

Examination of Chlorides in Municipal Solid Waste to Energy Combustion Residue: Origins, Fate and Potential for Treatment

by
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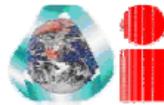
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Fate and Potential for Treatment (by Adam Penque)

EXECUTIVE SUMMARY

Each year the United States produces over than 380 million tons of municipal solid wastes (MSW) of which roughly 7.4 percent is combusted in modern waste to energy (WTE) facilities (Simmons et al. 2006). This process allows for the recovery of valuable energy and metals that would otherwise be lost from the productive lifecycle of material goods. During combustion roughly 10 percent of the MSW mass is converted to combustion residue in the form of ash (Liberti et al. 2005). The management of this ash presents a unique challenge to the operators of WTE facilities due to the complex and highly variable composition of the MSW feedstock. Heavy metals, petroleum derived compounds, salts and other such materials in MSW are not completely destroyed or rendered inert by the combustion process. Typically in the US this ash is landfilled however recent work has identified many potential reuse applications, including; using MSW ash as an amendment for cement and other building materials and trials in Pennsylvania has identified ash as a potential material for reclaiming abandoned coal mine sites.

One contaminant that poses a significant challenge to the beneficial reuse of MSW ash is the elevated concentration of chlorides. When ash is incorporated into building materials chloride can accelerate the oxidation of reinforcing steel, also in land reclamation projects ash chloride leaches out contaminating local ecosystems. As a result before ash can be practically incorporated into various reuse applications a sound mitigation mechanism for chloride must be developed.

Critical in understanding the means of managing this chloride is having an understanding of it's flow in a WTE facility. Plastics make up roughly 10 percent of MSW on a mass basis (Menke and Zwahr, 2003). Within plastics, the most significant contributor is polyvinyl chloride (PVC) as it is composed of 56.7% chlorine and makes up 0.7 percent of total MSW (Themelis 2005) (Menke and Zwahr, 2003).

After MSW is combusted in a WTE facility the chloride is distributed between the bottom ash and the fly ash with a small fraction lost to stack emissions. Research has found that roughly 60% of the total incoming chloride has its fate in fly ash (Chang and Huang 2002). By focusing mitigation of chloride to fly ash, the efficiency of chloride treatment can be maximized while minimizing overall material handling.

Fundamentally, the management of fly ash can be classified into two main schools of practice; treatment or stabilization for disposal or processing for reuse and recovery (Derie 1996), (ISWA 2003). In both of these scenarios a treatment step is critical to mitigate chloride and/or other contaminants. Due to the toxic nature of heavy metals concentrated in fly ash, most of the treatment processes currently available focus on the stabilization of heavy metals and fail to address the presence of chlorides. In fact some of the available heavy treatment mechanisms lead to a net increase in the leachability of chloride post treatment. In response to this problem a need for a simple treatment mechanism designed at targeting chloride was identified. Experimental work carried out

as part of this masters research project evaluated the potential for such a treatment process.

The experimental work investigated the potential of using a simple batch type water washing system to remove soluble chloride from fly ash. Fly ash samples from two US WTE facilities were used for this analysis. Extractions were done using several liquid to solid (L/S) ratios and at several process temperatures. The removal of chloride was monitored over time. Trials were done originally at high L/S ratios (>30) to build an understanding of this relationship, as well as test the method against similarly published experiments. After positive findings were presented to experienced industry personnel the research group was advised to use lower L/S ratios (≤ 10) as they would be more feasible to reproduce on an industrial scale. For the second phase of these tests, L/S ratios of 3, 5 and 10 were used for chloride extractions from fly ash.

The experimental results were successful in identifying the governing parameters of the extraction of chloride from the fly ash samples. It was observed that the amount of energy (in the form of heat) added to the extraction solution greatly affected the amount of chloride that was ultimately removed during extraction. Also, observed was the variability in the effect of L/S ratio at different temperatures. At 20°C all L/S extractions progressed rapidly with most of the chloride removed in the first 60 seconds, however the total amount of chloride removed varied greatly with L/S ratio. The trend demonstrated that greater amounts of chloride are removed at higher L/S ratios. When the same extractions were carried out at higher temperatures, 30°C , all L/S trials converged on the same final chloride removal equilibrium, suggesting that at this higher temperature near complete chloride removal was achievable for all L/S ratios. Also observed during these experiments was an energy release during each of the reactions, though the experiments were not designed to precisely measure this phenomenon.

All in all the investigation was successful in building an understanding of the driving parameters in a simple chloride water extraction system. From these findings areas of future work necessary before pilot or industrial scale up were identified.

ACKNOWLEDGEMENTS

I would like to thank my advisor Professor Nickolas J. Themelis for his constant support and patience during the completion of this work.

I dedicate this work to my father.

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Introduction

Annually the United States produces over than 380 million tons of municipal solid wastes (MSW) of which roughly 7.4 percent is combusted in modern waste to energy (WTE) facilities (Simmons et al. 2006). This process allows for the recovery of valuable energy and metals that would otherwise be lost from the productive lifecycle of material goods. As a byproduct, a large amount of combustion residues are generated in the form of ash. After metal removal, this material is equal to roughly ten percent of the incoming MSW (Liberti et al. 2005).

The management of this ash presents unique challenges to the operators of WTE facilities due to the complex and highly variable composition of the MSW feedstock. The heavy metals, petroleum derived compounds, and other such materials in MSW are not completely destroyed or rendered inert by the combustion process. These toxic substances are concentrated during the combustion process and lead to the contamination of the fly ash that is removed from the gas stream.

As in the case of the ash generated in the combustion of coal, much work has been done to find beneficial uses for the MSW combustion residues. These include building materials, fill for acid mine remediation projects, cement additives etc. However, before the fly ash can be used, it may require treatment of contaminants that may present a risks to both material application and human and environmental health.

Much of the research has been conducted on MSW ash has focused on the sources, behavior and mitigation of heavy metals, dioxins, furans and other toxic and carcinogenic materials found in the fly ash residue. As the management of ash moves from traditional land filling to beneficial use, treatment options must also expand to include compounds beside heavy metals and carcinogens. Compounds such as soluble chloride salts do not pose a threat to humans or the environment in landfill conditions; however they do pose a challenge to reuse applications such use in building materials where they can catalyze material decay or in mine reclamation projects where elevated chloride levels have been found in leachate that enters surface waters.

This thesis project is focused on building the understanding of the behavior of chlorides contained in MSW combustion ash. This study will examine the sources of chlorine ending in the ash, and its behavior and distribution within the WTE process. It will cover accepted and new treatment and mitigation processes available to waste management. Finally, the thesis will present and discuss the experimental work on chloride removal that was conducted in conjunction with this project at Columbia University's Earth and Environmental Engineering, supported by the Waste-to-Energy Research and Technology Council (WTERT).

Part I Chlorine Flow in Waste to Energy Facilities

The first step in understanding how to manage the chlorine contained in ash is to understand how it behaves in the energy recovery process. This is done by identifying its sources in MSW, tracing its path through the combustion process, and determining its ultimate fate in the ash and stack gases.

Chlorine is contained in dozens of materials that are found in municipal solid waste, plastics, computer boards, packaging, organic materials, etc. Its presence can be

attributed to its diverse applications; as an antiseptic, its effect on organic compounds, food additive etc. Chlorine is found in low concentrations in most materials however the sheer volume of these waste materials presents a difficulty in targeting and mitigating their sources. Table 1 below shows the concentration of chlorine in common components of municipal solid waste.

Table 1 Chloride Composition of MSW (Themelis, 2005)

| | % of component in MSW | Chlorine concentration in component, g/kg | Chlorine in MSW, g/kg |
|-----------------------|-----------------------|---|-----------------------|
| Paper | 29.4 | 2 | 0.59 |
| Plastics | 10.4 | 25 | 2.60 |
| Organics | 34.7 | 3 | 1.04 |
| Textiles | 4.4 | 12.5 | 0.55 |
| Wood | 2.7 | 12.5 | 0.34 |
| Miss. Combustible | 5 | 12.5 | 0.63 |
| Glass | 4 | 0.6 | 0.02 |
| Metals | 4.7 | 0.6 | 0.03 |
| Miss. Non-Combustible | 4.7 | 0.6 | 0.03 |
| Total | 100 | | 0.58 (5.82 %) |

Large amounts of chlorine are used each year by the paper industry. Chlorine is used during the paper bleaching process and often residue containing chlorine remains in the paper even after washing (Brunin 1995). Similarly bleaching and dyeing chemicals used to process textiles also contain chloride. When ever these products are discarded the trace amounts of chloride contribute to the presence of chloride in MSW. Additionally a considerable amount of chlorine that is found in MSW comes from organic material. This is a result of the salts, primarily NaCl, contained in food and plant material.

The major contributing source of chlorine to MSW is plastics. Plastics make up roughly 10 percent of MSW on a mass basis (Menke and Zwahr, 2003). Within plastics, the most significant contributor of chloride is polyvinyl chloride (PVC). PVC, a polymer of chloroethene ($\text{CH}_2=\text{CHCl}$) contains 56.7% chlorine by weight (Themelis 2005). From a mass balance point of view, PVC must be considered because alone it makes up 0.7 percent of the total composition of MSW (Menke and Zwahr, 2003).

Chemically, PVC is produced from salt and petroleum. In the first step, chlorine gas is produced by applying a high voltage current to a salt solution. Petroleum is put through a cracking process to yield ethylene. The chlorine gas is then reacted with ethylene to produce ethylene dichloride which is then transformed to produce vinyl chloride, the building block of PVC. The last step in the production process is a polymerization reaction where base units of vinyl chloride are attached to one another to produce the polymer (Lussier). Lead and cadmium are often used in the production of PVC as either plasticizers and or stabilizers. However in 2001 the plastic industry began to voluntarily phase out the use of cadmium as a plasticizer.

PVC is one of most commonly used plastics in the world and is the second largest commodity plastic produced in the USA behind polyethylene (Brunin 1995). As an organochloride, PVC has many diverse applications; due to its workability and resistance

to breakdown (Lussier). Commonly it is used to produce piping, plastic forms, molds, seals, and other materials. PVC is routinely mixed with other compounds to impart its chemical and physical properties. PVC's use as an additive to other materials also expands its application and usage in the market. Table 2 below summarizes the common applications of global PVC usage.

Table 2. Use of PVC in Various Materials.

| | |
|------------------------|-----|
| Building | 56% |
| Packaging | 15% |
| Consumer goods | 10% |
| Electronics industries | 9% |
| Agriculture | 5% |
| Others | 5% |

(Brunin, D. 1995)

This data shows that more than half of the PVC produced has long term applications in building supplies. These materials are not of direct concern for this analysis due to the fact that they are not incorporated in the municipal waste stream, as they are often used in long term applications. However, it should be noted that the presence of chlorine in these materials presents other environmental problems. When considering MSW, it is the PVC associated with packaging and consumer goods and to some degree electronic components that is of the most concern and importance. Of the total 23 million metric tons of annual PVC produced annually, roughly 5.75 million metric tons of the resin are used in consumer goods and packaging. (Brunin, 1995) Ultimately a large percentage of these goods and materials find their way into the MSW stream.

Recycling of PVC is considered to be the best approach from a waste management point of view. Recycled PVC can be easily processed to yield fresh raw material. However, the diverse applications of PVC in small amounts make recovery of PVC difficult, and as a result much PVC makes its way into landfills. As these plastic polymers break down heavy metals that were used as stabilizers and plasticizers are leached into ground water. A large effort has been made to avoid the landfilling of these materials; as a result, PVC often ends up in waste to energy facilities.

Research by Menke and Zwahr (2003) showed that in European countries 600,000 tons of PVC are incinerated annually. From the thermodynamic point of view, there is a tremendous amount of energy trapped in this waste PVC. The heating value of rigid PVC and flexible PVC are 16,000 and 20,000 kJ/kg respectively. This is considerably higher than the average 10,000 kJ/kg for MSW (Menke and Zwahr 2003). This high amount of energy presents an advantage to the combustion of PVC (and other energy rich plastics), however a complete understanding of the chloride chemistry and behavior must be known as they play a dynamic role in the production of acid gases and dioxins. During combustion, all materials containing chlorine behave in a similar fashion. As temperatures begin to rise, organic compounds decompose liberating chlorine, at higher temperatures chloride salts begin to volatilize. The two predominant chloride-containing gases that are produced during combustion are hydrochloric gas (HCL) and chlorine gas.

However, once chlorine gas (Cl_2) is produced it immediately reacts with water vapor found in the combustion gas to produce additional hydrochloric gas.

A significant amount of research has been done to identify other trace products from the combustion of chlorine containing materials. Some of these products include dioxins, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Particular interest is paid to these compounds because of their carcinogenic properties. The production of these compounds is tied to the chemistry of the HCl gas however because these compounds are found in such trace quantities and most WTE facilities have environmental control measures targeted at the capture of these materials, by means of activated carbon injection and fabric filters they are neglected from this analysis.

The presence of HCl in the exhaust gas presents several challenges to the running of a WTE plant besides the production of toxic trace compounds. At cooler temperatures, like those found at the surface of heat exchangers and boiler tubes, the very reaction that produced HCl proceeds in the reverse direction to produce Cl_2 gas, promoting the corrosion metals to metal chlorides (Themelis 2005). To prevent the production of these toxic and corrosive substances, the HCl found in the exhaust gas must be removed by the air pollution control system of the WTE facility. Most modern WTE facilities employ some type alkaline scrubbing system designed to remove acid gases (SO_4 and HCl). Typically, the alkaline material used is either limestone or more commonly calcium hydroxide. The calcium hydroxide reacts with the HCl gas to produce calcium salts and water. Industry accepts that the use of lime is 95-99% efficient at removing HCl from combustion gases (Cooper and Alley 1994). To understand how chlorine flows with in a waste to energy facility, it is important to understand the types of scrubber systems available for acid gas removal. Lime-acid gas scrubber systems can be classified into two main groups, wet and dry scrubbers. Each of these systems can be used in WTE facilities.

In a wet lime scrubber, lime is mixed with water to produce a slurry. The ratio of water to lime can be manipulated according to the amount of acid in the flue gas. Additional reagents may be added to this slurry to target certain compounds. The lime-water slurry is then sprayed into the flue gas scrubber. Several different types of spray systems can be used to maximize the interaction of the lime with the acid gas these include venturi scrubbers, baffle chambers, towers and air turbo-impactors. In general the acid removal efficiency of the scrubber system is a function of the residence time and more importantly the extent of the interaction between the lime and acid gas. The reaction of the acid gases and the lime produce solid salts that are suspended in the hot gas. This particulate material also known as fly ash must be collected down stream via a particulate collection system; this could include a baghouse or electrostatic precipitator. Due to the large excess amount of water used in wet scrubber systems large amounts of steam are often generated with the flue gas.

Dry lime scrubber systems operate similarly to wet systems only without the use of excess water. There are two types of dry scrubbers systems spray absorbers and dry sorbent injection. Spray absorber systems which make use of a small amount of water to produce a alkaline slurry, much like wet systems at a lower liquid to solid ratio. The flue gases are exposed to the slurry after it has been atomized. At the flue gases high temperatures the water is immediately evaporated leaving solid salts (fly ash) which is then removed with the system's particulate control system.

Dry sorbent systems are the only lime scrubbing system which uses no water. In this system a dry hydrated lime powder is injected into the flue gas. Injection can occur at several different steps either in the combustion chamber, in a separate reactor contact unit, or in a pre-particulate removal duct. Due to the shorter contact between the acid gases and the lime these systems have comparatively lower removal efficiencies than spray absorber or wet lime scrubber systems. Efficiency of these systems can be increased by increasing the humidity of the combustion gases (Cooper and Alley 1994).

The application of these different APC control devices plays an important role in determining the fate of chemical species in the overall mass balance and material flow of the MSW combustion facility. Research by Chang and Huang (2002) examined the flow of chlorine in two large MSW waste to energy facilities in Taiwan. In the analysis the concentration of chlorine was monitored by sampling at series of points through the incineration process. The tests were carried out on two MSW mass burn WTE facilities with different air pollution control systems, thus allowing for the comparison of the material flow of chlorine as it relates to air pollution control technology used in the facility.

The WTE facilities examined in this study were both built in the 1990's. WTE facility A was built with a design capacity of 450 tonnes MSW per day and WTE facility B a design capacity of 387 tonnes per day. The two plants were operating at rates of 300 tonnes per day and 220 tonnes per day respectively. The two facilities differed primarily in the installed APC equipment. WTE-A treated combustion gases first with a cyclone followed by dry lime scrubbing to remove acid gases and a fabric filter bag house for particulate removal. In WTE-B flue gases were first treated with an electro static precipitator followed by a wet scrubber. Figure 1a shows an over all schematic diagram of the two waste to energy facilities (Chang and Huang 2002).

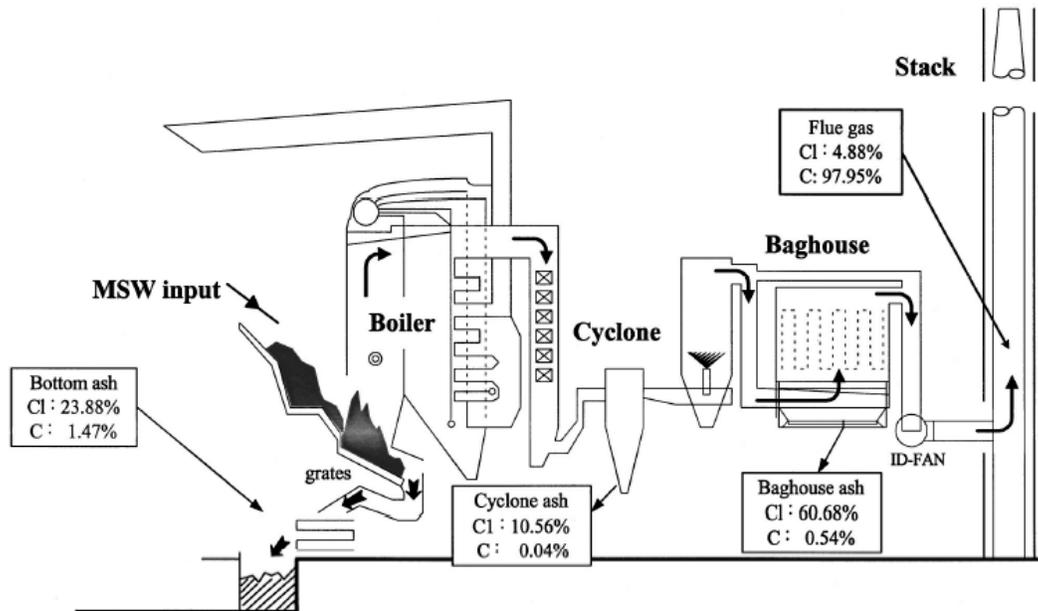


Figure 1a. Schematic of Facility A - Chang and Huang (2002)

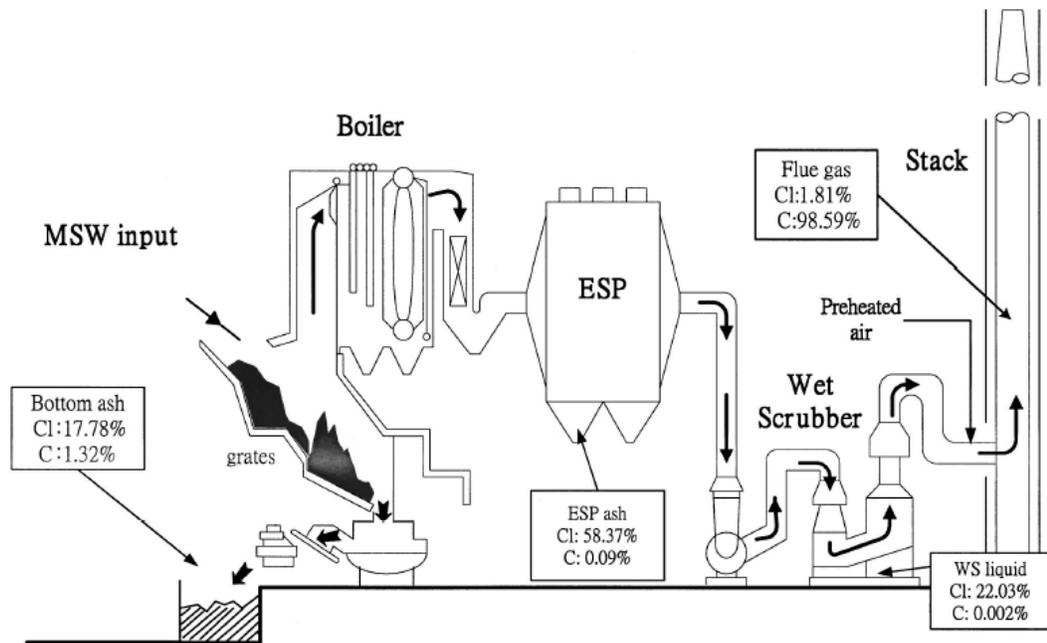


Figure 1b. Schematic of Facility B - Chang and Huang (2002)

In WTE facility A, combustion residue was generated at several steps and each of these *ashes* were sampled during the analysis. Unburned and inert bottom ash was removed from the combustion chamber grates, boiler ash was collected from the boiler unit, fly ash was collected from the cyclone prior to scrubbing and the remaining fly ash was collected by the bag house. In facility B, the combustion residue collected included: bottom ash, boiler ash, and all fly ash that was collected by the electrostatic precipitator. For both facilities, the concentration of HCl was also monitored before and after the air pollution control systems. Figure 2a summarizes the concentration of chloride in each of the residues sampled. As can be seen, the highest concentration of chloride was found in the baghouse ash. A result of collection post dry lime scrubbing.

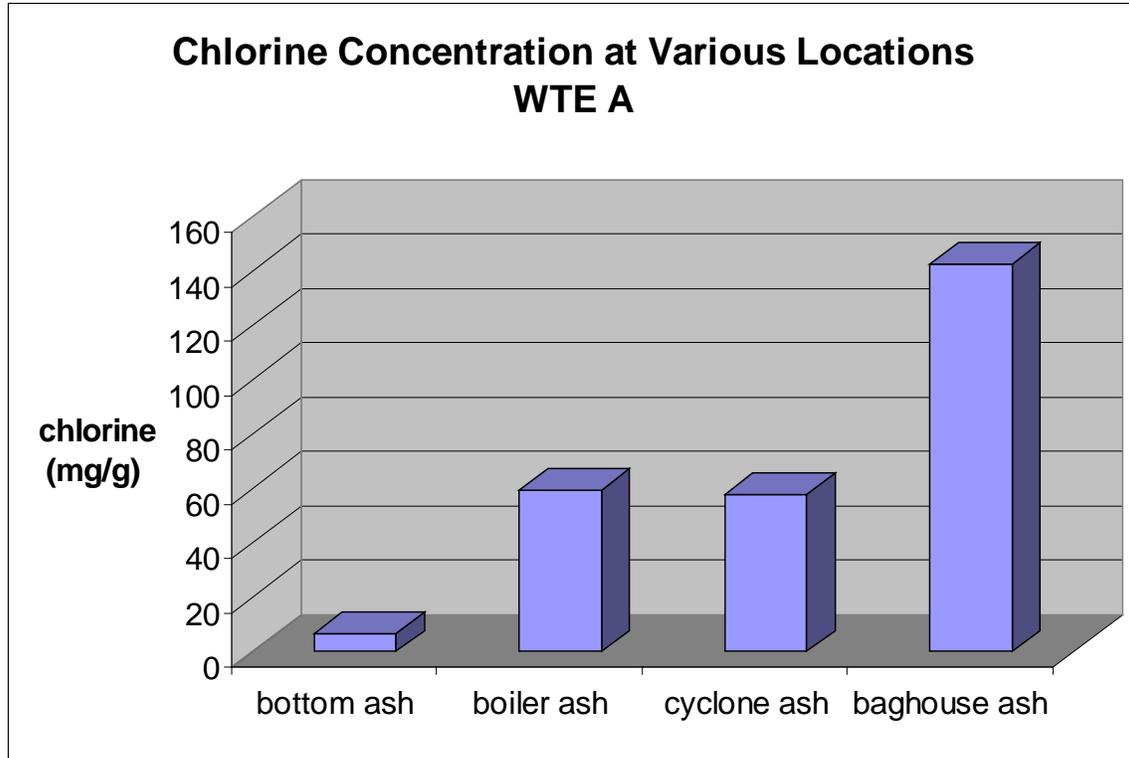


Figure 2a

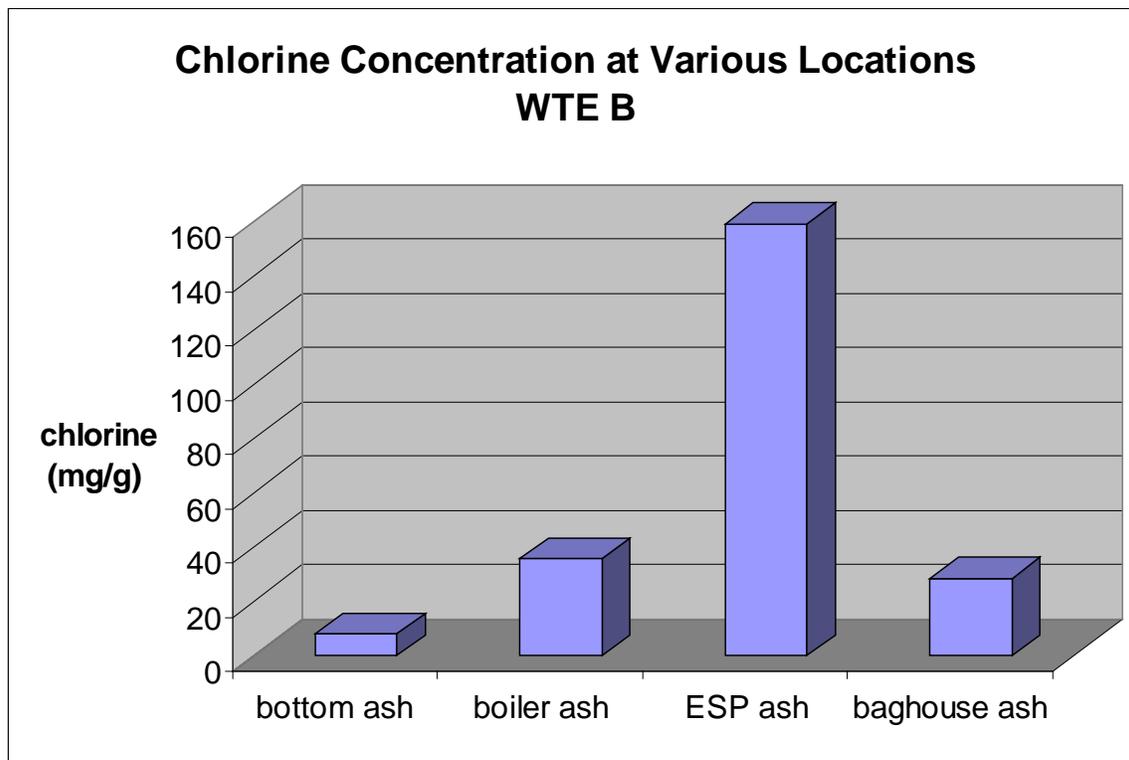


Figure2b (Data from Chang and Huang (2002))

The analysis by Chang and Huang revealed that bottom ash generated during combustion served as a sink for roughly 20-30 percent of the total chloride contained in the incoming MSW. Analysis of samples taken down stream of the combustion chamber revealed that the type of scrubber system and particulate removal system had little effect on the overall flow of chloride. In facility A, 60.68 percent of the total Cl was contained in the baghouse ash (post dry lime scrubbing), in facility B the Fly ash from the electrostatic precipitator contained 58.37 percent of the chloride. This shows that the type of scrubbing system used to treat acid gases has little effect on amount of chloride that finds its fate in the APC residue. However variation is observed between facilities reporting chloride concentrations (including facility A and B) as presented in Figure 3 below. Because the amount of chloride remains relatively constant, the variation in concentration is more a function of changes in the volume of residue that is generated by the different APC processes in place.

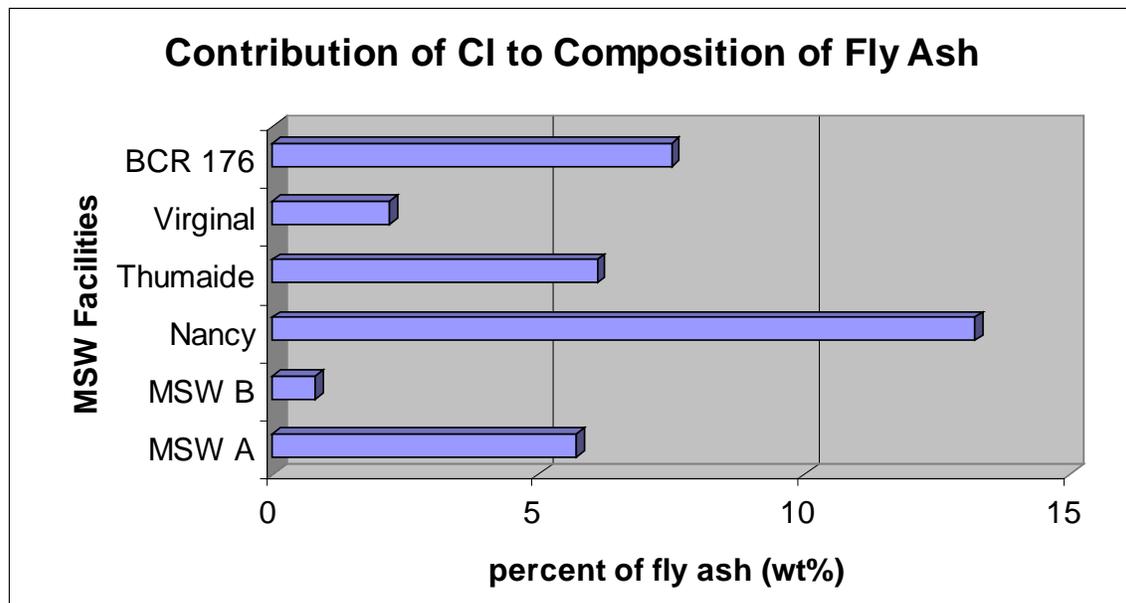


Figure 3 (Data from Chang and Huang, 2002; and Derie 1996)

Aside from combustion ash (bottom ash) and APC residue, the remaining chloride finds its fate up the stack of the WTE facility. Again, both of the two facilities examined by Chang and Huang showed remarkable similarities with average chloride stack concentrations of 170,157 mg chloride / Nm³ and 167,803 mg chloride /Nm³ for Facility A and B, respectively. These concentrations of chloride represent between 2-5% of the total chloride that was found in the originally incoming MSW (Chang and Huang 2002).

Part II Options for Ash Management

The handling of MSW incineration ash is driven primarily by the mitigation of toxic contaminants and their potential for both human and environmental harm. Typically, MSW contaminants include: heavy metals; notably lead and cadmium, dioxins, furans and elevated concentrations of salts. In MSW the concentration of these materials are usually very dilute representing only a small fraction of a few wastes. As illustrated in the

mass balance of chlorine presented earlier in this report it is important to understand the flow and sinks of these materials in order to identify where to effectively focus treatment steps. Due to the nature of the source material, the high temperatures of combustion and the volatility, most trace contaminants including chloride are concentrated into the fly ash. This was presented in the previous section, where in analysis of Taiwanese WTE facilities revealed that 60% of the chloride present in the combustion residues was concentrated in the fly ash (Chang and Huang 2002).

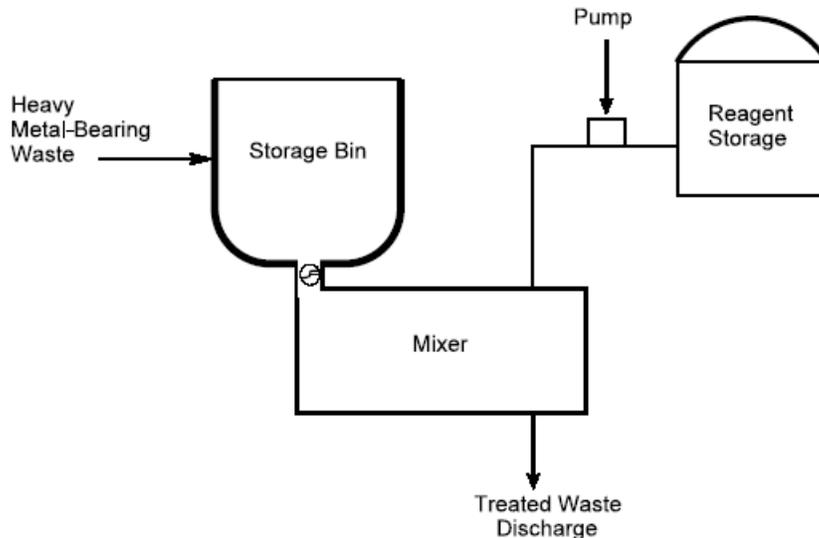
Fly ash represents only a small fraction (~10%) of the total combustion residue mass that is generated (Liberti et al. 2005). In Europe, fly ash is often handled as a waste stream separate from bottom and boiler ash that is generated by the system. This is due to its toxic nature and to prevent the contamination of the other ash streams (Zwahr). Ironically, for the same reason within the United States fly ash and bottom ash are routinely blended shortly after generation. In this case the two ash streams are joined to dilute contaminants contained in the fly ash with the larger volume of bottom ash. From a material flow point of view, heavy metals and salts were originally present in the solid waste entering the plant at concentrations and that did not present a threat to environmental health. They become a problem only after they are concentrated by combustion. The blending of bottom and fly ash to achieve dilution of these contaminate materials does hold merit as it returns them closer to their original distribution.

With increased legislation targeting the land filling of contaminated materials and the need for material recovery and reuse, the ability to mitigate the toxins found in APC residue is an important research focus. Currently there are many different methods for managing these materials beyond conventional landfilling. These processes vary from simple physical manipulation to more complex chemical treatments. Fundamentally the management of APC residue can be classified into two main schools of practice; treatment or stabilization for disposal or processing for reuse and recovery (Derie 1996), (ISWA 2003). Due to the threat that heavy metals, carcinogens, salts and other toxins pose to the environment and human health treatment the same steps are often needed whether the material is landfilled or reused. These treatment steps approach the problem from one of two schools of thought; removal or stabilization. By removing the contaminant from the ash, it eliminates the potential release years after processing. However, removal only requires the eventual treatment and/or disposal of secondary materials that are generated in processing be it wastewater or residue therefore the material management problem is rarely avoided. The second approach is to bind these contaminants to the ash, this usually involves a chemical treatment step. This process of binding contaminants to ash is referred to as ash stabilization, referring to the decreased breakdown of the material post treatment. In the following section two popular Stabilization techniques are examined and compared based on their ability to treat heavy metals and soluble chlorides (ISWA 2003).

The WES-PHix process

The Wes-PHix process is a chemical stabilization technique developed by Wheelabrator Technologies Inc. During the treatment soluble metal contaminants found in MSW ash are chemically bound to the ash in a phosphate stabilization reaction. The soluble metals

targeted by this process include cadmium, copper, zinc and chromium. Untreated these materials readily dissolve leaching from the ash substrate when the material is landfilled



WES-PHix® Stabilization Process

Figure 4 (from the SITE Technology Profile: Wheelabrator Technologies Inc. WES-PHix Stabilization process).

Figure 4 shows a schematic diagram of a typical WES-PHix process. Simply, combustion residue is flowed into a plug-mill type mixer. Due to the relatively rapid kinetics of the metal * PO₄ stabilization reaction the ash can be loaded to the plug-mill at rates of 40 – 200 tons per hour. While in the reactor the phosphate reagent is added with only one minute necessary for the reaction to reach completion. Application of the phosphate solution can be done at any point along the ash handling chain. In addition to wet application as described above, dry application can be done by spraying and/or sponging the phosphate reagent directly onto the combustion residue (Lyons 1999). Another advantage of this chemical treatment is that no curing or aging step is required (ISWA).

The WES-PHix process has been patented for the application of all forms of soluble phosphate (phosphoric acid, and/or salts) as the form of phosphate prior to application does not change the ultimate reaction progress. Additionally the patents scope includes the treatment of bottom ash, fly ash and various combinations of the two combustion residues (US patent no. 4,737,357, 1988) and (US patent no. 5,345,114, 1993). This increases the application of the WES-PHix, by allowing the treatment of combined ash streams, the WES-PHix process has been accepted by many US WTE facilities as ash streams are typically blended prior to disposal.

When ash is exposed to the phosphate solution the highly soluble metal compounds first dissolve then react with phosphate to precipitate as an insoluble metal phosphate. (Lyons 1999). During the stabilization process the porous ash residue is not physically

manipulated (ISWA). The metal phosphates are sorbed to the surface of the ash substrate. An advantage of the treatment process is in the lack of physical manipulation. After treatment, bottom ash residue retains its effectiveness as an aggregate of potential building material, less the risk of leaching heavy metals. Often treatments that involve crushing and or grinding of waste will increase surface area resulting in increased leachability of target and other contaminates.

Table 3. Results of WES-PHix Trials

| Parameter | EPA Test | University of New Hampshire | Field tests |
|-----------|----------|-----------------------------|-------------------|
| Cadmium | 32 % | 38 % | Below DTL |
| Copper | 51 % | 58 % | 43.5 |
| Lead | 99 % | 99 % | 90.2 |
| Chloride | Untested | Untested | - 19 % (increase) |

Data adapted from: Hyland (2005)

Analysis of the WES-PHix product was provided by Wheelabrator Technologies Inc., the evaluations included tests performed by the US EPA in 1993 and University of New Hampshire in 1996 as well as the results of an Independent 18 year long field test by Eighmy et al. (1997 and 2004). All of these different analyses were designed to gauge the leachability of heavy metals before and after the fly ash residues were treated with the WES-PHix process. As shown in Table 3 the results of these tests prove that the treatment was effective in significantly reducing the leaching of metals from the ash. In the case of lead the leaching was reduced 99% in both bench top tests and field tests support this high stabilization with greater than 90% reduction in leaching observed in the field. Copper behaved similarly with greater than 40% reduction for all tests, and cadmium showing a marked reduction in leachability. Only the field tests examined the effect of the WES-PHix process on the stabilization of chlorides found in the original ash sample. Unlike the heavy metals, the phosphate treatment had the opposite effect on chloride, increasing the leachability by nearly 19%. An explanation for this increased solubility can be given when examining the chemistry of the WES-PHix analysis. In the process of yielding insoluble metal phosphates, the metals originally as soluble as metal chlorides are dissolved, in the treatment these chlorides are substituted for phosphates. It could be that the chlorides made available by this reaction go on to form more soluble salts in the final product e.g. NaCl or CaCl₂. This would explain the increased leachability of these salts in the field. Another possible explanation could be that during the treatment the microscopic structure of the ash changes in such a way that chloride is less bound by the ash matrix. For both of these two theories future lab work should be done examining the presence and state of chloride before and after the phosphate treatment.

The Ferrox Process

Another unique chemical stabilization process is the Ferrox Process owned by Babcock & Wilcox Vølund. Like the WES-PHix process the Ferrox Process targets the release of heavy metals. The process is designed to immobilize heavy metals in an iron matrix while preventing the leaching of salts and other trace elements from MSW ash.. The aim

of them Ferrox Process is to bind trace elements (including heavy metals), in an iron complex and to remove via extraction easily soluble salts. This is to be done while minimizing the release of heavy metals into the wastewater associated with the process, a problem faced with many ash stabilization techniques

In the first step of the Ferrox Process ash is collected from fly ash handling equipment at a either pre or post lime scrubber location. The material is then washed with a ferrous sulphate solution. On contact, all soluble salts such as sodium and calcium chloride are dissolved in the solution. The iron(ii) contained in the ferrous sulphate solution is oxidized to iron(iii) oxides by the alkalinity of the APC residue. The exact details of the iron oxidation reaction are not known, partially because of the complex nature and composition of the APC residue. However, research has revealed ferrihydrite to be dominant over other crystalline iron-oxide forms in the Ferrox product. Regardless of the exact lattice form, the resulting iron oxides are insoluble. These products precipitate from solution crystallizing on existing APC residue found in the slurry or in the formation of new porous iron oxide particles.

The heavy metals and other trace elements found in APC residue become chemically stabilized when they are immobilized in the newly formed iron oxide. Chemically there are two fundamentally different mechanisms by which these materials are stabilized by the iron oxide; sorption and substitution. In sorption, charged sites on the surface of the iron oxide have an affinity for adsorbing specific chemical species, the heavy metals become bonded to these charged sites. The second mechanism that stabilizes heavy metals is substitution. In this case, substitution involves the one-for-one exchange of a heavy metal for a surface molecule of the iron oxide substrate. Substitution is a more permanent incorporation of the trace elements into the particles structure. These heavy metals are not released from the iron oxide matrix so long as the iron oxide remains in the solid form. Trace elements sorbed to the surface of these particles are less permanent. As the pH of the environment surrounding the alkaline APC residue starts to drop the binding ability of the iron oxide too begins to decrease. This liberation of heavy metals is the result of H^+ replacing the metals at the surface of the iron oxide. Figure 5 illustrates the relationship between pH and heavy metal surface sorbtion. The implications of this are important as in either beneficial use applications or landfilling the alkalinity of the Ferrox product must be preserved to insure the stabilization of the waste.

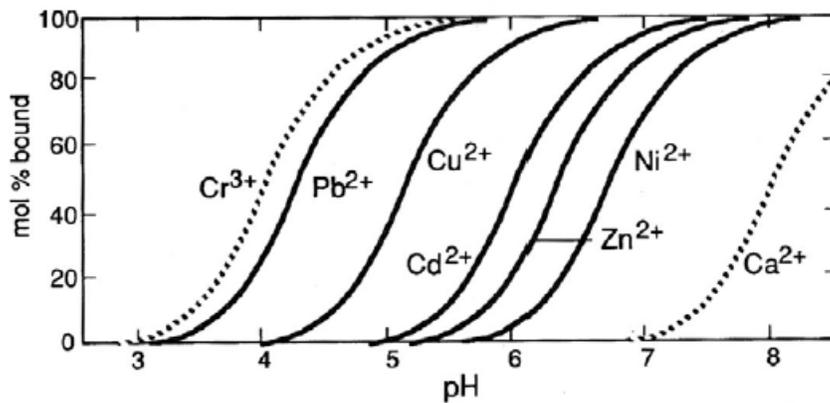


Figure 5 Relationship Between pH and Heavy Metal Surface Sorption (from Kasper, 2001)

The chloride salts and other soluble materials that were found in the ash remain dissolved in the ferrous sulphate solution while the iron oxide reaction progressed. In the next step of the Ferrox Process, the solid particles are removed via filtration leaving behind these dissolved constituents. This step removes a majority of the chlorides from the APC residue however this removal is optimized in the following step when the Ferrox product (filtrate) is washed with additional water (Kasper 2001).

Semi-Industrial trials were performed using the Ferrox process on three types of APC residue. APC residue treated via semi-dry scrubbing process, fly ash treated with a wet acid gas scrubber and raw (un treated for acid gas) fly ash were all examined representing material most types of material that could be found at waste to energy facilities. For each a mass balance with respect to lead and chloride was done to evaluate the binding of heavy metals and the extraction of salts by the Ferrox process. The result of this analysis is summarized in Table 4a for lead and Table 4b for chloride below.

Table 4a Ferrox Trial - Lead Mass Balance

| Material Type | Material-In | Water wash-Out | Ferrox product-Out |
|---------------------------|-------------|----------------------|--------------------|
| Semi-dry APC residue | 0.85 | 0.3×10^{-4} | 0.79 |
| Fly ash post wet scrubber | 1.18 | 0.2×10^{-4} | 1.22 |
| Raw fly ash | 1.16 | 0.1×10^{-4} | 1.10 |

Table 4b Ferrox Trial – Chloride Mass Balance

| Material Type | Material-In | Water wash-Out | Ferrox product-Out |
|---------------------------|-------------|----------------|--------------------|
| Semi-dry APC residue | 29.8 | 31.1 | 0.2 |
| Fly ash post wet scrubber | 9.8 | 11.4 | 0.6 |
| Raw fly ash | 12.5 | 13.9 | 0.2 |

Tables 4a and 4b are adapted from Kasper (2001)

As demonstrated by the data, the Ferrox treatment was effective in retaining nearly all lead present in the raw incoming ash material regardless of residue type. Though this simple washing step did not simulate leaching conditions in the field it does support that the lead is not dissolved or mobile during the washing of ash with water.

The mass balance of chloride demonstrated the effectiveness of the Ferrox process at removing soluble chlorides. In all cases chloride removal was greater than 92% with greatest removal for the semi-dry APC residue where original chloride concentrations were highest to start of the three samples. As seen in the data the amount of chloride that was found in the water wash was greater than the amount of chloride found in the original ash sample, meaning that there had to be an additional input of chloride to the system. This can be attributed to partial recycling of water that takes place in the process. Water used to rinse the filter press contained small amounts of residual chloride, this water was recycled and used in the following Ferrox batch treatment. Therefore incoming extraction water already contained levels of chloride prior to analysis (Kasper 2001).

In overall, the Ferrox process demonstrated its effectiveness at chloride removal, eliminating the potential for leaching of these salts in down stream management. It is important to keep in mind that the management of these salts is not eliminated, large amounts of wastewater are generated during the processing of ash material which must be treated (Kasper 2001)

Recovery and Reuse

Chemical management of contaminants contained in ash is traditionally done via stabilization. The other option that is available to manage these contaminants is removal. However, most often removal of these contaminants requires energy, and results in the transfer of contaminants from one waste material (ash) to another (eg wastewater) that in turn must be managed (ISWA 2003). This traditional way of thinking that stabilization is favorable over removal is being challenged with new research on material recovery for reuse in Germany. Not only has it been proven that contaminants can be removed from ash residue, but it can be done to produce industrially beneficial products.

The MVR Waste to Energy Facility

The Rugenberger Damm Waste to Energy Facility located in Germany, (MVR Waste to Energy Plant) uses an industrious mixture of energy and material recovery in their management. The facility is a cogeneration plant, handling 23 tons MSW per hour. A simplified lay out of the facility is given in Figure 6. The combustion of MSW at the plant yields 3MW of electricity which is fed to the local electricity power distribution grid, an additional 75 MW of thermal energy is also produced which is used in a district heating program. Beyond the power production and waste heat recovery, what makes this facility unique from other WTE plants is its unique material recovery system. The MVR plant has designed in to its APC system a chloride recovery process which produces a valuable industrial product. This process targets the recovery of chloride contained in the flue gas. Chloride is captured and recycled to yield a technical grade

30% HCl solution. By removing the chloride from the flue gases, downstream sinks for this chloride, either as deposited in fly ash residues or sent up the stack is avoided.

The first step in the air pollution control measures that are employed at the MVR facility involves the injection of ammonia into the combustion chamber. This step minimizes the NO_x that would have normally occurred at the combustor's 850°C operating temperature. Next fly ash is collected from the flue gas as it is passed through the system's boiler. The remaining flue gas is then treated with activated carbon, during this step heavy metals and dioxin/furans contained in the gas are adsorbed and removed. Following this all remaining particulates are collected using a baghouse filter. An overview of the MVR facility is provided in figure 6. Some of the hot flue gas which remains is recirculated back to the combustion chamber to aid in combustion. The remainder of the flue gas is then treated with a two-stage wet acid gas scrubber system. In its first stage HCl is removed from the flue gas yielding a crude acid byproduct. The second stage of the scrubber removes SO_2 . The by product of this step is gypsum which is sent for processing. The remaining flue gas is treated for a second time with activated carbon to adsorb any remaining gaseous heavy metals, PAHs, dioxins, and furans. The contaminated activated carbon is then collected by a second bag house unit before the gas is released to the stack. The need for raw materials is further minimized by regenerating the contaminated activated carbon for reuse within the air pollution control system.

The uniqueness of the MRV facility lies in the design of its Cl rectification process. In this process the crude HCl byproduct of the scrubber system is converted into reusable technical grade HCl. In the first step sodium hypochlorite is added to the crude HCl mixture with controlled amounts of NaCl and aluminum chloride. This is done to adsorb bromine and iodine from the mixture. Next hydrogen fluoride is removed by evaporating the gas and adding while adding aluminum chloride. From a mass balance point of view this step does increase the amount of chloride that is handled in the system. However in later steps this reagent chloride is recovered as salt solution. This salt solution is handled in an ecologically responsible manner by disposing of it in underground salt caverns.

The acid which remains, following fluoride removal is then distilled to increase the concentration of HCl to 11 percent. Off gas containing HCl which evolves during the distillation step is desorbed using calcium chloride and the final concentration of the HCl solution is brought to 30% using deionized water. An overview of the rectification process is shown in Figure 7.

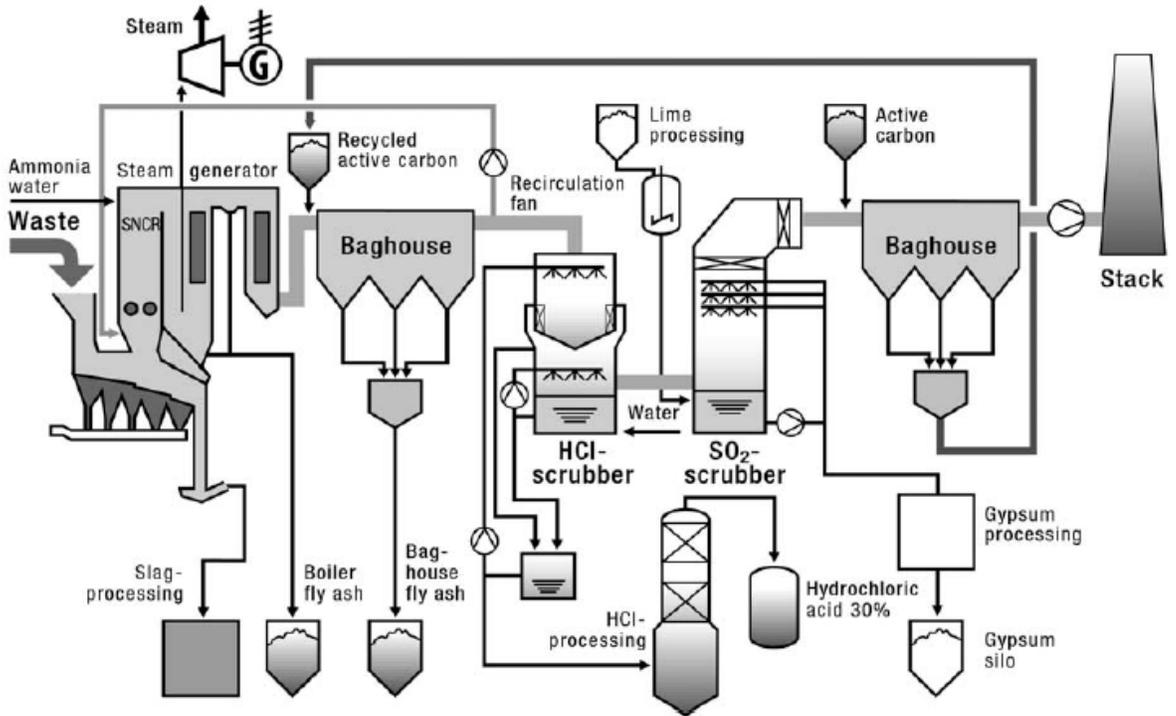


Figure 6 The MVR WTE Facility (from Menke and Zwahr, 2003)

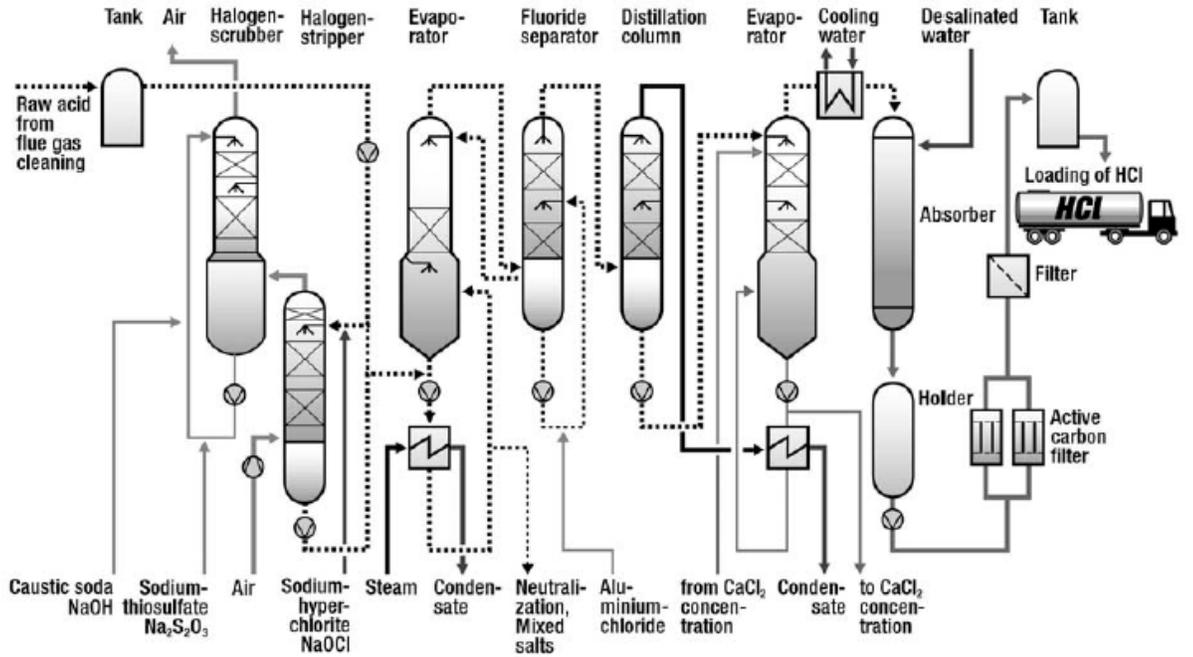


Figure 7. The MVR Chloride Rectification Process (from Menke and Zwahr, 2003)

When the plant is operated using an input of conventional MSW, with concentrations of 6 percent plastic and more specifically 0.7 percent PVC the rectification process yielded an average of 12 kilograms of HCl per tonne of waste. However the MVR facility is designed to accept additional amounts of PVC along with that contained in MSW. Trials were performed where the facility was run burning a combination of MSW and additional PVC. For the test the waste burned contained 5 percent PVC thermo plastics with a chlorine content of 16 percent. The result of this combined waste was the recovery of 22 kg HCl per tonne of waste (Menke and Zwahr 2003).

Ash as a Building Material

The application of MSW ash a building material and additive has been successfully demonstrated in many instances. In Rochester, Massachusetts, the SEMASS Resource Recovery Facility patented the production of Boiler Aggregate, a building material produced from bottom ash. The company used the material in the construction of an onsite road. In Wayne Pennsylvania, Rolite Inc. used MSW combustion residue to produce ash-cement balls that were used to cover landfills and mine sites (IEA and ISWA). A more advanced reuse project was successfully done by the State University of New York (SUNY) at Stony Brook where building blocks made of a combination of WTE ash and Portland cement were used to build a boat house.

Though all of these trials were successful, WTE ash still has limitations in its use due mostly to its chemical composition. One of these challenges that face use of the ash is the high concentrations of chloride. High levels of chloride complicate use scenarios, as it can have an impact on the quality and behavior of the produced materials. Additionally, negative environmental impacts have been associated with the dissolved chloride that leaches from these materials in to the local environment contaminating groundwater, receiving waters and soil.

In most trials, MSW used to produce simple building materials were successful, producing structurally stable building materials that did not leach contaminants into the environment. An extensive monitoring program was implemented at the SUNY Stony Brook boat house site. Both air and soil samples were analyzed pre-construction and after for a period of 30 months to gauge the stability of the construction materials. While elemental analysis of the soil showed increases in some metals, it was believed that this contamination was due to material handling and working during the construction process. Because the structural integrity of the blocks held up well over the monitored time period post construction (Roethel and Breslin 1995).

Although it has been demonstrated that MSW can be used as an additive for building blocks, its use as a structural cement additive is prevented by the high levels of chloride. The presence of chloride in concrete effects both its behavior in the setting process as well as its structural stability as it greatly increases the corrosion of the steel used for reinforcement. Thus before MSW ash can ever be considered as an additive for concrete with steel reinforcement, chloride mitigation must be considered (Liberti et al. 2005).

The presence of chloride can result in the breakdown of structural concrete when it causes corrosion of the reinforcing steel supports or rebar. Under normal conditions, chloride ions penetrate the porous surface of the material, often they originate from road

de-icing salts, marine wash etc. After, they begin to accumulate at the concrete-rebar interface until they reach a threshold at which, corrosion begins. This threshold is identified at roughly 0.05% chloride by weight (Nygaard and Geiker 2005). This threshold represents the chemical point at which corrosion begins to occur on the surface of the steel. Chemically, this corrosion is the chloride induced oxidation of the iron in the rebar to form hydrated iron (III) oxide [$\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ where x varies from 2 to 4]. There are a number of methods to under practice to inhibit the corrosion of steel rebar most often these involve coating the rebar with a protective layer. Though successful, the increased costs associated with the treatment of rebar can become prohibitively expensive.

When the concrete CI threshold for corrosion (0.05% chloride by weight) is compared to the chloride content of MSW fly ash, 6 - 12 % w/w it becomes clear that prohibitive levels of chloride are present in MSW fly ash (Derie 1996). Even when only small amounts of ash are added to cement mixtures levels of chloride rise dramatically, easily exceeding corrosion limits. This proves that steps must be taken to minimize or remove these ions before it can be added.

Though there are considerable challenges associated with the addition of MSW ash to cement, its potential benefit as an amendment can be seen when comparing the overall composition of the two materials. Table 5 below compares chemical compositions of each of these.

Table 5. Composition of Portland cement and MSW Fly Ash.

| Compound | Portland Cement | MSW Fly Ash |
|--------------------------------|-----------------|-------------|
| CaO | 67% | 35% |
| SiO ₂ | 23% | 21% |
| Al ₂ O ₃ | 6% | 7% |

Both Portland cement and MSW fly ash are composed of three dominant compounds SiO₂, Al₂O₃ and CaO. The relative concentrations of each mineral show striking similarities between the two materials, with SiO₂ and Al₂O₃ having nearly identical concentrations. It is these similarities in composition that allow for the substitution of fly ash for Portland cement on a partial basis when making concrete. Analysis by the US EPA reports that for every ton of fly ash that is recycled 5.3 million BTUs of energy are saved as a result thought the displacement of fossil energy (EPA Chapter 7).

The potential to amend structural concrete with MSW fly ash is of particular interest when considering the developing world where extensive use of concrete overlaps a desperate need for modern MSW management. The instillation of MSW-WTE in such places could stand to solve pressing waste and energy problems faced by millions of people. The use of MSW fly ash as an additive to structural concrete in these places would help to close the loop of WTE as the waste management solution for these people while conserving valuable energy.

WTE ash use in Reclaiming Abandoned Mine Sites

The Ms Thesis of Michael P Hyland, completed under WTERT sponsorship, examined results from a pilot project where MSW incineration ash among other materials was used

as a fill material to reclaim Bark Camp, an abandoned coal mine that is located in Western Pennsylvania. The Bark Camp site was originally identified as a remediation site by the Pennsylvania Department of Environmental Protection (PADEP). The PADEP's goal was to return the excavated mine site and gorges to its natural hillscape, to a condition that was capable of supporting vegetation and the local ecosystem. With many abandoned surface coal mine sites in Western PA (and through out the US) this project had the potential to demonstrate technologies that could be replicated elsewhere.

In a joint effort by a Penn State University research laboratory examining material properties of MSW ash and the Clean Ocean and Shore Trust of NJ/NY(COAST) which looked at beneficial uses for river sediment, a reclamation project was launched at the Bark Camp Site. Simply, the project was to evaluate the potential for backfilling different materials at the abandoned mine site. The materials that were evaluated by the research group included; dredged sediment from the NY and NJ waterways, degraded soils, fluidized bed combustion residue (FBC) from a clean coal fired power plant and MSW incinerator ash. The MSW incinerator ash that was used for the project was sourced from the Essex County NJ Waste to Energy Facility that at the time was under the direction of American Ref-fuel and is presently owned by Covanta Energy.

The remediation project was divided up into three phases. Phase I and II consisted of backfill trials using primarily river sediment and coal FBC, towards the end of Phase II FBC was blended with small fractions of MSW fly ash. Based on positive results from the first two phases of the project, the third phase of the project was initiated using combined ash in place of the FBC coal ash blended with the sediment. After successful trials, phase three launched a full scale operation. The *combined* MSW ash that was used for this trial was a blend of 90% bottom ash and 10% fly ash both from the Essex NJ WTE facility. Phase III began on June of 1998 and extended through the end of 2004 (Hyland 2005).

As part of the project, PADEP conducted an intensive sampling program designed to monitor compounds leaching from the remediation site. The program sampled surface and ground water wells in the vicinity of the mine site testing for; organic carbon, heavy metals and salts. The Results of this analysis ultimately led to the termination of the Bark Camp Remediation project due to elevated levels of chlorides that were found to be leaching from the Phase III site. The high levels of chloride liberated from the filled area posed a threat to soil and aquatic ecosystems located downstream of the site. It was determined that the MSW incinerator ash was the source of these chlorides.

Hyland's Masters Thesis examined in detail the results of the PADEP's data. As a cooperative effort with Hyland and Columbia University's WTERT the purpose of this masters thesis project was to examine chloride in MSW ash. Hyland's work concluded that because chloride is commonly found in MSW ash a chloride treatment step is required before any such land reclamation projects can be done using MSW ash. Hyland's work went on to propose developing a chloride stabilization process, one modeled after the WES-PHix heavy metal stabilization process, only in this case targeted at decreasing the leachability of chlorides. As stated earlier one of the purposes of this masters work was to evaluate the potential for adapting a WES-PHix type chemical stabilization technique for the treatment of chlorides in MSW ash. The following section will explore that possibility.

Chemical Stabilization of Chlorides

The goal of a stabilization process is to take a soluble contaminant present in waste and to react it in such a way that post-treatment the solubility of this material is significantly reduced. In doing so, the leachability of the compound is decreased or eliminated. Typically, stabilization processes are done in two ways, either by altering the chemical form of the contaminant, so that it is no longer soluble; or, through the reaction the chemical can be bound to the waste material and held by a matrix. Examples of these two different techniques are the Ferrox process, where heavy metals are bound in a iron oxide matrix, and the WES-PHix process, where soluble heavy metal salts are replaced by insoluble metal phosphates are presented in earlier sections of this report.

The first step in assessing the feasibility of a stabilization technique for chlorides is to examine the solubility of chloride and try to identify compounds that would be potential candidates for stabilization end products. In the case of heavy metals, by identifying that metal phosphates were insoluble a phosphate reaction became desirable and targeted in the WES-PHix process. Problems arise when applying this approach to chlorides due to its lack of insoluble forms. Solubility rules for chloride state that all chloride compounds are soluble except those of silver, lead and mercury (I). In the case of these insoluble compounds the solidification of chloride with silver would be too expensive, and stabilizing chloride with either lead or mercury would substitute one environmental problem with an even greater one.

The implications of this observation prevent further evaluation of a chemical stabilization treatment process for chlorides. If chloride is soluble irrespective of the chemical form it is found, no reaction will be able to prevent it from leaching. Furthermore, the high solubility of chloride makes the potential for binding the material in a matrix, either through substitution or surface sorption prohibitively challenging. Based on this conclusion the proposal of Hyland's work to develop a chemical stabilization technique for the treatment of chloride pre-land reclamation must be amended. Instead, it is proposed that a chloride extraction step must be developed to remove chloride prior to the use of MSW ash in future land reclamation projects. The third Part of this Masters Thesis presents experimental work that was performed in conjunction with this report to develop a simple chloride removal technique that could be used for such projects.

Part III. Extraction of Chloride from Municipal Solid Waste Fly Ash; The Feasibility of Fly Ash Quality Improvement

As noted earlier, the high solubility of chlorides contained in MSW incinerator ash presents a challenge to the reuse applications of ash, be it incorporation of ash into building materials or reclamation of abandoned mine sites. To cope with this problem a treatment step is required to eliminate the potential for liberation of these salts. Due to the solubility of most chloride compounds and the toxicity of insoluble forms stabilization is not an option. As a result the most feasible treatment for these salts is by means of removal. By taking advantage of the high solubility of chloride it is hypothesized that removal of chlorides can be done effectively via water extraction. In this approach water can be used as a solvent in a washing step to remove salts.

As with any industrial operation, sound understanding of the fundamental variables and controls is required at the bench top level before the system can be scaled up to a industrial scale operation. Much work has been done in the field of MSW ash examining the effects of water washing, however much of this work has been done to simulate leaching conditions to understand how toxic contaminates will behave in landfills. In such work the washing tests are often done at high temperatures and with excess water offering little information as to the behavior of chlorides under more feasible washing conditions. Furthermore, work that has been done on washing as a treatment step often is done by industry and is proprietary knowledge and is not available. This investigation sought out to build an understanding of how time, temperature, and the liquid to ash ratio of the extractions effect the degree of chloride removal. With this work, future research will be able to scale up extractions designed at chloride removal.

Background information

Typically in the United States, WTE bottom and fly ash are handled together as a combined ash mixture. As reported in Part I, 60% of the chlorinated compounds produced as a result of the combustion process are found in the fly ash (Chang and Huang 2002). Because chloride is concentrated in the fly ash there is great potential to target the removal of chloride from this fraction. By focusing the removal of chloride from the fly ash, the overall material handling (ash) can be decreased by nearly ten times vs treating the total combined ash. Also if materials such as water are used for removal the total wastewater generated is minimized during this targeted treatment. As a result this examination will focus on extraction of fly ash only, unlike similar work that has been done to wash bottom ash and/or combined ash fractions.

In order to understand what controls the extraction of chlorides from fly ash it is important to understand what is happening on a chemical level. The first thing that occurs when the fly ash is exposed to water is the rapid dissolution of the alkali chlorides, with this is calcium, magnesium, zinc, lead, and cadmium salts dissolve (Derie 1996) These free ions begin to diffuse out of the ash matrix into solution (Liberti et al. 2005) After, the slow hydrolysis of aluminosilicates contained in the ash begins to occur. Also occurring, is the free dissolution of calcium hydroxide, this step is of importance because it results in a pH increase to the solution (Derie 1996). As with most solvent/solute chemical reactions the rate or kinetics of this reaction is expected to be dependent on time, temperature and the ratio of water to the amount of ash or liquid to solid ratio (L/S). The following experiments will identify how these parameters effect the extraction of chloride from the fly ash. Because other potentially toxic compounds are present in the ash it is important to understand what conditions can be used to effectively remove chloride and then anticipate how to mitigate the removal of other undesirable compounds.

Chloride Extraction from FlyAsh

This experiment investigated the potential of using a simple batch type water washing system to remove soluble chloride from fly ash. Fly ash samples from two U.S.WTE facilities were used for this analysis. By varying the amount of water used during the extraction, the relationship between extracted chloride and liquid to solid ratio was investigated. Trials were done originally at high L/S ratios to build an understanding of this relationship, as well as test the method against similarly published experiments. Thus, the initial trials used liquid solid ratios of 30 and 60. After positive findings were presented to experienced industry personnel, the research group was advised to use lower L/S ratios as they would be more feasible to reproduce on an industrial scale. For the second phase of these tests, L/S ratios of 3, 5 and 10 were used for chloride extractions from fly ash. The following section reports the results of these tests.

Experimental Section

a) Apparatus

The reactor used for fly ash extractions was a bench top, complete mix batch type reactor, similar to the design used in an investigation carried out at the Technical University of Bari, by Liberti et al (2005). In the apparatus pictured below in Figure 8, the reactor consisted of a flask suspended in a temperature-controlled water bath. The water bath was fitted with a circulation pump, heating element and automatic thermostatic control device. For mixing within the batch reactor vessel, a variable speed stir rod was attached to the vessel. Variable speed settings were necessary to optimize mixing in samples of different viscosities.

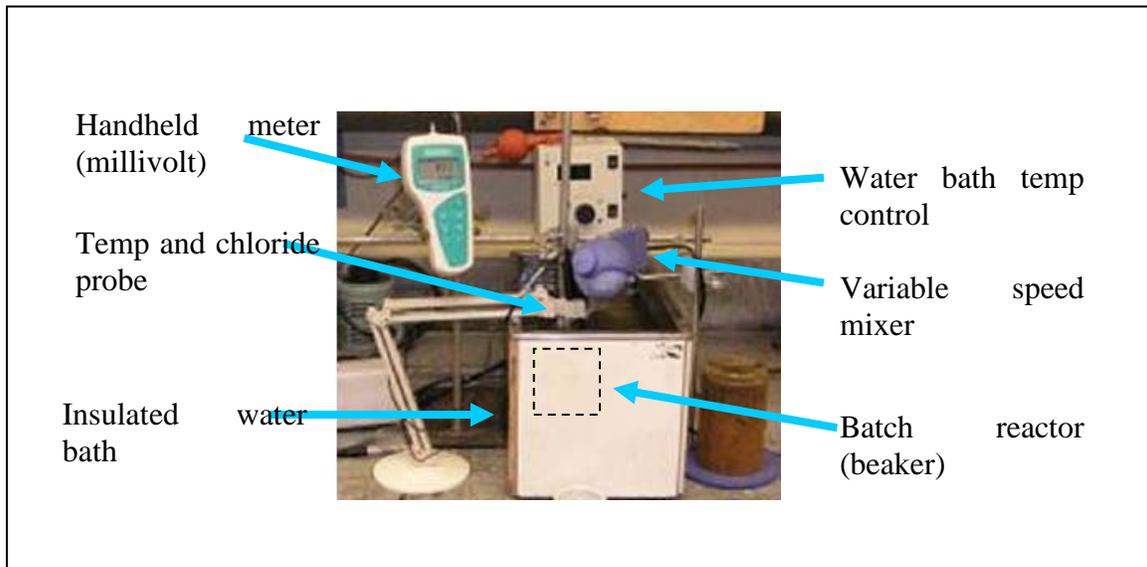


Figure 8 Experimental Extraction Apparatus

Chloride extraction was examined by monitoring the aqueous concentration of chloride as a function of time in the extraction fluid. As chloride was extracted from the fly ash sample the concentration of dissolved chloride rose in the solution. To measure the concentration of chloride in solution a refillable ion selective epoxy chloride electrode was used. The electrode was used in conjunction with a temperature probe, both probes

were connected to a hand held electrode meter that measured the millivolt response of the electrode. Chloride concentration was measured by calibrating this millivolt response to a series of standardized chloride solutions obtained from Cole-Palmer.

b) Reagents

A standardized chloride solution obtained from Cole-Palmer was used for preparing calibration standards. Standard solutions of 10, 100, 1,000 and 10,000 ppm chloride were prepared, using standard dilution methods with distilled H₂O. An ionic strength adjustment solution of NaNO₃ was used to buffer the ionic activity of chloride in the standard solutions. Also, this buffer solution made the standard more accurately representative of the ionic activity of the complex sample matrix.

Ultra pure deionized (UP-DI) water was used in the preparation of all dilutions, standards, buffer solutions and for the extraction of all fly ash samples. This was done to illuminate the effect of contaminate chloride on the results. Additionally all glassware was rinsed excessively with the UP-DI water to remove any contaminate material.

c) Experimental Method

Calibration of the Chloride probe was carried out using dilutions of a standard chloride solution. In accordance with the probe manual an ionic strength adjustment solution was added to each of the standard solutions. Due to the sensitivity of the probe to temperature, every 1 degree C change corresponds to a 2% error, calibrations were performed at each of the extraction temperatures. The results of the calibration tests were plotted on a semi-logarithmic scale, by fitting with a linear trend an equation solvable for chloride concentration was obtained. An example calibration curve is given as figure 9.

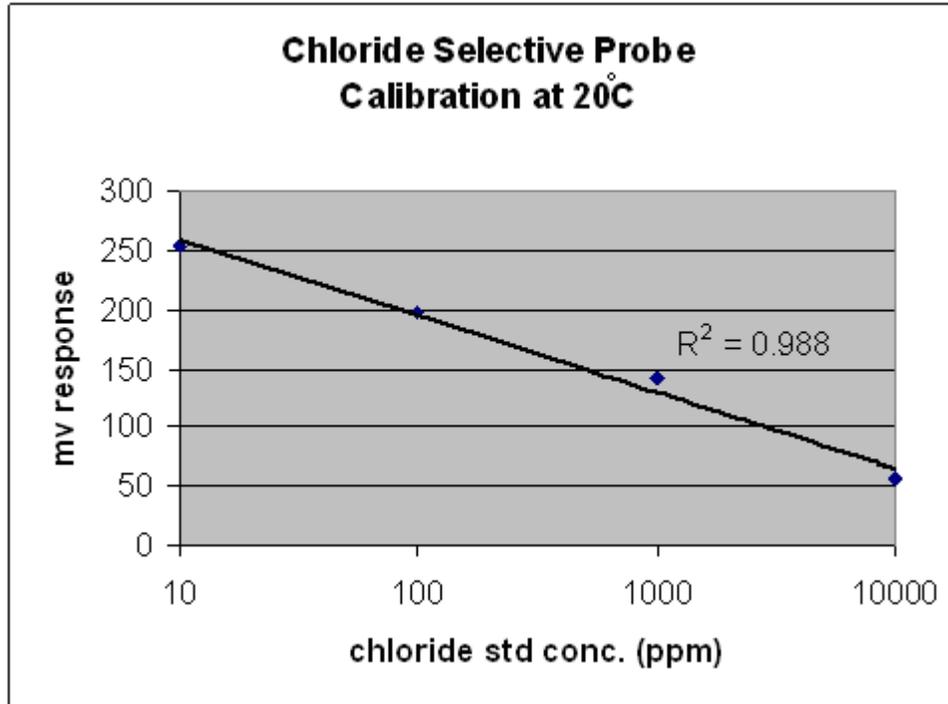


Figure 9

Extractions were carried out over a series of different liquid to solid ratio's (L/S) table 6 summarizes these L/S ratios giving the corresponding fly ash sample weights used as well as extraction volume of water. For each of the 3 L/S ratios extractions were performed at 20°C and 30°C.

Table 6. Liquid to Solid Ratios of Experimental Trials

| L/S ratio | Fly ash dry weight | Extraction volume |
|-----------|--------------------|-------------------|
| 10 | 10 g | 100 ml |
| 5 | 20 g | 100 ml |
| 3 | 50 g | 150 ml |

Before extractions started, the water bath was brought to the appropriate temperature. After the bath had stabilized, the appropriate amount of extraction water was added to the reactor flask. The flask was immediately covered with a watch glass to minimize evaporative losses while the extraction fluid was brought to equilibrium with the water bath. Once the temperature in the reactor stabilized, the mixing rod and chloride sensor were added to the reactor, temperature was allowed to re stabilize. Extraction began once the measured sample of fly ash was added to the reactor flask. Data collection commenced immediately, the extractions were allowed to progress for 20 minutes.

d) Experimental Results

Fly ash extractions were carried out under different conditions to gauge the effect of certain key operational conditions on the water-ash exchange of chloride. The operational

conditions that were tested were, temperature and liquid to solid ratio. Two liquid to solid ratio regimes were evaluated; high L/S ratios of 20, 30, 50 and low L/S ratios of 3, 5 and 10. Due to sample availability, the source of the fly ash was changed when the low L/S ratio tests were performed. Because the ash samples are not from the same WTE plant quantitative comparison of the results would be difficult to make. Rather, the results can be used to qualitatively understanding the extraction behavior in these two extraction régimes. For each of the fly ash types used a maximum theoretical chloride concentration was assumed based on general literature reports as well as the results of the analysis for each specific source of ash used. For the fly ash used in the low L/S trials this theoretical maximum amount of chloride was assumed to be 275 g chloride per kilogram of fly ash for the high liquid to solid ratio ash samples a chloride content of 250 g chloride per kilogram of fly ash was assumed. Variations in final chloride content of fly ash for different MSW WTE plants are explored in section 2 of this report.

e) Low L/S Ratio Extractions

L/S 10 at 20 °C

Immediately after the ash samples were added to the extraction solution, the millivolt response of the chloride probe began register chloride ions in solution. Nearly 90% of the total chloride extracted was achieved in the first 30 seconds of extraction. The extraction activity then tapered off as the chloride concentration of the extraction solution remained relatively constant at 8.55 g/l of solution.

The final equilibrium of the extraction resulted in the removal of 85.5 g of Cl⁻ per kilogram of fly ash extracted. This corresponds to 8.5 percent of the total weight of the fly ash sample.

L/S 5 at 20 °C

Again, chloride detection was immediate, after ash sample was added. 91.8 percent of the total chloride extracted was achieved in the first 30 seconds of extraction. The extraction rapidly tapered off as the chloride concentration of the extraction solution remained relatively constant from 3 to 20 minutes. The final equilibrium of the extraction yielded extraction fluid with a chloride concentration of approximately 12.97 g/l.

The yield was a steady state chloride extraction of roughly 64.9 g of Cl⁻ per kilogram of fly ash for a liquid to solid ratio of 5 at 20 °C, corresponding to 6.49 % of the total original fly ash sample weight.

L/S 3 at 20 °C

As with the other three 20 °C extractions, chloride extraction commenced immediately after the sample was added to the extraction vessel. Within 30 seconds of extraction 47.7 percent of the total extracted chloride was removed in this time the concentration of the deionized extraction liquid rose to 5.071 g/l. Over the remaining minutes of the extraction the concentration of chloride in solution rose to 7.97 g/l at 5 minutes, 8.80 g/l at 10 minutes and finally 10.63 g/l at 20 minutes.

The extraction resulted in the removal of 31.9 g of chloride per kilogram of fly ash extracted. This corresponds to 3.19 percent of the total weight of the fly ash sample.

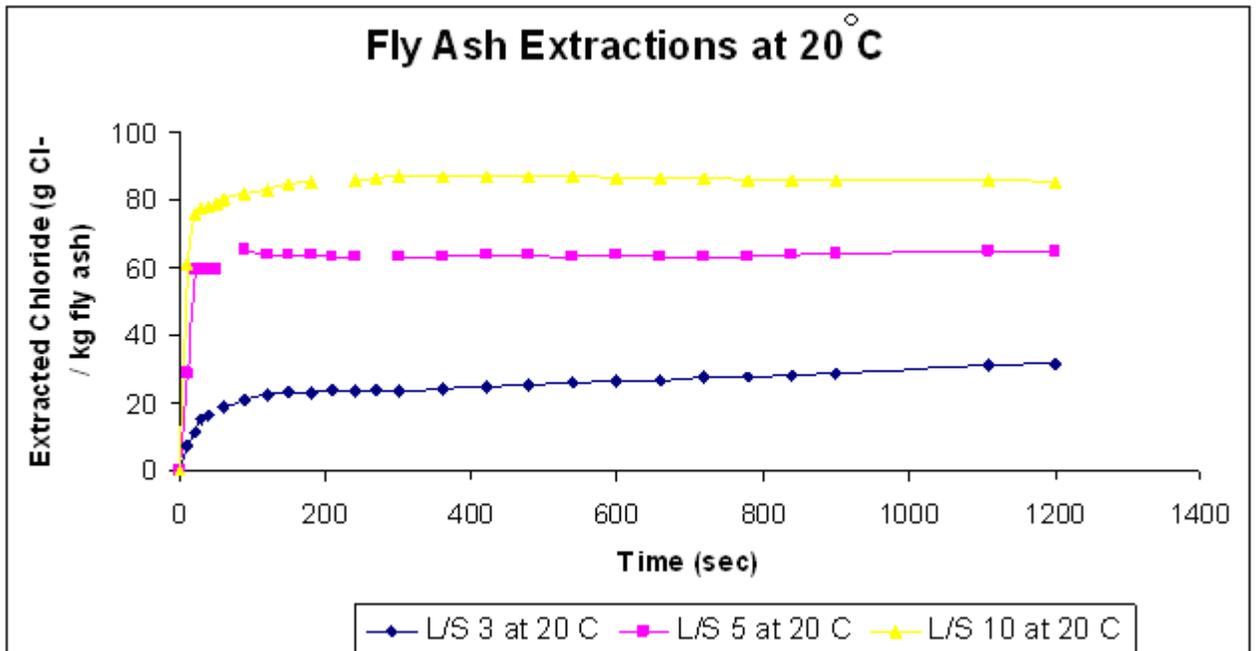


Figure 10

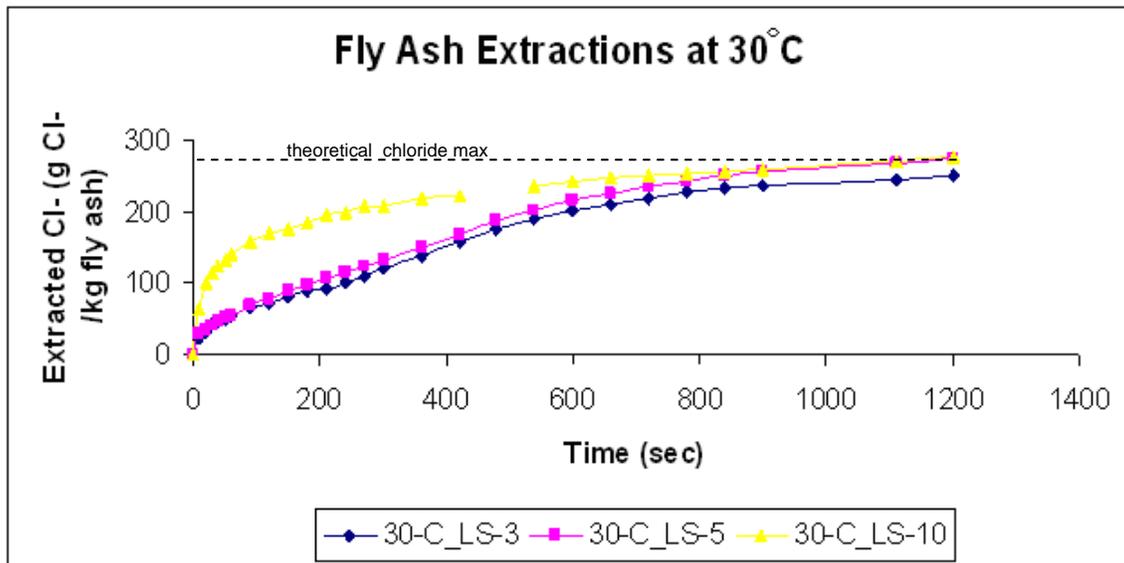


Figure 11

L/S 10 at 30 °C

Extraction of chloride progressed immediately after the fly ash sample was added to the extraction vessel, with in 20 seconds the extracted chloride was equivalent to 100 g of chloride per kilogram of fly ash. As shown in figure 10 the extraction began to quickly

taper off after 1 minute of extraction time. The rate of chloride removal began to slow 10 minutes, the extraction trial ended at 20 minutes with a total extracted mass of 2.759 g of chloride corresponding to removal ratio of 275.9 g chloride per kilogram of chloride.

L/S 5 at 30 °C

The concentration of chloride in the extraction solution rose quickly, removing 55.1 g of chloride per kilogram of fly ash in the first 1 minute of the extraction. After, the extraction progressed at constant rate, as shown in figure 12 with a linear slope of 0.295 corresponding to roughly a 18 g of chloride per minute. After, the extraction rate began to level off, at a final extracted mass of 5.45 g corresponding to a removal of 272.65 g of chloride per kilogram of fly ash.

L/S 3 at 30 °C

Behaving with similar behavior to the L/S 5 at 30 °C, the extraction rapidly progressed during the initial 60 seconds yielding a loss of 54.49 g of chloride per kilogram of fly ash. Again the reaction slowed and continued at a constant rate, as shown in figure 11 the slope of the linear plot was nearly identical to the L/S 5 trial with a slope of 0.2793 for the L/S 3 extraction.

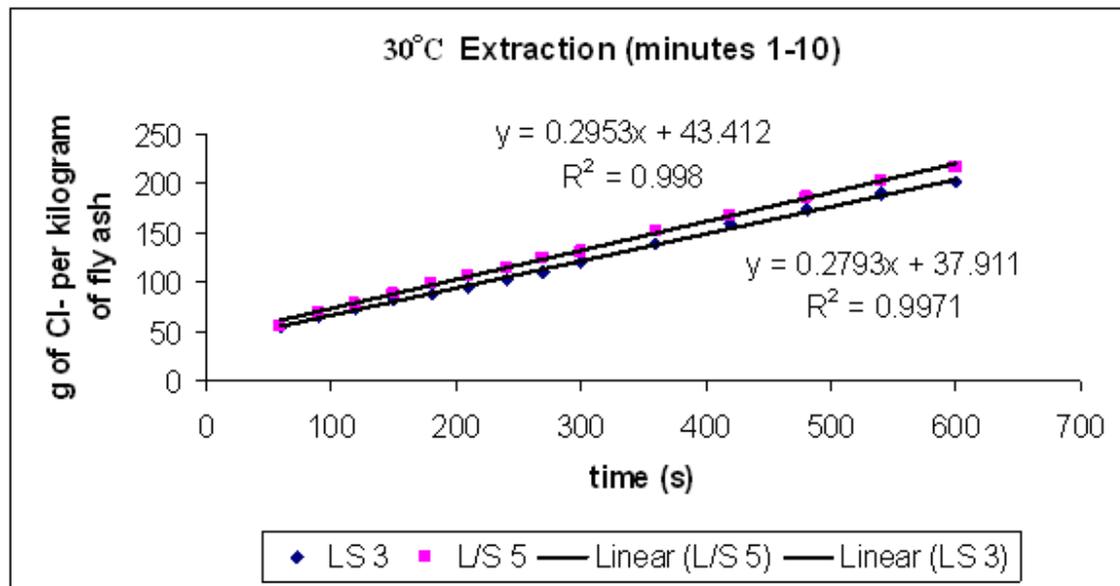


Figure 12

f) High Liquid to Solid Ratio Extractions

Originally chloride extractions were performed using L/S ratios of 30 and 60. These extractions were done to open an understanding of how chloride dissolved from the fly ash matrix as well as test the method used in this investigation against published data. Presentation of these preliminary results to industry professionals led to the design of low liquid to solid extraction tests.

The high L/S tests were performed at ratios of 30 and 60, an order of magnitude higher than the lowest of the later L/S extractions. Again the effect of temperature was examined

in these trials, for each of the two L/S ratios, extractions were performed at 30 and 50°C. Initially these temperatures were going to be used for the low L/S trials however during the high L/S experiments it was observed that at high temperatures (50°C) significant steps had to be taken to minimize the evaporative losses during the extraction. These losses led to the decision to use lower extraction temperatures for the low L/S trials.

The results of the high L/S trials provided in Figure 12, were very similar to the results published by research done by Liberti et al (2005), thus confirming the accuracy of the methods used in this investigation. For all trials the greatest loss of chloride from the sample occurred in the first 30 seconds. Again the low temperature (30°C) extractions, both L/S 30 and 60°C seemed to behave similarly showing rapid release of chloride then the extraction fluid stabilized with a minimal increase over the final 14 min of extraction. Interestingly, the initial release of chloride for L/S 30 at 50°C and L/S 60 at 50°C was nearly identical. However, after 30 seconds the lower L/S sample reached saturation with the extraction fluid coming to a stable equilibrium concentration of chloride. The higher L/S sample continued to release chloride under the same conditions.

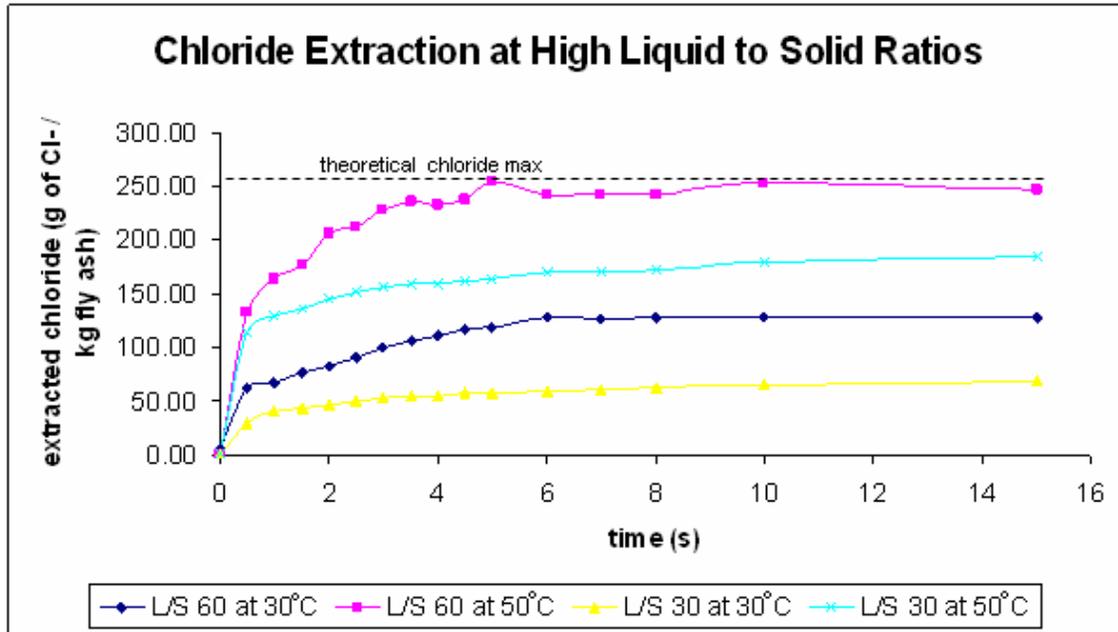


Figure 13

g) Discussion and Conclusions on Chloride Leaching

Overall the monitoring of extracted chloride was successful in helping to understand the removal of chloride from fly ash. After examining the effect of temperature, it is clear that the amount of energy (in the form of heat) added to the extraction solution greatly affects the amount of chloride that is ultimately removed during extraction. Simply, at higher temperatures more chloride could be extracted from the fly ash sample. For example, the final removal of chloride for L/S 10 trials was 85.50 and 275.77 g chloride/kg fly ash for 20°C and 30°C respectively. What is more interesting is that at 20°C each trial irrespective of L/S ratio progressed quite rapidly reaching near max

extraction in the first 60 seconds of extraction. In all 20°C cases, the extraction leveled off reaching a relatively constant chloride concentration in the solution. However, at 20°C each L/S leveled off at distinctly different points with the higher the L/S ratio the higher the extractability of chloride. When extraction profile for the 30°C extractions was examined, the same rapid removal of chloride was observed for each of the L/S ratios. However, after this initial release of chloride the extractions did not level off as in the 20°C case, but rather chloride continued to be removed. Though this secondary removal progressed at a slower rate, the addition of this removal regime increased the total removal of chloride nearly 500% from the 20°C trials. These observations have valuable implications when considering the scale up of this extraction for fly-ash remediation. At low temperatures the amount of water used has a dramatic effect on the removal of chloride. However when sufficient heat is added the differences from liquid to solid ratio are overcome with all extractions ultimately reaching the same level of chloride extraction.

Figure 11 shows that, as the 30°C extractions progressed, all of the L/S ratios converge on the same extracted amount of chloride. This convergence suggests that the amount of extractable chloride decreased towards the end of the extractions. This decrease in chloride solubility could be the result of either extraction fluid saturation or lack of additional chloride in the sample. Considering that when the removal leveled off the concentration of chloride in the extraction fluids were far below solubility of CaCl_2 (74.5 g/100 ml at 20 °C) it suggests that the removal was limited by the availability of chloride in the sample. Based on this assumption the composition of the fly ash used in these trials would be roughly 275 g chloride per kilogram of fly ash or 27.5%. Research by Liberti et al. (2005) at the Technical University of Bari found similar findings with fly ash* chloride concentrations of 200 g chloride / kg fly ash. (Liberti et al. 2005) The differences between these findings could be the result of differences in MSW composition as well as combustion conditions and chloride ash partitioning.

Another important observation is that the extraction of chloride is more sensitive to increases in temperature rather than liquid to solid ratio. A 10 degree increase in temperature corresponded to roughly a 300 percent increase in extracted chloride. In Figure 14, it is shown that the rate of chloride removal was identical for the two temperatures in the first 10 seconds of the extraction however as early as 20 seconds after the two extractions diverged, with significantly greater chloride extracted at the higher temperature. This relationship was observed in both the low and high L/S trials. Though no direct comparison can be made between the two series of experiments, the same fundamental trends are evident, the amount of extracted chloride increases steadily with increased temperature.

* Particulate range tested in Liberti analysis were consistent with fly ash particulate size.

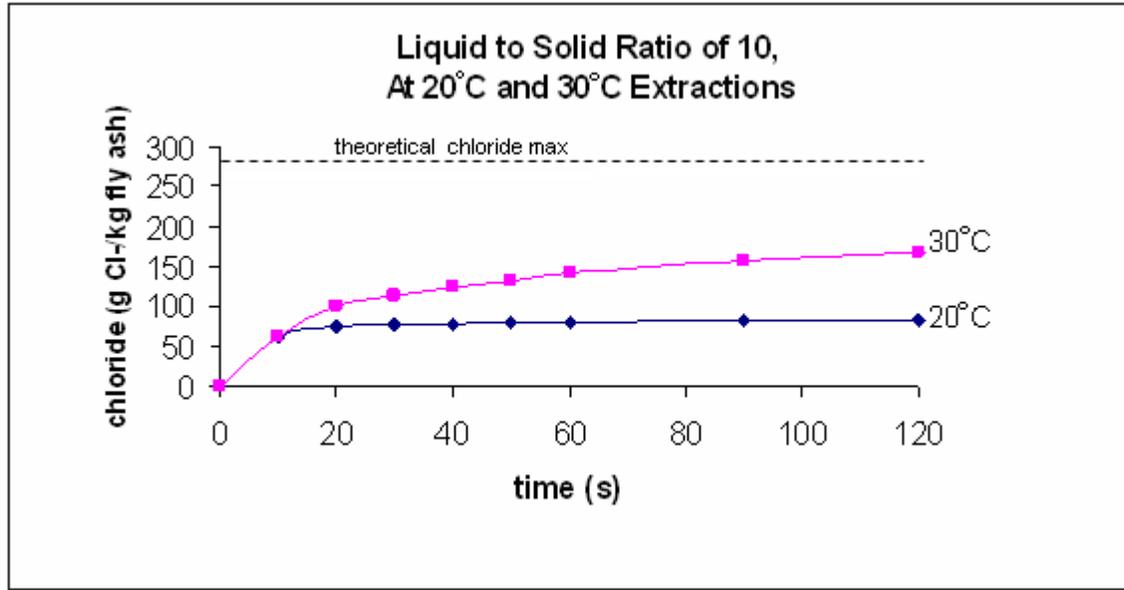


Figure 14

Temperature Change: The temperature of the extraction vessel was also monitored during each of the investigations. Originally done to calibrate the chloride probe, it was not the design of the experiment to collect temperature data for analysis. However after the analysis was complete a plot of the temperatures during each of the extractions revealed interesting results, shown in figures 7 and 8 for 20 degree and 30 degree trials respectively. All extractions showed a significant increase in temperature of the extraction solution immediately following the addition of the fly ash.

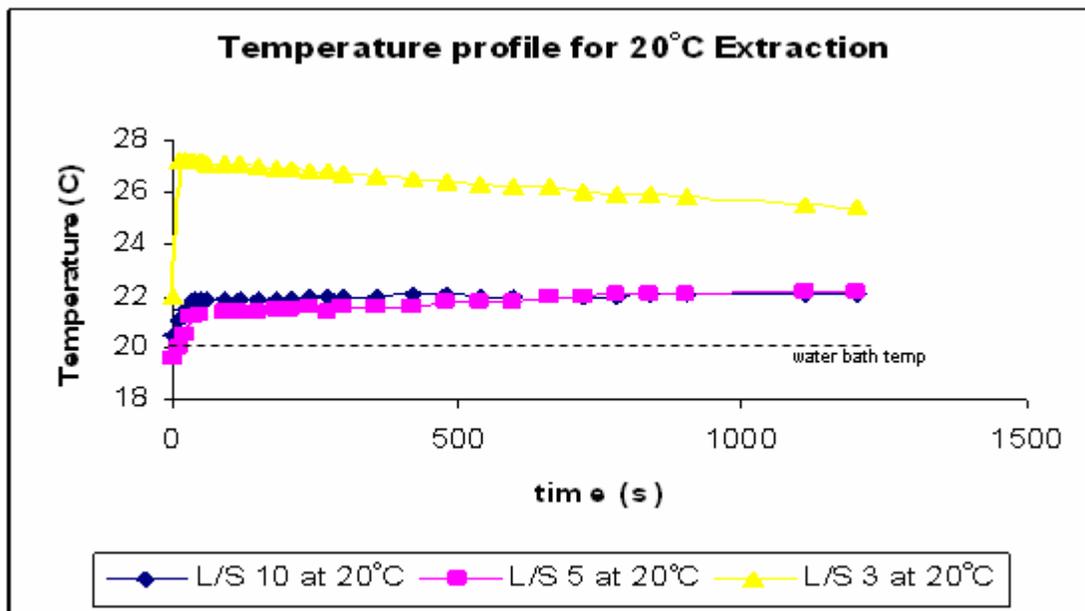


Figure 15a

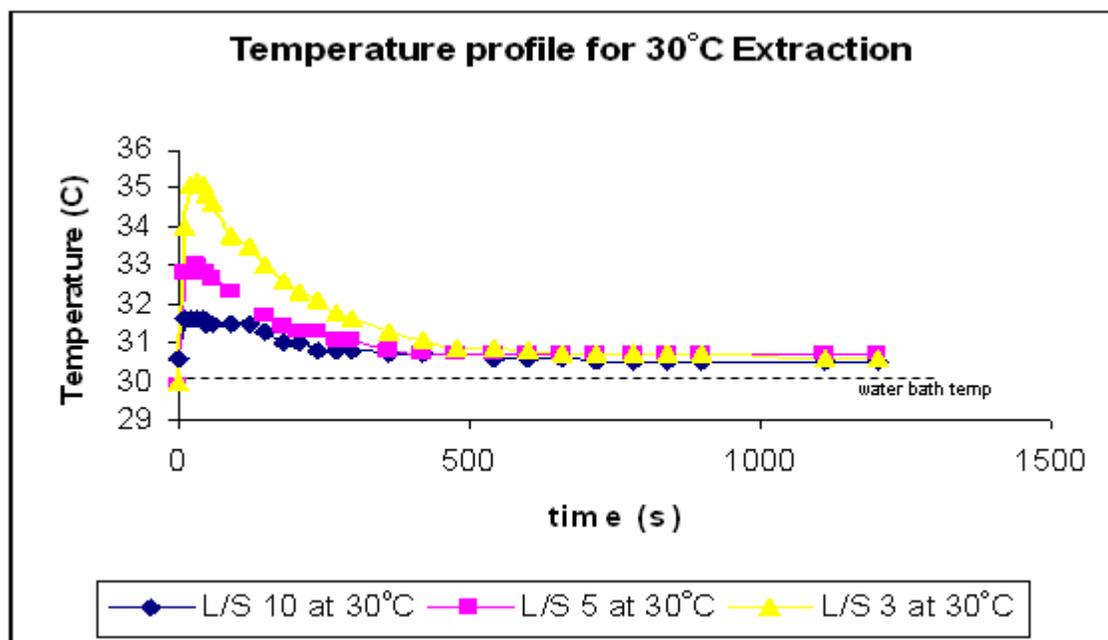


Figure 15b

As shown in figures 15a and 15b, each temperature profile increased dramatically to a maximum then began to taper off. Typically, this maximum was reached within the first 60 seconds of the extraction. The rise in temperature from initial equilibrium to maximum temperature was calculated as the delta temperature. From the delta temperature, the energy liberated to solution could be calculated. Table 7 below summarizes these values.

Table 7. Temperature and Energy Change During Chloride Extractions

| Temp (°C) | L/S ratio | Max time | ΔT (°C) | Joules |
|-----------|-----------|----------|-----------------|--------|
| 20 | 3 | 10 | + 5.2 | 3263.5 |
| | 5 | 30 | +1.6 | 669.4 |
| | 10 | 10 | + 1 | 418.4 |
| 30 | 3 | 30 | + 5.2 | 3263.5 |
| | 5 | 30 | + 3.1 | 1297.0 |
| | 10 | 10 | + 1 | 418.4 |

The values listed above are approximate. It is important to note that these calculations assume that all of the energy released by the extraction heats only the extraction solution and that there is no significant energy exchange with the water bath. This is a reasonable assumption because the time over which the delta temperature was observed was rapid (typically 30 seconds), thus the amount of time for energy exchange between the extraction fluid and the bath was limited. In the future more accurate analysis should be performed using an apparatus designed to minimize this interference of the water bath temperature.

Future Work

Based on the preliminary results obtained in this analysis there are several areas of future work which are advised in continuing to understand these extraction techniques. The first is a complete elemental analysis of the fly ash samples used in this test as well as bottom ash from the WTE facility, this will allow for more accurate mass balance accounting of chloride. As stated previously, more accurate temperature monitoring can be done to observe the energy release over the course of the extractions. This would involve a more advanced reactor for extractions to minimize losses of energy to the environment. Most important would be analysis of the extraction fluid that is generated in these extractions, the presence of heavy metals and other contaminants in these ash samples presents a significant challenge to the management of the wastewater generated during these extractions. An early understanding of contaminants in this water may help to develop potential mitigation techniques as the extraction is scaled up.

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