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**Processes for Treatment of Heavy Metals
in Ash from Municipal Solid Waste Incinerators**

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ABSTRACT

Modern municipal waste combustors (MWC's) process approximately 100 million tons of refuse each year in the United States, Europe and Japan, producing 30 million tons of ash. The incineration process has the effect of concentrating the toxic heavy metals normally present in municipal refuse. As a result, the ash may require treatment to reduce the quantity or the mobility of heavy metals within the ash. Four treatment categories are discussed: stabilization, extraction, vitrification and solidification. Within each category a variety of treatment processes are reviewed. Numerous methods have been shown to be successful in laboratory-scale tests and full-scale trials. Several processes have been in continuous, full-scale use for several years including: stabilization using cement; stabilization using phosphate; stabilization by lime addition; and vitrification processes.

INTRODUCTION

Waste-to-energy is an environmentally sound method for reducing the mass and volume of non-recyclable refuse that would otherwise require landfilling. Combustion typically reduces the volume of the refuse by 90% and reduces the solid mass by 70-80%. The resulting ash, while largely inert, can contain concentrations of heavy metals that require treatment in order to comply with regulations, meet standards for producing a usable product, and to provide for long-term stability of the metals when the ash is exposed in the environment. Heavy metals such as lead and cadmium can be toxic to biological systems when present in high enough concentrations.

In the United States, Europe and Japan approximately 100 million tons of refuse are combusted each year (Sawyers, 1996; Nilsson, 1997; Sandbongi, 1997). As a result, about 30 million tons of ash are produced in these regions. Proper management of the ash is an important component of municipal waste combustor operations.

Ash management, processing and treatment can consist of a variety of methods. On the most basic level, ash can be permanently stored in landfills or monofills. Additional processing can be employed to create a usable product (such as aggregate). In any case, heavy metals will be present in the ash. Any management method should include, at a minimum, analysis of the ash to determine the potential hazard of the heavy metals in the ash. If required, a variety of treatment processes may be employed to reduce the quantity and/or mobility of heavy metals present in the ash in order to meet applicable regulations and to ensure the safety of the ash when present in the environment.

MWC's produce several streams of ash: bottom ash (ash from the grates) and flyash (boiler tube residue and air pollution control residue). Treatment processes may be applied to the combined ash or to individual streams, and may be coordinated with other processing such as screening. Treatment for heavy metals falls into one of four general categories:

- Stabilization - treatment of the ash to reduce the solubility of the heavy metals.
- Extraction - removal of heavy metals from the ash.
- Vitrification - high temperature melting of the ash to form a uniform, glass-like substance.
- Solidification - conversion of the ash from powder or granular form into a more solid form.

ASH PROPERTIES AND CHEMISTRY

The ash streams from a typical mass burn MWC are defined as follows:

- Combined Ash (CA) - Composite of all ash streams.
- Bottom Ash (BA) - Composite of the grate ash and siftings
- Grate Ash - Ash discharged from the top of the grates
- Siftings Ash - Ash that falls through the grates
- Flyash (FA) - Ash carried out of the combustion chamber
- Boiler Tube Residue (BTR) - Residue dropping out of the flue gas stream or deposited on the tubes in the heat recovery section
- Scrubber Residue - Flyash, reacted lime and unreacted lime collected from the scrubber
- Fabric Filter (FF) Ash - Flyash collected in the fabric filter baghouse
- Electro-static precipitator (ESP) ash - Flyash collected in the ESP

Table 1 summarizes the concentration of five heavy metals in various streams of ash. The numbers in bold are approximate averages from the literature, with the range shown in parenthesis. Note that the literature survey is not comprehensive and the table is intended to show only the approximate level of metals in typical ash. Plants included in the table are generally mass-burn without secondary combustion chambers, rotary kilns, or other unique designs. The references provide more detailed data on the plant size, configuration and operations.

Table 1. Typical Metal Concentrations in Mass Burn MWC Ash

| Ash Stream | Pb | Cd | Cu | Zn | Cr (total) |
|---------------------|--------------------------|----------------------|-------------------------|-------------------------|-----------------------|
| Combined Ash | 1500 (1200-3000) | 30 (15-450) | 2300 (2188-2400) | 5000 (4043-6100) | 227 |
| Bottom Ash | 1000 (258-5000) | 15 (6-31) | 2200 (558-5910) | 3500 (1300-5783) | 300 (107-1419) |
| Boiler Tube Residue | 3000 (38-8000) | 150 (47-400) | 1000 (840-1120) | 3000 (1954-3900) | 100 (12-297) |
| Scrubber Residue | 3000 (2500-12000) | 100 (50-150) | 362 | 11770 | 132 |
| Baghouse Flyash | 2000 (1263-12000) | 500 (80-1000) | 2460 | 6200 | 36 |
| ESP Flyash | 3000 (2500-12000) | 200 (80-1000) | 1322 | 9382 | 365 |

Sources: Binner et al., 1997; Alba, et al., 1997; Arcangeli, et al., 1996; Eighmy, et al., 1997; Bäverman, 1997; Forrester, 1997; Plaue, et al., 1996; IAWG, 1994; Musselman, et al., 1994.

The heavy metals present in MWC ash are of concern primarily due to the potential for the leaching of soluble forms of the metals. Reduction of the solubility is important both when the ash is tested in the laboratory for compliance with regulations, and when the ash is exposed to the environment of its final destination. The leachability of hazardous constituents of waste materials are normally evaluated (in the United States) using the EPA's Toxicity Characteristic Leaching Procedure (TCLP). The TCLP involves grinding the waste material, digesting the waste in an acid solution, and measuring the concentration of metals in the acid. Similar tests are utilized by other environmental enforcement agencies in the U.S. and other areas of the world.

In addition to the solubility of the metals, the total metals content may also be of concern. While stabilization reduces the potential of the heavy metals to enter the environment by means of leaching processes, it does not reduce the total concentration or the long-term bioavailability (Forrester, 1997).

Typically bottom ash alone is not considered hazardous and can be disposed of or reused with minimal treatment. Flyash alone will generally not pass the TCLP and requires treatment or disposal as hazardous waste. Combined ash may require some treatment to pass TCLP.

Research has shown that most of the heavy metals in untreated ash are not soluble, but are present as insoluble lattice-substituted compounds or are bound in a glassy matrix. The portion of the heavy metal content that is soluble may be in a solid form on the surface of the ash particles or as aqueous complexes or metal cations dissolved in pore water and free water present in the ash (Lyons, 1996).

TREATMENT PROCESSES

Stabilization Processes

In general, stabilization describes techniques that convert a waste into a less soluble, mobile or toxic form. Many stabilization processes result in some solidification of the waste.

pH Adjustment

Adjustment of the pH of the ash can be effective in reducing the solubility of lead and cadmium as measured by the TCLP. Typically adjustment of pH is done by using more lime than is required for acid gas control in the scrubber, or by adding free lime to the ash itself. Both methods will have the effect of raising the ash pH into a range where the soluble lead compounds are less soluble. It is also possible that some of the lead and cadmium is converted to carbonates which have relatively low solubilities (Licata, 1997). In order to maintain lead and cadmium below the regulatory limits of 5 mg/l and 1 mg/l, respectively, the target free lime in the ash has been shown to be between 5 and 8 percent, resulting in a final TCLP pH of between 8 and 10. Figure 1 shows the TCLP behavior of lead and cadmium and the pH of ash with various free lime contents. Addition of magnesium oxide or magnesium hydroxide in place of lime for some of the alkalinity can help prevent the pH of the ash from rising above 10, where the lead can resolubilize (Licata, 1997)

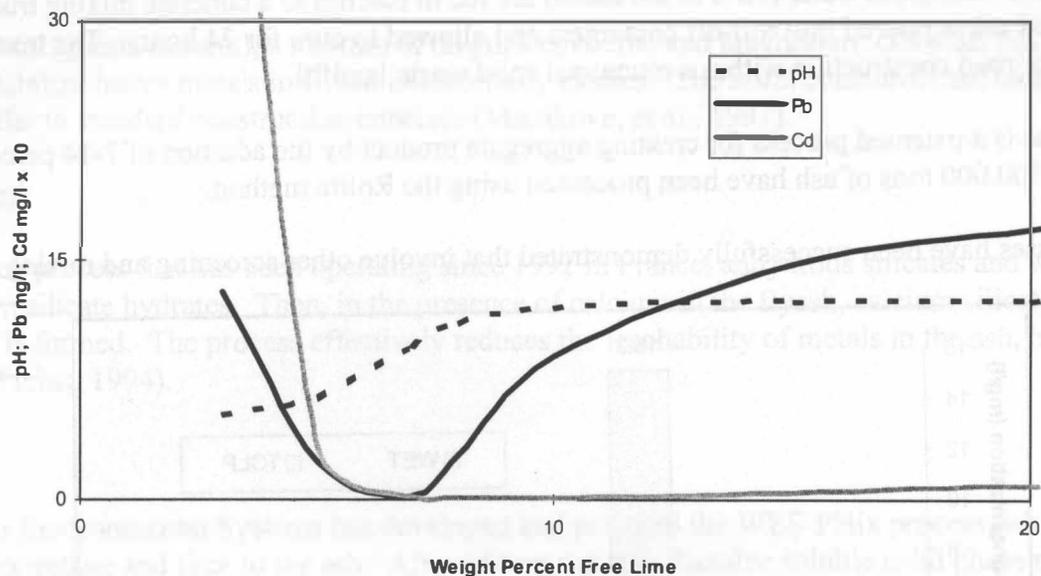


Figure 2. TCLP Lead, Cadmium and Final pH vs. Free Lime in Ash Blends (Lyons, 1996)

Cement Processes

Portland cement-based methods are widely used for treating a variety of hazardous wastes and have been successfully applied to MWC ash. Portland cement is widely available in a variety of types, but generally consists of calcium silicate compounds, that form calcium silicate hydrates when mixed with water (Conner, 1990). Treatment of ash with cement involves mixing ash (usually screened) with cement and water, and then allowing the mixture to set.

Cement treatment does not physically bind lead into the calcium silicate hydrate matrix. In fact, the hydration process leaves lead salts readily available on the surface of the hydrated cement (Cartledge, et al., 1990 and Akhter, et al., 1990). However, it appears that a portion of the lead forms insoluble silicate compounds. In fact, the lead leaching curve (cumulative lead leached vs. total acid added) closely follows that of silicon. The lead silicate compounds are probably not stoichiometric, but are of variable composition of the general form $yPb(OH)_x \cdot zSiO_2$ (Conner, 1990).

Cadmium immobilization appears to involve encapsulation on a microscopic scale. It is believed that the cadmium exists in the treated wastes as the insoluble solid $Cd(OH)_2$ encapsulated in the calcium silicate hydroxide and calcium hydroxide matrix (Cartledge, et al., 1990). While this mechanism is generally highly effective, at low pH cadmium can be solubilized from cement-stabilized waste (Conner, 1990).

The stabilization of chromium using cement may be effective, but it appears that a cure time of at least 28 days is required before significant reductions in the solubility is seen (Boy, et al., 1995 and Shin, et al., 1992). Data for other metals is limited.

Results from the Commerce Refuse-to-Energy ash treatment process are shown in Figure 2. The California's waste extraction test (WET) is similar to, but more stringent than, the EPA TCLP test. The Commerce process has effectively treated over 200,000 tons of ash during the last 7 years.

A typical portland cement treatment process is shown in figure 3. Flyash, screened bottom ash, Type II portland cement (11% of the batch) and water (18% of the batch) are fed in batches to a concrete mixing truck. After mixing, the treated ash is poured into roll-off containers and allowed to cure for 24 hours. The treated ash product is used for road construction within a municipal solid waste landfill.

The Rolite process is a patented process for creating aggregate product by the addition of 7-14 percent portland cement. Almost 500,000 tons of ash have been processed using the Rolite method.

Additional processes have been successfully demonstrated that involve other screening and mixing methods.

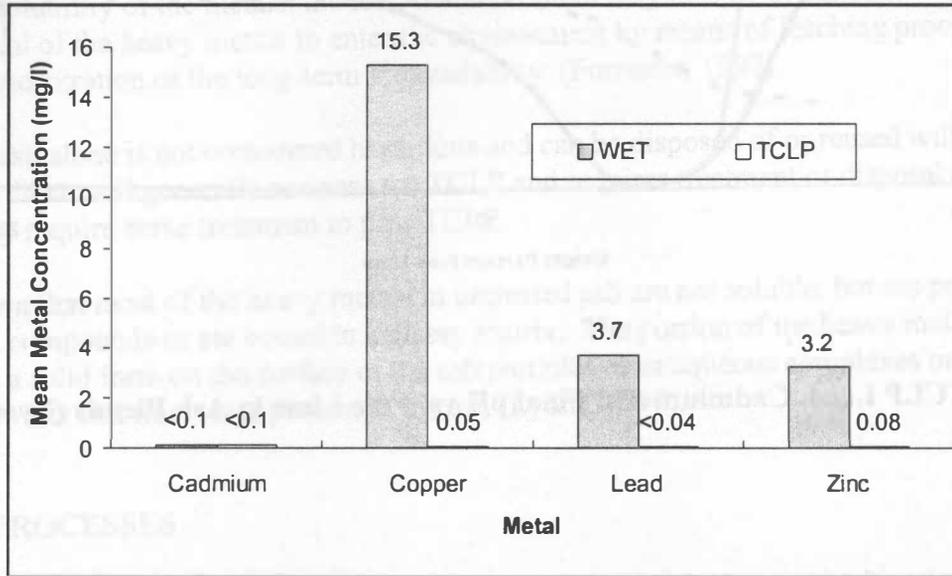


Figure 2. Commerce Refuse-to-Energy Treated Ash TCLP and WET Test Results

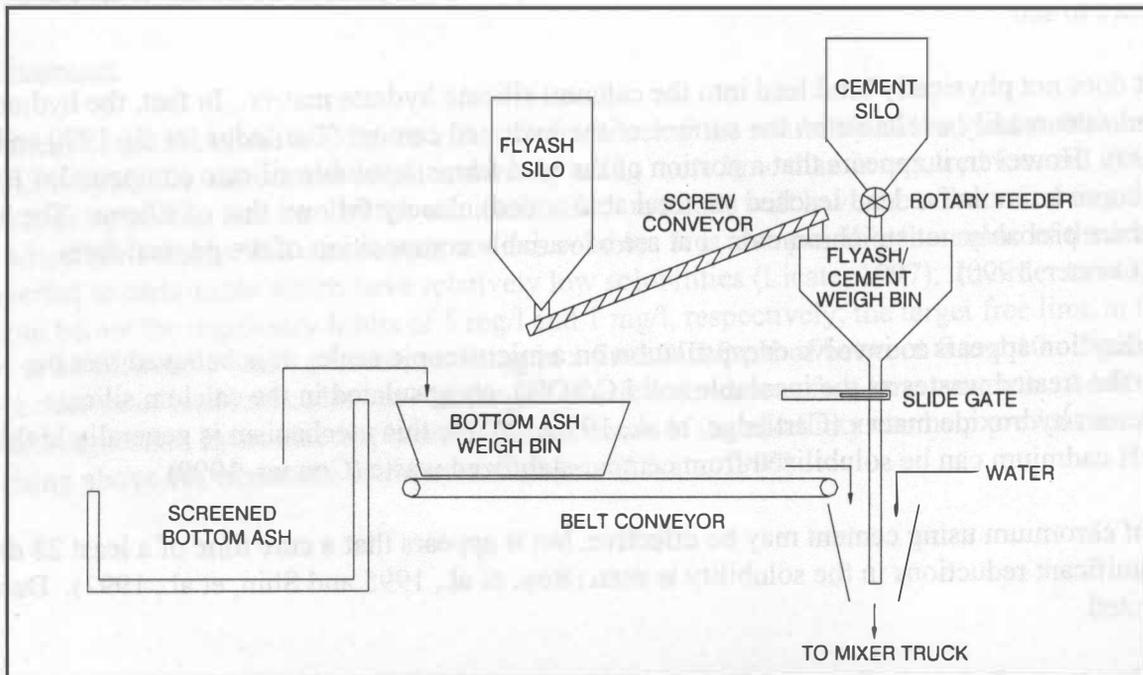


Figure 3. Schematic of the Commerce Refuse-to-Energy Ash Treatment Process

Sorel Cement

Sorel cement (magnesia cement), a mixture of magnesium oxide and magnesium chloride, has been shown to effectively stabilize heavy metals in flyash in laboratory studies. The Sorel cement-flyash concrete also has strength similar to standard construction concrete (Macakova, et al., 1997).

Other Cements

In the Ashrock process that has been operating since 1992 in France, anhydrous silicates and water are added to flyash to form silicate hydrates. Then, in the presence of calcium in the flyash, calcium silicate hydrate or Tobermorite is formed. The process effectively reduces the leachability of metals in the ash, but the mechanism is not clear (Pichat, 1994).

WES-PHix

Wheelabrator Environmental Systems has developed and patented the WES-PHix process, which involves the addition of phosphate and lime to the ash. After adding water to dissolve soluble solid phase metals, phosphate and lime are added to form insoluble metal phosphate and metal carbonate compounds. For lead, research indicates that this process produces a variety of highly insoluble lead phosphate compounds. For example, the low solubility of chloropyromorphite $[Pb_2(PO_4)_3Cl]$ (one of the principal minerals formed by WES-PHix) is shown in figure 4. For cadmium, research indicates that cadmium carbonate, and to a lesser degree cadmium phosphate compounds, are formed that render the cadmium less soluble. The solubility of copper and zinc is also reduced with the WES-PHix process. Approximately 10,000 tons of ash per day are now being treated by the WES-PHix process in the U.S. and Japan (Lyons, 1996).

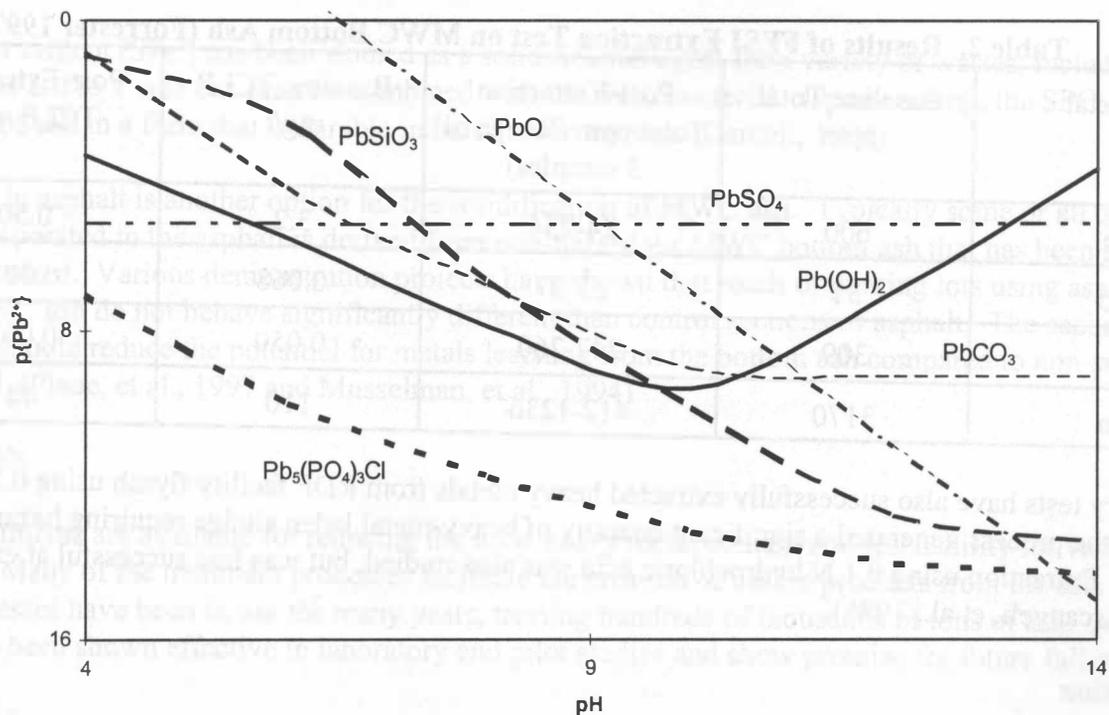


Figure 4. Lead Mineral Solubilities (Lyons, 1996)

ASHFIX

The ASHFIX process has been developed and patented by Ashland chemical. The process begins by creating a slurry of ash, and adding a proprietary coagulant. An organo-sulphur metals precipitant is added to precipitate out the metals, immediately followed by an alkaline earth metal (such as magnesium hydroxide) which gives the residue matrix cohesion. The resulting product is easy to handle and has potential reuse applications. Presently eight MWC's in France are using ASHFIX treatment on bottom ash. The process has also been successfully demonstrated on flyash alone (Kramer, 1997).

Extraction Processes

Extraction processes have the advantage of permanently removing toxic metals from the ash. This reduces the soluble metal content and also the total metal content, potentially reducing "cradle-to-grave" liability and allowing for additional reuse options.

FESI

Forrester Environmental Services Inc. (FESI) has developed and patented a process for extracting heavy metals from ash that has been laboratory tested on bottom ash and has been in full-scale use on other wastes. The process successfully removed over 90% of lead, zinc and other heavy metals in the ash test. To extract the metals, a solution of patent-pending Modified Complexing Agent ("MCA") was added to the ash in a 20:1 MCA to ash ratio and the combination was mixed for 48 hours. The ash was then dewatered, resulting in the ash metal content shown in table 2. Metals are precipitated from the MCA solution that is removed from the ash, and the MCA can be reused for further batches. The process leaves a sludge of precipitated metals that requires disposal, probably as hazardous waste (Forrester, 1997).

Table 2. Results of FESI Extraction Test on MWC Bottom Ash (Forrester 1997)

| Metal | Baseline Total ppm | Post-Extraction Total ppm (Range of 3 samples) | Baseline TCLP mg/l | Post-Extraction TCLP mg/l |
|-------|--------------------|--|--------------------|---------------------------|
| Pb | 600 | 24-234 | 3.2 | 0.50 |
| Cd | 31 | 25-27 | 0.068 | 0.007 |
| Cr | 309 | 247-260 | 0.050 | 0.001 |
| Zn | 3170 | 412-1236 | 110 | 44 |

Laboratory tests have also successfully extracted heavy metals from RDF facility flyash using 0.1 N nitric acid, although the process generated a significant quantity of heavy-metal laden sludge requiring hazardous waste disposal. Extraction using 0.1 N hydrochloric acid was also studied, but was less successful at extracting the metals (Arcangeli, et al., 1996).

Vitrification

Vitrification is the high temperature conversion of ash into a dense glass-like material. Vitrification can be achieved in one of several furnaces: a furnace utilizing fossil fuel burners; an electric arc; a plasma arc furnace; or furnaces integral to the MWC that utilizing electric heaters for additional heat input. The ash is typically heated to 1000-1500 C (Wakamura and Nakazato, 1994). When vitrified, the ash forms several products: vitreous product; metallic product and matte product. The vitreous product may be suitable for numerous uses,

typically as an aggregate in asphalt, concrete or tiles. The metallic and matte products can be recycled. A small fraction of the ash is captured from the fumes by condensation or in a fabric filter (Hollander, et al., 1994).

The vitrified processes consistently reduce the leachability of metals present in the ash. TCLP results for vitrified product produced from MWC's are shown in Table 3 (Hollander, et al., 1994).

Table 3. Vitrified Ash TCLP Results, mg/l (Hollander, et al., 1994)

| Metal | Mass Burn Combined Ash | RDF Flyash + APC Residue |
|-------|------------------------|--------------------------|
| Pb | 0.3 | 0.1 |
| Cd | 0.007 | 0.007 |
| Cr | <0.02 | 0.1 |

As of 1994, there were about 10 full-scale commercial vitrification processes operating in Japan with several more under construction or in planning (Wakamura and Nakazato, 1994). Vitrification is generally more costly than other treatment processes due to the energy input required (Hollander et al., 1994).

Solidification

Solidification alone does not reduce the inherent solubility of metals within the ash. Solidification processes will, however, further reduce the potential of leaching of heavy metals from ash that has already been shown to be non-hazardous.

Sulfur polymer cement (SPC) has been studied as a solidification agent for a variety of wastes, including MWC ash. SPC melts at 115 C and can then be combined with the waste material. Upon cooling, the SPC encapsulated the ash in a form that is durable in harsh environments (Darnell, 1994).

Encapsulation in asphalt is another option for the solidification of MWC ash. Typically some or all of the aggregate incorporated in the asphalt is derived from non-hazardous MWC bottom ash that has been screened or otherwise processed. Various demonstration projects have shown that roads or parking lots using asphalt containing MWC ash do not behave significantly different than control sections of asphalt. The asphalt encapsulation should reduce the potential for metals leaching from the bottom ash compared to non-solidified use or disposal. (Plaue, et al., 1997 and Musselman, et al., 1994)

CONCLUSION

Numerous treatments are available for reducing the toxic heavy metal content and leachability for various types of MWC ash. Many of the treatment processes facilitate the creation of usable products from the ash. Several treatment processes have been in use for many years, treating hundreds of thousands of tons of ash. Additional processes have been shown effective in laboratory and pilot studies and show promise for future full-scale use.

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