure 1: Mass of metal per kilogram of ash (mg/kg) extracted by different agents (average of six values).

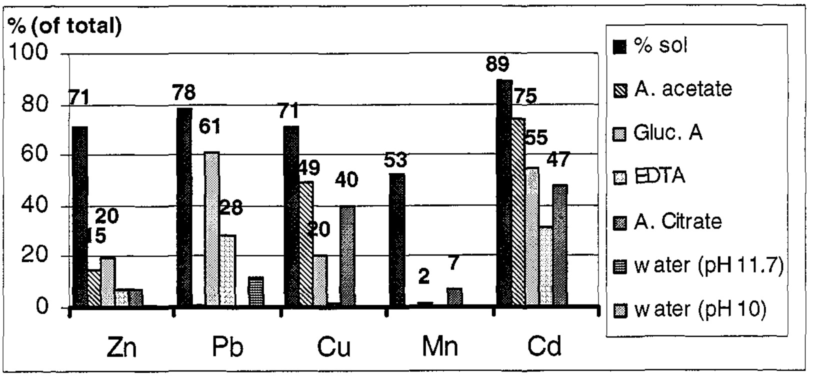

Figure 2: Percentage of readily soluble metal (% sol) and percentage of metal extracted from fly ash with different assisting agents.

4.2 Extraction with Na-gluconate at different pH

Concentration of metals in solution was plotted against pH for water, 3% Na-gluconate and 6% Na-gluconate (see figures 3 to 7).

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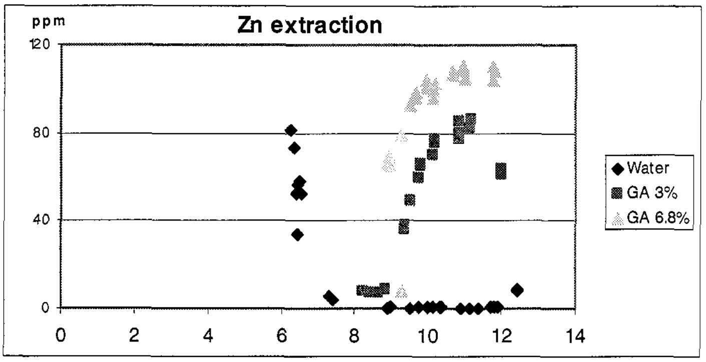

Figure 3: Concentration of Zn in solution in function of pH for water, 3% Na-gluconate and 6% Na-gluconate.

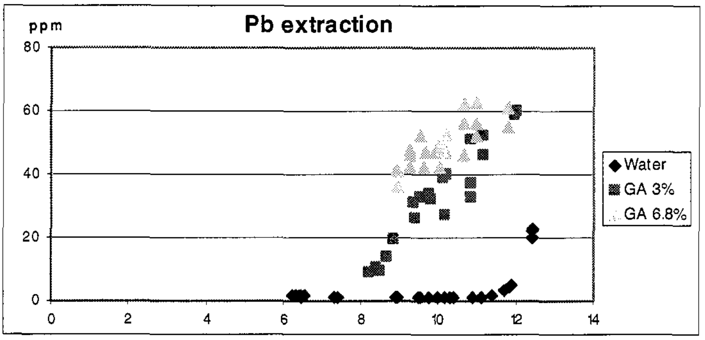

Figure 4: Concentration of Pb in solution in function of pH for water, 3% Na-gluconate and 6% Na-gluconate.

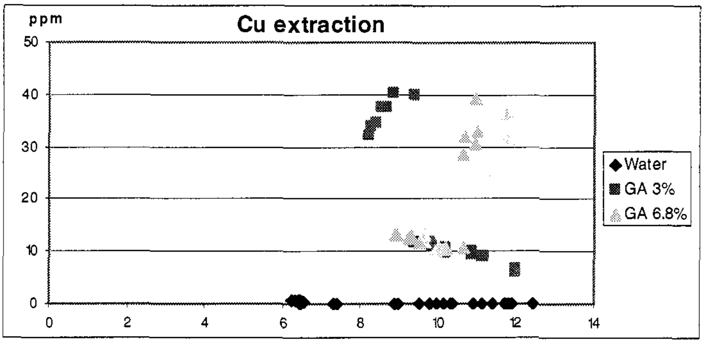

Figure 5: Concentration of Cu in solution in function of pH for water, 3% Na-gluconate and 6% Na-gluconate.

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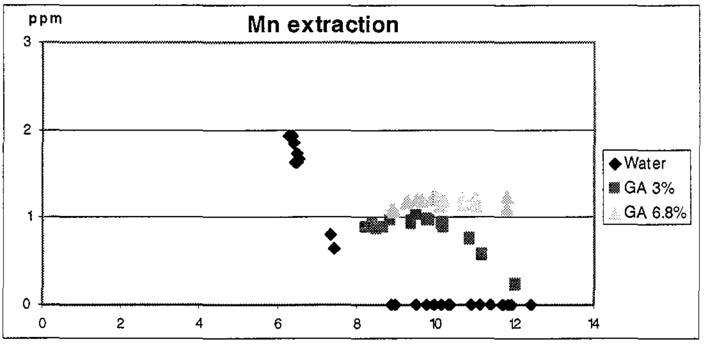

Figure 6: Concentration of Mn in solution in function of pH for water, 3% Na-gluconate and 6% Na-gluconate.

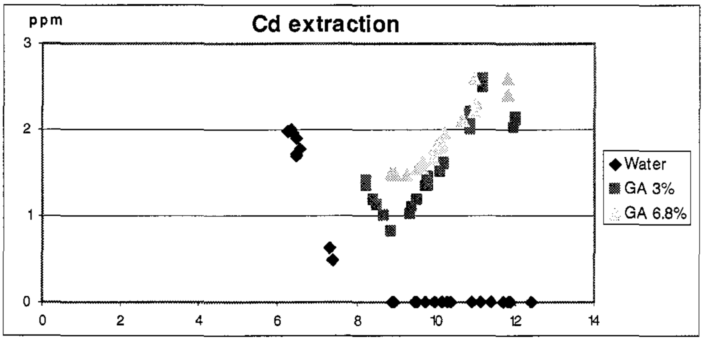

Figure 7: Concentration of Cd in solution in function of pH for water, 3% Na-gluconate and 6% Na-gluconate.

5 Discussion

5.1 Batch extraction with different assisting agents

This series of experiments were conducted to evaluate the capacity of different assisting agents to remove heavy metals from fly ash into solution. Discussion of the results will focus first on the comparison between the heavy metals extracted and then on the comparison between the assisting agents.

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5.1.1 Extraction of heavy metals

The highest extraction (percentage of total) achieved for the studied heavy metals was (figure 2), in descending order: 75% for cadmium (extracted with acetate), 61% of lead (extracted with Na-gluconate), 49% of copper (extracted with acetate), 20% of zinc (extracted with Na-gluconate), and 7% of manganese (extracted with citrate).

The low extraction values for manganese are partially related to the fact that only 53% of manganese is readily soluble while the other 47% is either strongly bound or part of the solid matrix (figure 2). This means that almost half of total manganese is not easily extractable. Nevertheless, the amount extracted represents only approximately 14% of the readily soluble fraction.

The highest extractions were for cadmium, with the mass extracted representing 75% of total mass and 84% of the readily soluble fraction.

5.1.2 Comparison between different assisting agents

Metal solubilization with water was very low, as expected due to the alkaline conditions. Only a small amount of zinc (1%) and lead (12%) were extracted with water at pH 11.7, while extraction was null for all other metals and pH.

Citrate performed well with cadmium and copper, removing 47% and 40%, respectively. However it was not able to solubilize any lead, performing even worse than water. On the contrary, it presented the best results on extraction of manganese.

Acetate presented the best results for cadmium (75%) and copper (49%). However, extraction of lead was very low, only 1%.

EDTA is considered very effective in complexing heavy metals so it was expected that it would present the best results. However, this was not the case. From figures 1 and 2 it can be seen that although EDTA has reasonable good results for zinc and lead, it was not the best extractant for neither of these metals. For copper, manganese and cadmium it presented the lowest removal values, performing only better than water. The fact that final pH was 12.9, which is the highest alkalinity, might partially explain the low performances.

Na-gluconate is the best extraction agent for both zinc (20%) and lead (61%). For lead, it is approximately 2 times more efficient than EDTA (the second best) and 61 times better than ammonium acetate. Other than citrate, it is the only agent capable of extracting manganese, although in lower percentage (3,5 times less than citrate). It also performs reasonably well with copper (2,5 times less than the best) and with cadmium (1,4 times less than the best). It is therefore the only agent from the ones tested that is able to extract all of the selected heavy metals.

5.2 Extraction of heavy metals with Na-gluconate

According to the results of the first batch extractions, Na-gluconate seems to perform better than the other assisting agents tested. The second series of experiments (discussed below) was conducted to evaluate the behaviour of Na-gluconate in function of pH, for two different concentrations.

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As can be seen from figures 3 to 7 concentrations of Na-gluconate of 6% generally worked better than the 3% concentration (with the exception of copper).

Extraction with water covered a pH range of approximately 6 to 12,5. However, for Na-gluconate this range started with 8, because the interest was in extraction at alkaline media. This implies that no comparison can be made between Na-gluconate and water between pH 6 and 8. For water extraction, it can be seen that as pH decreases, that is becomes more acidic, the concentration of zinc, cadmium and manganese increases, as expected. As discussed previously, the aim is to extract metals at alkaline media, near pH 12, the natural pH of fly ash. Around this pH it can be seen (from figures 3 to 7) that Na-gluconate always performs much better than water. When pH decreases to 8 the performance of Na-gluconate also decreases to practically the same level as that of water, with the exception of lead and copper, for which it still presents higher values. This is probably due to the stability of the chelates, which are higher at higher pH.

6 Conclusion

Results indicate that Na-gluconate presents the best results for both zinc and lead, while performing also well for all the metals. Na-gluconate stands out as a good assisting agent in the working pH around 12, which is the natural pH value for fly ash. This means that no additional acidification is necessary, which is important for MSW fly ash because of its high buffering capacity. Besides the good performance observed in the extraction tests at high pH values, Na-gluconate also presents some additional characteristics such as its non-toxicity, formation of charged complexes with the metals and reasonable price, that points out at the possibility of using it as an assisting agent in the electrodialytic remediation of fly ash.

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