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Metal Leaching from MSW Fly Ash Before and After Chemical and Thermal Treatments

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Municipal Solid Waste (MSW) incineration fly ash was collected in the industrial facilities in the city of Toulouse, equipped with recent gas scrubbing equipment which collects daily 15 t of lime treated fly ash. The fly ash contains a large proportion of water soluble chlorides, besides trace elements such as iron, zinc, titanium and copper. Presently, the fly ash is landfilled after a cement solidification process. Matrix stability and leaching behavior of heavy metals (Cd, Cu) from samples of doped MSW fly ash were examined before and after chemical and thermal treatments. A new phosphate process leading to hydroxylapatite formation is described. To evaluate its performance as a stabilization process, cupric and cadmium ions were added as typical pollutant tracers and their distribution was studied as a function of different treatment parameters. The hydroxylapatite process used effectively removes chloride ions in the water extract and retains most of the added metal ions in the solid residues. Evaluation of this procedure as a cold process shows 50% reduction in leachable metal ions. Calcination of the solid residues at 900°C results in agglomerated particles with increased resistance to metal ion dissolution. This is attributed to heavy metal incorporation in the hydroxylapatite matrix formed during the thermal treatment. Thus, combined chemical and thermal treatments are efficient for heavy metal stabilization in MSW fly ash.

INTRODUCTION

Management of municipal solid waste (MSW) requires the consideration and understanding of many diverse environmental and ecological impacts that result from the ultimate disposal of these wastes. Landfilling is the most expedient, inexpensive disposal method for MSW; however, groundwater pollution from landfill leachate is of concern, as are gas emissions. Furthermore, any toxic products present in

the original waste will remain in unknown, uncontrolled form in the landfill. Legislation in France calls for the ban of standard landfilling sites in the year 2002. Only non-recyclable waste, so-called "ultimate waste", will be admitted in authorized, well-equipped sites. To meet these requirements, recyclable MSW will have to be removed in an efficient and cost-effective manner. One method of organic waste separation is combustion. This process recycles or converts waste to steam or energy. The non-combustible residues from this process are classified as bottom ash (which contains the ferrous, magnetically removed metals) and fly ash. Comparative studies of bottom and fly ash have shown that fly ash is enriched in more volatile metals such as mercury, lead and cadmium [1,2]. The bottom ashes are generally considered to be suitable for use as an additive in concrete, or for use as roadbase material. Contamination of fly ash with toxic heavy metals is controlled by the volatility of these metals and their chlorides at high temperature and their effective precipitation and retention in gas scrubbing equipment. Demanding atmospheric emission standards have led to efficient neutralization techniques for hydrochloric acid and heavy metals contents. The procedure usually involves lime injection, with sodium carbonate as an alternative [3].

As an alternative method to the actually used cement solidification process prior to landfilling, we have developed a new process consisting in a phosphate chemical treatment followed by a thermal treatment. The phosphate treatment is an aqueous sol-gel process which produces agglomerated fly ash particles and extracted chlorides. The thermal treatment consists, after drying at 60°C, in calcining the fly ash

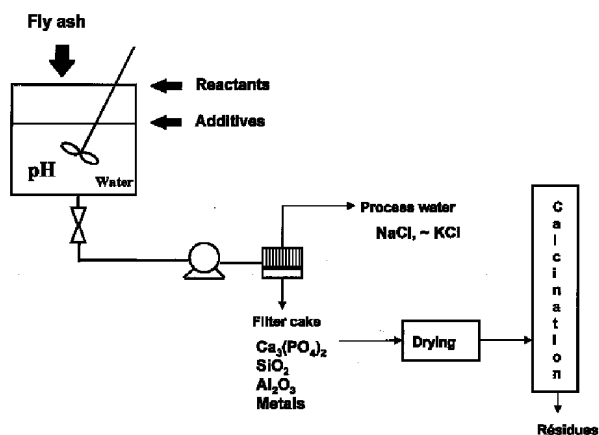


FIGURE 1. Chemical treatment diagram showing wet process followed by filtration and further heat treatment.

agglomerates in air at 900°C.

We have added small amounts of heavy metals (Cu, Cd) to generate doped fly ash in order to study matrix stability and leaching behavior of treated samples. Our main objective was to determine whether or not the chemical treatment, alone or combined with a thermal treatment, stabilizes the residues by decreasing the amounts of metal ions released in leaching tests carried out with water and complex forming solutions.

MATERIALS AND METHODS

1- Sample collection. The fly ash used in this study was collected as a homogeneous 10 kg sample from the municipal waste incinerator in Toulouse. This facility burns 450 tons of waste daily and produces 15 tons of fly ash. The stack scrubber was installed in 1994 and includes a lime injection unit followed by filters which collect the fly ash. Gases are then sent through a gas washing unit which collects residual hydrochloric acid and heavy metals. The process water is treated, and filter cake residues are produced. These cakes were not included in the present study.

2- Sample composition. The collected fly ash contains calcium, silica, alumina and chloride ions as major constituents characterized by energy dispersive X-ray analysis (EDX). Major elements include, by weight : Ca (8.2%), Na (3.1%), and Cl (9.0%) ; the trace elements include Cu (0.08%) and Cd (0.02%).

3- Process description and experimental procedure. In a first series of experiments, 1 kg of fly ash and 2 l of distilled water were introduced in a stirred tank reactor of 10 l capacity. 10 g of copper or cadmium was added in the form of a concentrated solution. To homogenize the mixture, the suspension was stirred 30 minutes at room temperature (20°C). The suspension was filtered and the cakes were air-dried in a Jouan oven at 60°C. The process waters were sampled for chemical analysis. The solid residues were sampled as 100 g aliquots and calcined in sintered alumina crucibles under air atmosphere at 900°C in a Thermolyne muffle furnace. In a second series of experiments, to a mixture containing 1 kg of fly ash and 2 l of distilled water and 10 g of copper (or cadmium) was added 20 g of $\text{Ca}(\text{OH})_2$ and 60 g of H_3PO_4 . The suspension was stirred 30 minutes and treated as described above. The various steps of the process are

illustrated in Figure 1.

4- Quantitative chemical analysis. 2.0 g samples were digested 15 minutes with 30 ml concentrated nitric acid under reflux. The suspensions were cooled and filtered. The filtrates were diluted to 100 ml and examined for various elements. The chloride contents were analyzed by a silver nitrate titration method using potentiometric end point determination.

5- Leaching tests. Experiments were carried out using water or 1% EDTA or tartaric acid solutions with a liquid to solid ratio of 200 ml of solution for 100 g of solids. The suspensions were stirred for half an hour and filtered on Buchner funnels to separate the solid and liquid phases. Leach liquors were analyzed for Cu, Cd, Ca, Na and Cl. The solids were analyzed for the same elements following nitric acid digestion.

6- Analytical techniques Atomic absorption measurements were made with a Unicam model 919 spectrophotometer using air-acetylene and multielement discharge lamps for calcium, copper and cadmium. A Corning model 410 emission spectrophotometer was used with air-natural gas to determine sodium concentrations. A Jeol scanning electron microscope was used to observe the samples, which were analyzed with no sputtered coating by spreading small samples of powder on conductive tape. Identification and semi quantitative analysis were performed with a Link analytical EDX analyzer. A Sieffert XRD diffractometer was used to obtain powder X-ray diffraction patterns for the phosphate treated fly ash and a commercial hydroxylapatite reference sample.

RESULTS AND DISCUSSION

The analytical results concerning the fly ash used in our experiments show that copper and cadmium are present in negligible amounts. 1% of copper was added as a typical transition metal and 1% of cadmium as a representative heavy metal [4]. The presence of these metals in easily quantified concentrations helps to study their leaching behavior.

Distribution of copper and cadmium: Table 1a presents the results obtained when fly ash spiked with 1% copper is treated with water. 100% of the copper remains in the solid phase. On the other hand, the majority of soluble chloride salts are extracted by water, as has been previously reported [5] The insolubility of copper may simply be explained by the

TABLE 1a. Behavior of Fly Ash Spiked with Copper

Element (weight %) in:	Cu	Ca	Na	Cl
Water extract	0	8	52	53
Solid residue	100	92	48	47
Solid residue leaching test				
Element (% extracted)	Cu	Ca	Na	Cl
With water	0	13	32	47
With EDTA (at pH = 6)	41	20	-	-
With tartaric acid (at pH = 6)	66	5	-	-

TABLE 1b. Behavior of Fly Ash Spiked with Cadmium

Element (weight %) in:	Cd	Ca	Na	Cl
Water extract	0.4	8	19	74
Solid residue	99.6	92	81	26
Solid residue leaching test				
Element (% extracted)	Cd	Ca	Na	Cl
With water	0	12	58	21
With EDTA (at pH = 6)	53	12	-	-
With tartaric acid (at pH = 6)	9	4	-	-

formation of cupric hydroxide at the pH resulting from water treatment (pH= 11.5). Further water extraction of the solid residues at neutral pH was unable to dissolve cupric hydroxide. EDTA or tartaric acid, both adjusted to pH= 6 to accelerate the leaching process, removed partly cupric ions from the solid phase (from 41 to 66 % of the copper contents). Similar results were observed at pH= 8, showing that dissolution is related to metal-ligand complex formation, as could occur with organic material in the environment.

Table 1b presents the distribution of cadmium ions in solid and liquid phases following analogous treatments. In this case, very little cadmium is soluble at high pH, which may be accounted for by the formation of sparingly soluble hydroxycadmides and insoluble cadmium hydroxide. These results show that the distribution of metals depends on the nature of the considered elements, its capacity to interact with organic ligands or hydroxide ions to form stable, soluble or insoluble complexes.

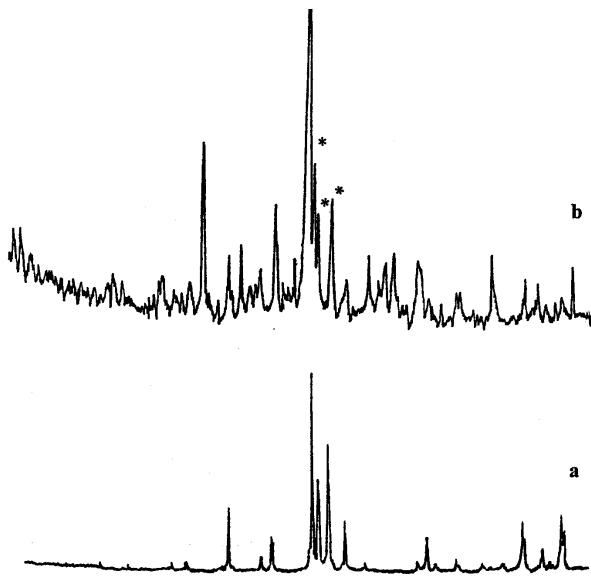
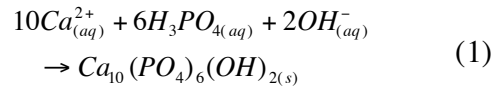


FIGURE 2. X-ray diffraction patterns of treated fly ash (b) showing matching peaks (*) and (a) reference hydroxylapatite.

Calcium phosphate treatment: When calcium and orthophosphate ions are mixed in solution at neutral pH, a gel forms which may precipitate hydroxylapatite when the proper calcium to phosphorous ratio is present. Reaction 1 occurs to completion because of the very low solubility product of hydroxylapatite [6].



By isomorphic substitution, metal ions may be incorporated in the solid matrix according to reaction 2.

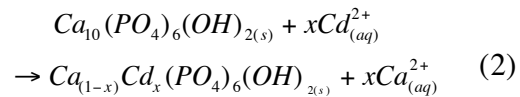


Figure 2 compares the powder diffraction pattern of a reference hydroxylapatite to that obtained for the fly ash treated by the previously described phosphate process. Hydroxylapatite is identified in the treated fly ash residues by the presence of the characteristic diffraction peaks for interplanar distances of d= 2.81; 2.78 and 2.71 Å and labeled * in figure 2.

When a calcium phosphate gel was formed, no major change was observed with respect to water solubility as shown in Table 2a. On the other hand, a significant decrease in cupric or calcium ion extraction by complexing ligands was observed, reaching over 50%. Interestingly, some cadmium is released near neutral pH following calcium phosphate treatment, as shown by the results presented in Table 2b. This may be related to the high concentration of chloride ions observed under our experimental conditions, leading to the dissolution of cadmium hydroxide in the form of water soluble chlorocadmides. Once again, the main effect of calcium phosphate treatment is to reduce the calcium and heavy metal dissolution in leaching tests.

Heat treatment and SEM-EDX evaluation. SEM-EDX examination of fly ash shows a heterogeneous mixture of

TABLE 2a. Behavior of Calcium Phosphate Treated with Copper

Treated fly ash				
Element (weight %)	Cu	Ca	Na	Cl
Process water	0	6	63	45
Treated solid residue	100	94	37	55
Treated solid residue leaching test				
Element (% extracted)	Cu	Ca	Na	Cl
With water	0	15	33	47
With EDTA (at pH = 6)	20	11	-	-
With tartaric acid (at pH = 6)	14	0.1	-	-

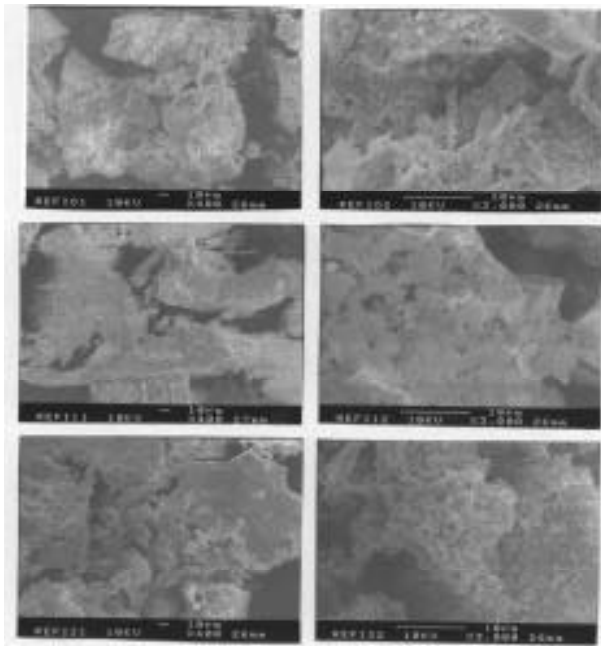


FIGURE 3. SEM pictures of fly ash (top), treated fly ash (middle) and treated and calcined fly ash (bottom).

elements and shapeless particles (Figure 3). Washing fly ash with water to remove soluble salts caused an increase in surface microporosity of the remaining particles. Some of the larger particles are observed to have finer particles stuck on their surfaces. Fly ash treated with calcium phosphate gel shows agglomerated particles with over 100 micrometers diameter and surfaces covered with 1micrometer nodules. The calcium phosphate treated fly ash examined after air calcination at 900°C showed a reduced size for the surface nodules, with retention of a porous, non-dense structure. This can be explained by the crystallization and partial sintering of the solids.

Table 3 presents the effect of calcination on heavy metal dissolution by aqueous ligands. A further significant decrease in copper and cadmium leachability is observed. This effect may be related to the incorporation of metal ions in a more compact, crystalline and insoluble calcium phosphate matrix. Substitution of calcium by other metals accounts for the

TABLE 3. Effect of Calcination on % Metal Extracted in Leaching Tests

Fly ash spiked with:	Cu	Cu	Cd	Cd
Leaching test with:	EDTA	tartaric acid	EDTA	tartaric acid
Fly ash solid residue at 20°C	41	66	53	9
Fly ash calcined at 900°C	2.0	0	2.0	0
Treated fly ash at 20°C	20	14	35	0.2
Treated fly ash calcined at 900°C	0.1	0	19	0.01

TABLE 2b. Behavior of Calcium Phosphate Treated Fly Ash with Cadmium

Treated fly ash				
Element (weight %)	Cd	Ca	Na	Cl
Process water	13	11	18	69
Treated solid residue	87	89	82	31
Treated solid residue leaching test				
Element (% extracted)	Cd	Ca	Na	Cl
With water	0.2	11	75	23
With EDTA (at pH = 6)	35	9	-	-
With tartaric acid (at pH = 6)	0.2	1	-	-

decreased solubility of heavy metals in the hydroxylapatite structures [7,8]. The cadmium spiked untreated fly ash has a low concentration of leacheable cadmium (2%), possibly due to the loss of cadmium as volatile chloride during the calcination step. The treated fly ash shows higher retention of cadmium in the phosphate matrix during calcination. This leads to some cadmium release during the EDTA leaching test (19%).

CONCLUSION

Chemical treatment of MSW fly ash by a calcium phosphate gel addition effectively reduces heavy metal ion solubility, particularly under aggressive chelating conditions. This conforms to present knowledge on heavy metal removal from contaminated soils [9]. Thermal treatment also significantly affects the solubility of metal ions with respect to chelating ligands. The observed decreases in metal ion leachate concentrations may be attributed to the incorporation of the metals in a calcium phosphate matrix. The thermal treatments under mild conditions (900°C) generally avoid excessive metal loss by evaporation [10], but contribute to apatite crystallization, as confirmed by SEM and X-ray diffraction analysis.

The chemical treatment method proposed presents the advantage of eliminating some soluble chlorides combined with the advantage of leading to a low temperature thermal treatment for the solidification-stabilization step. In order to optimize the best combination of chemical and thermal treatments, several parameters need to be explored and include: heavy metal concentration, particle size control, drying technique, and temperature and duration of calcination, nature and quantities of phosphate additives. In parallel with this experimental approach, thermodynamic equilibrium and mass transfer of metal ions in mineral matrixes are being examined to evaluate the distribution of pollutants. These combined efforts should yield new processes [11,12] for municipal solid waste incinerator fly ash disposal or recycling.

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