

**Removal and Recovery of Heavy Metals From
Incinerator Ash Residues**

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P.O. BOX 2008

Hampton, NH 03843-2008

Peer Review

INTRODUCTION

This paper presents results of a novel and state-of-the-art patent-pending processes developed jointly by Forrester Environmental Services Inc. ("FESI") and Brookhaven National Laboratories ("BNL") for the extraction and recovery of lead (Pb), Cadmium (Cd), Copper (Cu), Zinc (Zn) and other heavy metals from heavy metal bearing wastes including but not limited to solid waste incinerator bottom ash, flyash and combined ash.

The heavy metal extraction and recovery processes were found to be capable of high percentage of heavy metals extraction and recovery at a relatively low cost under bench scale and full-scale refuse incinerator facility conditions. This paper presents empirical data from bench scale studies only, as the full-scale data is currently under review. The ash product remaining after extraction passed all TCLP regulatory limits and retained only minimal Pb, Cd, Cu, and Zn content and other water insoluble heavy metal compounds.

The extraction efficiency of the processes exceeded expectations for Pb, Zn and other key heavy metals at 90%+ levels, thus yielding post-extracted ash heavy metal contents well within current USEPA and state allowable levels in residential soils. The process capital and operating expenses were also determined to be highly cost competitive against conventional and currently used ash stabilization methods. The FESI/BNL Heavy Metal Extraction and Recovery Process is currently under contract for use at industrial applications throughout the world including waste incinerators and is expected to enhance the acceptance of incinerator ash use by significantly reducing the content, solubility and availability of heavy metals therein.

Results of heavy metals recovery and low cost from ongoing field applications of this technology are consistent with the bench scale data presented within this paper.

BACKGROUND

Waste-to-Energy Ash Production and Type

Waste-To-Energy ("WTE") facilities employ a form of recycling, involving the use of solid waste as a fuel to produce steam which in turn is used to produce electricity. In the combustion process the total volume of solid waste is reduced by 90%, resulting in an ash generation of nearly 10% by volume and 30% by weight. In most modern WTE facilities, refuse is combusted at temperatures approaching 1800 to 2500 degrees Fahrenheit. Most organic materials in

the solid waste are reduced to base elements such as Carbon, Oxygen and Nitrogen. Inorganic materials such as iron, aluminum, calcium, sodium and silicates make up the major components of ash residue, along with much smaller weight fractions such as Pb, Cd and Zn which are regulated due to their relative toxicity and potential threat to the environment.

The ash residues are collected at various points throughout the system, producing three distinctive types -- bottom ash (BA), fly ash (FA), and flyash scrubber residue (FASR). As the words imply, bottom ash is collected at the bottom of the furnace grates following the combustion process. Flyash is composed of small particles which are carried by the combustion flue gas and then captured by the air pollution control devices or drop-out hoppers. Bottom ash typically represents roughly 85 to 90 percent by weight of the total ash produced in a mass burn facility, with flyash and scrubber residues comprising the remaining 10 to 15 percent ("scrubbers" are combustion gas cleaning systems that neutralize acid gases). The BA/FA+FASR ratio for Refuse-Derived Fuel ("RDF") combustion facilities which remove a fraction of ferrous, non-ferrous and certain non-combustible wastes prior to combustion has been measured by FESI at full-scale operations at 50/50.

The use of lime scrubbers can significantly alter the leachability of FA by increasing or decreasing Pb solubility and decreasing Cd solubility based upon the pH-log solubility characteristics of those elements and compounds thereof. The water solubility of FA without lime scrubbing is often relatively low due to the neutral pH condition of FA, yet as lime scrubbing products and unreacted lime as hydroxide are added, the water solubility of the Pb in the newly produced FASR can greatly increase ... this due to the amphoteric nature of Pb that remains water soluble under low and high pH conditions.

The use of the acidic TCLP #2 test to measure the leachability of FASR under an assumed acid leaching condition actually lowers the pH of the FASR in solution with dilute acetic acid, and now presents FASR Pb solubility at a semi-neutral pH condition, as compared to the more probable high pH condition likely to occur in the field under much less acidic leaching conditions. Consequently the TCLP test can greatly under-predict the leaching potential of FASR.

Current Ash Management

Most commonly, FA/FASR and BA are combined at the WTE

facility and transported to permanent disposal sites. BA is usually wetted in a water quench system to allow for a boiler air seal and to cool the 1800 to 2500 degree F mass of silica and non-combustibles. The larger fractions of BA such as slag often fractures upon wetting due to sudden cooling in the water quenching tank.

FA and FASR are bone dry as generated from air pollution control devices after dry scrubbing towers, and are collected in enclosed hoppers due to their dust-like fugitive nature and human exposure risk. These FA/FASR residues are often wetted to control dusting, and thereafter added to the BA for disposal, thus producing a combined ash ("CA").

Landfill disposal remains the simplest and most cost effective method of disposing both BA and FA/FASR. The preferred practice is to dispose of the residue at the residue-only landfill, referred to as an ash "monofill".

Various concerns have been raised by regulators, public interest groups and scientists alike regarding the safe handling, disposal and possible use of ash residues. One of the most common concerns raised relates to the total compositional content of Pb and Cd in ash the fate of those elements over the long-term use and handling of ash products in the open environment.

Some opponents to ash use argue that: (a) heavy metals contained in residue are concentrated at unacceptable levels and (b) the metals are "leachable components" which have the potential to reach groundwater supplies. "Leachable components" are those elements or compounds which have the potential to dissolve in water. Ash use critics often also claim that as rainfall percolates through ash, it has the potential to leach these heavy metals and transport them into the water supply.

However, scientific tests throughout the international community have demonstrated that ash residues from modern WTE facilities, when properly managed at ash landfills do not leach contaminants at significant risk levels. In fact, CA leachate closely resembles seawater. As a matter of extra safety, these CA leachates are often collected and stabilized prior to disposal in accordance with strict federal and state environmental standards.

THE NEED FOR METALS CONTENT REDUCTION

In addition to the above mentioned leaching of heavy metal

bearing wastes, human and biological exposure to heavy metal content has long been of concern to environmental regulators and waste producers. Under the Resource Conservation and Recovery Act (RCRA) solid waste is classified by the U.S. Environmental Protection Agency (USEPA) as hazardous waste if excessive amounts of heavy metals leach from the waste when tested under the Toxicity Characteristic Leaching Procedure (TCLP). EPA also regulates the land disposal of certain heavy metal bearing wastes depending on the content of the heavy metals regardless of the leaching potential. In addition, several state governments require solid wastes with elevated levels of heavy metals be disposed of as a hazardous waste. Disposal of waste at a hazardous waste landfill is typically more expensive than disposal at non-hazardous waste landfills.

In an attempt to reduce the expenses associated with the landfill disposal of heavy metal leachable waste, particularly lead bearing waste, various methods to control heavy metal leaching and reduce heavy metals have been developed. These methods include the stabilization of lead bearing waste with, for example, portland cement, silicates, sulfates, phosphates and combinations thereof as well as acid digestion and metals recovery. However, these methods are often expensive and involve complex handling equipment and operations. Additionally, some of these methods use chemicals, such as strong acids, which in the amounts used, are hazardous to workers and corrosive to the waste handling and treatment equipment.

The stabilization methods most commonly used do not reduce compositional level or bioavailability of Pb and other regulated metals, and thus fail to reduce the risks of direct exposure to the waste after treatment. Given that many states now require limitation of heavy metal content for use or RCRA Subtitle D solid waste disposal of industrial wastes, the stabilization methods fail to provide the required technology for waste reuse or local landfilling.

Accordingly, a need exists for means of reducing lead content beyond leachable fractions, particularly when considering reuse of the ash outside of a landfill where environmental sensitivity to newly introduced heavy metals such as Pb and Cu can be extreme.

FESI/BNL PROCESS

In late 1993 FESI and BNL entered in the first of two Cooperative Research Agreements (CRADA) for development of a

safe, simple and inexpensive method of extracting and recovering inorganic compounds from industrial wastes. The process method is not disclosed herein given its pending patent status, although key results are presented.

The materials evaluated by FESI/BNL to date have included various heavy metal bearing wastes and materials, firstly bottom ash from solid waste combustion and the ferrous and non-ferrous metals normally produced along with the bottom ash, leaded paint contaminated soils, metal finishing sludges, foundry sands, K061 waste, Pb bearing soils and industrial site wastes. Such wastes, materials and residues often contain high levels of lead and cadmium which can be leached at levels in excess of 5 ppm (5 mg/l) and 1 ppm (1 mg/l) as determined by the USEPA TCLP leaching test and copper and zinc in excess of 25 ppm and 200 ppm as determined by the California state leaching test method. Such wastes also often contain total compositional heavy metals such as lead, cadmium, barium, chromium, copper, magnesium, manganese, nickel, strontium, tin, and zinc at levels which are higher than those allowed by the USEPA, state regulators and local officials for ash use in engineered products such as cement blocks and/or application to the environment such as roadbase aggregate.

Incinerator Bottom Ash Evaluation

Water quenched bottom ash from a solid waste combustion facility was first subjected to ten (10) separate composited baseline total metals and TCLP analyses in order to define the character of the ash prior to extraction. Total metal content in the ash was determined by acid digestion after grinding of an ash composite sample of 0.5 grams with a mortar and pestle.

Analytical Method: The composited bottom ash sample was placed in a 30-ml platinum crucible. Five ml of concentrated HNO₃ was added to each crucible. The mixture was then heated on a hot plate to almost dryness. An additional 3 ml of HNO₃ plus 2 ml of HClO₄ was added to the crucible. The mixture was then heated until fumes of HClO₄ appeared. The crucibles were cooled and then 5 ml of 30% HF was added. The mixture was then reheated and evaporated to dryness. Finally, 5 ml of concentrated HNO₃ and 5 ml of deionized water was added, heated until the solution boiled gently, transferred into volumetric flasks, and diluted to 100-ml with deionized water. Metals were then analyzed by ICP-MS.

The bottom ash baseline sample was also subject to the Toxicity Characteristic Leaching Procedure (TCLP) as set

forth in the Federal Register Vol. 55, No. 61 (Mar. 29, 1990) which corresponds in pertinent part to the procedure set forth in Federal Register, Vol. 55, No. 126, pp 26985-26998 (June 29, 1990). This test procedure is also referenced in EPA SW 846, 3rd Edition. The TCLP test produces an aliquot of filtered solution containing soluble metals which were analyzed by ICP-MS.

Extraction Method: In this first study, 100 grams of <3/4" size reduced BA was subjected to three separate solutions of a FESI patent-pending Modified Complexing Agent ("MCA") at an ash to solution ratio of 1:20 for 48 hours using a wrist action shaker to maintain mixing contact. During extraction, 5 ml aliquot samples were taken in order to assess the time variance of the extraction efficiency. After the 48 hour extraction period, the ash was dewatered via centrifuge (12,000 rpm, 20 min.) and then subjected to a post-extraction TCLP and total metals analyses. Extractions were conducted at 25 degree C and 85 degree C in order to assess the impact of temperature on the extraction of metals, given that the bottom ash incinerators often quench the bottom ash at elevated temperatures.

The use of an ash centrifuge for dewatering and removal of residual MCA solution from the ash solid matrix, 48 hour batch mixing of the ash with the MCA solution and contact with varied solutions were all considered by FESI to define certain upper boundaries of removal efficiencies of metals under aggressive mixing, dewatering and contact conditions. Field and laboratory evaluations of less aggressive and more likely full-scale applications of the technology including press dewatering, extraction in a semi-mixed batch reactor, contact times of 5 to 60 minutes and lower MCA concentration extract conditions were also conducted. These more probable field operating conditions don't preclude the use of one or more of the aggressive methods described if needed to achieve target removal percentages.

The chemical constituents of the extract remaining after the removal of ash from the extraction vessel was of great interest during the research effort. The recovery and management of complexed metals and free MCA in solution after contact with the ash through biodegradation and/or precipitation are an important aspect of commercialization of the process.

In order to define the ability to control residual MCA and soluble metal complexes in the ash porosity after extraction as well as define a possible supporting wastewater treatment scheme, the MCA extract was subjected to biological

treatment to recover the metals from solution. For this purpose, a FESI patent-pending Engineered Bacteria ("EB"), was developed to consume MCA as a sole carbon source. A series of tests using EB were conducted to establish degradation efficiencies and rates.

After treatment, the extract samples were centrifuged (12,000 rpm, 20 min) to separate the solids biomass and metal precipitates from the solution which resulted in complete recovery. The solid phase was dried overnight at 70 degree C 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 extract correlated for relative mass.

Extraction Results

Metals Extraction. The ash baseline and post-48 hour extracted heavy metals concentrations and percent metal extracted are presented in Table 1 in rounded average values. The results clearly confirm the MCA extractability of major metals Aluminum, Iron and Magnesium as well as trace metals such as Cadmium and Lead in all solutions evaluated. The measurement of extract metals concentration over time indicated that a majority of the metals from ash were recovered in the first 5 hours with a classical inflection of diffusion rate from surface to bulk mobility occurring at 5 to 10 hours with a gradual transition to flat slope of extraction after 20 hours.

Total Pb was 85% extracted at only 5 hours ... having a very steep extraction rate from 0 to 5 hours, 100% of total extractable amount at 25 hours with a 10 degree slope from 5 to 25 hours and a flat extract-to-time relationship after 25 hours. This time-effect observation was important, as long-term extractions such as 48 hours would likely require separate ash handling facilities due to the high tonnage production of ash and the need to store 48 hours production of ash while waiting on batch baths, or the need to have a higher batch production system to handle batch reaction times. Shorter extraction periods would allow for extraction and ash processing in-line or along side existing ash production facilities.

Temperature Effects. The ash extractions were also found to vary with temperature. Most metals showed an increase in extraction efficiency at 85 degree C as compared to 25 degree C, with the exception of Fe, Sr and Ti. This temperature effect could prove useful when applying the MCA

to ash quenching tanks or when timing the bath reactor loading such that hot ash is subjected to extraction. A hot batch extraction process may also prove very useful in post-combustion ferrous and non-ferrous scrap metal polishing and cleaning prior to sale, as the removal of surface oxidized metals and contaminants from the combustion process such as bottom ash or ash fines will increase the value of the scrap metal. Table 2 presents results of temperature effect on ash metals extraction. Extraction results were somewhat different from previous extraction testing due to sample variability common with incinerator ashes.

TCLP Control. The ash TCLP baseline and post-extraction, post-centrifuge dewatering results presented in Table 3 also confirm that the MCA removes the more readily soluble forms of metals as determined under the TCLP extraction method, thus reducing the residual metals available after ash dewatering for leaching within the buffered acetic acid solution used within the TCLP-1 test for BA.

Biodegradation. Biodegradation of residual MCA remaining in the extract after ash contact was found to occur rapidly and at a somewhat linear rate within 43 hours. The initial degradation rate of MCA was 80 mg per liter per hour. The removal of metals from solution and conversion of such to a precipitate was observed to be very high for metals as shown in Table 4.

The rate of metals removal varied, yet generally remained linear during the 48 hour period up to the point of reduction to levels less than 0.5 ppm where the metal concentration to time relationship flattened. Lead removal rates of 0.045 mg per liter per hour were observed. These results confirm that the residual metals in solution, and/or within the pores and on surfaces of the processed ash remaining after the ash MCA extraction, can be converted through biodegradation to insoluble precipitates within a liquid or solid ash matrix by addition of EB.

It is further possible that addition of common heavy metal precipitating agents could reduce the remaining soluble metals within the ash, yet such methods would not enhance the reduction of available MCA within the ash and thus would allow the residual MCA to remain available and possibly continue to allow for reduction and conversion of metals to soluble complexes. It is thus desired to reduce the MCA residual to a low level within the ash, as remaining MCA in solution will possibly increase the potential for metals to become water soluble at some time in the future, thus increasing the potential of metals release.

MCA Recycling. The use of EB for degradation of MCA in solution and/or within ash void liquids will provide useful for control of residual MCA and reduction of soluble metals when recycling of MCA to the primary extraction vessel is not considered necessary. As an alternative method, recycling of MCA from the ash batch reactor, ash drainage or ash rinsing solutions may be considered valuable to operators using high concentrated solutions of MCA.

Several evaluations of post-batch extractions revealed only 0.5 to 1.0 percent reduction of available MCA for bath durations of 5 minutes to 48 hours. Such a low consumption rate presents the opportunity to include MCA recycling in a process where loss of MCA by solution biodegradation is not desirable. Consequently, the heavy metal precipitating agents sodium sulfide and hydroxylapatite were evaluated in order to determine their capability to recover heavy metals from MCA recycle wastewaters and ability to return free MCA in solution to the reactor tank.

Both sodium sulfide and hydroxylapatite were found to precipitate over 99% of Pb out of solution within several minutes of contact. The recovery of MCA after addition of 1% sodium sulfide to extract of ash was found to be 98.7%. The comparison of fresh MCA against recycled MCA in the batch ash reactor as shown in Table 5 also supports that recycled MCA provides similar and often superior metal extraction efficiencies.

Process Costs

The process chemical costs for a full-scale extraction and recovery operation are less than \$0.50 per US ton of waste processed. The scale-up process application can vary in cost from \$150,000.00 capital and \$60,000.00 operating and maintenance for a 100 ton per day extraction facility to \$700,000.00 capital and \$270,000.00 operating and maintenance for a 500 ton per day facility as determined by FESI at several ongoing industrial waste extraction projects. The amortized capital and operating cost is less than \$2.50 per US ton, resulting in a net \$3.00 per ton of waste processed operating and installation cost.

Given \$60.00+ per ton landfill disposal costs in the Northeast, the \$3.00 extraction to enhance ash reuse and consequently avoiding landfilling is highly attractive. The estimated \$3.00 per ton processing cost is also competitive with existing TCLP stabilization methods and is often less expensive given that the extraction process reduces ash weight required for haul and disposal.

CONCLUSION

FESI and BNL researched and demonstrated a novel method for extraction and recovery of heavy metals from industrial wastes and materials. The projects primary objective of defining a safe, simple, cost effective method of extracting and recovering Pb from incinerator ash was achieved through use of a Modified Complexing Agent ("MCA") for single stage ambient temperature extraction of Pb in combination with an Engineered Bacteria ("EB") which targeted and consumed remaining MCA in the wetted ash and bioconverted MCA complexed lead in extract solution to insoluble Pb bioprecipitates.

Although the process method and application rates remain proprietary at this time pending patent issuance, the results of the extraction at 96% + for Pb, 90% (+) recovery rates by biodegradation, TCLP metals control to less than required by the USEPA and simple ambient temperature application confirm the method as beneficial for incinerator ash processing and production into a more reusable nature than baseline.

Table 1. Total Metals Extraction Results

Metal	Baseline (ppm)	Percent Metals Extracted		
		A	B	C
Aluminum	33,700	40	51	52
Barium	873	25	28	26
Cadmium	31	14	18	16
Chromium	309	16	17	20
Copper	558	54	74	90
Iron	47,300	9	22	29
Lead	600	61	74	96
Magnesium	4,200	91	94	94
Manganese	534	46	73	97
Nickel	1,090	21	26	24
Strontium	324	43	60	60
Tin	120	39	41	47
Titanium	6,280	13	14	17
Zinc	3,170	61	83	87

Table 2. Temperature effects on extraction

Metal	Percent Metal Extracted	
	25 C	85 C
Aluminum	25	53
Cadmium	7	13
Chromium	8	21
Iron	23	20
Lead	>99	>99
Magnesium	95	>99
Manganese	75	>99
Nickel	18	68
Strontium	34	43
Tin	37	>99
Titanium	13	23
Zinc	>99	>99

Table 3. TCLP results pre and post-extraction

Metal	Baseline TCLP	Extracted TCLP
Cadmium	0.068	0.007
Chromium	0.050	0.001
Lead	3.2	0.50
Zinc	110	44

Table 4. Biodegradation recovery of heavy metals

Metal	Percent Metal Recovered from Extract
Barium	99
Cadmium	88
Iron	99
Lead	93-99
Magnesium	99
Nickel	87-91
Strontium	99
Tin	89-98
Zinc	99

Table 5. Recycled versus fresh MCA extraction

Metal	Baseline (ppm)	Percent Metal Extracted	
		Fresh MCA	Recycled MCA
Aluminum	35,200	44.9	52.8
Cadmium	22	63.2	67.7
Chromium	148	39.9	46.3
Lead	1010	70.2	76.1
Magnesium	7140	64.6	70.2
Manganese	578	58.3	63.7
Nickel	72	56	51.2
Zinc	4740	74.7	78.1

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