# Stabilization and hydrometallurgical treatment of flyash from a municipal incinerator

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#### Abstract

Flyash from municipal solid waste (MSW) incinerators is frequently classified as a characteristic hazardous waste due to lead and cadmium content. Two alternate processing schemes for the treatment of flyash obtained from the MSW incinerator in Tuscaloosa, AL have been investigated; one involves stabilization of the flyash with portland cement, and the other involves the recovery and recycling of metal values by leaching and subsequent precipitation. Results indicate that flyash can be successfully stabilized in a 1:1 mixture of flyash and portland cement which meets environmental requirements. It has also been demonstrated that extraction of the metal content from flyash, specifically lead, cadmium and zinc, can be accomplished quickly and efficiently by leaching in hydrochloric acid solutions. Preliminary experiments on the subsequent recovery or precipitation of metallic lead and cadmium from these leaching solutions by cementation with zinc dust appear to be promising. Various means were used for characterization of the as-received material and several leaching residues including X-ray diffraction, particle size analysis, inductively coupled plasma spectroscopy, and atomic absorption spectroscopy. Results indicated that at least some of the lead in the flyash is present in the form of PbSO<sub>4</sub> with smaller amounts of PbCl<sub>2</sub>.

# Introduction

Proposed federal regulations for landfills for municipal solid waste and state and local legislation mandating recycling are causing communities across the nation to re-evaluate their methods of treatment and disposal of their solid waste. At the present time most solid waste is disposed of in sanitary landfills, but the cost of this option must be reconsidered in light of the new regulations. There will be significant economic incentive to reduce the volume of waste that must go into the landfill. While recycling is one option to reduce waste, there will still be a significant volume of waste to dispose of after recycling. Incineration coupled with a recycling effort offers the means for maximum reduction of the volume of waste that must be disposed of in the landfill. There is an increase in activity in planning and construction of municipal incinerators

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which include energy recovery as a major component of solid waste management.

The major materials remaining after incineration requiring disposal are bottom ash and flyash. Bottom ash is seldom classified as a hazardous waste and can be disposed of in a sanitary landfill without further treatment. Flyash, on the other hand is a characteristic hazardous waste, and it cannot be disposed of in a sanitary landfill. Without further treatment, it must be disposed of in a hazardous waste landfill with the attendant cost and liability. This study took two approaches to the problem. The first approach addresses waste minimization coupled with recycling in which hazardous or valuable metals in the flyash are extracted using hydrometallurgical techniques, followed by recovery of the extracted metals. The residue could then be safely disposed of. The second approach addresses stabilization of the flyash so that the hazardous components would not leach out, allowing safe disposal in a sanitary landfill, but without recovery or recycle of any of the metal values.

## Background

When discussing emissions from MSW incinerators, some consideration must be given to the type of incinerator and to whether the fuel has been pretreated. One classification of incinerator is mass burn, which burns waste as delivered with only minimal pretreatment. Some incinerators are designed to burn refuse derived fuel, RDF, which is normally in the form of pellets containing only combustible material processed from the raw refuse. Mass burn incinerators can be classified into large field erected units versus modular units. The large field erected units generally contain the large water-wall boiler and traveling grate similar to those found in power plant boilers. These incinerators are usually large, with a normal capacity of a single furnace of 200-300 tons per day of raw refuse. Modular incinerators are generally smaller, with a single furnace capacity of less than 100 tons per day of raw refuse. Most of the modular incinerators have a two-stage combustor, with the first stage oxygen starved and excess air added to the second stage. Steam generation is by a waste heat boiler in the flue gas downstream of the boiler. Particulate emissions from modular incinerators per pound of refuse fed are less than 10% of the emissions from a large field erected incinerator [1].

Because the concern about the toxicity of MSW flyash has arisen only recently, the literature on the characteristics of the flyash is not extensive, although some recent publications have appeared. Savage et al. [2] studied the air pollution implications of a two-stage modular municipal incinerator. Their studies included an analysis of heavy metal content in the combustible fraction of the raw refuse as well as in the flyash from a two-field electrostatic precipitator. Law and Gordon [3] also present an analysis of the metals in the combustible fraction of MSW. Kosson and coworkers [4,5] characterized ashes

# **Experimental studies**

# Flyash source

The flyash used in the present study came from the municipal incinerator at Tuscaloosa, AL. The mass burn incinerator is a Consumat Systems Inc. modular incinerator processing raw refuse. There are four furnaces each with a capacity of 75 tons per day operating in parallel to feed two waste-heat boilers, followed by a single economizer. Each furnace contains a starved air first stage which contains three hydraulic rams for moving the refuse down the tiers to a water ash quench. All of the air in the first stage is supplied under the fuel bed through the rams. The designed operating temperature of the first stage is  $800^{\circ}$ C. The second stage of each furnace has excess air fed tangentially to give a minimum operating temperature of  $1000^{\circ}$ C. After the waste-heat boiler and economizer, flyash is removed in a two-field electrostatic precipitator (ESP). The flyash sample used in the characterization and leaching studies was a composite of samples removed from the ESP over a three day period and blended for uniformity.

# Flyash characterization

# Particle size distribution

The particle size distribution of the flyash was determined by dry-sieve analysis. The results are shown in Table 1. These results should be viewed with caution, however. The flyash is hygroscopic, and microscopic examination showed that many of the particles are agglomerates. Analysis of the material

# TABLE 1

Particle size (µm)	Percentage retained on sieve		
- 45	20.3	· ·	
49	10.4		
64	23.8		
91	11.5		
128	8.6		
181	7.7		
256	6.0		
450	7.8		
+600	3.9		

Dry sieve analysis of incinerator flyash

in a Microtrac particle size analyzer which uses a water dispersion to avoid agglomerates could not be used because of the high degree of water solubility of the sample. Thus the dry sieve analysis is the best indication of the effective size distribution of the material, as long as one remembers that many of the particles are agglomerates.

# Chemical analysis

The flyash was subjected to several different analyses to determine the chemical nature of the material.

X-Ray analysis. X-ray powder diffraction analysis was performed on the asreceived flyash, as well as the residue remaining after water dissolution, and the residue remaining after dissolution in aqua regia (3:1 ratio of HCl to $\text{HNO}_3$ ). X-ray diffraction is a classical method for the identification of chemical compounds. These analyses revealed the presence of the following compounds.

As-received sample: PbSO<sub>4</sub>, PbCl<sub>2</sub>, $\gamma$ -CaSO<sub>4</sub>, PbTi<sub>3</sub>O<sub>7</sub>, Na<sub>21</sub>MgCl<sub>3</sub>(SO<sub>4</sub>)<sub>10</sub>, K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.

Residue/water dissolution: PbSO<sub>4</sub>, PbCl<sub>2</sub>, γ-CaSO<sub>4</sub>.

Residue/aqua regia dissolution:  $SiO_2$ ,  $TiO_2$ .

X-Ray diffraction analysis did not confirm the presence of lead oxide or any zinc compounds. This is likely due to the presence of lead oxide or zinc compounds in amorphous forms which cannot be detected through X-ray diffraction analysis.

Energy dispersive X-ray analysis (EDX) for the as-received flyash was also performed on the scanning electron microscope (SEM). The elements detected are consistent with inductively coupled plasma analyses (ICP) performed externally and the X-ray diffraction data presented above. The particles in the flyash were too small to allow mapping to determine form and crystallinity. A summary of the SEM/EDX results follow.

As-received sample: Zn, Al, Si, K, Ca, Ti, Fe, S, Cl

Residue/water dissolution: Zn, Mg, Al, Si, K, Ca, Ti, Fe, Cu, Cl

Residue/aqua regia dissolution: Al, Si, Cl, Ca, Ti, Cu

ICP and AA analyses. As-received and various size fractions from the dry sieve analysis were evaluated for metal content by dissolution in aqua regia and subsequent analysis for lead, cadmium and zinc by atomic absorption spectroscopy (AA). The same samples were analyzed by ICP in an independent laboratory. Results indicated very little variation in chemical composition between a relatively coarse size and a very fine size. This is likely due to the "sticky" nature of the flyash and the difficulty in sieving. Examination of the material on a scanning electron microscope indicated that small particles tend to stick together to form larger agglomerates. Thus it is not surprising that the composition is relatively uniform. As a result the as-received flyash, without sieving, was used for the leaching experiments. The ICP analysis of the asreceived flyash used in this study is presented in Table 2 under the heading "Tuscaloosa". The AA analyses for cadmium, zinc. and lead confirmed the ICP analysis and are not presented here. Chemical analyses of the Tuscaloosa flyash are ouite similar to results for flyash from the Red Wing incinerator presented by Savage et al. [2], both regarding the ions present and the concentrations. The only notable difference is that the flyash from the Tuscaloosa incinerator contains more sodium and potassium. The Red Wing incinerator, like the Tuscaloosa incinerator, is a two-stage modular incinerator with a two-field electrostatic precipitator. The flyash analysis for the Red Wing incinerator is also included in Table 2. Ontiveros et al. [4] present analyses for several different types of incinerators. Two of the incinerators in Canada had waterwall furnaces and used electrostatic precipitators for flyash collection. The averaged flyash analyses for these incinerators is listed in Table 2 under "Canadian". Note the significant difference in flyash composition between the field erected waterwall Canadian incinerators and the two-stage modular units.

The as-received flyash was also contacted with deionized water for 36 hours at 30°C in order to determine the nature of water soluble materials in the flyash. Results in weight percent are presented in Table 3 for three pertinent metals. The percent metal extraction is calculated on the basis of total metal

Element	Canadian	Red Wing	Tuscaloosa	
Cadmium	195	2,000	2,100	
Zinc	-	110,000	133,000	
Lead	5555	15,000	19,200	
Barium	2390	490	500	
Sodium	21,350	48,000	115,400	
Potassium	15,200	34,000	58,800	
Arsenic	-	300	<900	

Flyash analyses  $(\mu g/g)$ 

TABLE 2

#### **TABLE 3**

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Element	Extraction percentage					
Zinc	26					
Lead	3.5					
Cadmium	55					

content as determined by ICP, given in Table 2. A total of 36% of the original weight of sample dissolved during the experiment. As can be seen only a small portion of the lead is water soluble. The 3.5% lead extraction represents a dissolved lead concentration of 3.1 ppm. Dissolution experiments with 1.0 Macetic acid vielded 18% extraction of lead (16.1 ppm). In order to determine the likely chemical compounds present in the flyash which contribute lead, solubilities of PbCl<sub>2</sub>, PbSO<sub>4</sub>, and PbO were measured experimentally in 1.0 Macetic acid and solubilities in water were obtained from the literature. These data showed PbCl<sub>2</sub> to be readily soluble in water (10.980 ppm) or acetic acid (3280 ppm). Lead sulfate, however, was only slightly soluble in water (32.8 ppm) and was only slightly more soluble in 1.0 M acetic acid (130 ppm). Lead oxide is not readily soluble in water (16 ppm), but it is readily soluble in 1.0 M acetic acid (6500 ppm). A comparison of the solubility data with results of the leaching experiments suggest that a significant portion of the lead present in flyash is in a low solubility form, perhaps as  $PbSO_4$ . The presence of sulfate was confirmed by ion chromatographic analysis, which indicated that the predominant water soluble anions were chloride and sulfate, with traces of fluoride, bromide and nitrate.

# Leaching

Leaching experiments have been performed on flyash in a 1 liter reactor fitted with a stirrer, condenser, and sampling device. Constant temperature was maintained by immersion in an oil bath. Experiments were initiated by placing one liter of leaching solution in the reactor and turning on the stirrer. After the solution had reached the desired temperature, an accurately weighed sample of flyash (about 5 g) was placed in the reactor, and this time was designated as the initial starting time. Samples of the aqueous solution were taken at designated time intervals which were then analyzed by atomic absorption spectroscopy to determine the concentrations of dissolved metals extracted as a function of time. Lead, zinc and cadmium concentrations were followed in the flyash extract.

Figure 1 (a) presents results for cadmium extraction from flyash using three different lixiviants, namely 1 M HCl, 1 M acetic acid and 2 M NaCl. Both the rate of cadmium extraction as well as the extent of extraction were found to be almost the same for the three lixiviants. Figures 1(b) and (c) show similar results for lead and zinc extraction, respectively, using the same three lixiviants. Initial leaching rates are again relatively rapid for both lead and zinc. On the other hand, in the case of lead the extent of extraction is quite high in 1 M HCl, somewhat reduced in 2 M NaCl and drastically reduced in 1 M acetic acid. This is likely due to the occurrence of a large portion of the lead in flyash as lead sulfate which has a relatively low solubility. The presence of chloride either as HCl or NaCl allows much greater levels of lead extraction owing to the formation of soluble lead-chloro complex ions.



Fig. 1. Fraction of (a) cadmium, (b) lead, and (c) zinc extracted from flyash at 350 rpm and 30 °C.



Fig. 2. Fraction of (a) cadmium, (b) lead and (c) zinc extracted from flyash using HCl at 350 rpm and  $30^{\circ}$ C.

Figures 2 (a)–(c) show the dissolution rates for cadmium, lead and zinc, respectively, using 1 M and 0.1 M HCl. Figures 3 (a)–(c) show similar results for cadmium, lead and zinc, respectively, using 1 M and 0.1 M H<sub>2</sub>SO<sub>4</sub>. A comparison of these data show that the concentration of lixiviant does not have a significant effect on the leaching behaviour of cadmium. However, the concentration of lixiviant does seem to have an effect on the leaching behavior of lead and zinc. Also, it can be seen from Fig. 3(b) that lead dissolution is again quite low in sulfuric acid, similar to results obtained in acetic acid.

Figures 4(a)-(c) show the temperature effect on the dissolution rates of cadmium, lead and zinc, respectively, using 0.1 *M* HCl. Results of these experiments, performed at two different temperatures, 30°C and 60°C, indicate that temperature does not have a strong effect on the leaching rate of cadmium. In the case of lead and zinc, temperature has a more noticeable effect on the leaching rate.

The effects of varying the lixiviant volume (i.e. the solid/liquid ratio) and stirring speed on the leaching rate of lead, cadmium and zinc were also examined. The fraction of metal extracted was affected by the variation in the lixiviant volume only in the case of lead, as shown in Figs. 5 (a)–(c). Variation in the stirring speed in the range of 30 to 500 rpm in 1 M HCl at 30°C had no noticeable effect on the leaching rates of any of the metals.

These results indicate that cadmium extraction is very fast and almost complete, regardless of the leaching solution, temperature, or stirring speed. Austin et al. [6] observed similar behavior and have suggested that the rapid extraction of cadmium may be due to the adsorption of cadmium species on the surfaces of flyash particles. On the other hand, lead and zinc extraction are more strongly affected by the choice of lixiviant, concentration of lixiviant, and temperature. The level of lead extraction in 1 M acetic acid and in 1 M sulfuric acid were quite low, probably due to the low solubility of lead sulfate in these solutions. At least in the case of lead, this seems to be a solubility effect rather than a rate effect, since the initial rate of extraction was quite rapid and nearly the same in both 1 M acetic acid and 1 M sulfuric acid.

A summary of the final concentrations of dissolved zinc, lead and cadmium observed at the end of the various leaching experiments is shown in Table 4. The data presented in Table 4 were taken from the experiments represented in Figs. 1 through 4. As can be seen the solutions contain significant amounts of dissolved metals. Dissolved lead and cadmium can be recovered by cementation, results of which are presented in the following section.

The primary purpose of the leaching process is to detoxify the solid and render any remaining residue as non-hazardous. As a result the toxicity of several residues was determined by the toxic chemical leachate procedure (TCLP) and compared with the as-received flyash. Results of the TCLP tests are shown in Table 5. Before performing the TCLP tests the residues were filtered and washed seven times with deionized water to remove any entrained



Fig. 3. Fraction of (a) cadmium, (b) lead and (c) zinc extracted from flyash using  $H_2SO_4$  at 350 rpm and 30 °C.



Fig. 4. Fraction of (a) cadmium, (b) lead and (c) zinc extracted from flyash using 0.1 M HCl at 350 rpm.



Fig. 5. Fraction of (a) cadmium, (b) lead and (c) zinc extracted from flyash using 1 M HCl at 30 °C and 350 rpm.

## TABLE 4

Lixiviant	Temp. (°C)	Zinc	Lead (ppm)	Cadmium	pH		
		(ppm)		(ppm)	begin	end	
1.0 M HCl	30	563	79.4	10.0	0.04	0.05	
1.0 <b>M HAc</b>	30	524	16.1	9.8	2.33	2.92	
2.0 <i>M</i> NaCl	30	430	52.7	9.4	6.61	7.04	
0.1 M HCl	30	407	66.0	9.4	1.01	1.17	
1.0 M HCl	30	571	<b>79.4</b>	10.0			
$0.1 M H_2 SO_4$	30	407	11.6	9.5	1.03	1.10	
1.0 M H <sub>2</sub> SO <sub>4</sub>	30	571	15.2	9.7	_	0.07	
0.1 <b>M</b> HCl	60	509	76.8	9.5	1.10	1.19	
0.1 M HCl	30	399	65.2	9.2	1.10	1.17	

Final	concentrations	of dissolved	l Zn.	Pb and	Cd attained	l in 1	the	leaching	exi	periments
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## TABLE 5

A comparison of the response of leaching residues with as-received flyash on the basis of TCLP tests

Element	0.1 <i>M</i> HCl 30°C (ppm)	0.1 <i>M</i> HCl 60°C (ppm)	1.0 <i>M</i> HCl 30°C (ppm)	As-received (ppm)	EP toxicity limit (ppm)
Pb	30.5	21.0	0.43	54.0	5.0
Cd	1.25	1.0	0.09	82.0	1.0
Zn	19.0	8.5	6.8	1080.0	-

leaching solution. As shown, the residue from the 1.0 M HCl leaching experiment meets the EP (extraction procedure) toxicity limit for both lead and cadmium. Although zinc is not considered to be toxic, it is included in Table 5for comparison.

## Recovery

Recovery experiments are essentially the reverse of the leaching experiments. Legiac et al. [5] conducted preliminary experiments using electroplating to recover metals from flyash leach solution and showed that it is a possible means of metal recovery. In the present work, cementation is investigated as a means of metal recovery. Cementation was chosen because it is simple, direct and does not require electrical energy.

After the leaching experiment approximately 0.8 liter of solution containing dissolved metals is produced; any non-reacted residue is filtered off. Recovery of dissolved metals from the filtered leaching solution was evaluated by the addition of Zn dust at room temperature. The addition of Zn dust causes cementation of metallic lead and cadmium according to the reactions:

 $Pb^{2+} + Zn \rightleftharpoons Pb + Zn^{2+}$  $Cd^{2+} + Zn \rightleftharpoons Cd + Zn^{2+}$ 

Accurately weighed amounts of zinc powder were added to the solution, samples were taken at various time intervals, and concentrations of dissolved cadmium and lead as a function of time were determined by AA. In these experiments lead and cadmium are precipitated as solids, leaving behind a solution containing primarily dissolved zinc. Although eventual recovery of the zinc will be an important part of an overall recycling process, the recovery of lead and cadmium are emphasized here.

Recovery experiments were performed by adding 5 g of zinc (-400 mesh) to 0.8 liters of two selected types of leaching solutions. One type of leaching solution was produced under the following conditions: lixiviant 1 *M* HCl, temperature 30°C, stirring speed 350 rpm, flyash added 5 g, and solution volume 0.8 liter. The recovery experiment was performed at the same temperature and stirring speed as the leaching experiment. More than 80% of the cadmium



Fig. 6. (a) Cadmium and (b) lead concentration in 1 M HCl leaching solution after zinc addition.

precipitated out by cementation in about 5 min after the addition of zinc. The cadmium left in the solution after 5 min was only 0.0025 grams/l. However, when the recovery experiment was continued beyond 5 min, almost all of the precipitated cadmium had redissolved, as shown in Fig. 6(a), due to the relatively high concentration of HCl. The pH initially was 0.04 and only rose to 0.09 at the end of the experiment. Similar observations were made in the case of lead, as shown in Fig. 6(b).

A second type of leaching solution was produced under identical conditions as above except the lixiviant concentration was decreased to 0.1 M HCl and temperature was increased to 60°C. The recovery experiment was again conducted at 30°C and 350 rpm with the addition of 5 g zinc. As can be seen in Fig. 7 (a), more than 95% of the cadmium precipitated out in about five minutes after the zinc addition. The cadmium level in the solution dropped to 0.3 ppm, and remained below the EP toxicity limit of 1 ppm. The initial pH of the solution was 1.17, rising to 3.41 at the end of the experiment. Similarly lead was more than 95% precipitated five minutes after the addition of zinc, as shown in Fig. 7(b). The final lead concentration in the solution, 3.5 ppm, remained below the EP toxicity limit of 5 ppm.

The cementation experiments reported here are preliminary and were per-



Fig. 7. (a) Cadmium and (b) lead concentration in 0.1 M HCl leaching solution after zinc addition.

formed to determine the feasibility of the cementation process for the leachates encountered. The amount of zinc required to recover the lead and cadmium is considerably more than would normally be used in a commercial process. It is apparent that high concentrations of HCl in the lixiviant require excessive amounts of zinc and should be avoided. Additional research is underway to reduce zinc consumption in the cementation process to acceptable levels.

## Stabilization

The flyash used in the stabilization studies was from the same source as used in the leaching studies, but samples were taken several months earlier. The basic characteristics were essentially the same for both materials, except for slight differences in composition. A more detailed discussion of the stabilization investigation is available elsewhere [7].

The results of the TCLP test, presented in Table 5, indicate that lead and cadmium are the metals of concern regarding disposal of flyash. Therefore the focus of the stabilization study, was to reduce the leachability of these two metals. The test was designed to simulate the long-term leaching characteristics of the waste, with the acetic acid simulating the action of rainwater and bacteria. The leachability tests used in this study can be viewed as modified TCLP or EP Toxicity tests.

## Stabilization procedure and results

The two stabilization agents used were sodium bentonite and portland cement. The cement was used to solidify the mixture and give strength to the resulting solid, and the sodium bentonite was added in the hope of greatly reducing the permeability of the solid. Various combinations of cement, sodium bentonite, and flyash were attempted. The cement was sieved to remove any large particles. In one set of experiments cement and the sodium bentonite were mixed in two ratios, 1:1 and 4:1, cement to sodium bentonite by weight. The materials were carefully blended to obtain a homogeneous material which was then mixed with equal amounts of flyash, by weight. Deionized water was added to produce a thick slurry which could be formed into cubes using a die especially designed for the purpose. Two sizes of cubes were made, 0.5 in. and 0.375 in. In a second set of experiments, flyash and cement were combined, without sodium bentonite. Two ratios of cement to flyash were used, 1:1 and 4:6, by weight. After allowing the cubes to set for 48 hours, samples were immersed in 0.25 liter of aqueous acetic acid solution in which the pH of the solution was maintained at  $5 \pm 0.2$ . The solution was stirred for fixed times and analyzed for lead and cadmium by AA.

Tests on cubes containing sodium bentonite were not successful. Cubes with 25% (w/w) sodium bentonite disintegrated immediately upon immersion in the acetic acid solution. Cubes with 10% sodium bentonite did not break up immediately, but showed signs of fracturing and did so after a few hours im-

mersion. Such structural failure is attributed to the nature of sodium bentonite which, when hydrated, swells to 13 times its dry volume. This large volume increase breaks down the cement matrix, causing the cube to disintegrate.

The cubes composed only of flyash and cement were stronger than the cubes containing sodium bentonite. The flyash and cement mixture must be homogeneous, however, or the cube disintegrates upon immersion in the solution. Homogeneous flyash and cement cubes maintained their structural integrity when immersed in the acidic solution.

Leaching experiments were performed on both the intact cubes and cubes crushed to a fine particle size (-30 mesh) with a hammer. The experiments on the crushed cubes were performed in order to determine the maximum amount of lead and cadmium that could be leached from the cubes without having to run experiments for a very long time. The concentration of lead leached from a crushed cube was higher than from the intact cube but was significantly lower than that of lead leached from an equivalent amount of flyash alone. The crushed flyash cubes contained 5 g of flyash and the lead concentration in the solution after 7 days was 0.31 ppm. Leaching experiments on the same amount of untreated flyash resulted in a dissolved lead concentration of 7 ppm after 1 day. This large reduction in leachability by stabilization indicates that most of the lead present in the flyash has chemically bonded with the cement, since even in the crushed cube, where diffusional resistance has been made small enough for equilibrium to be established, the concentration never reaches the levels found with untreated flyash.

The concentration of cadmium similarly leached (pH 5) from a crushed cube or from a whole cube was quite low, close to the limits of the analytical technique. This indicates that the immobilization of cadmium is primarily chemical in nature. The cadmium concentration in the leachate from the crushed cubes was 0.03 ppm. The concentration in the leachate from the plain flyash was 27.8 ppm. A possible explanation for the chemical immobilization is the formation of insoluble silicates and hydroxides in the highly alkaline environment of the cement as suggested by Bishop [8] and Shively [9].

A disadvantage of the stabilization process is the large increase in mass of the final disposal product. The mass of the final product is twice that of the original quantity of waste. Reducing the cement fraction adversely affects the strength of the cube, causing the cube to fracture upon immersion for a few hours. The final ratio of 1:1 is the minimum ratio of cement to flyash for effective stabilization and structural strength. The loss of structural integrity is felt to be caused by the large fraction of the flyash which is water soluble. It is felt that the ratio of cement to flyash can probably be reduced if the water soluble components are removed prior to stabilization. Additional tests are underway in which solid residue from leaching experiments are stabilized by cement.

#### **Summary and conclusions**

As stated previously, municipal incinerator flyash is a characteristic hazardous waste, primarily due to the presence of lead and cadmium. Various means for characterizing the flyash used in this investigation have been employed, including X-ray diffraction, SEM examination, ICP and AA analyses, and ion chromatography. ICP and AA analyses are consistent with those reported in previous investigations on flyash from similar incinerators [2]. X-Ray diffraction revealed the presence of lead in the form of PbSO<sub>4</sub> and PbCl<sub>2</sub>. Although specific compounds for zinc could not be identified, the results of the characterization along with the leaching experiments suggest that a large portion of the zinc is present as an amorphous oxide. Similarly it is likely that a significant portion of the lead is also present in amorphous form, and that the amount of lead sulfate exceeds that of lead chloride. This would be consistent with the initially rapid dissolution of zinc and lead in the various leaching solutions used.

Two very different processing schemes for the treatment of flyash have been investigated. The first approach is relatively simple and involves stabilization with portland cement. Results indicate that flyash can be stabilized with a 1:1 mixture of flyash and portland cement which meets environmental requirements. Cadmium appears to be primarily chemically immobilized by this procedure, since the leachability is independent of particle size. Lead, on the other hand, appears to be mostly chemically immobilized, but the leachability of the unreacted lead is also slowed by diffusion from the solid matrix. This is an attractive approach, since it is simple, but suffers from the fact that the amount of waste to be disposed of is essentially doubled, unless some use can be found for the material.

The second approach to treatment of flyash involves the recovery and recycling of metal values by leaching and subsequent precipitation. It has been demonstrated that extraction of the metal content from the flyash, specifically lead, cadmium and zinc, can be accomplished quickly and efficiently by leaching in hydrochloric acid solutions. Preliminary experiments on the subsequent recovery or precipitation of the lead and cadmium by cementation with zinc dust appear to be promising. Further research on the cementation process is continuing, especially with regard to minimizing the consumption of metallic zinc by the acid in the leaching solution while still maximizing the extraction of lead, cadmium and zinc from the flyash. This may be accomplished by the addition of NaCl, using an HCl concentration between 0.1 and 1.0 M or both. Eventual recovery of metallic zinc by electrolysis or a purified zinc compound by chemical precipitation is also under investigation.

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