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Informal Report

CITRATE EXTRACTION OF HEAVY METALS FROM INCINERATOR BOTTOM ASH

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Final Report

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Abstract

The Brookhaven National Laboratory (BNL) Citric Acid Process, developed to remove and recover toxic metals and radionuclides from contaminated soils and wastes, was tested with municipal solid waste incinerator bottom ash (BA) as a first step to evaluate the environmental and regulatory acceptability of the treated ash. Bottom ash was selected, given that with most mass burn facilities, this ash is 85 to 90% of the total ash weight and has the highest reuse potential. The metals in the ash were first extracted with citric acid and later recovered through biodegradation of the citric acid extract. Greater than 90 % of Cu, Mg, Mn, Pb, and Zn were extracted from the ash. The extraction efficiencies were probably dependent upon the nature of association of the metal with the mineral phase of the ash. Biodegradation of the extract resulted in the complete metabolism of the citric acid and recovery of ~ 99% of Ba, Fe, Mn, Sr, and Zn, 96% of Pb, 94% of Ti, and 90% of Ni in the solid phase with the biomass. These results show that the BNL citric acid process can be effectively used to treat incinerator ash for environmental compliance. Future efforts will be directed at bench scale optimization of the process, recovery of citric acid for recycle, scale up, and demonstration at a full-scale ash production facility. The recent US Supreme Court ruling requires ash generators to test, and if required, treat the ash as hazardous waste. The BNL treatment process may improve the potential of ash to be reused as an aggregate versus disposal at the expensive and decreasing landfill space. In the long run this technology is expected to mitigate problems of ash disposal and end use.

I. Introduction

Incinerator bottom ash generated from the combustion of residential and commercial solid wastes contains metals of potential environmental concern (Roethel and Breslin, 1988; Breslin et al., 1988). Out of 196 million tons of municipal solid waste (MSW) generated yearly in the U.S., 32 million (16%) is incinerated (Federal Register, 1994). During combustion, the weight of the waste is reduced by 60 to 75%, resulting in over 8 million tons of incinerator ash annually.

Although ash generated in the waste-to-energy MSW incinerators contains high levels of potentially toxic metals such as Pb, Cd, Zn, Ni, and Cu, in the past it has been exempted from regulations as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) (Federal Register, 1994). However, on May 2, 1994, the Supreme Court ruled that ash generated by the combustion of the MSW or a combination of MSW and non-hazardous industrial or commercial wastes in waste-to-energy facilities is no longer exempt from the RCRA and thus is subject to Toxicity Characteristics Leaching Procedure (TCLP) testing. In addition, the Court indicated that this decision in fact annulled the 1980 exemption (40CFR261.4(b)(1)) of waste-to-energy refuse generated by MSW alone (Federal Register, 1994). In accordance with this ruling, the facilities generating incinerator ash will have to determine if incinerator ash is hazardous under Subtitle C¹ of RCRA and manage it in compliance with the hazardous waste regulations if characterized as TCLP hazardous (Federal Register, 1994).

This recent ruling has forced the entire incinerator industry to look into new technologies to treat the ash so that it will pass the TCLP test. In particular, the ruling on ash is predicted to have a direct impact on the current garbage disposal policies on Long Island. Currently, the towns of Brookhaven and Hempstead have a cooperative arrangement for waste disposal, whereby Brookhaven's garbage is incinerated in Hempstead and the ash

¹ Subtitle C is a program within RCRA which deals only with present and future generation of hazardous waste (EPA 530-SW-86-001, 1986).

from the incinerator is landfilled in Brookhaven. Recently, the town's lack of testing of the incinerator ash, prior to landfill, has engendered criticism from the Department of Environmental Conservation. This means that disposal of the incinerator ash in accordance with EPA regulations may cost 3 to 10 times more in the future if it is not stabilized by the American Ref Fuel Hempstead facility in order to pass routine testing.

Presently, the available treatment processes offered to incinerator ash generators are stabilization, solidification and vitrification. These techniques essentially trap the contaminants in a matrix or renders the metals less soluble so that their leaching potentials, as measured under TCLP, are reduced (Chesner, 1994). None of the current Pb and Cd stabilization processes used in the U.S. or the world, produce a Pb or Cd bearing ash which is less hazardous or toxic in regards to ash dermal, ingestion, or inhalation exposure. The TCLP test is limited to evaluating leachable RCRA metals (Ag, As, Ba, Cd, Cr, Hg, Pb, Se), and thus ignores the hazards of incinerator ash under the other exposure routes. In addition to the ongoing need for TCLP control in all U.S. states and composition control in specific states, the reuse of BA is also currently criticized by environmental agencies and groups due primarily to the Pb and Cd contents of BA.

In response to the above regulatory, political and environmental control needs, the extraction, and hence compositional and TCLP reduction of Pb and Cd from incinerator ash residues is a needed technology.

Brookhaven National Laboratory (BNL) has recently developed a process for the removal and recovery of radionuclides and toxic metals from contaminated soils, sludges and wastes (Francis and Dodge, 1994). This patented technology uses citric acid to extract the metals from contaminated materials and subsequently converts the metals and radionuclides to a concentrated form suitable for disposal or recycle (Francis et al., 1992; Francis and Dodge, 1992). This technology also has the potential to cleanup toxic metal contaminated wastes such as incinerator bottom ash.

Objective

The primary objective of this research is to define a cost effective method of solubilizing the surface active lead in bottom ash thus reducing the Pb oxide availability in the environment and under TCLP.

The bottom ash is no longer exempt from RCRA TCLP testing and it will often fail this test for Pb at > 5.0 ppm. The controlled leaching of heavy metals within BA should allow BA to pass TCLP and greatly increase the end-use market potential for BA. Secondary metals and salts recovery via controlled extraction would also improve the potential use of BA. BA uses are currently restricted to low leach potential applications such as asphalt aggregate due to the initial surge of Pb and salts from BA as a loose aggregate.

As an alternative to stabilizing Pb in BA, FESI/BNL will evaluate the feasibility of intentionally solubilizing Pb by the use of citrate chelation within or outside of the BA quenching system which is currently used to control ash dust, temperature, and provide boiler seal. Following the chelation and complex formation, the resultant Pb bearing solution would be processed through coprecipitation or digestion in order to extract Pb complexes and return treated wastewater as make-up water to the ash quench system.

II. Materials and Methods

Incinerator Bottom Ash

BA contains a variety of trace heavy metals such as Pb, Cd, Ba, Zn, and Cu, and is primarily a semi-vitrified Si matrix with Fe, Al, Ca, S, Cl, Ti, and K in order of concentration. The particle size of this material varies greatly due to the processing facility type and post combustion materials handling systems used. In most cases the BA is quenched with H₂O at 160-180°F in a drag of ram expeller device immediately after the final zone of combustion. The predominant soluble metal of concern to regulators and end-users is Pb. The Pb is found mostly as an oxide.

Incinerator bottom ash from a mass-burn facility with a superheater and primary boiler section flyash direct discharge to the BA wet rams was provided by Forrester Environmental services. The ash contained approximately 28% water. The sample was sieved into two size fractions: mesh 30 (< 0.6 mm) and mesh 4 (< 4.75 mm). Only these particle size fractions were used in this study.

Total Metal Determination

Total metal content in ash was determined by acid digestion (Lim and Jackson, 1982). Prior to the actual acid digestion, the ash sample was ground to a powder with a mortar and pestle. Three replicates of 0.5 g were placed in three separate 30-ml platinum crucibles. Five ml of concentrated HNO_3 (Ultrex, J. T. Baker Chemical) was added to each crucible. The mixture was heated on a hot plate to almost dryness. An additional 3 ml of HNO_3 plus 2 ml of HClO_4 were added to each crucible. The mixture was then heated until fumes of HClO_4 appeared. The crucibles were cooled and then 5 ml of HF (30%) was added. The mixture was then reheated and evaporated to dryness. Finally, 5 ml of concentrated HNO_3 and 5 ml of deionized water were added, heated until the solution boiled gently, transferred into volumetric flasks, and diluted to 100-ml with deionized water. Metals were analyzed by ICP-MS.

Selective Extraction

A selective extraction was conducted to determine the mineralogical associations of metals in the ash (Figure 1). Sequential extraction determines the metals in the water soluble, exchangeable, carbonate, iron-manganese oxide, organic and inert fractions (Tessier et al., 1979). Ten grams of duplicate ash samples (mesh 30) were placed in two 500-ml polyethylene bottles. The ash samples were extracted with 100 ml deionized water to determine the soluble fraction and then with 200 ml of 1.0 M MgCl_2 to determine the exchangeable fraction of the metals. In the next step, the residue was extracted with 200 ml of 1.0 M sodium acetate at pH 4-5 for 5 hours to determine the metals associated with the

Figure 1. Selective Extractions of Metals

carbonate fraction. Metals in the Fe-Mn oxides fraction were then determined by treating the residue with 100 ml of 0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ at 96°C for six hours. The extraction was done by shaking the bottles at periodic intervals. The metals associated with the organic fraction were determined by oxidizing the residue after Fe-Mn extraction with 15 ml of 1.0 N HNO_3 and 30 ml of 30% H_2O_2 at 85°C for five hours. At the end of each step the solids and the liquids were separated by centrifugation. The supernates from each extraction step were analyzed for metal contents by ICP-MS. Blanks containing no bottom ash were also subjected to selective extraction and analyzed for metals.

Effect of Citric Acid Concentration on Extraction Efficiencies of Metals

Bottom ash was extracted with different concentrations of citric acid to determine the removal efficiencies of the metals. Fifteen grams of dried ash (mesh 30) was placed into 500-ml polyethylene bottles and extracted with 300 ml citric acid (ACS Reagent grade, Sigma) solution using a wrist action shaker (Burrell Corporation, Pittsburgh) at 25°C for 48 hours. Three different concentrations of citric acid, 0.1 M, 0.2 M and 0.5 M, were used to determine the metal extraction efficiency. During extraction, the bottles were wrapped with aluminum foil to avoid possible photodecomposition of the metal-citrate complexes. Periodically, 5 ml samples were taken from each bottle and filtered through a 0.45 μm Nuclepore filter. The samples were then acidified to pH ~ 2 using concentrated HNO_3 (Ultrex, J. T. Baker Chemical) and analyzed for metals by ICP-MS.

Effect of Temperature on Extraction Efficiencies of Metals

Extractions were conducted at 25°C and 85°C to compare the effect of temperature on extraction efficiency. Variations in extraction temperatures is of interest given that BA is quenched at an initial ash drop temperature of 1370-980°C on the wet rams or wet drags. Thirty-five grams dry ash (mesh 4) was placed in 500-ml polyethylene bottles to which 300 ml of 0.5 M citric acid was added. All extractions were carried out in duplicates. Extractions at 25°C were carried out as described earlier. The extractions at 85°C were

performed by placing the bottles in a heated oven and mixing the contents frequently. Samples were taken periodically from each bottle, filtered through a 0.45 μm filter, and analyzed for metals by ICP-MS.

Biodegradation of Citric Acid Ash Extract

The citric acid extract was subjected to biodegradation to recover the metals. For this purpose, *Pseudomonas fluorescens* biovar II (ATCC 55241) capable of degrading citric acid as a sole carbon source was used. The bacterium was grown in modified Simmon's citrate medium containing: 2 g citric acid, 0.2 g MgSO_4 , 1 g NH_4Cl , 1 g K_2HPO_4 and 5 g NaCl in one liter of deionized water. The pH of the medium was adjusted to 6.2 with 2 N NaOH. The bacterium was grown at $26 \pm 1^\circ\text{C}$ in the dark in a rotary shaker.

Duplicate diluted citric acid extract solutions ($\sim 18 \text{ mM}$ citric acid) were amended with nutrients consisting of 0.1% of NH_4Cl , K_2HPO_4 and KH_2PO_4 . The pH of the extract was adjusted to 6.3. One hundred milliliters of each sample were placed in 250 ml flasks and then inoculated with 4 ml of an 18-hour old culture of *P. fluorescens*. One control flask for each sample was prepared but not inoculated. The samples were incubated on a shaker at $26 \pm 1^\circ\text{C}$ and 150 rpm. All experiments were carried out in the dark to minimize possible photodecomposition of metal-citrate complexes. Following the incubation, 3 ml aliquots from each flasks were removed periodically and filtered through a 0.22 μm filter. The filtered samples were analyzed for pH, citric acid and metals as described later. Three separate sets of biodegradation experiments (Experiments 1, 2 and 3) were carried out. Experiments 1 and 3 were periodically monitored for pH, citric acid, and metal concentration in the liquid phase, while in experiment 2 the samples were analyzed only at the beginning and the end.

Metal Recovery

After biodegradation, the samples were centrifuged (12,000 rpm, 20 min.) to separate the solids (biomass and metal precipitates) from the solution. The solid phase was dried

overnight at 70°C and then weighed. The solid was dissolved in 5 ml concentrated Ultrex HNO₃, diluted to 200 ml with deionized water and analyzed for metals by ICP-MS. Metal recovery was calculated as a percentage of the initial metal concentration of the citric acid extract.

Chemical Analysis

Citric acid was analyzed by a Shimadzu LC-10AS high pressure liquid chromatography (HPLC) and a SPD-10A UV-vis detector at 210 nm. The mobile phase used was 0.003 N H₂SO₄ at a flow rate of 0.6 ml/min. For both standard and samples, a 20 µl volume was injected into a 25-cm, 5 µm Aminex HPX-87H column. Identification of citric acid was made by comparison with standard retention time (ACS Reagent grade, Sigma). Sample concentrations were calculated from sample peak areas compared to that of the standard curve. The analytical precision of replicated injections was < ± 5%.

Metals were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). For both standard and samples, indium was added as an internal standard. Based on the concentration, samples were diluted with 1% HNO₃ (Ultrex, J.T. Baker Chemical). The concentrations for each metal were calculated according to standard curves determined by SPEX Multi-Element Plasma Standard (SPEX Industries Inc.) and corrected for a blank.

III. Results

Total Metal Analysis

The metal content of the BA is given in Table 1. The BA contained high concentrations of Al (3.4%), Fe (4.7%), and Mg (0.42%), and varying levels of toxic metals. In particular, the BA contained approximately 590 ppm of Pb, 1090 ppm of Ni, and 32 ppm of Cd.

Table 1. Analysis of Metals in Mass Burn Bottom Ash

<i>Major metals (%)</i>		
Aluminum (Al)	3.37	$\pm 1.23^a$
Iron (Fe)	4.73	± 1.44
Magnesium (Mg)	0.42	± 0.15
 <i>Trace metals ($\mu\text{g/g dry wt}$)</i>		
Barium (Ba)	873	± 80
Cadmium (Cd)	31.6	± 7.9
Chromium (Cr)	309	± 53
Copper (Cu)	558	± 180
Lead (Pb)	593	± 170
Manganese (Mn)	534	± 73
Nickel (Ni)	1090	± 330
Strontium (Sr)	324	± 36
Tin (Sn)	120	± 21
Titanium (Ti)	6280	± 1020
Zinc (Zn)	3170	± 460

^a Standard deviation.

Selective extraction

The results of the selective extraction of bottom ash are presented in Figure 2. Metals were associated with the carbonate, oxide, organic and inert fractions to varying degrees. The soluble and exchangeable forms of the metals in the BA were very low. Substantial amounts of Al, Cd, Cr, Fe, Ni, Sn, and Ti were associated with the inert fraction which is predominantly silicate. Other metals were associated in varying degrees with the carbonate, oxide, and organic fractions. For example Zn was mostly associated with the carbonate fraction, Cd with the inert fraction and Pb with the organic and Fe-Mn oxide fractions.

Extraction efficiencies of metals

The extraction efficiencies of metals using three different concentrations of citric acid are summarized in Table 2 and Figure 3. The extraction efficiencies generally increased with increasing citric acid concentration. With 0.1 M citric acid, approximately 91% Mg was extracted and 40 to 60% extraction efficiencies were achieved for Cu, Pb, Mn, Sr and Zn. With 0.5 M citric acid, Mg, Cu, Pb, and Mn had extraction efficiencies greater than 90%. However, the extraction efficiencies for Ba, Cd, Cr, Fe, Ni, and Ti with 0.5 M citric acid were less than 30%. As shown in Figure 3, it appears that most metals were extracted from the ash within 5 hours. For metals with low extraction efficiencies such as Fe, the extraction efficiency increased slowly with time. The variation in the amount of metals extracted was related to the mineralogical association in the ash. Metals associated with the silicate fraction had lower extraction efficiencies. TCLP tests of BA before and after 0.2 M citric acid extraction is shown in Table 3. TCLP for lead in the BA used in this study showed that it was 3.2, ppm which is well below the regulatory requirement of 5 ppm (Table 3). However, treated BA showed much less TCLP lead indicating the potential applications of citric acid extraction process.

Figure 2. Mineralogical Associations of Metals in Bottom Ash

Figure 2. (cont'd) Mineralogical Associations of Metals in Bottom Ash

Table 2. Effect of Citric Acid Concentration on Metal Extraction Efficiency

Metal	% metal extracted ¹		
	0.1 M	0.2 M	0.5 M
Aluminum (Al)	40 ± 5 ^a	51 ± 5	52 ± 6
Barium (Ba)	25 ± 0	28 ± 0	26 ± 0
Cadmium (Cd)	14 ± 1	18 ± 1	16 ± 1
Chromium (Cr)	16 ± 1	17 ± 1	20 ± 1
Copper (Cu)	54 ± 7	74 ± 9	90 ± 10
Iron (Fe)	9 ± 1	22 ± 2	29 ± 2
Lead (Pb)	61 ± 6	74 ± 8	96 ± 9
Magnesium (Mg)	91 ± 5	94 ± 4	94 ± 5
Manganese (Mn)	46 ± 1	73 ± 1	97 ± 2
Nickel (Ni)	21 ± 2	26 ± 3	24 ± 2
Strontium (Sr)	43 ± 1	60 ± 1	60 ± 1
Tin (Sn)	39 ± 2	41 ± 2	47 ± 3
Titanium (Ti)	13 ± 0	14 ± 1	17 ± 1
Zinc (Zn)	61 ± 2	83 ± 2	87 ± 2

¹ Percent extraction was determined at 48 hours. Extractions were done with a mesh 30 size fraction at 25°C, and a ash to liquid ratio of 0.05 (g/ml).

^a Standard error.

**Table 3. Metal Concentration in Pre and Post-Citrate TCLP
Leachate of BA**

Metal	TCLP Before Citric Acid	TCLP After Citric Acid	Citric Acid (0.2 M)
<i>(mg/l)</i>			
Al	48	15	743
Fe	1.8	6.1	237
Mg	36	6.9	140
Ti	3.4	0.2	24
Bi	8.5	2.8	148
Pb	3.2	0.5	21
Cu	2.5	3.7	16
Sn	n.d.	n.d.	6.1
Zn	110	44	413
Sr	2.5	0.3	5.6
Mn	1.7	0.2	12
Ni	0.2	0.1	4.4
<i>(µg/l)</i>			
Cr	50	n.d.	800
Cd	68	7.0	150

n.d. = not detected.

Figure 3. Effect of Citric Acid Concentration on Metal Extraction from Incinerator Bottom Ash

Effect of temperature on extraction efficiencies

Extractions were carried out at 25°C and 85°C. The latter temperature is the quenching temperature of ash after combustion. Figure 4 shows the percentage of metal extracted during extraction at both temperatures. Most metals showed an increase in extraction efficiency at 85°C, with the exception of Fe, Sr, and Ti (Table 4). The extraction efficiency of cadmium increased by ~ 1.8 fold at 85°C.

Biodegradation of citric acid ash extract

Citric acid was completely degraded in 43 hours (Figure 5). The initial degradation rate of citric acid was ~ 80 mg l⁻¹ h⁻¹. During biodegradation, the pH increased from 6.3 to 9.0 (Figure 5). The removal of metals during biodegradation (experiment 1) is shown in Figure 6. There was no change in metal concentration in the uninoculated samples.

In Tables 5A, 5B, and 5C the metal removal efficiencies for the three sets of biodegradation experiments are compared. Lead removal efficiencies ranged from 93-99 percent. Significant amounts of other metals Fe(99%), Ba (99%), Mg (99%), Ni (87-91%), Sn (99%), Ti (89-98%), Zn (≥99%), and Cd(88%) were also removed after biodegradation of the citric acid extract.

Lead removal rates of 0.045 mg l⁻¹ h⁻¹ and 0.022 mg l⁻¹ h⁻¹ were obtained for experiments 1 and 3, respectively (Figure 7). The removal of metals during experiment 3 is presented in Figure 8.

Metal Recovery

The concentration of metals recovered along with the biomass is listed in Table 6. Approximately 0.47 g of biomass was produced per gram of citric acid metabolized.

Figure 4. Effect of Temperature on Metal Extraction from Incinerator Bottom Ash

Table 4. Temperature Effect on Metal Extraction Efficiencies

Metal	% metal extracted ¹	
	25°C	85°C
Aluminum (Al)	25 ± 3 ^a	53 ± 6
Cadmium (Cd)	7 ± 0	13 ± 1
Chromium (Cr)	8 ± 0	21 ± 1
Copper (Cu)	>99	69 ± 11
Iron (Fe)	23 ± 2	20 ± 2
Lead (Pb)	>99	>99
Magnesium (Mg)	95 ± 4	>99
Manganese (Mn)	75 ± 2	>99
Nickel (Ni)	18 ± 2	68 ± 10
Strontium (Sr)	34 ± 1	43 ± 1
Tin (Sn)	37 ± 1	>99
Titanium (Ti)	13 ± 1	23 ± 1
Zinc (Zn)	>99	>99

¹ The percent extraction was determined at 72 hours. Extractions were done with 4 particle size, with 0.5 M citric acid, and a ash to liquid ratio of 0.12 (g/ml).

^a Standard error.

Figure 5. Biodegradation of Citric Acid Ash Extract

Figure 6. Removal of Metals from Citric Acid Ash Extract During Biodegradation

Figure 6. (cont'd.) Removal of Metals from Citric Acid Ash Extract During Biodegradation

Table 5A. Biodegradation of Citric Acid Extract
(Experiment 1)

Component	Concentration (ppm)		Percent Removed
	Before Biodegradation	After Biodegradation	
Citric Acid	3467	< 1	> 99
<i>Metals</i>			
Barium (Ba)	0.17	n.d.	> 99
Copper (Cu)	1.20	0.14	88
Iron (Fe)	46.0	0.12	> 99
Lead (Pb)	2.90	0.20	93
Magnesium (Mg)	16.0	11.2	30
Manganese (Mn)	1.46	0.02	99
Strontium (Sr)	0.66	0.11	83
Titanium (Ti)	2.10	0.24	89
Zinc (Zn)	51.0	0.50	99

Reactions were carried out at $26 \pm 1^\circ\text{C}$ for 72h.

n.d. = Not detected.

Table 5B. Biodegradation of Citric Acid Extract**(Experiment 2)**

Component	Concentration (ppm)		Percent Removed
	Before Biodegradation	After Biodegradation	
Citric Acid	3840	< 1	> 99
<i>Metals</i>			
Aluminum (Al)	118	1.1	99
Barium (Ba)	0.20	n.d.	> 99
Copper (Cu)	3.90	0.300	92
Iron (Fe)	98	1.0	99
Lead (Pb)	3.84	n.d.	> 99
Manganese (Mn)	4.30	n.d.	> 99
Nickel (Ni)	2.10	0.20	91
Strontium (Sr)	1.40	n.d.	> 99
Tin (Sn)	0.28	n.d.	> 99
Titanium (Ti)	4.80	0.02	94
Zinc (Zn)	36.8	n.d.	> 99

Reactions were carried out at $26 \pm 1^\circ\text{C}$ for 72h.

n.d. = Not detected.

Table 5C. Biodegradation of Citric Acid Extract**(Experiment 3)**

Component	Concentration (ppm)		Percent Removed
	Before Biodegradation	After Biodegradation	
Citric Acid	3136 ± 52 ^a	n.d.	>99
<i>Metals</i>			
Cadmium (Cd)	0.015 ± 0.001	0.002 ± 0.001	88
Copper (Cu)	1.25 ± .05	0.399 ± 0.026	68
Iron (Fe)	11.3 ± 0.9	0.116 ± 0.027	99
Lead (Pb)	1.01 ± 0.05	0.006 ± 0.000	99
Magnesium (Mg)	10.5 ± 1.3	1.61 ± 0.15	85
Manganese (Mn)	14.4 ± 0.8	0.777 ± 0.03	95
Nickel (Ni)	0.158 ± 0.011	0.020 ± 0.000	87
Strontium (Sr)	0.252 ± 0.003	n.d.	>99
Tin (Sn)	0.124 ± 0.000	n.d.	>99
Titanium (Ti)	1.14 ± 0.07	0.028 ± 0.003	98
Zinc (Zn)	7.27 ± 0.33	0.009 ± 0.004	>99

Reactions were carried out at 26 ± 1°C for 72h. Results are an average of triplicate observations.

ND: Not Determined.

n.d.: Not detected.

^a Standard deviation.

Figure 7: Lead Removal During Biodegradation

Figure 8: Metal Removal During Biodegradation (Experiment 3)

Table 6. Metal Content in Solid Phase after Biodegradation

Metal	Concentration ($\mu\text{g/g}$ dry wt.)	
	Experiment 2	Experiment 3
Aluminum (Al)	26500	ND
Barium (BA)	44.0	ND
Cadmium (Cd)	n.d.	24 $\pm$ 11 ^a
Copper (Cu)	534	757 $\pm$ 89
Iron (Fe)	18400	9530 $\pm$ 1290
Lead (Pb)	-	653 $\pm$ 69
Magnesium (Mg)	5480	6700 $\pm$ 900
Manganese (Mn)	453	12900 $\pm$ 1800
Nickel (Ni)	306	142 $\pm$ 18
Strontium (Sr)	201	118 $\pm$ 30
Tin (Sn)	49.0	82.2 $\pm$ 13
Titanium (Ti)	581	920 $\pm$ 110
Zinc (Zn)	4840	5690 $\pm$ 650

^a Standard deviation.

ND: Not Determined.

- : error in determination.

Experiment 3 is an average of duplicate samples.

IV. Discussion

Citric acid is a multidentate chelating agent which forms stable bidentate, tridentate, binuclear or polynuclear complexes with metal ions (Ekstrom and Olin, 1978; Hedwig et al., 1980; Francis et al., 1992). We have shown that citric acid can remove toxic metals, especially Pb, Cu, and Zn from incinerator bottom ash. Some metals like Mg, Cu, Pb, Mn, and Zn were readily extracted while other metals such as Fe, Cd, Ti, and Ni had lower removal efficiencies. This difference in efficiency is probably due to the nature of the association of the metals with the different mineralogical fractions in the ash. The selective extraction results provided further evidence to this assumption. For example, Zn was mostly associated with the carbonate fraction and Pb with the inorganic, Fe-Mn oxide and carbonate fractions. However, metals such as Sn, Ti, Ni, and Fe, which are associated with the inert fraction had lower extraction efficiencies. The higher extraction efficiencies of Pb and Zn as compared to Sn, Ti, Ni, and Fe, is due to their association with the inorganic and carbonate fractions which were more amenable to citric acid extraction than metals associated with the inert fraction. The overall metal concentrations in the ash sample prior to extraction are comparable to the ones reported for various bottom ash samples from different facilities (Forrester, 1989).

Typically, in these batch experiments, 0.47 g of biomass was produced per gram of citric acid metabolized during biodegradation. This corresponds to the production of 0.9 g of biomass per gram of ash treated. Recovery and reuse of the free citric acid from the metal citrate complexes prior to biodegradation, should further reduce the ratio of biomass produced to ash treated by the BNL process.

The mechanisms of metal removal from citric acid extract are due to a combination of factors: (1) the degradation of citric acid by *P. fluorescens* releases the metals as free ions; (2) biosorption of released metal ions by the biomass; and (3) pH increase during biodegradation of citric acid which facilitates the formation of metal hydroxide precipitates, especially for Fe and Al. Formation of these metal hydroxides are known to help coprecipitate trace metals out of solution (Stumm and Morgan, 1981; Bodek et al., 1988;

Schneider, 1988; Schindler, 1990) and also act as retainers and complex flocculent nuclei which further provide for a matrix stabilization and/or particle enhancement.

V. Significant accomplishments

Based on the results obtained from the laboratory batch studies, it is evident that citric acid is an effective extraction agent for the removal of toxic metals from incinerator bottom ash, especially Pb (>95% removal efficiency). Subsequent microbial treatment results in 93 - 99% Pb recovery from the citrate extract. The recovered Pb may be recycled or disposed off.

VI. Significant problems

- Extraction efficiency for Cd was low.
- Extraction efficiencies of other toxic metals also need to be improved.
- In this process, citric acid is completely destroyed. Methods are needed to recover and recycle citric acid used as extraction fluid to reduce the unit cost of ash extraction.

VII. Industry and laboratory benefits realized

The capability of the BNL citric acid process to remove Pb metals from incinerator bottom ash has been successfully demonstrated on a bench scale. This technology is expected to provide a dual method of reducing ash hazardousness under TCLP as well as mitigating problems of ash disposal and end use by reducing ash heavy metal content. However, scale up and implementation of the process on a pilot plant scale will be necessary to evaluate its commercialization prospects.

VIII. Recommended follow up work

- (i) In this CRADA, only bottom ash was used to evaluate the BNL citric acid treatment process. Future work will include all waste-to-energy facility refuse, namely bottom

and fly ash as well as scrubber residues from the acid gas control systems required on most modern waste-to-energy facilities.

- (ii) Design of processes to recover the citric acid and/or the heavy metals. These will include citric acid removal and/or heavy metal recovery from extraction fluids via solvent extraction, ion exchange, adsorption and chemical precipitation.
- (iii) Optimization of the extraction, biodegradation and/or recovery steps will be followed by scale up and demonstration at a full-scale ash production facility.
- (iv) Removal of any residual trace metal contaminants in the waste water for its recycle and reuse.
- (v) Stabilization of final solid waste heavy metal sludge concentrate by standard available methods, including BNL solidification and encapsulation technology.

IX. Potential benefits from pursuing follow-up work

Completion of the recommended follow up work is expected to yield a full fledged ash remediation technology. The treatment technology is expected to benefit the MSW incinerator industry.

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Bibliography

- Bodek, I., Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H. 1988. *Environmental Inorganic Chemistry*. Pergamon Press, New York.
- Breslin, V. T., Roethel, F. J., and Schaeperkoetter, V. 1988. Physical and chemical interactions of stabilized incineration residue with the marine environment. *Marine Pollution Bulletin*, 19 (IIB), 628-632.
- Brynhildsen, L. and Rosswall, T. 1989. Effects of cadmium (II) and citrate ion. *Annali di Chimica*. 65, 593-607.
- Chesner, W. H. 1994. Options for Stabilizing Municipal Waste Combuster Ash. *Preprinted Extended Abstract Presented at the I&EC Special Symposium American Chemical Society*.
- Ekstrom, L. G. and Olin, A. 1979. On the complex formation between lead (II) and citrate ions in acid, neutral, and weakly alkaline solution. *Chemica Scripta*. 13, 10-15.
- Environmental Protection Agency, May 1994. Sampling and Analysis of Municipal Refuse Incinerator Ash DRAFT. EPA530-R-94-020.
- Environmental Protection Agency, January 1986. RCRA Orientation Manual. Office of Solid Waste, EPA 530-SW-86-001.
- Federal Register, Rules and Regulations, Vol. 59, No. 108, Tuesday, June 7, 1994.
- Forrester, K. E. 1989. State-of-the-Art in refuse-to-energy facility ash residue characteristic, handling, reuse, landfill design and management: A summary. Presented at: Materials Research Society 1989 MRS Symposium, Boston, MA.
- Francis, A. J., Dodge, C. J., and Gillow, J. B. 1992. Biodegradation of metal citrate complexes and the implications for toxic metal mobility. *Nature* 356, 140-142.
- Francis, A. J. and Dodge, C. J. 1992. Reclamation with recovery of radionuclides and toxic metals from contaminated materials, soils, and wastes. *Conference Proceedings-The Third National Technology Transfer Conference & Exposition*, December 1-3, 1992, Baltimore, MD.
- Francis, A. J. and Dodge, C. J. 1994. Waste site reclamation with recovery of radionuclides and metals. U.S. Patent No. 5,292,456.

- Hedwig, G. R., Liddle, J. R., and Reeves, R. D. 1980. Complex formation of nickel (II) ions with citric acid in aqueous solution: A potentiometric and spectroscopic study. *Aust. J. Chem.* 33, 1685-1693.
- Lim, C. H. and Jackson, M. L. 1982. Dissolution for total elemental analysis. In *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*- Agronomy Monograph No. 9 (2nd Edition).
- Roethel, F. J. and Breslin, V. T. 1988. Interactions of stabilized incineration ash with the marine environment. In *Proceedings of the 1988 conference on solid waste management and materials policy*. New York City.
- Schindler, P. W. 1990. Co-adsorption of metal ions and organic ligands: formation of ternary surface complexes. In *Mineral-Water Interface Geochemistry* (Eds. M. F. Jr. Hochella and A. F. White), Mineralogical Soc. of America, Washington, DC, 281-307.
- Schneider, W. 1988. Iron hydrolysis and the biochemistry of iron- The interplay of hydroxide and biogenic ligands. *Chimia*, 42, 9-20.
- Stumm, W. and Morgan, J. J. 1981. *Aquatic Chemistry* 2nd Ed., John Wiley and Sons, New York, 796 pp.
- Tessier, A., Campbell, P. G. C., and Bisson M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, Vol. 51, 844-851.