Ultrasonic treatment of municipal solid waste fly ash for utilization as construction material

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**ULTRASONIC TREATMENT OF MUNICIPAL SOLID
WASTE FLY ASH FOR UTILIZATION AS
CONSTRUCTION MATERIAL**

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Interdisciplinary Graduate School
Nanyang Environmental and Water Research Institute

2020

ULTRASONIC TREATMENT OF MUNICIPAL SOLID WASTE FLY ASH FOR UTILIZATION AS CONSTRUCTION MATERIAL

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**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute**

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy

2020

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ABSTRACT

In recent years, the use of municipal solid waste incineration for waste management is becoming more and more popular due to the potential of energy recovery and high-volume reduction. However, the use of incineration gives rise to the generation of more hazardous by-products such as fly ash (FA) and air pollution control (APC) residues. In Singapore, the FA and APC were not treated but instead disposed of at an offshore landfill. Due to the rapid increase in waste generation, this offshore landfill is only expected to last till 2035 and there is an urgent need to divert away some of these by-products for utilization purposes. However, these by-products contained high salt and heavy metal contents that could result in many problems during utilization. Therefore, proper treatment must be done before these by-products could be utilized and diverted away from the landfill. This research proposed using ultrasonication as a form of treatment for the FA before partial cement replacement. The ultrasound method has not been studied widely yet in the past but as ultrasound technology advances and lowering in cost of ultrasonic devices, this method showed great potential to become a sustainable and economically feasible method for ash treatment in the future.

During ultrasonication, both stable and transient cavitation can occur to give rise to various physical and chemical effects. The hotspot theory postulates that when the bubble undergoes transient cavitation, localized hotspots of high pressure and high temperature in excess of 500 atm and 5000 K are formed to increase the rate of reaction and also generate OH and H radicals. Also, ultrasound has been known to increase the rate of dissolution in many solid-liquid systems due to the increase in the driving force for mass transfer due to the formation of micro-jets and other microstreaming effects.

Before ultrasonication, detailed characterizations such as TCLP leaching, variable pH leaching, total elemental composition, morphology studies and mineralogy studies were conducted. The characterization results agreed with other literature, highlighting the concern over leaching of Cr, Cd, Pb and Zn. It was shown that both FA and APC had both high natural pH but FA had low acid-neutralizing capacity thus making it more susceptible to enhanced leaching of heavy metal if pH decreases. The results from the variable pH leaching test indicated that the leaching of most metals was highly dependent on the pH based on the respective dominant mineral phase.

After the in-depth characterization and variable pH leaching study, ultrasound treatment was applied to both FA and APC with washing treatment as a control. It was found that washing

treatment could only remove mostly soluble metal chlorides while ultrasound showed enhanced extraction and particle size reduction. Further characterization of the sonicated FA using SEM and XRD revealed the presence of needle-like micro-ettringite which was a natural weathering product in FA capable of immobilizing various heavy metals within its matrix. These results showed that treated FA exhibited reduced heavy metal leaching and increased homogeneity of the cementitious contents.

An optimization study applying ultrasound with different extracting agents at various concentrations on FA was also carried out. It was found out that 5 mins of sonication were enough to promote the accelerated mineral formation and enhanced leaching from FA. 15 to 30 mins was the optimal duration for better performance. However, re-adsorptions of heavy metals were observed at a prolonged sonication duration of 60 mins. FA with 60 mins sonication showed the best leaching results indicating relatively high stability of re-adsorbed metals, possibly due to chemisorption. Acidic leaching agents such as citric and nitric acid showed good enhanced leaching yields, but the lowering of pH affected the formation of ettringite and increased the mobility of Pb and Zn significantly. EDTA was found to be the best extracting agent due to high extraction yield independent of pH which gave relatively good leaching results. However, at a higher concentration of EDTA at 0.15 M, the formation of ettringite was also affected and no characteristic peaks were detected from the XRD.

The final phase of this study was to use the ultrasound treated FA (FA Probe) as a partial replacement for cement in construction material. It was found that the FA Probe performed much better than the untreated FA (FA Raw) and washing treated FA (FA Wash) in terms of compressive strength reaching a maximum of 36.2 MPa at 28 days (>75% strength of pure cement) even at 30% replacement. It was revealed that the concrete samples with FA Raw and FA Wash had much lower compressive strength due to the high amount of large air void due to the reaction of non-ferrous metallic content with highly alkaline cement powder. Samples with FA Raw showed even lower compressive strength due to the presence of high chloride content delaying the hydration process and the recrystallization cycle of salts disintegrated the integrity of the structure. Assessment of the long-term environmental impact of sonicated FA samples shows low leachability and indicated that it was suitable for utilization.

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LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Description
APC	Air Pollution Control
DI	Deionized
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
FA	Fly Ash
MSWI	Municipal Solid Waste Incineration
SEM	Scanning Electron Microscopy
S/S	Solidification and Stabilization
TCLP	Toxicity Characteristic Leaching Procedure
TEM	Transmission Electron Microscopy
US	Ultrasound
XRD	X-Ray Diffraction

1 Introduction

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1.1 Background

Due to rapid urbanization and development, the rate of generation of municipal solid waste (MSW) in cities is increasing at an exponential rate and is projected to hit 2.2 billion tonnes per year by 2025 (Bhada-Tata 2012). Therefore, in addition to improving the recycling rate, the management of municipal solid waste also needs to move away from landfilling towards other more efficient and sustainable methods (Council 2003).

One of the most commonly used waste management methods in the world is municipal solid waste incineration (MSWI). The incineration process can achieve a high volume reduction of MSW by up to 90% and allows energy recovery (Chandler et al. 1997, Leckner 2015). However, the incineration process also generates various potentially toxic by-products that require further treatment before disposal.

The three main by-products are the bottom ash, fly ash (FA) and air pollution control (APC) residues. The bottom ash consists of mainly the non-combustibles portion of the MSW which is generally larger in particle size and collected at the bed of the incinerator, while the FA consists of very fine particles that are entrained with the hot rising flue gas and typically collected by an electrostatic precipitator. Lastly, the APC is the product of the reaction between the acidic flue gas and the lime additives during the scrubbing process to reduce the harmful emissions. Currently, most of these by-products are disposed of in landfills (Reijnders 2005) while only a small amount are being utilized with the implementation of environmental policies and subsidies (Sakai et al. 1996).

Owing to the large quantities of FA and APC produced, there have been researches focusing on the treatment and utilization of these incineration by-products. However, most of these treatment methods require high capital cost and the final products are usually not stable enough for utilization. Currently, in Singapore, all the non-recyclable waste is incinerated and up to 20 tons of FA is being generated daily, which is mixed with APC and bottom ash before being sent to the Semakau landfill. This is not sustainable, and given the high cost of constructing another offshore landfill, there is an urgent need to explore ways to treat and utilize the FA.

However, the use of FA can cause serious durability issues in construction material due to the delayed ettringite formation which causes the concrete to crack resulting from the expansive forces developed within the hardened concrete. This limitation results in treated FA not being utilized for construction purposes.

1.2 Knowledge gap and research motivation

Although similar in total elemental composition, the leachability and alkalinity of different MSWI ashes vary drastically depending on the incinerator conditions, air pollution control devices used and many other factors. At times, the leaching results of the ashes from different studies without proper characterization and classification can be inconsistent and appear to have contradicting results between studies. More detailed characterization of the ashes in terms of their microstructures and mineral composition could be the key to differentiate them to explain the variations and also further explain certain leaching properties.

Next, accelerated extraction procedures using ultrasonication have been widely adopted due to the ease of operation and low cost. However, most studies only used ultrasound as a means to accelerate the extractions of metals but did not try to investigate ultrasound's effect on the residue ash products. Low-frequency high-intensity ultrasound is known to be capable of producing cavitation which not only accelerates the extraction but also causes physical and chemical changes to the FA samples. Ultrasound induced changes such as the formation of more stable minerals and enhanced extraction of heavy metals could potentially be used to make FA more suitable for utilization as a construction material.

Lastly, most of the existing methods for the treatment of fly ash are usually costly and the final products cannot be utilized as construction materials due to the delayed formation of the mineral ettringite, which can cause durability issues. Studies had shown that there could be up to 5-10% of delayed ettringite content formed during the setting process (Yang et al. 1999) starting from day 25 to 400 of the concrete age. This delayed ettringite formation could lead to a reduction in the compressive strength of concrete by up to 25% of the control that did not involve ettringite formation (Ronne and Hammer 1999).

1.3 Objective and scope of the study

The purpose of this research is to investigate the physicochemical mechanism of low-frequency ultrasonication and its effect on the leaching behavior and mineralogy of FA and APC, evaluated using Toxicity characteristic leaching procedure (TCLP) and variable pH leaching tests and other analytical methods such as Scanning electron microscopy (SEM), X-ray powder (XRD) and Transmission electron microscopy (TEM). The sonicated FA was tested for the suitability for usage as a cement replacement in mortar in terms of product durability and strength. The main objectives are as follows:

1. Studying the leaching behavior of FA and APC under TCLP and variable pH leaching and total elemental composition.
2. Investigating the microstructure and mineralogy of FA and APC to explain some of the variations in leaching behaviors.
3. Use of ultrasonication for enhanced heavy metal extraction and accelerated stabilization of FA.
4. Evaluating the early strength properties and durability of concrete with FA substitution.

1.4 Organization of thesis

This thesis consists of 8 chapters. This chapter covers the background, current knowledge gap and research motivation followed by the scope and objectives of this study to address some of the deficiencies in understanding. Lastly, this chapter also provides an organization outline of the thesis as follows:

Chapter 2 provides a relevant updated literature review of the incineration process and the characterization and treatment of FA and APC. It also discusses the basic mechanism of ultrasound cavitation that can be used for accelerated extraction of soluble constituents in FA and APC. Lastly, the durability problem of delayed ettringite formation was presented to explain the lack of utilization of FA in construction material.

Chapter 3 describes some of the materials and methods used in this study.

Chapter 4 evaluates the microstructure of both FA and APC using SEM, XRD and TEM experiments while the leaching behavior and total elemental composition were performed via TCLP and microwave digestion. Also, the variable pH leaching test was conducted to study the effects of pH on the heavy metal leaching for both FA and APC.

Chapter 5 describes preliminary experiments on applications of ultrasound to treat APC residue and FA as compared to using simple stir washing as a control, to determine the effects of sonication on these by-products in terms of mineralogy and TCLP leaching.

Chapter 6 describes the differences between ultrasonication and a simple washing extraction procedure of FA in terms of mineralogy and extraction efficiency. The ultrasound leaching process was also optimized by varying the types of leaching agent and concentration.

In Chapter 7, the treated FA was used as cement replacement at a 30% level and the strength and durability of the product were studied to evaluate the possibility of FA utilization. The early strength and leaching of the final product were evaluated.

Chapter 8 is a summary of all the findings of the thesis and concludes with some discussions on the potential for utilization of the final products with recommendations for future works.

2 Literature review

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2.1 Municipal solid waste incineration

2.1.1 Composition of waste generated in Singapore

Municipal solid waste is highly heterogeneous in composition and the proportion varied over time which resulted in differences in the physical and chemical properties of the MSWI fly ash generated (Sabbas et al. 2003). Therefore, a good understanding of the composition of the waste that is incinerated is important when comparing ashes from different sources. In 2013, 7,851,500 tons of waste was generated in Singapore, of which 61% was recycled, 36% sent for incineration while 3% incombustible were sent for direct landfilling (Figure 2-1). For the waste sent for incineration, the three major components were the food waste & organics (32%), plastic (26%) and paper (20%) (Figure 2-2). The majority of the waste disposed of consisted of mainly combustible organics from residential waste with a small proportion of industrial waste such as glass, metal and construction debris.

Figure 2-1: The fate of the waste generated in Singapore, 61% recycled, 36% incinerated and 3% incombustible directly landfilled (National Environmental Agency 2013).

Figure 2-2: Composition of combustible waste sent for incineration in Singapore (National Environmental Agency 2013).

2.1.2 Incineration process

To understand the physical and chemical properties of the different types of MSWI by-products generated, it is important to understand the incineration process. The typical modern incineration plant with energy recovery consists of the followings (Figure 2-3):

- Storage bunker
- Combustion system
- Heat recovery system
- Air pollution control system

Figure 2-3: Incineration process of Tuas South Incineration Plant (National Environmental Agency).

The purpose of the storage bunker is to ensure that the incineration plant has a consistent feedstock and to allow the waste to dry for better combustion efficiency. The waste from the bunker is fed directly to the furnace via the overhead cranes controlled by the operators.

In the combustion system, auxiliary burners are used to initiate the combustion process and the burning is sustainable by the waste feed once fired. The combustion temperature was to be maintained at high temperatures to destroy the organics and to achieve volume reduction (Kilgroe et al. 1990). The combustion rate is controlled by the moving grates which spread the waste evenly and air nozzles under the grates also introduce air to the waste to facilitate the combustion.

The heat recovery system includes a boiler that transfers the heat from the hot flue gas to boil the water into steam which then drives the turbine to generate electricity. Some plants will have an economizer installed downstream of the boiler to make use of the lower temperature flue gas to heat the water for the boiler.

Lastly, due to the introduction of air during the combustion process, fine particles might be released into the flue gas. Other than these particles, minor trace metals such as Hg and Cd with low boiling point also volatilize into the gas stream (Song et al. 2004). Zn, Cd and Pb

were also found to evaporate significantly at the combustion temperature especially when chlorides were present (Jakob et al. 1995, Lu-shi et al. 2003). These metals are hazardous and therefore must be removed from the gas stream before releasing to the environment. Generally, an electrostatic precipitator (ESP) is installed to remove the fine particles followed by a wet scrubbing system with lime injection further downstream to remove the acidic gases and volatilized metals by lime injection. After the lime addition, the reaction products were collected by a fabric filter for disposal.

2.2 Composition of incineration by-products

2.2.1 Electrostatic precipitator fly ash

As mentioned, due to the introduction of air, some particles will enter the flue gas stream. These fine fractions will be removed from the flue gas via the ESP located downstream of the boilers. In general, the ESP was found to be efficient for removing larger particles while the finer particles and vapor has to be treated further downstream (Le Forestier and Libourel 1998). This will lead to a major difference in the composition of the FA and APC, therefore proper characterization is required to understand their chemical properties such as elemental composition, mineral phase and alkalinity to determine the best treatment process.

Firstly, for consideration of fly ash utilization, the two most important physical properties are the particle size distribution and morphology. The particle size distribution of the FA is as shown in Table 2-1. On average, 74% of the FA particles were found to be in the range of 2-5 microns while 20% were between 5 to 20 microns and only 6% of the particles were larger than 20 microns. However, it was observed that 90% of the mass was contributed by the largest 6% fraction (Glen and Howarth 1988).

Table 2-1: Particle size distribution data for FA (Chandler et al. 1997).

	% of particles in each size range (Microns)				
	2-5	5-10	10-20	20-40	40-200
By Mass	0	0	4	11	85
	0	1	2	11	86
	0	0	2	0	97
By Frequency	64	9	16	5	5
	76	12	5	4	4
	80	9	7	0	4
Average Mass	0	<1	3	7	90
Average Frequency	74	10	10	3	3

For the morphology, it was found that FA consisted of thin polycrystalline platelets (O, K, Na, Zn, Cl, Pb, Ca and S) which tend to agglomerate to form a larger particle as shown in Figure 2-4. The SEM image of a leached sample in Figure 2-5 revealed spherical aluminosilicate (O, Si, Al, Ca, Na, K) which was commonly found in coal fly ash (Eighmy et al. 1995). Other than physical properties, chemical properties such as total composition and leaching characteristics were studied more widely due to their impact on the environment.

Figure 2-4: SEM image of FA (Eighmy et al. 1995).

Figure 2-5: SEM image of leached FA (Eighmy et al. 1995).

As shown in Table 2-2, the major elements in FA were Al, Ca, Cl, K, Pb, Si and Zn and trace heavy metals such as Cr, Ca, Hg and Ni were also detected. The presence of these metals might be due to the volatilization-condensation mechanism of the volatile metals that vaporized in the furnace and then condense onto the particles before the electrostatic precipitator.

Table 2-2: Total elemental composition of FA (Eighmy et al. 1995).

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Cl	232000	Ni	69.8
K	109000	Mo	47.1
Zn	104400	V	35.2
Ca	46300	Na	24.7
Si	38000	Se	17.4
Pb	27000	Cs	13.5
Al	20800	Co	13.3
Ti	6100	Ce	12.9
Sn	5900	Hg	9.77
Ba	2400	Dy	9.75
Br	2380	La	4.72
Cu	2220	In	3.23
Sb	2073	U	3.05
Cd	1660	Yb	2.4
Fe	1600	Sc	2.3
Mg	1100	Hf	1.25
As	960	Sm	1.11
Zr	600	Au	0.95
Cr	494	Tb	0.94
Mn	448	Ta	0.87
Rb	206	Eu	0.86
Ag	192	Th	0.2

Other than the total composition, the leachable fraction of the FA is also an important criterion during classification. From Table 2-3, it could be seen that some elements such as Al, Fe and Si were less leachable as they were usually associated with the residual fraction, therefore concern should be given to Pb, Zn, Cd, Mn and Mo which were very leachable and toxic and considered to be hazardous.

Table 2-3: Leachable fraction after 24 h leaching at constant pH 7 adjusted with 0.1 M HCl.

Major elements	% Released	Trace Elements	% Released
K	100	Cd	100
Ca	80	Mo	97
Na	63	Ni	26
Mg	37	Mn	19
Zn	23	Co	12
Si	9	Cr	9
V	3	Cu	3
Sn	2	Sn	2
Fe	<1	Pb	1
Al	<1	Ti	<1

2.2.2 Air pollution control residue

Due to increasing concerns over emissions of hazardous contaminants, incineration plants are now required to install air pollution control system to remove acidic gases and heavy metals. The APC system consists of a lime injection system followed by a bag filter to capture the solid residues generated during the reaction. The lime is usually added in excess to ensure better removal efficiency. However, a better removal efficiency also meant that the APC fly ash generated will become more hazardous.

As seen from Table 2-4, APC residue consisted of relatively much smaller particle size as compared to FA with over 90% of the particles in the 2-5 μm region. This difference is due to the ESP device installed upstream which removes the larger particles from the flue gas stream.

Table 2-4: Particle size distribution for APC (Chandler et al. 1997).

% of particles in each size range (μm)					
	2-5	5-10	10-20	20-40	40-200
By Mass	12	7	81	0	0
	2	2	17	78	0
By Frequency	11	19	79	0	0
	92	3	5	0	0
	87	5	5	3	0
	90	5	5	0	0
Average Mass	8	6	59	26	0
Average Frequency	90	4	5	1	0

As seen from Table 2-5, the chemical composition of APC residue consisted of a large proportion of Ca due to the lime injection in the form of calcium chlorides or calcium oxide/hydroxide. Chloride is a major component as well as a lot of plastics and food waste is present in most of the waste incinerated. Calcium chloride which accounted for up to 60% of the APC fly ash was readily soluble which can be a major issue that could contaminate water sources if not properly dealt with. Besides, these chlorides might further increase the solubility of lead and zinc which are considered detrimental to health.

Table 2-5: Composition range for APC dry/semi-dry system(Chandler et al. 1997).

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Ca	110,000-350,000	Pb	2,500-10,000
Cl	52,000-380,000	P	1,700-4,600
Si	36,000-120,000	Cu	16-1,700
Al	12,000-83,000	Sb	300-1,100
Fe	2,600-71,000	Mn	200-900
K	5,900-40,000	Ni	19-710
Na	7,600-29,000	As	18-530
S	1,400-25,000	Cr	73-570
Zn	7,000-20,000	Cd	140-300
Mg	5,100-14,000	Ag	0.9-60
Ba	51-14,000	Hg	0.1-5.1

2.3 Leaching characteristics of heavy metals and different protocols

2.3.1 Mechanism of diffusion

Leaching refers to the mass transfer between the solid matrix and the liquid leachate during contact and can be simplified as a second-order diffusion model for leaching from a small unit area as illustrated in Figure 2-6.

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \quad \text{Eq 2-1}$$

Where,

C is the concentration of a potential solute in the particle (mole/cm³)

t is the leaching time frame (seconds)

x is the distance from the leaching region in the particle to the particle shell (in cm)

D_e is the effective diffusion coefficient (cm²/second)

Figure 2-6: Conceptual model of ash dissolution (Hinsenveld 1991).

Other than the molecular diffusion, advection and hydrodynamic dispersion are another two major transport mechanism controlling the mass transfer between the particle and the leachate. The impact of each mechanism on the particle varies depending on the particle size, fluid velocity and molecular diffusion coefficient. These factors are investigated to come out with the Peclet Number:

$$P_e = \frac{dv}{D_m} \quad \text{Eq 2-2}$$

Where,

d is average particle diameter (cm)

v is fluid velocity (cm/s)

D_m is the molecular diffusion coefficient (cm^2/s)

Rose has studied the relation between the Peclet number of fly ash and bottom ash to come up with the conclusion that molecular diffusion is the most dominant mechanism for the mass transport due to small particle size (Rose 1977).

2.3.2 Factors affecting the rate of diffusion

From the physical aspect of leaching, the factors governing the rate of diffusion include:

- Particle Properties
- Temperature
- Agitation

Particle properties such as particle size, specific surface area and average pore diameter will affect the internal diffusional resistance. A larger particle with smaller pore diameter will result in much longer diffusion path lengths while a very high specific surface area indicated that the diffusion pathway would be very tortuous (Hartlén and Elander 1986).

Temperature also affects the rate of diffusion; the rate of leaching will increase as temperature rises. From the thermodynamic and solubility product's point of view, the Van't Hoff equation showed that temperature is directly proportional to the rate of diffusion while from the kinetic adsorption and diffusion point of view, the Arrhenius relationship also shared similar conclusion.

Lastly, agitation of the solid and liquid phase promotes contact between the two phases and reduces the boundary layer thicknesses which increases the rate of diffusion and reduces the time required to reach the equilibrium.

2.3.3 Factors affecting the leaching of heavy metal

Some of the main factors affecting the leaching of heavy metal from the solid includes:

- L/S ratio
- Particle size and surface area
- pH conditions
- Complexation on dissolution
- Mineralogy and metal speciation

The L/S ratio refers to the ratio of extraction fluid added to a solid matrix during the leaching process. Generally, an increase in the L/S ratio will lead to higher amounts of heavy metal leaching for most metals as reported by many studies (Mizutani et al. 1996, Abbas et al. 1999, Wilewska-Bien et al. 2007). The correlation between L/S ratio and the amount leached indicated that the limiting factor for these metals was the solubility equilibrium in the solution (Van Herck et al. 2000). However, some metals like Cu, Pb and Zn exhibited a negative correlation whereby an increase in L/S ratio resulted in a decrease in the amount leached (del

Toro et al. 2009). This behavior was thought to be due to the precipitation between the metals ions and other anions that were leached with the increasing L/S. It was also found out that the highly soluble metals such as Ca, Na and K present in FA were independent of L/S ratio while highly reactive metals such as Al and Cr were affected by the L/S ratio due to the kinetic controls (Guyonnet et al. 2008).

Other than L/S ratio, the particle size can also influence the amount of heavy metal leaching, in general, smaller particle size and higher specific surface area leads to higher amounts of heavy metal leaching (Mizutani et al. 2006). Particle size reduction methods such as grinding or ultrasound treatment was found to enhance the leaching of minor metals due to fragmentation of the matrix and exposure of the encapsulated metal components (Lim et al. 2004, Li et al. 2010). The increase in porosity after the dissolution of the readily soluble mineral such as NaCl and KCl was also found to increase the internal specific surface area from 10 times to 70 times the external specific surface area (Wilewska-Bien et al. 2007). However, the increase of total porosity could also lead to a reduction in leaching for metals such as Cu and Zn due to increased adsorption due to the presence of more available mineral surfaces (Karlfeldt and Steenari 2007). Depending on the total chemical equilibrium in the leachate and the content of the ash matrix, the reduction in particle size could lead to different results.

The pH is also another key factor in the leaching of heavy metals. Generally, under acidic conditions, the leaching of most heavy metal is significantly increased while precipitation and/or sorption could reduce the leaching of some of these metal at alkaline conditions (Pagnanelli et al. 2004). However, the effects of pH variation are not monotonous and largely dependent on the types of leaching behavior of the metal such as cationic, oxyanionic and amphoteric leaching patterns. Cationic elements exhibit a high concentration of leaching at low pH which decreases as pH increases while the oxyanionic elements exhibit an opposite trend. For amphoteric elements such as Pb and Zn, the leaching decreased first then increased as the pH increases giving a “V” shaped graph (Komonweeraket et al. 2015).

Formation of the complex via the use of ligand-based extracting leachate such as EDTA would be able to bind heavy metals in the dissolved state and thus increase the dissolution of the metal. This is due to that the bounded heavy metals are not included in the dissolution equilibrium and thus resulting in more heavy metal to diffuse from the bulk ash particle.

2.3.4 Extracting agent

The use of different extracting agents other than water was known to be able to enhance the leaching of heavy metals from ash. The most common extracting agent is strong mineral acid such as HCl (Zhang and Itoh 2006, Tang and Steenari 2016), HNO₃ (Nagib and Inoue 2000, Okada et al. 2007) and H₂SO₄ (Fedje et al. 2010, Zhang and Ma 2013) as most heavy metals tend to be more soluble at a lower pH. The use of these mineral acids showed significant enhancement in the extraction of Cu, Pb and Zn. However, the acidic extraction method for ash with high alkalinity and acid-neutralizing capacity is not suitable as a large amount of acid would be consumed to decrease the pH. Furthermore, the use of strong mineral acid during extraction can result in the dissolution of the ash matrix which affects further utilization of the residual ash.

Another popular alternative is the use of chelating agents such as EDTA, citric acid and NTA that can react with metal ions to form water-soluble complexes (Youcai et al. 2002, Zhang and Itoh 2006, Fedje et al. 2010). The chelating agents were found to be effective in the removal of Cr, Cu, Zn and Pb by binding them to the ligands (Song et al. 2016). One key factor affecting chelating efficiency is the stability constant of the chelant-metal complexes based on the affinity between the chelating agent and the different metals (Huang et al. 1997). It was found that EDTA is more efficient in the extraction of Pb and Cd while EDDS is more efficient in the extraction of Cu and Zn (Luo et al. 2005). The order of stability of EDTA and its complexes is as shown in Table 2-6, however, common cations such as Ca²⁺, Fe²⁺, Mg²⁺ and Al³⁺ can also compete for binding sites with heavy metals. Therefore, the overall efficiency is also influenced by the metal speciation in a given matrix (Elliott and Brown 1989).

In the literature, one of the most commonly used chelating agents used is EDTA due to its high metal complexing capacity, high stability and low cost. The high stability of EDTA is due to the hexadentate structure that can bind with the metal ion in a 1:1 stoichiometry as shown in Figure 2-7. The EDTA-metal complex is made up of a central metal ion surrounded by the six EDTA ligands. The metal ion acts as a Lewis acid (electron acceptor) while the ligands act as Lewis bases (electron donor). The formation of a ring around the metal ion by the polydentate EDTA has a chelating effect on the metal ions enhancing EDTA's affinity for metal ions and reducing the metal ions reactivity.

Table 2-6: Stability constant for EDTA-metal complexes.

Metal	Log K
Cr^{3+}	23.0
Hg^{2+}	21.8
Cu^{2+}	18.7
Ni^{2+}	18.6
Pb^{2+}	18.3
Cd^{2+}	16.4
Zn^{2+}	16.4
Al^{3+}	16.1
Fe^{2+}	14.3
Mn^{2+}	13.8
Ca^{2+}	11.0
Ag^{+}	7.32

Figure 2-7: Complexation of a fully deprotonated EDTA with metal ion

2.3.5 Leaching test: toxicity characteristic leaching procedure (TCLP)

2.3.5.1 Toxicity characteristic leaching procedure (TCLP)

One of the most common leaching tests used to classify waste for disposal is the TCLP from the U.S. Environmental Protection Agency. TCLP is a standardized batch leaching test that can measure the amount of leachable fraction from the waste with regards to heavy metals and organic pollutants.

Figure 2-8 and 2-9 show the procedures of TCLP: 2 L of extraction liquid (Glacial Acetic Acid ACS grade) will be added to 100 g of waste and leached for 18 hours under constant agitation of 30 revolutions per minute. Also, if the sample is larger than 9.5mm, it must be milled to decrease the size to below 9.5mm before the leaching procedure. After the leaching, the leachate must be filtered using acidified glass fiber filter (0.6-0.8 microns) and acidified (if testing for heavy metals) (USEPA 1990).

Figure 2-8: TCLP method 1311 part A (USEPA 1990).

Figure 2-9: TCLP method 1311 part B (USEPA 1990).

2.4 Existing treatment technologies for FA

Heavy metal leaching of untreated FA and APC tends to exceed the regulatory limits and treatment is usually required before disposal. The main treatment methods consist of Separation & extraction methods, Stabilization & solidification methods and thermal methods. Despite the variation in strategies, the primary objective is to reduce the leachability rate and total availability to the environment to reduce any negative impacts. Although there are various proven existing treatment technologies, some of which are too costly while other low-cost methods increase the volume significantly. Therefore, more researches are still ongoing to improve existing methods to become more effective and/or economically feasible.

2.4.1 Separation method

Separation refers to the extraction of certain species to isolate them from the bulk residue to improve the quality of the treated residue. Other than reducing the negative environmental impacts of the residue, most separation processes target valuable contaminated resources and aim to treat them for utilization purposes. Separation methods include washing, leaching, ion exchange and electrochemical processes.

The washing treatment is generally used as a pre-treatment procedure before other treatment processes as it is very effective in removing soluble salt contents which can cause problems in other treatment processes (Mangialardi 2003, Piantone et al. 2003, Chimenos et al. 2005). However, due to the extremely high pH of fly ashes, the direct washing method is not very efficient in extracting many metals that are more soluble at lower pH. Another problem of this method is that amphoteric metals such as Lead and Zinc were relatively soluble and the leachate from the washing method requires further treatment which increased the cost of treatment (Quina 2005).

Next, one of the most studied treatment processes is leaching with chemical additives which aim to extract the target component to acquire leachate with high enough concentration for recovery. Among all the leaching processes, acid leaching is the most efficient for extracting trace metals as most metals were soluble at low pH (Chandler et al. 1997, Nagib and Inoue 2000, Lundtorp et al. 2003, Zhang and Itoh 2006). However, waste such as APC has a very high acid-neutralizing capacity and requires a lot of acids to lower the pH, which raises the cost of the treatment. To overcome this, leaching with chelating agents such as ethylenediaminetetraacetic acid (EDTA) which is not affected by pH were studied (Di Palma et al. 2005). However, EDTA does not degrade easily and can be a problem itself, therefore currently more emphasis was placed on bioleaching instead (Krebs et al. 2001, Tiwari et al. 2013).

Lastly, electrochemical treatment processes make use of the potential differences from the electrode to induce various redox reactions for separation of the waste into a concentration stream for extraction and a diluted stream for disposal (Kirkelund et al. 2010, Pazos et al. 2010, Kirkelund et al. 2013). The main benefit of this method is that no additional chemicals are required and thus does not create new substances that require further treatment (Yang et al. 1998). However, the main gap in this method is the efficiency drops and more current is

required when the waste becomes diluted which raises the cost of this method if the disposal limit is very stringent.

2.4.2 Stabilization and solidification (S/S)

The S/S process is the most well studied and widely adopted since 1960 due to its simplicity and effectiveness. Solidification controls the physical aspects such as the surface area and permeability through encapsulation and confinement of the contaminants to reduce their mobility. Stabilization, on the other hand, controls the chemical aspects such as solubility through the formation of insoluble salts (such as carbonates, silicates and hydroxides). Together, S/S processes can modify both the physical and chemical properties of the contaminant and reduce its environmental impact. S/S processes can be categorized into mainly S/S without additives, S/S with additives and accelerated carbonation.

Next, although S/S with additives will eventually increase the overall volume, it is still preferred over other S/S methods as it is a well-developed technology at a reasonable cost (Yang et al. 1998). One of the most researched additives is the Ordinary Portland Cement and it had been shown that the formation of ettringite and Friedel's salt was effective in reducing the mobility of the toxic component in the MSWI fly ashes (Auer et al. 1995).

Lastly, accelerated carbonation can also be considered as an S/S process which is a diffusion-controlled reaction whereby carbon dioxide is diffused into the MSWI fly ash to form calcite. Carbonation was found to reduce the mobility of Pb, Zn, Cd and Hg (Ecke 2003, He et al. 2006) but it was not effective in stabilizing chlorides and sulfates (Todorovic and Ecke 2006).

2.4.3 Thermal method

Thermal treatment processes make use of high temperatures to treat contaminated waste. One of the main benefits is that in thermal treatment, the treated residue volume is much lesser than that of original waste. Also, some thermal methods can destroy harmful organic compounds such as dioxin which is a carcinogen. However, thermal methods are also considered to be one of the most expensive treatment methods as they require the use of extremely high temperatures. The three different thermal methods are vitrification, sintering and evaporation.

Vitrification is the formation of a rigid glassy matrix by melting crystalline/amorphous materials at elevated temperature (1100-1500°C) and then quenched rapidly without crystallization to occur. The homogenous glassy matrix formed was capable of immobilizing the contaminant within itself and thus forming a stabilized product (Quina et al. 2008).

Although alkalis which act as a network modifier can be added to lower the melting point to reduce the cost of treatment, excessive addition affects the chemical properties of the glassy product. Therefore, this process is generally not applicable to APC residues due to the high cost involved.

Sintering is an alternative approach to stabilize ashes using a lower temperature (800-1000°C) which is lower than the melting point of the ashes. The main mechanism of sintering is based on the acceleration of atomic diffusion at elevated temperature to fuse powder material into a larger piece thus reducing the surface area and modifying the mobility of the contaminants. However, particle size and distribution are very significant during sintering and it might not be effective to treat heterogeneous MSWI ashes for utilization purposes (Mangialardi 2001).

Lastly, the volatilization process involves heating the waste to about 1000°C to encourage the volatilization and recovery of the target contaminants (melting point higher than 1000°C). Jakob and Stucki also discovered that the introduction of chlorides and the presence of a reducing environment promotes this process and a high volatilization rate was obtained for lead, cadmium and chromium (Jakob et al. 1996).

2.5 Successful utilization and benefits

2.5.1 Coal fly ash

The pioneer studies on coal fly ash were conducted by R.E. Davis in the 1930s due to the rise of coal-fired power plants (Davis et al. 1937). His studies set the foundations for future studies on specifications and testing methods for the coal fly ash. The successful construction of the Hungry Horse Dam in the USA was the first major utilization of coal fly ash and it helped to encourage the further usage of coal fly ash.

Later in the 1980s, Idorn's studies revealed that the reaction product from the coal fly ash is similar to that of the hydration of Ordinary Portland Cement (OPC) (Idorn 1983). In 1988, RILEM reported that the fly ash possesses pozzolanic and cementitious properties which means that the fly ash can be used as an additive or serves as an OPC replacement in the cement mix (RILEM and Committee 1988).

Hydration Reaction: **Pozzolanic Reaction:**

In general, the coal fly ash is very heterogeneous and consists of both amorphous and crystalline phases. The main chemical composition is 25-60% silicon dioxide, 10-30% aluminum oxide, 5-25% iron oxide and a variable amount of calcium oxide. If the calcium oxide is more than 20%, the fly ash will be classified as a Class C fly ash which is cementitious and pozzolanic, while if the calcium oxide content is less than 20%, it will be classified as a Class F fly ash which generally possesses pozzolanic properties. (Committee 1987)

2.5.2 Benefits of coal fly ash

The addition of coal fly ash into cement not only lowers the cost but also brings in benefits such as better workability, improved compressive strength and better durability of the resulting concrete.

The ultra-fine coal fly ash can physically disperse the floc to free more water to lubricate the mixture resulting in better workability (Dhir 1986). Brown also exhibited that the workability improvement is the result of the spherical morphology and fineness of the coal fly ash (Brown 1980).

By the inclusion of more fines such as coal fly ash, bleeding of the concrete can be controlled and thus resulting in a more durable concrete (Idorn and Henriksen 1984). The underlying mechanism is that the fly ash fines can block the bleeding-water channels as explained by Lane (Lane 1983).

Other than durability, the replacement of up to 30 % of coal fly ash can also improve the compressive strength of the concrete. This is due to coal fly ash having a smaller particle size and is thus able to fill into the gaps between the cement particles. This decrease in porosity leads to an increase in concrete strength (Ramachandran and Beaudoin 1981). Bakker also discovered that the addition of coal fly ash could also increase the compressive strength by the formation of more cement gel product (Bakker 1983). The increase in late strength and formation of more cement gel products is due to the pozzolanic effects from the coal fly ash (Bloem 1954).

2.5.3 Problems with FA and APC

Despite having similar compositions as coal fly ash, FA and APC also contained a high amount of heavy metals, chlorines and sulfates (J.E.Aubert 2006) which reduces their utilization potential. The two main concerns are the concrete quality (workability, strength and durability) and the environmental impact such as the release of the heavy metals. Many studies had shown that the leachability of various heavy metals was controlled due to the stabilization effects from binding with the cementitious matrix and would not cause much negative environmental impact. However, many studies also showed a correlation that a higher amount of FA often led to lower quality of the final product due to various effects such as ingress of chloride ions (Ahmad 2003) and expansion stress from delayed ettringite formations (U. Muller 2006). Also, the presence of high aluminum content could give rise to the generation of hydrogen gas which might result in high porosity and decrease in concrete strength (J.-E. Aubert 2004)

A common strategy used is the washing of FA with water to reduce the amount of Cl and other soluble salts to reduce the chlorides corrosion attacks (Mulder 1996) while others suggest limiting the quantity of the MWSI ash used to reduce the negative effects or make use of the hydrogen generated as usage for aerated concrete (X. Gao 2008, T.Y. Huang 2015, Yuanming Song a 2016). However, not much research has been done on treatment on FA to reduce the long-term durability of concrete due to delayed ettringite formations.

It can be seen from Figure 2-10 that delayed ettringite formation tends to start after 25 days and could continue to grow beyond 400 days. Depending on the type of cement and ash composition, the ettringite content formed could be up to 5-10% of the concrete mass, leading to a 0.5% expansion (Yang et al. 1999). Such expansions are detrimental to the ultimate strength of the concrete and Figure 2-11 showed that the ultimate strength of concrete with higher ettringite content (cured at a higher temperature) tends to be up to 25% lesser than those with lower ettringite content (Ronne and Hammer 1999).

Figure 2-10: (a) Ettringite content of cement paste in the mortar at 20°C and 100°C. (b) Corresponding expansion data for mortar cured at 20°C and 100°C. (Yang et al. 1999).

Figure 2-11: Effects on compressive strength development for concrete mixes with w/b 0.5 and 0% SF due to delayed ettringite formation (Ronne and Hammer 1999).

2.6 Ultrasound

2.6.1 Ultrasound development and mechanism

At high enough intensity and low frequency (20 kHz), the sound wave generated is capable of inducing cavitation bubbles within the liquid medium via alternating positive pressure cycle (compressive) and negative pressure cycles (rarefaction) (Pilli et al. 2011). During the low-pressure cycle, if the hydrostatic pressure is lower than the applied acoustic pressure, the liquid pressure will become negative and if this pressure can overcome the surface tension of the fluid medium, the fluid will be “pulled” apart to form the cavitation (Suslick 1989, Rastogi 2011).

The cavity will then expand and reach a critical size before violently imploding to give rise to a region with high temperature (5000°C) and pressure (500 atm). During this implosion, high impact micro-jets with a high velocity of up to 100 ms^{-1} are also formed and are capable of causing fragmentation to the solid phase (Kuppa and Moholkar 2010). Another physical effect caused by the implosion is the formation of micro-streamers which induces motion in the fluid to enhance the mass transfer process (Tang 2003, Pang et al. 2011). Other than physical aspects, the formation of hydroxyl and hydrogen radicals during the cavitation also helps to enhance the stability of the waste via chemical fixation (Suslick 1989, Capelo et al. 2005).

Figure 2-12: Three reaction zones of sonochemical reactions (Wu et al. 2013).

One popular model is the hotspot theory that separates the sonochemical activities into three different regions with different reactions occurring in each zone. The three zones are as shown in Figure 2-12, and are as follows:

Zone 1: Hot spot region, the core of the cavitation bubble with high temperature and pressure where water molecules are pyrolyzed to form $\text{OH}\cdot$ and $\text{H}\cdot$ in the gas phase.

Zone 2: Gas-liquid transition region with similar reactions taking place as per the hot spot except in the liquid phase instead of the gas phase. Additional recombination reactions of $\text{OH}\cdot$ to form H_2O_2 also occur in this region.

Zone 3: Bulk liquid phase reactions mainly involving radicals and H_2O_2 with the mixture at ambient conditions.

Under the hotspot theory, each cavitation bubble is believed to serve as a microreactor with high temperature and pressure to break the bonds of gaseous volatile molecules and return them to the bulk solution for further reactions with other species. While substances with low volatility are unlikely to enter the bubble, their reactions can still be accelerated due to the exposure to a high energy environment or reacting with the radical species generated by the sonolysis of the solvent (Cravotto and Cintas 2006).

Figure 2-13: Micro-jet fragmentation of particle mechanism from the asymmetric collapse of the ultrasound bubble (adapted from Banks & Compton, 2003a).

In the case of a heterogeneous system consisting of solid-liquid slurry, the mechanical effects of ultrasound can also lead to enhancement of the reactions as illustrated in Figure 2-13. The primary mechanical effect is caused by the asymmetric collapse of the cavity due to the non-uniformity of the surrounding to a solid surface. Such collapse results in micro-jets of high velocity of up to 111 ms^{-1} that hits the solid surface with tremendous force, which gives rise to mechanical effects such as surface cleaning, particle size reduction and improved mass transfer.

2.6.2 Factors affecting the ultrasound process

Ultrasound processes depend mainly on cavitation and implosion, and therefore the parameters affecting cavitation such as the frequency, intensity, temperature and solvent properties are very important for the efficiency of ultrasound processes.

Firstly, the frequency of the ultrasound device is very important. Generally, a low frequency is more favored to produce cavitation at a given intensity. This is because, at very high frequency, the duration of the compression-rarefaction cycles is not long enough for the molecules in the solvent to separate (Vajnhandl and Majcen Le Marechal 2005). Next, the intensity is a very important parameter and there is a threshold intensity that must be reached for cavitation to occur. However, using extremely high intensity is not applicable as it will result in liquid agitation and reduce the efficiency of the ultrasound (Adewuyi 2001).

Temperature is also a very important factor in controlling cavitation. Low temperature is preferred as although higher temperature results in more cavitation, the increase in vapor pressure will cause rapid diffusion of air into the voids which can reduce the impact of the implosion (Chimenos et al. 2005).

Lastly, the properties of the solvent such as surface tension, vapor pressure and viscosity. Lower surface tension and viscosity results in more cavitation at a given intensity as less cohesive forces are needed to overcome and “pull apart” the fluid to form voids. Vapor pressure of the solvent is tricky as high vapor pressure results in the ease of cavitation but reduces their impact, therefore a balance must be made for the best effect (Mason 1991, Tarr 2003).

2.6.3 Application of ultrasound in MWSI accelerated extraction and treatment

With the advances in ultrasonic technologies, ultrasound has become a very popular pre-treatment method for the rapid extraction of metals from different matrices. Compared to other emerging technologies such as microwaves (dipolar species), electrochemistry (conduction medium) and photochemistry (chromophore), ultrasound devices are more versatile as it only requires a liquid medium for energy transmission (Swamy and Narayana 2001). In general, power ultrasound is capable of generating cavitation which is favorable for extraction processes and has been reported to reduce the extraction time from hours to minutes (Filgueiras et al. 2002). The extraction efficiency was revealed to be strongly dependent on the target metal; extraction of Cr was found to be poor due to the likelihood of the formation of radicals and oxidizing H_2O_2 while other metals such as Zn are also found to decrease on prolonged sonication time due to re-adsorption (Luque-García and Luque de Castro 2003).

Many researchers studied the effects of applying ultrasound as pre-treatment for the samples or simply as a form of acceleration for their extraction scheme and agreed that ultrasound was indeed beneficial and showed better performance than the control without ultrasound (Luque-García and Luque de Castro 2003). Swamy showed that only 3.83% of copper was extracted in 40 min under mechanical agitation, which increased to 11.52% under ultrasound agitation (Swamy et al. 1995). Elik (2007) showed that the leaching time of Cu, Pb, Ni Zn and Mn could be reduced from 12 h to 25 mins with the use of ultrasound and showed potential as a reproducible and inexpensive method for rapid analysis.

2.7 Summary

Although some research of FA and APC residue treatment had been performed, there are still many debates ongoing to determine the best method with the lowest life-cycle cost. The ultrasound had proven to be one of the up and coming technologies due to the low cost and rapid processing but there are a lot of gaps in the state of the current knowledge when it comes to FA and APC residues. Some of the major issues are identified as follows:

1. Most of the characterization studies for FA and APC residues only assess the ultrasound-based on various leaching tests and total elemental composition but never the examined mineralogy.
2. Some studies worked on the mixed ash and residue while others worked on either MWSI FA or APC residue but not many studies evaluate the effects of mixing of FA and APC residue under variable pH conditions.
3. Many types of research made use of the ultrasound as a form of pre-treatment to increase extraction yield but there is a major gap in the literature about the stabilizing effect due to accelerated formation of various mineral forms.
4. The usage of coal FA for construction purposes has well been studied and widely used in construction material while utilization of FA has not been realized due to its high Cl and S contents that might cause product durability issues.

3 Materials and methods

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3.1 Materials

3.1.1 FA and APC

The FA and APC used in this study were collected from a Waste-to-Energy (WtE) incineration plant capable of handling 3,000 tons/day of MSW. An electrostatic precipitator (ESP) was used to remove the entrained FA from the flue gas before the use of any additives while the APC was collected from a ten-compartment catalytic bag filter after a semi-dry lime scrubbing process. The collected FA and APC were dried for 24 h at $105^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ before storing it in an air-tight container.

3.1.2 Chemicals

All the chemicals used in this study were of analytical grade and were diluted to the right concentration before use. The chemicals were glacial acetic acid (Sigma-Aldrich), sodium hydroxide (Sigma-Aldrich), citric acid (Merck), nitric acid (Sigma-Aldrich) and EDTA (Sigma-Aldrich). All the experiments were conducted using DI water ($18.2\text{ M}\Omega\text{ cm}$).

3.2 Analytical methods

3.2.1 SEM-EDX

The surface morphology and size of FA and APC were examined by a field emission scanning electron microscope (FESEM JEOL 6340F) operated at 5 kV accelerating voltage and 8 mm working distance. The bulk elemental distributions of the selected regions of FA and APC were studied by obtaining the electron micrograph and element mapping using an energy-dispersive X-ray spectroscopy (EDX, Oxford Xmax80 LN2 Free) attached to the FESEM operated at 20 kV and 15 mm working distance.

3.2.2 XRD

The mineralogy of the crystalline phases of FA and APC were characterized by X-ray powder diffraction performed by a Bruker D8 diffractometer (Bruker D8 Advance XRD) operating on a $\text{Cu-K}\alpha$ X-ray source ($\lambda=1.5418\text{ \AA}$) at 40 kV and 40 mA. The samples were scanned over 2θ values from 10° to 80° at a scan rate of $0.05^{\circ}/\text{s}$.

3.2.3 XRF

The major elements of the materials were analyzed by using an X-ray fluorescence (XRF) spectrometer (Panalytical Axios).

3.2.4 Microwave acid digestion

To determine the metal element contents, FA and APC were digested with 9 mL of concentrated nitric acid in a polymeric microwave digestion tube. The mixtures were heated to 180 °C in 10 mins and then maintained for another 10 mins. After digestion, the solution was acidified to pH 2 with nitric acid and tested for metal analysis using inductively coupled plasma optical emission spectrometry (ICP-OES).

3.2.5 ICP-OES

The solution from leaching tests and microwave digestion were analyzed for cations by the ICP-OES (Optima 8300, Perkin Elmer). Three major elements (Ca, K and Na) and 21 trace elements (Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V and Zn) were quantified. The calibration was done with a standard solution diluted to give a range of concentration from 0.1 mg/L to 50 mg/L. Triplicates were done to calculate the mean and standard deviation.

3.3 TCLP leaching test

TCLP test was performed using the TCLP extraction fluid 2 due to the high natural pH of the samples following closely to the procedure set by USEPA (Environmental Protection Agency 1992). The extraction fluid 2 was prepared by diluting 11.4 mL of glacial acetic acid ACS reagent grade with DI water to obtain a 2 L solution of pH of 2.88 (± 0.05). 2 L of extraction fluid was added to 100 g of sample and leached for 18 h in extraction vessels under constant agitation of 30 rpm. After extractions, slurries were centrifuged at 8000 rpm for 5 min. The supernatant was filtered with a 0.6 μ m borosilicate glass fiber and acidified to pH 2 and stored for further analysis for heavy metals.

4 Characterization and effects of pH on leaching of heavy metals in FA and APC

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4.1 Introduction

During the waste incineration process, heavy metals present in the waste are released into the flue gas as condensates or entrained particles which form highly polluted fly ash (FA) (Sørum, Frandsen et al. 2003, 2004). Subsequently, the flue gas containing acidic gases (NO_x, SO_x, etc.) and volatilized metal chlorides/sulfates are captured by the lime scrubbing neutralization process producing the air pollution control residue (APC) (Kirby and Rimstidt 1993). Both FA and APC are considered major environmental concerns due to the presence of heavy metals and the ease of leaching into the environment (Lisk 1988). Typically, FA and APC are enriched in Cd, Cr, Cu, Pb, and Zn due to paint pigments, batteries, and electronics good present in the municipal waste, while the chlorides in plastic waste enhance the formation of volatile metal chlorides (Belevi and Langmeier 2000, Jung et al. 2004, Lima et al. 2008, Luan et al. 2014). Elements like Al, Ba, Mn, Ni and Si are also commonly found in FA in the forms of entrained particulates due to higher melting points (De Boom and Degrez 2012).

Owing to the hazardous nature of FA and APC, these residues require proper treatment to meet environmental legislation before disposal to landfill. On the other hand, FA and APC exhibited pozzolanic and cementitious behavior similar to that of commercially available coal fly ash (Hartmann et al. 2015, Chen et al. 2019). Therefore, the application of FA and APC as construction materials attracted great research interests for a sustainable option to recycle and reuse these residues (Qian et al. 2006, Colangelo et al. 2012). In places with limited natural resources and land, proper management of the FA and APC can become a viable and cost-effective solution. Therefore, proper characterization should be carried out to understand (i) the total and leachable heavy metals under various conditions, and (ii) other properties such as mineralogy and microstructure that can affect their utilization potential (Sawell et al. 1995, He et al. 2004, Song et al. 2004, Li et al. 2018).

FA and APC are expected to have different properties and therefore it is important to differentiate them before further treatment or utilization. Improper standardization and inappropriate classification have led to misinterpretation of FA and APC and their mixture (Quina et al. 2008). These residues may contain similar elements but in different mineral phases and the difference in mineralogy can affect the leaching potential of heavy metals due to the differences in their stability and acid buffering behaviors (Kitamura et al. 2016). pH is also an important factor that affects the mobility of the heavy metals in FA and APC. The understanding of the mineralogy to leaching behavior as a function of pH will enable us to

estimate the leaching potential of FA and APC under different conditions. However, the pH-dependent leaching mechanism of the effects of ash mixing and interaction based on mineralogy is not well understood.

In this study, the mineralogy, elemental composition, morphology and microstructure of FA and APC were investigated to identify their differences and to provide experimental data illustrating the need for proper classification of these residues. Heavy metals leaching, which is a key concern for disposal or utilization of FA and APC, was evaluated by using toxicity characteristic leaching procedure (TCLP). Also, the impacts of pH on the leaching behavior of heavy metals from FA, APC and their mixture were investigated.

4.2 Materials and method

4.2.1 FA and APC characterization

The FA and APC used for characterization and leaching in this study were collected and prepared for storage as discussed in Chapter 3. To study the effect of mixing FA and APC, mixed ash (denoted as MIX) consisted of FA and APC at 1:1 ratio was additionally prepared according to the actual ash output of the WtE facility.

The total elements were determined by microwave acid digestion followed by ICP-OES as discussed in Chapter 3.

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to determine the morphology and obtain a semi-quantitative composition. X-ray powder diffraction (XRD) was also performed on the ground samples to determine the main mineralogical compositions.

4.2.2 Leaching test

Two compliance leaching tests, TCLP and EN12457-2, and one pH-dependent leaching test were performed on FA APC and MIX samples. The acid-neutralizing capacity and the leaching behavior at different pH of the samples were studied. The tests used were TCLP (TCLP 1992), EN 12457 water leaching test (EN 2002) and EN 14429 pH-dependent leaching (CEN 2006).

4.2.2.1 TCLP

TCLP test was performed using the TCLP extraction fluid 2 due to the high natural pH of the samples in this study following closely to the procedure set by USEPA (Environmental Protection Agency 1992). The details were as discussed in Chapter 3.

4.2.2.2 EN 12457-2 leaching test

EN 12457-2 leaching test was performed to investigate the leaching behaviors of FA, APC and MIX at their natural pH. 1 L of DI water was added to 100 g of sample and leached for 24 h in extraction vessels under constant agitation of 30 rpm. After extractions, slurries were centrifuged at 8000 rpm for 5 mins and the supernatant was filtered through a 0.45 μm membrane.

4.2.2.3 pH-dependent leaching test

To study the effects of pH on the leaching behavior of heavy metals, a pH-dependent leaching test following BS EN 14429 was conducted for FA, APC and MIX. Samples were acidified at a liquid-to-solid ratio of 10:1 by weight to achieve different mixtures with final pH values ranging from 0 to 12. Different amount of HNO_3 (5M) and DI were used. A contact time of 48 h was set to achieve chemical equilibrium conditions and multiple pH readings were taken using a pH meter at 44, 46 and 48 h to ensure that pH values had been stabilized within ± 0.1 . After 48 h of extraction, the slurries were filtered through 0.45 μm membrane and the filtrates were acidified to pH 2 for heavy metal analysis using ICP-OES. The experimental conditions of pH-dependent leaching tests are presented in Table 4-1.

Table 3-1: Amount of HNO₃ and DI used for pH-dependent leaching test and the pH values of the leaching solutions at equilibrium.

Sample	FA			APC			MIX		
Parameter	HNO₃ (mL)	DI (mL)	48 h pH	HNO₃ (mL)	DI (mL)	48 h pH	HNO₃ (mL)	DI (mL)	48 h pH
Test 1	55	245	2.70	100	200	0.10	65	235	1.80
Test 2	50	250	3.74	95	205	0.33	60	240	4.97
Test 3	45	255	4.13	90	210	0.46	55	245	6.02
Test 4	40	260	4.72	85	215	1.73	50	250	7.50
Test 5	35	265	5.49	80	220	6.39	45	255	9.85
Test 6	30	270	6.36	75	225	9.20	40	260	10.17
Test 7	25	275	6.84	70	230	10.64	35	265	10.77
Test 8	20	280	8.25	65	235	11.68	30	270	11.55
Test 9	15	285	9.29	60	240	11.73	25	275	12.27
Test 10	10	290	9.86	55	245	11.77	20	280	12.39
Test 11	5	295	10.53	50	250	11.80	15	285	12.43
Test 12	0	300	11.26	45	255	12.05	10	290	12.46

4.3 Results and discussion

4.3.1 FA and APC characterization

4.3.1.1 Total metal composition

The total concentration of the metal elements from acid digestion is shown in Table 4-2. These values were compared to the typical minimum and maximum values from the literature summarized as FA_{min} , FA_{max} , APC_{min} and APC_{max} (Eighmy et al. 1995, Chandler et al. 1997, Wang et al. 2001, He et al. 2004, De Boom and Degrez 2012, Stegemann 2014, Huber et al. 2016, Kirkelund and Jensen 2018). The results for both FA and APC were within the typical ranges reported in previous studies. It could be observed that both FA and APC in this study contained similar metal elements, but with very different distributions.

FA contained a high amount of Ca (16.8%) and Al (3.4%) due to the entrainment of calcium-alumino-silicates in the hot flue gas during waste incineration. However, the amount of Al could be underestimated as the HNO_3 used in the 3050B method could not completely dissolve silicate compounds. Therefore, the metals usually associated with silicates such as Al, Fe, and Mg might not be fully released (Bogush et al. 2015). High content of Na, K, Pb and Zn in FA was ascribed to their speciation with their chlorides ($NaCl$, KCl , $PbCl_2$ and $ZnCl_2$) which has a lower boiling point and can be vaporized and adsorbed onto the FA.

APC contained a significant amount of Ca (39.4%) as excess $Ca(OH)_2$ was added during the scrubbing process to neutralize the acidic flue gas. Ca contents found in different studies varied due to the differences in the scrubbing process and the amount of $Ca(OH)_2$ added (Bodéan and Deniard 2003). It was also observed that APC contained lesser lithophilic elements such as Fe and Al due to prior removal of the FA by the ESP before the scrubbing process. Similar to FA, high contents of Na, K, Pb and Zn were also found in APC as some of these chlorides were highly volatile and were not completely removed by the ESP. The lower concentrations as compared to FA might be due to the dilution effect from the scrubbing additives.

These results showed that the fate of heavy metals distribution was affected by the chloride content which is abundant in municipal solid waste from sources such as food waste and plastic. Also, the total content of various heavy metals such as Pb and Cd in this study was high compared to some other studies may be due to the lack of segregation of batteries and electronics before the incineration process. Therefore, it is important to identify potential

means to recycle food waste, plastic, batteries and electronics and divert them away from the waste stream sent for incineration to obtain a much cleaner FA and APC.

Table 4-2: Total metal composition of the FA and APC used in the study. Minimum and maximum values from the literature were listed for comparison.

Elements (mg/kg)	This study	From literature		This study	From literature	
	FA	FA _{min}	FA _{max}	APC	APC _{min}	APC _{max}
As	323	2	960	43	4	210
Ag	5	2	192	6	10	23
Al	33880	6100	93400	2200	2000	39000
Ba	1116	96	3100	131	41	1600
Ca	168140	46000	322000	394200	87000	583000
Cd	149	20	1660	61	16	1400
Co	21	1	87	N.D.	0.5	31
Cr	180	26	1100	12	80	8130
Cu	1292	37	3200	272	110	5400
Fe	19466	1600	44000	1309	1900	97000
K	47340	21000	109000	13990	810	44000
Mg	14490	1100	19000	8954	9	170000
Mn	589	400	1900	121	140	12000
Mo	36	6	150	4	2	44
Na	50760	15000	84000	16122	720	70000
Ni	90	9	260	10	20	310
Pb	3972	316	27000	1143	254	22000
Sb	75	81	1500	183	80	682
Se	4	0.4	81	1	3	3
Sn	303	106	5900	155	340	814
Sr	226	40	640	109	5	350
Ti	306	1000	14000	216	270	4400
V	45	25	150	N.D.	7	86
Zn	15632	1048	104000	5380	1100	53000

N.D. = below detection limit of ICP-OES (< 0.10 mg/L)

4.3.1.2 Morphology and bulk elemental composition

Figure 4-1 (a), (b) illustrates the morphology of FA examined by SEM and the selected region for semi-quantitative analysis using EDX was as shown in Figure 4-2 (a). Amorphous and polycrystalline platelets with particle size ranging from 5 to 50 μm with different shapes such as spheres, flakes and fine-grained irregular agglomerates were observed. The spherical particles were mainly glassy silicate or alumino-silicate droplets melted during the incineration process and solidify due to the subsequent cooling in the ESP. SEM-EDX semi-quantitative results in Table 4-3 indicated that the bulk elemental compositions in FA mainly consisted of Ca, Cl, K, Na, O, S and Si agreed with the results of total metal composition from acid digestion.

From Figure 4-1 (c), (d), it can be seen that APC comprised of mainly irregularly shaped polycrystalline particles with finer particle size between 0.5 to 10 μm . The composition of APC was dominated by the reaction products between the scrubbing lime and acidic flue gas and other condensation products. The finer particle size of APC could be attributed to the prior removal of larger particles through electrostatic precipitator which formed FA, before the scrubbing process. Table 4-3 indicates that APC mainly consisted of Ca, Cl and O and with a trace amount of Na, K, S and Zn based on the selected region as shown in Figure 4-2 (b).

Figure 4-1: SEM images of FA and APC at 1000x to 5000x magnification: (a) 1000x FA; (b) 5000x FA; (c) 1500x APC; (d) 5000x APC.

Figure 4-2: EDX spectra of (a) FA; (b) APC for semi-quantitative analysis of the entire selection region as indicated on the top right corner.

Table 4-3: Semi-quantitative elemental analysis for FA and APC using SEM-EDX

Elements	Weight % in FA	Weight % in APC
Ca	11.7	24.3
Cl	17.8	17.7
K	5.2	1.2
Na	17.3	2.9
O	34.1	52.6
S	10.4	1.1
Si	3.5	N.D.
Zn	N.D.	0.2

N.D. = not detected by SEM-EDX

4.3.1.3 Mineralogy

Mineralogy information is essential to understand the leaching behavior as some specific mineral phases can exhibit control to the leaching of different trace metal elements (Comans et al. 1993). Figure 4-3 shows the XRD results of powdered FA and APC.

The XRD diffractogram of FA shows well-defined peaks for Anhydrite (CaSO_4), Sylvite (KCl), Halite (NaCl) and Corundum (Al_2O_3). Other than well-defined crystal peaks, FA also comprised of a significant amount of amorphous silicate phases with broad peaks in the region $2\theta = 30\text{-}35^\circ$. This broadening effect was due to the scattering of X-rays in various directions as amorphous materials atoms were randomly distributed instead of orderly arranged in lattice planes. In other literature, a high amount of glassy silicate phases were also found to be contributing up to 40% amorphous content found in FA (Le Forestier and Libourel 1998, Bayuseno and Schmahl 2011).

The XRD diffractogram of APC identified the crystalline phases to be mainly Calcium-based compounds such as CaClOH , CaCO_3 , Ca(OH)_2 , CaSO_4 , and CaO with other soluble salts such as NaCl and KCl . The presence of NaCl and KCl might be due to the limitation of the electrostatic precipitator to remove particles with particle size smaller than $10\text{ }\mu\text{m}$. As for the major components such as CaClOH and CaSO_4 , they were formed due to the reaction of hydrated lime and acidic flue gas according to these reactions:

The proportion of CaClOH , CaSO_4 , CaO and Ca(OH)_2 varied across the literature due to the different practices of the amount of excess lime addition.

Figure 4-3: XRD diffractogram of (a) FA; (b) APC.

4.3.1.4 TEM

Based on the TEM results from Figure 4-4 (a), (b), (c) and (d), FA consisted of mainly the Si-rich, S-rich and Na/K-rich particles. From Figure 4-4 (a), the Si-rich particle was found to be spherical and contained mainly Si and O. The selected area electron diffraction (SAED) pattern further showed that Si-rich particles were highly amorphous, which was in agreement with the XRD results. It was suggested that the rapid cooling of the melted Si-particles did not allow enough time for proper crystallization to occur while the spherical shape was formed because of more favorable mineral surface energy. The presence of Ca and Zn could be due to the adsorption of their chlorides onto the surface or incorporation into the complex silicate structure.

S-rich particles exhibit an irregular shape without any defined structure. In Figure 4-4 (b), CaS is agglomerated with other particles. In Figure 4-4 (c), CaSO₄ was embedded as a coating over spherical SiO₂. The SAED patterns indicate that both the S-rich particles are crystalline in structure and should show clearly defined peaks in the XRD but in Figure 4-4 (d) only CaSO₄ was shown while CaS is not reflected in the diffractogram. This is possibly due to the low abundance and therefore below the detection limit (approximately 1%) for the XRD.

S-Na/K-rich particles showed a poly-crystalline structure consisted of Ca, S, O, K and Na, suggesting that it could be a mixture of CaSO₄, K₂SO₄ and Na₂SO₄. This could be due to the heterogeneous chemical reaction between NaCl, KCl, and CaCl₂ with SO₂.

Figure 4-4: TEM of FA with SAED and EDX (a) amorphous spherical particle rich in Si and O; (b) crystalline particle rich in Ca and S; (c) crystalline coating rich in Ca, S and O; (d) polycrystalline rod rich in C, Ca, O, S, Na and K.

From Figure 4-5, TEM images of APC showed that it contained mainly polycrystalline Ca-rich particles. As supported by the XRD results, the main compositions of the APC were CaCl_2 , CaSO_4 and CaCO_3 which could be formed during the use of scrubbing additives added to the flue gas to neutralize the acidic gases such as HCl and SO_2 . This finding was in agreement with the XRD results, indicating that the APC mainly consisted of the reaction products between the acidic flue gas and the lime additive while most of the entrained particles were effectively removed by the electrostatic precipitator. The removal of the spherical amorphous Si-rich particles before the scrubbing process also reduced the amount of other less volatile metals found in APC as Si-rich particles could interact with other less volatile metals by adsorption.

Figure 4-5: TEM of APC with SAED and EDX (a) polycrystalline particle rich in Ca, Cl and O; (b) irregular crystalline structure rich in Ca, Cl, S, C and O.

4.3.2 Leaching test

4.3.2.1 TCLP

The leaching behaviors of heavy metals in FA and APC by TCLP is shown in Table 4-4. Under the EPA TCLP regulations (Environmental Protection Agency 1992), the leaching of Cr, Cd and Pb for FA was below the limits while the leaching of Cr and Cd for APC was also well below regulatory limits. However, the leaching of Pb in APC exceeded the limits by over 3 times at 17.92 mg/L due to the high pH and ANC. These results showed that proper treatment is required before the disposal of APC especially for amphoteric metals such as Pb and Zn.

Pb demonstrated higher mobility in APC than FA when tested by using TCLP which can be attributed to the final leaching pH of FA (~pH 10) and APC (~pH 12) as Pb is known to be amphoteric and leach at high or low pH condition. Therefore, it is important to study the effects of variable pH on the leaching for FA due to its low acid-neutralizing capacity and the high content of Pb to fully evaluate its toxicity.

The leaching of Zn, Cu and Fe were also studied but since there are no standard limits for these metals in EPA TCLP regulations, the landfill disposal limits in Singapore (National Environmental Agency 2020) were employed as a supplementary standard. The leaching of Zn, Cu and Fe in both FA and APC are lower than the limits and thus considered suitable for landfill disposal.

Table 4-4: TCLP leaching for FA and APC.

Elements (mg/L)	FA	APC	TCLP Limits	Landfill disposal limit, Singapore
As	N.D.	N.D.	5.0	5.0
Cr	1.46	N.D.	5.0	5.0
Cd	N.D.	N.D.	1.0	1.0
Pb	N.D.	17.92	5.0	5.0
Zn	0.31	3.13	N.A.	100
Cu	0.13	0.32	N.A.	100
Fe	0.12	N.D.	N.A.	100

N.D. = below detection limit of ICP-OES (< 0.10 mg/L)

4.3.2.2 EN 12457-2 leaching test

FA was found to be enriched in amphoteric heavy metals such as Pb and Zn and APC possesses high alkalinity which could facilitate the release of these heavy metals when mixed. Leaching tests based on EN 12457-2 were conducted on FA, APC and MIX to investigate the effects of ash mixing before disposal. A calculated value, MIX (Calculated), based on the average release of FA and APC were used as a reference to compare with the actual release denoted by MIX (Actual).

Table 4-5 illustrates the leaching of Cd, Cr, Pb and Zn from FA, APC and MIX. For Cd, the leaching was below the detection limit of ICP-OES (< 0.1 mg/L) across all three samples. This could be due to the high leaching pH of 11.3, 12.7 and 12.1 in FA, APC and MIX (Actual) respectively as the DI water used in EN 12457-2 is not able to promote the release of Cd due to the high natural pH of the samples.

The leaching of Cr across all samples was below regulatory limits at 1.46 mg/L, < 0.1 mg/L and 0.28 mg/L for FA, APC and MIX (Actual). The leaching of MIX (Actual) exhibited a lower leaching amount of 0.28 mg/L than MIX (Calculated) at 0.73 mg/L. This result indicated that the mixing of FA and APC could be effective in reducing the leaching of cationic metals due to the increase in pH.

The leaching of Pb for FA, APC and MIX (Actual) was < 0.1 mg/L, 17.92 mg/L and 17.82 mg/L. Both APC and MIX (Actual) exceeded the regulatory limits of 0.5 mg/L (for inert waste) and 10 mg/L (for hazardous waste) and treatment must be done before disposal. Based on the leaching of Pb for FA and APC, MIX (Calculated) was expected to only leach out 8.96 mg/L but almost twice the amount was leached from MIX (Actual). This could be likely due to the additional release of Pb in FA that was not released at pH 11.3 due to its amphoteric nature. However, when FA and APC were mixed, the increase in pH from 11.3 to 12.1 facilitated the release of Pb.

The leaching of Zn for FA, APC and MIX (Actual) was 0.31 mg/L, 3.13 mg/L and 5.51 mg/L respectively. Only MIX (Actual) exceeded the regulatory limits of 4 mg/L (as inert waste). The leaching of MIX (Actual) was higher than predicted than in MIX (Calculated) as FA was also found to be highly enriched in Zn which follows an amphoteric leaching pattern.

From this result, it could be seen that mixing FA and APC before disposal could be beneficial in reducing the release of cationic heavy metals due to higher pH. However, the increase in pH after mixing might also result in the additional release of amphoteric heavy metals such as Pb and Zn from FA. Measures such as waste sorting to remove certain heavy metals from the FA should be taken if the mixing of ash for disposal is the only option. However, if utilization is the goal, mixing should be avoided as the mixture would become more heterogeneous and difficult to process.

Table 4-5: Leaching of Cd, Cr, Pb and Zn for FA, APC, MIX (Calculated) and MIX (Actual) under EN 12457-2.

Elements (mg/L)	FA	APC	MIX (Calculated)	MIX (Actual)
pH	11.3	12.7		12.1
Cd	N.D.	N.D.	N.A.	N.D.
Cr	1.46	N.D.	0.73	0.28
Pb	N.D.	17.92	8.96	17.82
Zn	0.31	3.13	1.72	5.51

N.D. = below detection limit of ICP-OES (< 0.1 mg/L).

N.A. = leaching amount below the detection limit (<0.1 mg/L) and no values for calculation

4.3.2.3 pH-dependent leaching test

The leaching characteristics of metals are affected by the L/S ratio, pH and the other bulk contents within the ash. In this study, the analysis of the influence of pH on the release of the As, Ba, Cd, Cr, Cu, Fe, Pb and Zn was carried out according to EN 14429. The leaching of major elements such as Na and K were not included as both are described to be highly soluble and not dependent on pH (Kida et al. 1996) but rather more on solubility controlled affected by the L/S ratio. The natural pH of both FA and APC were the high therefore different amount of nitric acid was added to adjust the pH of the leaching solutions and reach different final pH across the range of 2-12.

As seen from Figure 4-6, FA demonstrated low acid-neutralizing capacity (ANC) and the pH started to decrease with 5 mL of nitric acid added. APC demonstrated high ANC and requires at least 50 mL of nitric acid for the pH to start decreasing. This is probably due to the need to react and consume the excess lime additives added in APC. The ANC results from this study are similar to those reported by Margarida with ANC values for pH 7 to be 6.2-6.8 meq g⁻¹ (Quina et al. 2008). The high ANC and high pH of APC might have positive effects in controlling the leaching of some heavy metals such as Cd but it also enhanced the leaching of some amphoteric metals like Pb (Quina et al. 2009). On the other hand, FA has low ANC and will be more susceptible to pH changes from natural conditions such as acid rain and soil conditions and natural weathering.

Figure 4-6: Acid neutralizing capacity curve of FA, APC and MIX with an increasing amount of nitric acid added.

Figure 4-7 and 4-8 illustrates the pH-dependent leaching of heavy metals under different pH conditions for FA, APC and MIX. The natural pH of FA, APC and MIX were represented by the vertical lines while the regulatory limits for TCLP and landfill disposal limit in Singapore were represented by the red and blue horizontal lines. The availability of each heavy metal could be estimated by the leaching value at low pH below pH 2 (Hong et al. 2000). The three main distinct patterns include cationic, oxyanionic and amphoteric. In cationic pattern, the leaching of the heavy metal decreases as pH increases while in oxyanionic pattern, the leaching increases as pH increases. In amphoteric pattern, leaching occurs at either extremely acidic or alkaline conditions showing a typical “V” shape pattern.

For As, the leaching behavior followed a cationic pattern for FA, APC and MIX with concentrations of 4.3 mg/L, 2.4 mg/L and 5.4 mg/L at pH 2.7, 0.1 and 1.8 respectively. As pH increases to above pH 4, the amount of As leaching decreased sharply to below the detection limit. Cd, Cu, Fe and Zn also exhibited similar cationic leaching patterns. Cd and Zn exceeded the TCLP regulatory limits and Singapore landfill disposal limit respectively for FA, APC and MIX below pH 8 and 6. However, the leaching of both Cd and Zn for FA, APC and MIX decreased to below the respective limits at their natural pH.

For Ba, the leaching of Ba from both FA, APC and MIX seemed to be independent of pH from pH 1 to 10 with maximum concentrations of 1.8, 3.3 and 3.0 mg/L for FA and APC at pH of 5.5, 9.2 and 4.97 respectively. However, as the pH increased beyond 10, the leaching of Ba for FA, APC and MIX decreased sharply. Similar leaching behavior was reported for APC in other studies (Astrup et al. 2006), it was also found that the solubility of Ba seemed to be associated with BaSO_4 and therefore controlled by the dissolution-precipitation of barite and celestite (Fällman 2000).

The leaching of Cr demonstrated amphoteric behaviors as shown in Figure 4-7 (d) for FA. Leaching of Cr decreases from 5.5 to 0.3 mg/L as pH increases from 2.7 to 3.7 but at pH 10.5, the amount leached increased to 2.3 mg/L showing a U-shape graph. At high pH and under oxidizing conditions, the Cr(VI) would form oxyanions and become more mobile due to reduced sorption (Hyks et al. 2009) which can be a concern as Cr(VI) is more toxic than Cr(III) (Astrup et al. 2005). The leaching of Cr from APC was 0.5 mg/L at pH 0.1 and reduced to below the detection limit as pH increases.

The leaching of Pb showed amphoteric behavior in APC but not in FA from Figure 4-8 (c). The maximum leaching for Pb in FA and APCs is 58.7 mg/L at pH of 2.70 and 55.4 mg/L at pH of 0.3 respectively. For FA, the leaching behavior of Pb decreased gradually from 58.7 mg/L to 1.9 mg/L as the pH values increased from 2.7 to 5.5. For APC, leaching of Pb also decreased with the increasing pH but when the pH reaches 10.6, the leaching started to increase and reach 43.5 mg/L at pH of 11.8 demonstrating a typical V-shape amphoteric curve (Kida et al. 1996). One reason for the non-amphoteric behavior in FA for Pb leaching could be due to the maximum pH tested was lower, at pH 11.3, however, from the hydroxide solubility curve of Pb, the increased in leaching should be observed even at this pH. Other plausible explanations are that the leaching of Pb is governed by other minerals such as ettringite or due to sorption of Pb onto iron oxide surfaces which suppressed its leaching (Oehmig et al. 2015). The APC neither contains sufficient sulfates to form ettringite mineral nor enough iron oxides for the sorptive surface due to their lithophilic nature.

In general, FA and APC, the availability of heavy metal were in the order of $Zn > Pb > Fe > Cu > Cd > Ba > Cr > As$ and $Zn > Fe > Cu > Pb > Cd > Cr > Ba > As$ respectively. The enrichment of Pb and Zn in FA and APC were associated with the formation of their respective volatile metal chlorides which condenses onto small particles entrained in the flue gas (Wang et al. 1997, Belevi and Langmeier 2000).

For FA, leaching of heavy metals such as As, Cd, Cu, Fe and Zn were reduced with increasing pH starting from pH 3, 4, 5.5 and 6, respectively. This variation in pH of leaching for different metals was found to be closely related to their hydroxide solubility with minor variations due to complexing factors (Dou et al. 2017). The maximum leaching of As, Cd, Cu, Fe and Zn were 2.4, 9.0, 78.2, 100.9 and 232.9 mg/L, respectively, at pH of 2.7 and the leaching decreases to below detection limits as the pH increases to above 11.

For APC, the maximum leaching from APC for As, Cd, Cu, Fe and Zn are 2.4, 4.0, 17.9, 46.5 and 144.2 mg/L, respectively. The amount of these metals in APC was lower than that of FA due to the addition of lime to neutralize the acidic gas for APC during the scrubbing process. Lithophilic elements such as Fe and Cu were also lower in APC as they tend to solidify at a higher temperature and were removed by the electrostatic precipitator before the scrubbing process.

Figure 4-7: pH-dependent leaching of trace elements (<10 mg/L) from FA, APC and Mix ash (a) As; (b) Ba; (c) Cd; (d) Cr. The natural pH of FA, MIX and APC are represented by the vertical lines and the TCLP limits of each metal are represented by the red dash except for Ba which has a limit of 100 mg/L.

Figure 4-8: pH-dependent leaching of minor elements (>10 mg/L) from FA, APC and Mix ash (a) Fe; (b) Cu; (c) Pb; (d) Zn. The natural pH of FA, MIX and APC are represented by the vertical lines. The TCLP limit of Pb is represented by the red dash and the limit of landfill disposal in Singapore represented in blue is used as a reference for Fe, Cu and Zn as they are not regulated by TCLP.

4.4 Conclusion

The characterization of FA and APC, which included elemental metal composition, mineralogy, morphology and TCLP leaching, was evaluated in this study.

Total metal composition shows that APC was mainly composed of Ca due to the lime additives while FA was enriched in other heavy metals, which are of environmental concerns. Results from XRD, SEM and TEM studies provided insights into the mineralogy present within FA and APC to explain some of the mineral phases controlling the leaching. All these results and findings contributed to expanding the understanding of the properties of FA and APC to plan for a better life cycle strategy for these incineration by-products.

The mixing of FA and APC was found to be effective in increasing the overall ANC for higher stability which decreased the leaching of Cr but increased the leaching of Pb and Zn. Also, the mixing of FA and APC resulted in even more heterogeneity and render further treatment and utilization even harder.

The pH-dependent leaching studies were conducted on FA, APC and MIX to investigate how variation in pH affects the leaching of different metals. It was found that the APC had an extremely high natural pH above 12 and high ANC which required a high amount of acid to alter the pH. FA was also found to have a high natural pH of 11.5 but had low ANC. The low ANC and high heavy metal composition in FA were of environmental concern as the variation in pH was found to affect the mobilization of many metals. From this study, it could be seen that Pb and Zn exhibited amphoteric behavior with minimal solubility observed at pH 9 for Pb and pH 10 for Zn.

5 Effect of washing and ultrasound treatment on FA and APC

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5.1 Introduction

FA consisted of CaO, SiO₂, Al₂O₃, Na₂O, K₂O, SO₃ and Fe₂O₃ with a microstructure consisting of thin polycrystalline platelets agglomerated on spherical particles (Leckner 2015). APC consisted of mainly the reaction products from the added lime and acidic gases, therefore it contained a high amount of CaO and a lesser amount of SiO₂, SO₃, Na₂O and K₂O (Lisk 1988). Both FA and APC also contained a significant amount of heavy metals such as Cr, Zn and Pb which can be considered as hazardous when leached out. Due to the heterogeneous and hazardous nature, proper characterization and detailed analysis must be carried out for both FA and APC to determine a suitable disposal or treatment strategy.

As compared to disposal, utilization of these residues after proper treatment is a more sustainable solution as the amount of FA and APC produced increases over the year. Many research groups had already investigated different methods such as thermal treatments (Chandler et al. 1997), solidification and stabilization (Sawell et al. 1995), and selective extractions (Buekens and Huang 1998) to treat both FA and APC. However, recent works making use of novel energy-efficient low-frequency ultrasonic methods have shown great potential in accelerating extraction, homogenization and promoting other reactions (Kishimoto et al. 2001).

When ultrasound is applied, the sound waves will travel through the medium which results in rarefaction and compression cycles within the medium. During the rarefaction cycle, negative pressure will be produced and if this negative pressure is higher than the surface tension of the liquid, cavitation will occur. These cavities will continue to absorb energy from the ultrasound and eventually implode to produce a region of extremely high temperature (5000 °C) and pressure (1000 atm). This extreme condition increases the solubility and diffusivity of the heavy metals and results in the formation of radicals which can accelerate other reactions. Also, high impact micro-jets of up to 100 m/s were produced and could cause fragmentation to the solid phase while micro-streaming effects also enhanced the mass transfer process (McKay 2002).

In this study, washing and ultrasound treatments were applied to both FA and APC. The leaching of heavy metals, changes in mineralogy and microstructures of FA and APC were investigated to evaluate the effects of washing and ultrasound treatments. The purpose of this study is to understand and harness the potential of ultrasound to convert hazardous FA and APC into useful construction materials.

5.2 Materials and methods

5.2.1. Washing and ultrasound treatments of FA and APC

For the washing treatment, 50 g of samples were added to 500 mL of DI water and agitated with rapid magnetic stirring for 30 mins to ensure all the samples were suspended throughout the entire duration.

For the ultrasound treatment, 50 g of samples were added to 500 mL of DI water and underwent ultrasound treatment by an ultrasonic generator (Vibra Cell VC-505 from Sonics & Materials, USA) with a net power output of 500 W and a frequency of 20 kHz with constant magnetic stirring.

After the treatments, all slurries as shown in Figure 5-1 were centrifuged for 5 mins at 8000 rpm, filtered with 0.45 μm membrane and dried at 55 °C to recover the treated samples for further analysis.

Untreated FA, FA treated with washing and FA treated with ultrasound were denoted as FA Raw, FA wash and FA Probe, respectively. Untreated APC, APC treated with washing and APC treated with ultrasound were denoted as APC Raw, APC Wash and APC Probe, respectively.

5.2.2. Characterization and analytical methods

The properties of FA and APC before and after the treatments were determined by using acid digestion, SEM-EDX and XRD as described in Chapter 3, Section 3.2. The environmental impacts of the heavy metal release before and after treatment were also evaluated with TCLP as discussed in Chapter 3, Section 3.3.

Figure 5-1: Image of FA Probe and FA Wash slurries after treatments, respectively.

5.3 Results

5.3.1 TCLP leaching results

The TCLP leaching of Ba, Cr, Pb and Zn were studied as these were the main elements of concern based on abundance and potential toxicity. The TCLP results of these elements for both FA and APC before and after treatment were shown in Table 5-1 and Figure 5-2.

For FA Raw, the leaching of Pb were below the detection limit (< 0.1 mg/L) while for the APC samples, the leaching of Pb and Zn were significantly higher. On the other hand, the leaching of Cr was significantly higher for FA than APC. This was mainly caused by the variation of the final leaching pH of these mixtures due to the difference in alkalinity and acid-neutralizing capacity of the FA and APC as found in Chapter 4 (Alba et al. 1997). The use of acetic acid (pH 2.88 as the extraction fluid for TLCP caused the pH of FA Raw to decreased to pH 10, which corresponded to the lowest leaching for amphoteric Pb and Zn while the pH of APC Raw remained above pH 12.5 which facilitated the release of Pb and Zn. Therefore, it would be recommended that both FA and APC be treated before disposal.

After treatment of FA, the leaching of Ba decreased to 0.23 mg/L and 0.21 mg/L for FA Wash and FA Probe while the leaching of Cr increased to 1.52 mg/L and 1.43 mg/L. The decrease in Ba leaching after treatment could be due to the removal of soluble Ba compounds during the treatment. The increase in Cr leaching could be due to the higher enrichment in the less soluble Cr content available. However, the higher leaching of Cr in FA Wash was unexpected as FA Probe had smaller particle size than FA Wash and the oxidizing condition during ultrasound treatment could convert Cr(III) to a more soluble Cr(VI) with higher solubility. This result indicated the possibility of the incorporation of Cr into a more stable matrix formed during ultrasound treatment.

For the treatment of APC, the leaching of Ba, Pb and Zn were significantly reduced and were all below the TCLP regulatory limits after treatment. The leaching of Pb decreased from 21.64 mg/L in APC raw to 2.51 mg/L and 4.62 mg/L in APC Wash and APC Raw respectively.

In general, these results indicated that both washing and ultrasound treatment was effective in reducing the leaching of various heavy metals by the separation while ultrasound treatment showed possible stabilizing effects on the FA.

Table 5-1: TCLP results for FA and APC samples for Ba, Cr, Pb and Zn with average and standard deviation calculated from triplicates (Ag, As, Cd and Se were excluded as all values across all samples were below detection limits).

Element (mg/L)	FA Raw		FA Wash		FA Probe		APC Raw		APC Wash		APC Probe	
	Ave	S.D.	Ave	S.D.	Ave	S.D.	Ave	S.D.	Ave	S.D.	Ave	S.D.
Ba	0.64	0.02	0.23	0.01	0.21	0.01	1.37	0.61	0.49	0.03	0.19	0.03
Cr	1.15	0.27	1.52	0.03	1.43	0.02	N.D.	N.A.	N.D.	N.A.	N.D.	N.A.
Pb	N.D.	N.A.	N.D.	N.A.	N.D.	N.A.	21.64	2.51	3.54	0.19	4.62	0.82
Zn	0.31	0.03	N.D.	N.A.	N.D.	N.A.	7.03	2.24	1.79	0.14	1.99	0.34

N.D. = below detection limit of ICP-OES (< 0.1 mg/L).

N.A. = not applicable due to TCLP leaching amount below the detection limit (<0.1 mg/L)

Figure 5-2: TCLP leaching: (a) leaching for Ba, Cr and Zn for FA Raw, FA Wash and FA Probe, Pb was below the detection limit for all FA samples; (b) leaching for Ba, Pb and Zn for APC Raw, APC Wash and APC Probe.

5.3.2 Elemental concentration

The total elemental concentrations in FA and APC, before and after the treatments were shown in Table 5-2. FA Raw was enriched in both volatile elements such as As, Cd, Pb and Zn and lithophilic elements such as Al and Fe. On the other hand, APC Raw was mainly enriched in more volatile metals such as Pb and Zn. The high contents of Al and Fe in FA Raw suggested the potential of metals recovery while the high content of Pb and Zn in APC Raw suggested a need for treatment. This is because Pb and Zn exhibited high mobility at high pH due to their amphoteric behavior as seen from the TCLP results and could be of environmental concern.

Figure 5-3 compares the concentration of elements remained in the FA and APC after washing and ultrasound treatments, respectively. Generally, there was an increase in proportion in Al, Ba, Cr, Pb and Zn in the washed or sonicated samples as compared to the raw samples. This could be due to the dissolution of highly soluble species such as NaCl and KCl. This showed that washing treatment or ultrasound treatment could reduce heterogeneity and improve the quality of the treated residue.

FA Probe showed similar metal composition as that of the FA Wash, however, the leaching of heavy metals from TCLP was significantly different. This showed that the total composition might not always be the best way to evaluate the toxicity as the type of mineral phase also played an important role in terms of heavy metal leaching.

Table 5-2: Elemental concentrations for FA and APC.

Elements (mg/kg)	FA Raw		FA Wash		FA Probe		APC Raw		APC Wash		APC Probe	
	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
Al	17966	1085	31443	7419	29544	7530	1724	298	1756	945	2416	1293
Ba	674	45	1072	384	1060	433	N.D.	N.A	N.D.	N.A	N.D.	N.A
Cr	123.8	10	357	53	333	40	N.D.	N.A	N.D.	N.A	N.D.	N.A
Cu	779	58	1649	246	1624	222	238	68	275	137	399	202
Fe	9869	660	22061	2390	24059	1463	1231	312	1678	1093	2410	1033
Mg	7354	467	16166	2564	15121	2313	6252	1862	7695	4012	10503	4667
Mn	393	31	907	139	901	126	N.D.	N.A	N.D.	N.A	N.D.	N.A
Pb	1815	194	3469	522	3805	263	962	365	826	289	880	478
Sr	N.D.	N.A	280	19	274	18	N.D.	N.A	N.D.	N.A	N.D.	N.A
Zn	7550	867	18047	2822	17600	2547	3551	1119	4350	2343	6849	3522

N.D. = below detection limit (< 2 mg/kg)

N.A. = not applicable due to TCLP leaching amount below the detection limit (<2 mg/kg)

Figure 5-3: Elemental concentration for FA.

5.3.3 Mineralogy and structural effects of ultrasound on FA and APC

In Figure 5-4, the main mineral phases in FA Raw contained CaSO_4 , Ca_2SiO_3 , Ca_3SiO_3 , KCl , NaCl and CaCO_3 . Also, FA Raw contained a significant amount of amorphous content as seen from the broad peaks around 30° to 40° . Additional peaks of ettringite, $\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$, could be detected in FA Probe which could be due to the effects of ultrasound treatment as ettringite peaks were not found in FA Wash. This early formation of ettringite could be likely due to the particle size reduction resulting in a higher reacting surface and also the elimination of the passivating aluminum oxide layer.

Figure 5-4: XRD diffractogram of FA samples.

In Figure 5-5, the XRD diffractogram showed the crystalline phase present in APC Raw consisted of Ca(OH)_2 , NaCl , KCl , CaSO_4 , CaClOH , MgO , CaCO_3 and CaO while in APC Probe and APC Wash, similar phases can be seen except for the soluble compounds such as NaCl , KCl and CaClOH . This indicated that the washing treatment was enough to remove the soluble components while the ultrasound treatment did not yield any major changes to the crystalline phases as compared to APC Raw.

Figure 5-5: XRD diffractogram of APC samples.

Figure 5-6 (a) and (b) illustrate the SEM-EDX results for the FA Probe. FA Probe was found to contain ettringite with a needle-like structure (consisted of mainly Al, Ca, O and S) and calcium aluminosilicate which had a spherical structure (consisted of mainly Al, Ca, O, and Si). These results were consistent with the XRD for the formation of a new mineral phase due to ultrasound and indicated the surface cleaning effects of ultrasound treatment to reveal a spherical structure.

Figure 5-6: Element identification of SEM-EDX of FA Probe: (a) needle-like structure containing Al, Ca, S and O; (b) spherical structure containing Al, Ca, Si and O (region selected for identification circled in red).

5.4 Discussion

From the results, it could be seen that ultrasound treatment is different from washing treatment due to the chemical and physical effects occurring during transient cavitation. In terms of the physical aspect, the micro-jet fragmentations and microstreaming effects could be observed from the change in particle size during SEM analysis for both FA and APC. The morphology of FA Probe was also changed as spherical and rod-like crystals were observed after ultrasound treatment but no observable change was found in FA Wash, APC Wash and APC Probe.

In terms of the elemental composition, after ultrasound treatment, the metal contents in FA Wash and FA Probe were similar but significant differences were observed between APC Wash and APC Probe. In general, all Wash and Probe samples were more enriched in various metals such as Al, Cr, Fe, Mg, Pb and Mg due to the dissolution of readily soluble chlorides such as KCl and NaCl. Despite the increase in total metal composition of Cr, Pb and Zn, both FA Probe and APC Probe showed lower TCLP leaching than the Raw and Wash samples, this indicated that ultrasound treatment had resulted in some forms of stabilization of the metals.

Despite similar composition between FA Probe and FA Wash, XRD results revealed that sonochemical effects were prevalent in the form of accelerated formation of the ettringite mineral. The formation of ettringite mineral is a slow natural process in aging FA which followed this equation:

It was understood that ettringite can be formed with the presence of Ca^{2+} , SO_4^{2-} with ionic Al species and were stable under alkaline conditions of around pH 9 to 13.4 and temperature of below 80°C (Santhanam et al. 2001, Shimada and Young 2004) and would slowly be converted to other forms of mono-sulfate as pH and temperature continues to rise. The accelerated formation of ettringite in FA Probe was likely to be an effect of sonocatalysis whereby fragmentations of the particle increased the reaction rate while the hotspot provided a good environment for the conversion of Al_2O_3 to more reactive forms to react with the Ca^{2+} and SO_4^{2-} which were in high abundance within the slurry. Ettringite was known to have ion exchangeability to reduce the leaching of Pb and other heavy metals (Xiang et al. 2018) and this stabilization process might also be accelerated by ultrasound. On the other hand, despite the differences in elemental composition, there was no observable difference in the mineral phase between APC Probe and APC Wash, this might be due to the high homogeneity of APC

and low contents of other minerals formed which were below detection limit of the XRD (Lim et al. 2004).

5.5 Conclusion

FA Raw and APC Raw were both found to be highly heterogeneous and had a high risk of releasing hazardous metal elements such as Cr, Pb and Zn into the environment and require treatment before disposal. In this study, washing treatment and ultrasound treatment were applied to both FA and APC followed by evaluating their elemental concentration, TCLP and XRD, SEM-EDX.

Washing treatment was effective in removing soluble compounds such as NaCl, KCl and CaClOH to obtain a more homogenous product with higher utilization potential. However, XRD results of APC Probe showed no significant difference as that of the APC Wash, thus showing that washing treatment was sufficient for the treatment of APC. Another possible reason was that the new mineral forms in APC Probe were too low to be detected by XRD (detection limit of 1-2%) and other methods could be used to identify these changes. The total composition for both washed and sonicated FA showed similar elemental concentration but differs in terms of leaching under TCLP, thus indicated a possible change in mineralogy due to ultrasound irradiation. This formation of the new mineral phase was thought to improve the leaching results of FA Probe due to the incorporation of the metals into the newly formed mineral matrix. Results from XRD also detected peaks of the ettringite mineral in FA Probe but not from the control FA Wash, thus indicative of the effects of ultrasound on FA. Further evidence from SEM-EDX of FA Probe also confirmed the formation of ettringite and the presence of spherical calcium alumino-silicate products after ultrasound treatment. This early ettringite formation could reduce the delay expansion problem and limit the leaching of heavy metals, thus increasing the potential of utilization for FA treated with ultrasound.

6 Influence of duration and extracting agent on ultrasound treatment of FA

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6.1 Introduction

In the previous chapter, ultrasound treatment was found to be effective in reducing the leaching of various heavy metals and able to accelerate the formation of the mineral ettringite in FA. The use of ultrasound can produce enhanced extraction efficiency to reduce the heavy metal content resulting in a more homogenous product that has better utilization potential. Also, the accelerated formation of ettringite from the ultrasound treatment is beneficial as it prevents durability issues due to delayed ettringite formation in fly ash concrete.

In this study, various optimizations of the ultrasound treatment were studied individually to determine the optimum operating conditions to enhance the extraction of various metals while ensuring the formation of ettringite at the early stage. The effects of duration were studied to determine the feasibility and viability of the ultrasound treatment. The higher temperature increases the extraction efficiency for normal extractions but in the case of ultrasound extraction, a higher temperature can reduce the cavitation effect which reduces extraction efficiency.

The objective of this study is to investigate the effects of duration and different types of extracting agents such as NaOH, citric acid, nitric acid and EDTA on FA. Further investigation of the various concentrations of EDTA was also studied as it showed promising extraction results.

6.2 Materials and method

6.2.1 Materials

The FA and chemicals used in this study were the same as discussed in Chapter 3.

6.2.2 Ultrasound experiments

Sonication was done using a horn transducer with an ultrasound generator (Vibra Cell VC-505 from Sonics & Materials, USA) with a net power output of 500 W and a frequency of 20 kHz. The resulting slurries were centrifuged and dried at 55°C before other analyses.

For the feasibility study, the duration of 5 mins, 15 mins, 30 mins and 60 mins sonication were studied to determine the time required. For the investigation of different chelating agents, the duration and temperature were fixed at 15 mins and 25°C respectively with 30 g of FA in 300 ml of 0.1 M of NaOH, 0.1 M of citric acid, 0.1 M nitric acid and varying concentrations of EDTA ranging from 0.01 M to 0.15 M.

6.3 Results and discussion

6.3.1 Duration

One of the key factors in ultrasound treatment is the sonication time taken and it is a complex parameter based on the leachate and ash matrix interaction, particle size, the concentration of the leachate and the type of ultrasound device used (Capelo et al. 2005). Typical time of sonication can range from as low as 1 min in probe systems to 180 mins in bath systems (Júnior et al. 2006). As a general rule, the more “inorganic” the matrix is, the more time is required for total extraction, biological and plant samples will typically take 5 mins to 15 mins (Minami et al. 1996, Bermejo-Barrera et al. 2001) while sediments require a longer time for extraction (Siaka et al. 1998). In this study, a duration of 5 mins to 60 mins was chosen for evaluation as the probe system possesses higher acoustic power while FA is considered to be “inorganic” sediment which requires longer extraction duration.

From Figure 6-1, the extraction yield of the Cd, Cr, Pb and Zn is illustrated. The extraction yield was calculated using the amount of heavy metal in the extraction leachate divided by the sum of the extraction leachate and the concentration in the residue after the treatment. It could be seen that Cd and Zn showed a high extraction yield under the sonication using DI water as the solvent regardless of the sonication duration. This could be due to the high natural pH of the final mixture which limits the effectiveness of ultrasound extraction of certain metals and

suggested the need for other solvents such as acid to adjust the pH or chelating agent for complexation.

The extraction yield of Cr increased from 2.5% to 4% before dropping to 2% at 5 mins, 30 mins and 60 mins respectively. Pb also showed a similar trend of decreased extraction yield with longer ultrasound duration. The initial increase could be attributed to the mechano-chemical effects from the ultrasound irradiation resulting in fragmentation of the FA which facilitated the metal dissolution (Hong et al. 2000, Hasegawa et al. 2013). The drop in the extraction yield at prolonged sonication duration might be due to re-adsorption or formation of other more stable forms of the initially leached Cr and Pb (Filgueiras et al. 2002). From these results, a sonication time of 15 to 30 mins was the most efficient for the extraction of FA to maximize the extraction yield and reduce re-adsorption of the extracted metals.

Figure 6-1: Extraction yield of Cd, Cr, Pb and Zn from FA for 15 mins using DI water.

Figure 6-2 shows the TCLP leaching of Cd, Cr, Pb and Zn after different durations of sonication. The leaching of Cd, Cr, Pb and Zn all met the TCLP requirements with the leaching of $Cr > Zn > Pb > Cd$. There is a correlation between longer sonication duration and lower leaching, this is surprising because the metals extracted from FA at 60 mins were lower than that of 15 and 30 mins, this suggested that in addition to enhanced extraction, sonication also had certain stabilization effect on FA. Similar result of increased Pb stability despite lower extraction yield under alkaline condition was also reported (Lim et al. 2004). It was suggested that new lead complexes with low solubility could form during the sonication simultaneously with the enhanced dissolution of other metal species. Other reasons for the reduction in TCLP leaching could be due to the removal of soluble chlorides and the enrichment in Fe and Mn content after the sonication process (Wei et al. 1998).

Figure 6-2: TCLP leaching for Cd, Cr, Pb and Zn for 5 mins, 15 mins, 30 mins and 60 mins.

XRD results from Figure 6-3 shows that NaCl and KCl were removed and a new mineral phase, ettringite, was formed after sonication. This finding is in agreement with the TCLP leaching results. The mineral ettringite was known to reduce the leaching of divalent cations such as Cd^{2+} , Pb^{2+} and Zn^{2+} by incorporating them into the lattice to substitute Ca^{2+} (Zhen et al. 2013),. Although ettringite can be formed through natural weathering, it was believed that sonication accelerated this formation as results from the previous chapter showed that no ettringite was formed after washing treatment.

Figure 6-3: XRD of treated FA after different sonication duration: (a): 5mins; (b): 15 mins; (c) 30 mins; (d) 60 mins.

6.3.2 Extracting agent

Due to the high natural pH of the FA, the extraction efficiency would be low as pH is one of the dominant factors in the dissolution of metals, however, FA also had low ANC which made the pH easier to control for optimization. The extraction of Cr, Cd, Pb and Zn with different acids, alkaline and chelating agents was investigated in this optimization study. Nitric acid was chosen as the acid extractant as it is the most extensively used acid for such extractions in the literature due to the high solubility of nitrate salts (Bradshaw and Slavin 1989, Miller-Ihli 1995, Santos et al. 2009). NaOH was used to study the effects of selective leaching of amphoteric metals under alkaline conditions. EDTA and citric acid were chosen as chelating agents due to their binding stability with metals across a wide range of pHs (Hong et al. 2000). To reduce the environmental impact and concern over the cost and usage of chemicals, this study limits the concentration of the extractants to 0.1 M.

The extraction yield of Cd, Cr, Pb and Zn from FA using NaOH, citric acid, nitric acid and EDTA is shown in Figure 6-4. The initial pHs were 13.0, 5.6, 7.0 and 9.1 for NaOH, citric acid, nitric acid and EDTA respectively while the final pH after the sonication increased to 12.8, 6.1, 8.1 and 9.9. This result showed that when acidic leachate such as citric acid, nitric acid and EDTA were used, sonication might have resulted in better hydrolysis of Ca, K, Na and Mg oxides to increase the pH of the solution.

65% and 45% of Cd were extracted when EDTA and citric acid were used as the solvent respectively while the Cd extracted was below the detection limit when NaOH and nitric acid were used. This showed that pH was not the only factor contributing to the extraction yield as EDTA at a relatively high pH of 9.1 showed high extraction yield for various metals.

For extraction of Cr, citric acid was the most effective extractant followed by EDTA and nitric acid. The pH was the most dominant factor for extraction as compared to the chelate stability as there is a correlation between the extraction yield and the pH of the mixture despite EDTA having a higher stability constant than citric acid for Cr. This result indicated that higher acid concentration could enhance the extraction of Cr by increasing its mobility. On the other hand, although Cr is known to show amphoteric behavior in FA, the use of NaOH as a solvent fails to extract any Cr at pH 12.8.

Due to the amphoteric behavior, Pb exhibited high extraction yield when NaOH and EDTA were used as the solvent at extraction pH of 12.8 and 9.9. It is known that Pb is an amphoteric metal that can be easily extracted at extremely high or low pH therefore high extraction rate

was obtained by NaOH at pH 12.8. However, the high extraction of Pb when using EDTA at pH 9.9 indicated that leaching of Pb using EDTA was mainly due to the chelating effect as pH 10 corresponds to the lowest solubility range for the amphoteric Pb (Hong et al. 2000). The use of acidic treatment to lower the pH of FA to extract Pb was not effective as shown by the low extraction yield using nitric acid and citric acid, although higher concentration of acid could be used to further lower the pH to increase the extraction of Pb but that would require a higher reagent cost and might not be feasible.

Citric acid leaching showed the highest extraction yield of Zn as the pH of the mixture's final pH was 6.1, this acidic condition encouraged the leaching of Zn while EDTA showed the next highest extraction efficiency at pH 9.9 due to the chelating effects.

For extraction, the addition of NaOH did not improve the extraction yield of most of the metals except for Pb, this result could be useful to selectively extract Pb from the FA. The addition of nitric acid at a low amount was also not capable of lowering the pH of FA for effective acidic extraction. The use of citric acid and EDTA showed promising extraction yield with EDTA giving the best extraction effect while not altering the pH of the FA as much as citric acid. Due to the high extraction efficiency, after the ultrasound treatment, the extraction fluid would require proper treatment or metal recovery before disposal.

Figure 6-4: Extraction yield of Cd, Cr, Pb and Zn from FA for 15 mins using 0.10 M of NaOH, citric acid, nitric acid and EDTA.

From the TCLP results of the FA after ultrasound treatment from respective solvent shown in Figure 6-5, the leaching of Cd, Cr, Pb and Zn were within the limits except for Pb after citric acid leaching. The usage of acidic extracting agents consumed the natural alkaline buffering effects of the various mineral phase in FA resulted in the increased mobility of other heavy metals during the TCLP. Figure 6-6, XRD of the treated FA shows that after the ultrasound treatment of nitric acid and citric acid, there was no ettringite mineral formed while in the FA treated with NaOH and EDTA, ettringite mineral was detected. The formation of ettringite is pH sensitive and only stable at the pH of above 10 (Havlica and Sahu 1992) while the final pH of the mixture of nitric acid and citric acid were 8.1 and 6.1 respectively.

Figure 6-5: TCLP leaching values of Cd, Cr, Pb and Zn from the treated FA after 15 mins of extraction using 0.10 M of NaOH, citric acid, nitric acid and EDTA.

Figure 6-6: XRD of treated FA using different extracting agent: (a) 0.1 M EDTA; (b) 0.1 M NaOH; (c) 0.1 M nitric acid; (d) 0.1 M citric acid.

6.3.3 EDTA concentration

Previously, it was found that EDTA is capable of achieving high extraction yield of many different types of metals with independent on the pH of the FA mixture. However, EDTA's binding effect on trace metals could be affected considerably when used on FA due to low selectivity and the high amount of Ca, K and Na present (Jung et al. 2004). However, other than relative abundance of the various metallic ions, different EDTA-metal complexes have different stability orders (Begum et al. 2012) and the stability of Cr, Cd, Pb and Zn are of many orders higher than that of Na, K and Ca. To understand the effects of ionic abundance against EDTA-metal stability, different concentrations of EDTA were used in this study. The effects of EDTA concentration on the extraction yield of different metals and the stability of the treated FA based on TCLP were investigated.

Figure 6-7 shows that as the concentration of EDTA increases from 0.01 M to 0.15 M, the extraction yield of Cd, Cr, Pb and Zn also increased. For Cd, when the concentration of EDTA increased from 0.01 M to 0.05 M, the extraction yield increased significantly from 42% to 59% but eventually flattened out at 0.15 M with an extraction yield of 64%. This indicated that most of the available Cd already form complexes with EDTA even at low concentrations.

The extraction yield of Cr increased steadily as the concentration of EDTA increases, especially from 0.10 M to 0.15 M. This indicated that the extraction yield could further increase with a higher EDTA concentration. This result is surprising as Cr^{3+} has the highest stability constant of $\log K_f$ values of 23.4 with EDTA which meant it should attain high extraction yield even at low EDTA concentration. One likely explanation was the increase of EDTA concentration also brought about the drop in pH which could affect the mobility of Cr in the solution.

For Pb, the extraction yield of Pb followed a similar trend as Cd, increasing at a decreasing rate with a higher concentration of EDTA. The increase in EDTA concentration from 0.01 M to 0.15 M increased the extraction yield from 18% to 65%, this result showed that EDTA is promising to selectively extract Pb from FA.

The extraction yield of Zn was low at 0.01 M and even at the maximum tested EDTA concentration of 0.15 M, only 12.87% of Zn was extracted. The reason for such low extraction yield might be due to Zn binding to the residual fraction of FA. Another plausible explanation could be due to the high amount of Zinc present in FA that this concentration of EDTA was unable to completely extract all of them.

Figure 6-7: Extraction yield of Cd, Cr, Pb and Zn from FA using 0.01 M, 0.05 M, 0.10 M and 0.15M EDTA for 15 mins.

Figure 6-8 illustrates the TCLP results of different EDTA concentrations, the leaching of Cd, Cr and Pb are below the standard limits. The TCLP leaching of Cd and Pb shows a significant increase with increasing EDTA concentration. This was likely to be caused by the decrease in pH with increasing EDTA concentration. The pHs of the treated FA using 0.01 M, 0.05 M, 0.10 M and 0.15 M EDTA are pH 10.9, 10.35, 9.9 and 9.6 respectively. The leaching of Zn, however, showed a few orders of magnitude in terms of leaching in TCLP despite a higher extraction amount during the ultrasound treatment. The maximum TCLP leaching of Zn when 0.15 M was 14.7 mg/L as compared to 3.1 mg/L (for 0.10M), 0.2 mg/L (for 0.05M) and 0.1 mg/L (for 0.01 M). Another interesting finding was that from Figure 6-9, the XRD using 0.01 M, 0.05 M and 0.10 M EDTA showed a similar pattern with the presence of the mineral ettringite while in the XRD of 0.15 M EDTA, no ettringite was detected.

Figure 6-8: TCLP leaching of Cd, Cr, Pb and Zn from FA using 0.01 M, 0.05 M, 0.10 M and 0.15M EDTA for 15 mins.

Figure 6-9: XRD for different EDTA concentrations: (a) 0.01 M EDTA; (b) 0.05 M EDTA; (c) 0.10 M EDTA; (d) 0.15 M EDTA.

6.4 Conclusion

This study evaluated the effects of ultrasound duration and the extraction and stabilization potential using a different extracting agent and varying the EDTA concentration for FA. The leachate after extraction and the TCLP of the residue were evaluated for the optimization of ultrasound application to treat FA in terms of extraction yield and after the stability of the residues.

It was found that the optimal duration required for sonication of FA was between 15 mins to 30 mins, prolonged duration of ultrasound showed reduced extraction yield which might be attributed to re-adsorption of Cr and Pb. However, in terms of stabilization, the duration of ultrasound showed a positive correlation with the stabilization of the residue with lower TCLP leaching from the treated FA. From the XRD results, it could also be seen that the formation of ettringite was accelerated even with 5 mins of ultrasound treatment.

In terms of leachate, NaOH had the lowest extraction yield due to a high extraction pH of 12.8 and could only extract Pb due to its amphoteric nature and exhibited a lower extractability for other metals than the DI water control. This, however, could be useful for stabilization purposes only as the leachate will contain mainly Pb, Na, Ca and K which could be dealt with more easily before disposal. On the other hand, citric acid and nitric acid could lower the pH of FA to pH 6.1 and 8.1 respectively to enhance metal mobility to increase the extraction yield. Citric acid extraction showed a high extraction yield especially for metals that are dependent on pH for dissolution. However, acidic treatments resulted in negative environmental impacts as it consumed the natural buffering effects of FA and increased the mobility of various metals such as Zn and Pb. It was revealed that no ettringite mineral was detected in the residue but instead peaks of gypsum were found for FA residues which were extracted by acidic leaching. The most versatile extracting agent in this study was EDTA as it was proven to increase the extraction yield of various metals independent of the pH due to its chelating properties.

Further investigation with varying EDTA concentrations showed that higher concentrations led to higher extraction yield for Cd, Cr, Pb and Zn. However, the trend of the increase is different for respective metals, an increase to 0.05M of EDTA was shown to effectively extract the most of the Cd and subsequent increase in concentration saw very little increase which could be attributed to the increased mobility and lower pH instead of more chelating sites for metals binding. For Cr, Pb and Zn, high EDTA concentration increases the extraction yield proportionally and the maximum extraction yield was not reached in this study. Another

explanation for low extraction yield is because it is understood that the sample FA contained a relatively large amount of Pb & Zn compared to Cd and the majority of them might belong to the residual fraction with low mobility. Despite higher extractability with higher concentration, it could be seen that at 0.15 M EDTA concentration, the mobility of various metals such as Pb and Zn increases sharply and leaches in order of magnitudes higher than the 0.01 M to 0.10 M EDTA samples. XRD results of the different EDTA concentrations showed that ettringite mineral was not detected at 0.15 M EDTA concentration.

In conclusion, it is not possible to determine the best leaching agents as the decision depends on many factors such as the properties of the ash matrix and the purpose of the treatment. For FA with low acid-neutralizing capacity, acidic extraction using nitric acid may be the better choice. However, the use of EDTA which exhibits high extraction yield independent of pH might be less costly for other ash types with high acid-neutralizing capacity. Furthermore, if the purpose of the treatment is for utilization, acidic extraction might not be suitable as such an aggressive extraction method can dissolve more than 50% of the original ash content. Also, the leaching of heavy metals from the ash after acid extraction increases due to the decrease in pH. Given the high cost of risk of environmental pollution and the lack of construction material, the extraction of FA to produce a safer product suitable for construction purposes now has an economical driving force on top of the environmental concerns. Lastly, with improved extraction yields, the metal extracted can also be recovered instead of landfilled, thus moving a step closer to the circular economy of metal.

7 Accelerating ettringite formation of fly ash and application in cement

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7.1 Introduction

In the previous chapter, treated FA was shown to have a similar composition as coal fly ash which is known to be beneficial to concrete products in terms of compressive strength and durability. Studies using MSW FA as a replacement also produced similarly promising results (Hamernik and Frantz 1991, Collepardi 2010). However, the high sulfate and chloride contents of FA could be detrimental for long term durability and limits its utilization (Mangialardi et al. 1999). Ultrasound treatment was found to be effective in simultaneously release the chlorides and heavy metals from the fly ash using different extracting solvent (pH 8 to 14) while accelerating the formation of ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, to reduce the amount of gypsum. Furthermore, in addition to mitigating the durability problem, the early formation of ettringite was also found to affect reducing the leaching of various heavy metals (Hassett et al. 1989, McCarthy et al. 1991, Chrysochoou and Dermatas 2006).

Compared to other treatment methods, the ultrasound process achieved higher extractions of various metals to produce a more homogenous and stable treated FA (Anjum et al. 2014). In addition to increasing homogeneity, accelerated formation of ettringite could increase the utilization potential of the final product by mitigating the problem of delayed ettringite formation in fly ash concrete which reduces the long term compressive strength of concrete (Leklou et al. 2017). The use of ultrasound is safe in operation since it does not require the use of any corrosive substance or high temperature as compared to other forms of treatment and uses a lesser amount of extraction agents due to more efficient mixing which results in less secondary by-products generated and less reaction time required.

Other than delayed ettringite formation and chloride attacks, another problem with FA is the presence of metallic aluminum can produce a lot of hydrogen gas when mixed with the highly alkaline OPC. The production of the hydrogen gas during the mixing and curing of the concrete resulted in entrapment of large voids that affected the compressive strength (Bertolini et al. 2004). Efforts had been made to reduce this excessive aluminum content by treating it in alkaline solution for up to 24 hours before using sees the potential of up to 50% replacement without durability concerns (Pera et al. 1997).

In this chapter, 30 % of FA Raw, FA Wash and FA Probe would be added as a partial replacement for cement. The concrete samples were tested for both the compressive strength and the environmental impact of leaching from the final product. The purpose of this study is to evaluate the utilization potential of ultrasound treated FA as a construction material.

7.2 Materials and methods

7.2.1 Materials

The fly ash used in this study was collected from a Waste to Energy (WtE) Incineration Plant with the capability of handling 3000 tons/day of municipal solid waste. The FA was collected from the two-zone electrostatic precipitator prior addition of any other additives. After collection, the fly ash was oven-dried and kept in airtight containers pending experiments. The cement used was obtained from a local supplier, as a premixed of Ordinary Portland Cement (OPC) with fine sand at approximately 3:2 ratio. The composition of the raw materials as illustrated in Table 7-1.

Table 7-1: XRF of FA Raw and cement powder.

Element Composition	FA Raw (%)	Cement (%)
Al ₂ O ₃	4.52	13.60
Br	0.28	N.D.
CaO	33.07	36.84
Cl	11.54	N.D.
CuO	0.22	N.D.
F	0.61	N.D.
Fe ₂ O ₃	3.67	5.78
I	0.21	N.D.
K ₂ O	5.66	1.03
MgO	1.61	1.42
Na ₂ O	8.63	0.59
P ₂ O ₅	1.27	0.32
PbO	0.49	N.D.
SiO ₂	8.34	36.09
SO ₃	15.50	3.07
TiO ₂	1.29	0.89
ZnO	2.24	N.D.

7.2.2 Ultrasound and washing treatments

The ultrasound and washing treatments for the FA in this study followed the same conditions as mentioned in Chapter 4.

7.2.3 Mixing method and mix design for concrete blocks

To study the feasibility of the FA concrete, specimens with different water to cement (W/C) ratio and different types of FA (FA Probe, FA Wash and FA Raw) were cast. The water to cement (W/C) ratio of 0.45, 0.50 and 0.55 was selected to ensure reasonable workability and prevent segregation or poor compaction. The fresh mortars were cast in 50 x 50 x 50 mm pre-oiled molds and removed after 24 h for curing at a temperature of 23 ± 2 C° until tested for compressive strength at the age of 3, 7 and 28 days. The molds were pre-oiled to ensure the proper removal of the samples from the molds. The compressive strength of the specimens was determined using a constant loading rate of 50 kN/min until failure and the mean was calculated with three specimens for each concrete age.

A total of six different blends were designed and labeled as FA-Raw45, FA-Wash45, FA-Probe45, FA-Probe50 and FA-Probe55 based on their respective types of FA added and W/C. A control mix, OPC45, with no replacement was also cast to serve as the reference. A cement replacement rate of 30% was chosen to maximize the amount and impact of SCM used while ensuring an acceptable concrete quality.

7.2.4 Diffusion test: NEN 7375 monolithic leaching of concrete cubes

The leaching of a monolithic concrete cube under normal exposure conditions is known to be governed by the diffusion process affected by the permeability of the finished product (van der Sloot et al. 2007). The most suitable test to evaluate the leaching behavior of the concrete cube is the tank test based on NEN 7375:2004 (NEN 2005). For the compliance testing, the most promising FA-Probe45 cubes that were cured for 28 days at 23 ± 2 C° and >90% relative humidity (RH) were immersed in DI water at an L/S ratio of 4 and kept in static conditions. At the end of each normalized immersion step (3, 7, 14 and 28 days), the leachate was collected and filtered using a 0.45 µm membrane filter and stored for further analysis.

7.3 Results

7.3.1 Elemental composition and TCLP leaching of treated FA

Table 7-2 shows the TCLP leaching and total elemental composition of various metals for FA Raw, FA Wash and FA Probe. After washing or sonication, the treated FA exhibited higher homogeneity and lower leaching under TCLP in general. It could be seen that with the removal of readily soluble contents such as the chlorides of Na and K, the treated FA became more homogenous and enriched in Ca and Si which could be beneficial for cement replacement (Tan et al. 2016). The leaching of Cr reduced from 18.63% in FA Raw to 8.51% and 8.6% in FA Wash and FA Probe respectively showing that Cr had lower mobility after treatment. The TCLP leaching of Mg also decreased significantly from 12.92% in FA Raw to 1.43% and 3.06% in FA Wash and FA Probe. Although Pb and Zn were present in significant amounts across FA Raw, FA Wash and FA Probe, the amount leached during TCLP was below the detection limit due to the high natural pH of all the FA samples. In general, the treated FA was non-hazardous and suitable for utilization as the leaching of heavy metals would be limited at high pH conditions when mixed with cement. The washing treatment and ultrasound treatment were both effective in treating FA for utilization based on this result.

Table 7-2: TCLP leaching and elemental composition for FA Raw and FA Probe.

Elements	FA Probe			FA Wash			FA Raw		
	TCLP (mg/L)	Elemental composition (mg/kg)	Leach (%)	TCLP (mg/L)	Elemental composition (mg/kg)	Leach (%)	TCLP (mg/L)	Elemental composition (mg/kg)	Leach (%)
Al	0.30	29544	0.02	0.46	31443	0.03	0.28	17966	0.03
Ba	0.21	1060	0.39	0.23	1072	0.44	0.64	674	1.91
Cr	1.43	333	8.60	1.52	357	8.51	1.15	124	18.63
Cu	N.D.	1624	N.A.	N.D.	1649	N.A.	0.13	779	0.33
Fe	N.D.	24059	N.A.	N.D.	22061	N.A.	0.12	9869	0.02
Mg	23.14	15121	3.06	11.52	16166	1.43	47.50	7355	12.92
Mn	N.D.	901	N.A.	N.D.	907	N.A.	N.D.	393	N.A.
Pb	N.D.	3805	N.A.	N.D.	3469	N.A.	N.D.	1815	N.A.
Sr	2.35	274	17.16	2.48	280	17.72	3.04	116	52.45
Zn	N.D.	17600	N.A.	N.D.	18047	N.A.	0.31	7550	0.08

N.D. = below detection limit of ICP-OES (<0.1 mg/L)

N.A. = not applicable due to TCLP leaching amount below the detection limit (<0.1 mg/L)

7.3.2 Effects of different FA treatment on compressive strength

Figure 7-1 (a) to (h) illustrates the 7 days images of all the concrete surfaces before and after compression testing. Typical lateral cracks parallel to the compression force could be observed across all specimens after cracking. From Figure 7-1 (b) and (d) it could be observed that OPC45 and FA-Probe45 remained intact with cracks while Figure 7-1 (f) and (h) showed that FA-Wash45 and FA-Raw45 experienced larger cracks and deformity with parts falling off after the compression test. This indicated FA-Wash45 and FA-Raw45 were more brittle due to the presence of imperfections and the strength might be affected (Ince and Arici 2004).

From Figure 7-1 (a) and (c), it could be seen that OPC45 had no visible voids or imperfections on the surface while some small evenly spread voids could be seen on FA-Probe45 while Figure 7-1 (e) and (g) showed that FA-Raw45 and FA-Wash45 contained a high number of large voids that could be due to the high amount of metallic aluminum (or other non-ferrous metal) which reacted aggressively with mixed with OPC in the following reaction to produce hydrogen gas (Jones 1996):

Even with proper compaction after the mixing, the evolution of the hydrogen gas continued due to the highly alkaline environment produced by the hydration of OPC. These hydrogen gas became entrapped within the matrix and forms a network of bubbles that could result in lower compressive strength and higher permeability. The ultrasound treatment was thought to be effective in promoting the corrosion of aluminum by the elimination of the passivation aluminum oxide film during the cavitation process (Milinchuk et al. 2015). Also, during the ultrasound treatment, the final pH of the slurry was increased to above 12.5 due to the enhanced hydrolysis of other alkaline oxides which further accelerated the corrosion of the aluminum.

FA Raw contained up to 4.52% of Al_2O_3 content based on XRF and is capable of generating up to $28.3 \text{ cm}^3 \text{ H}_2/\text{g FA}$ based on stoichiometric calculations and could cause major detrimental effects on the compressive strength if not treated properly. This result showed that ultrasound treatment or other forms of treatment is necessary to treat the FA before utilization to reduce the amount of hydrogen gas produced.

On top of the visible voids, the color of the 7 days concrete could also be an indication of the rate of the cement hydration. It could be seen that FA-Probe45 appeared to be lighter in color

similar to that of OPC45 while FA-Wash45 and FA-Raw45 showed a darker color which might suggest that the hydration reaction in FA-Wash45 and FA-Raw45 might be delayed and not completed after 7 days of aging.

Figure 7-1: Images of concrete surface before and after compression testing: (a) OPC45 with smooth even surface with no visible voids; (b) OPC45 compression failure with standard cracks developing on one side; (c) FA-Probe45 with low amount of visible voids on the surface; (d) FA-Probe45 compression failure with standard cracks developing along both sides; (e) FA-Wash45 with large amount of larger visible voids on the surface; (f) FA-Wash45 with a crack developing on both sides and across the middle possibly along the large voids; (g) FA-Raw45 with a darker surface with uneven white areas and visible uneven flaws; (h) FA-Raw45 with cracks developing along the two sides.

From Figure 7-2, OPC45 had the highest 3 days, 7 days and 28 days compressive strength at 36.9 MPa, 44.9 MPa and 46.9 MPa respectively. More than 90% of final compressive strength had been reached for OPC45 samples by 7 days. FA-Probe45 showed similar strength growth patterns as the OPC45 with 7 days compressive strength of 34.82 MPa which was also over 90% of its final compressive strength of 36.2 MPa at 28 days. However, FA-Probe45 had a low 3 days compressive strength of 23.6 MPa compared to its final compressive strength due to high cement replacement of 30%. The high level of dilution of OPC reduces the number of hydration products formed at an early age and the increase in the number of heavy metals such as Zn and Pb could also hinder the normal hydration of OPC (Tashiro et al. 1977). However, the FA contained reactive pozzolanic contents that could react with excess portlandite to compensate for the loss in early strength at a later age (Rukzon and Chindaprasirt 2008). From Figure 7-3 (a) and (b), it could be observed that there were no additional defects or cracks

development at 28 days age for both OPC45 and FA-Probe45 indicating that despite the presence of high SO_3 detected by XRF, there was no delayed ettringite formation.

FA-Wash45 showed poor performance in terms of compressive strength and only attained a compressive strength of 26.3 MPa at 28 days which is only half of the control OPC45. The main reason might be due to the weakness caused by the presence of a network of air voids as shown in the finished surface in Figure 7-2 (e) and (g). Another cause could be the new cracks developed at 28 days possibly due to delayed ettringite formation as shown in the 28 days images of FA-Wash45 from Figure 7-3 (c) due to the high content of CaSO_4 present in the FA. In addition to low compressive strength, FA-Wash45 also exhibited the highest variation in compressive strength across all age as shown on Table 7-3 and the coefficient of variation increased from 5.24% to 9.60% and 12.25% at 3, 7 and 28 days concrete age which indicated that possible defects formed as concrete aged.

FA-Raw45 had the lowest 28 days compressive strength of 23.3 MPa. Despite having lesser visible voids than FA-Wash45 and even FA-Probe45, it was believed that the high amount of salt content such as ZnCl_2 could delay the hydration of the OPC and reduce the compressive strength. Another likely cause could be due to the recrystallization pressure from the NaCl and KCl as layers on the pore walls (Lubelli et al. 2006). The crystallization cycle is irreversible and generates a dilating disaggregating effect in the mortar as seen from Figure 7-3 (d).

Table 7-3: Coefficient of variation (%) of OPC45, FA-Probe45, FA-Wash45 and FA-Raw45 at 3, 7 and 28 days concrete age.

Coefficient of variation in compressive strength				
FA-Probe45				
Days	OPC45 (%)	(%)	FA-Wash45 (%)	FA-Raw45 (%)
3	2.27	0.76	5.24	5.32
7	1.29	1.54	9.60	6.39
28	0.61	0.71	12.25	3.52

Figure 7-2: 3, 7 and 28 days compressive strength results of OPC45, FA-Probe45, FA-Wash45 and FA-Raw45 with mean and standard deviation calculated from triplicate values.

Figure 7-3: Images of the concrete after 28 days aging of (a) OPC45 with no visible defects; (b) FA-Probe45 with multiple small air voids evenly spread; (c) FA-Wash45 with large air voids and cracks developing on the surface ; (d) FA-Raw45 with darker surface suggesting that some water might still be left unreacted.

7.3.3 Mineralogy of 7 days concrete powder

Calcium silicate hydrate (C-S-H, $2\theta = 29.1^\circ$), ettringite (15.8°), portlandite ($18.0, 34.1^\circ$), calcite ($29.6, 48.5^\circ$), quartz (26.7°), alite ($C_3S, 31.1^\circ$), belite ($C_2S, 31.1^\circ$) and anhydrite (25.5°) are identified in the XRD patterns (Lee et al. 2017, Qoku et al. 2017, Maddalena et al. 2019, Jansen et al. 2020) of the 7 days concrete specimens prepared as shown in Figure 7-4. A significant quartz peak was detected due to the addition of sand pozzolan in the cement mix and pozzolanic reaction had not taken place yet as it is known to be a slow process occurring at later concrete age.

Strong anhydrite peaks were observed for FA-Probe45, FA-Wash45 and FA-Raw45. This observation agreed with the high sulfur contents found in FA from the XRF results and other studies (Hewlett and Liska 2019). Delay of the hydration of concrete specimens mixed with ashes can be observed based on the relatively higher intensity of C_2S and C_3S peaks as compared to the control OPC45. The retardation in the hydration could be caused by the presence of metals and salts present in the ashes and partly due to the high replacement ratio of 30% used in this study.

Additional peaks of ettringite were also observed for FA-Probe45 but not in FA-Wash45 and FA-Raw45, this result suggested that natural delayed ettringite formation has not taken place yet. The ettringite found in FA-Probe45 was formed during the ultrasound treatment and would not cause any detrimental expansion problem at a later age in agreement with the high 28 days compressive strength from previous results.

Peaks of halite and sylvite were detected for FA-Raw45 as no prior treatments were done to remove these soluble salts. These peaks were not detected in FA-Probe45 and FA-Wash45 and these results suggested that both treatment methods were highly efficient in the removal of chloride salts. It is important as it could be seen from the compressive strength results that chloride salts not only affected the compressive strength but also caused the concrete to disintegrate and fall apart.

Figure 7-4: XRD of 7 days OPC45, FA-Probe45, FA-Wash45 and FA-Raw45.

7.3.4 Leaching stability of FA concrete

Other than compressive strength, the leaching stability of the MSWI concrete is also one major concern for using FA as a construction material. Although it is known that heavy metals concentrations in MSWI concrete will be extremely low due to further fixation and stabilization after binding with the cement matrices. Nevertheless, extra precaution had to be taken as the overall integrity of the concrete might be compromised by cracks or other weathering processes, therefore proper evaluation of risks of leaching from the final concrete product should be studied to account for any possible risk (Bertolini et al. 2004).

The monolithic leaching of different heavy metals from FA-Probe45 was shown in Figure 7-5. The leaching of Cd and Cr were below the detection limit (<0.1 mg/L) while Pb and Zn were 0.31 mg/L and 0.77 mg/L respectively. Most of the leaching occurs during the early stages between 3 days and 7 days but slowed down significantly after 7 days for Pb and Zn indicating a depletion of the available metals for release.

From the literature, it was proven that pure diffusion-controlled release could be implied by a 1:0.5 slope (Van der Sloot and Dijkstra 2004). The leaching curve of Pb at the early stage was parallel to the diffusion slope which suggested that the main release mechanism of the less soluble Pb could be governed by diffusion of the element from the concrete. From the initial release for Zn was likely the surface leaching while it is believed that diffusion was the governing release mechanism at the later stage in between 7 to 14 days as the gradient of the leaching curve of Zn decreased to lower than 0.5.

In general, the leaching amount for all metals was low at the later stage because the diffusion of metals was heavily dependent on the porosity and permeability of the concrete while FA concrete was known to have a reduced porosity and permeability due to pozzolanic reaction between the reactive amorphous Si and excess $\text{Ca}(\text{OH})_2$. The total leaching amount for all metals after 28 days was below the regulatory limits which meant that the solidification of FA Probe with cement was capable of immobilizing the heavy metals while producing a reliable strong and durable construction material.

Figure 7-5: Leaching of Pb and Zn from monolithic concrete leaching with black dotted lines with a slope of 1:0.5 to represent pure diffusion release.

7.4 Conclusion

The feasibility of using treated FA as a construction material was evaluated based on both the structural functionality in terms of compressive strength and environmental issues of leaching of heavy metals. It was found that FA Probe replacement of up to 30% cement was suitable except for a low 3 days compressive strength which meant that the FA concrete might be more suitable for precast purposes. The negative effects of hydrogen production from aluminum in alkaline condition and the expansive durability issue of delayed ettringite formation were eliminated using ultrasound treatment on FA.

XRD of the 7 days concrete powder showed evidence of delayed hydration due to the high replacement rate of FA while proving the ettringite found in FA-Probe45 was likely to be formed during the ultrasound treatment and not a product from the natural aging process as no ettringite peaks were detected in FA-Wash45 and FA-Raw45. Peaks of halite and sylvite were detected in FA-Raw45 but not FA-Probe45 and FA-Wash45 which suggested that both washing and ultrasound treatment were effective in the removal of chlorides which affected compressive strength and caused the disintegration of the concrete at later age due to the recrystallization cycle.

The leaching of Cd and Cr from the FA-Probe45 was below the detection limit while Pb and Zn were well below the regulatory limit. The main mechanism of release from Zn was surface leaching at the early stage (before 7 days) followed by diffusion from the concrete at a later stage (after 7 days) while the release of Pb was mostly associated with diffusion. The total leaching of Cd, Cr, Pb and Zn was low due to the reduced permeability of the FA-Probe45 concrete from the pozzolanic reactions. The leaching test over 28 days confirmed that solidification of ultrasound treated FA further immobilized any leachable heavy metals and can produce an eco-friendlier concrete with sufficient strength for structural applications.

8 Conclusion and recommendations

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8.1 Conclusion

The motivation for this research was to improve the situation of lack of natural resources as construction material and the lack of land for ash landfilling in Singapore. This study explored the use of ultrasound as a treatment to extract various metals and stabilize the fly ash for utilization purposes. This study first characterized both the FA and APC and investigated their leaching properties under different pH conditions when mixed. A preliminary accelerated extraction and stabilization ultrasound procedure was carried out to evaluate the effects on both FA and APC. After the preliminary experiments, FA was selected for treatment optimization in the second part of the study to determine the effects of duration and different leaching agents of different concentrations. The sonicated FA underwent a series of characterizations such as SEM, TEM and XRD to determine the mineralogy changes in addition to conventional leaching tests and total elemental composition evaluation. With the study of mineralogy, this study gave insight into the use of ultrasound in terms of enhanced extraction and accelerated stabilization in terms of ettringite formation. Lastly, the treated FA was utilized in partial replacement for cement and tested for structural strength and environmental stability.

The characterization of FA and APC in Chapter 3 revealed that the composition of many trace elements had lesser variations compared to other countries due to the lack of seasonal changes. FA consisted of a wide variety of major and minor elements $\text{Ca} > \text{Na} > \text{K} > \text{Al} > \text{Fe} > \text{Zn} > \text{Mg}$ and trace elements $\text{Pb} > \text{Ba} > \text{Cr}$ while APC consisted of mainly Ca and Cl with trace amounts of $\text{Zn} > \text{K} > \text{Mg} > \text{Na} > \text{Al} > \text{Fe} > \text{Pb} > \text{Ba}$. It was revealed that FA contained a high amount of amorphous content consisting of spherical Si-rich particles from the XRD and TEM results. pH-dependent leaching of FA and APC also indicated that both FA and APC had high pH but FA had a low ANC while APC had a high ANC which meant that FA was more susceptible to pH changes. It was found that a significant amount of Cr leached from FA and Pb from APC at their natural pH. The mixing of FA and APC could suppress the leaching of Cr in the mixed ash while not increasing the Pb leaching. This result showed that mixing could be appropriate if the disposal was the only option as it increased the ANC to resist natural weathering. However, a better option would be to separate FA and APC if utilization was the goal.

Chapter 4 investigated the effects of ultrasound on both FA and APC with simple DI water washing as a control. It was found that both ultrasound and washing treatments were effective in the removal of highly soluble minerals such as NaCl, KCl and CaClOH as their peaks were no longer detectable by XRD after treatment. Interestingly, the early formation of ettringite

was detected XRD and SEM also indicated the presence of this needle-like micro-ettringite. Improved leaching results from FA showed the potential of using ultrasound as a form of treatment for FA. A significant size reduction effect from the ultrasound could also be useful for the enhanced extraction of selective metals for recovery purposes.

Chapter 5 investigated the extraction yield of different metals under different ultrasound conditions and extracting agents. It was found that an ultrasound duration of 5 mins is enough while 15 mins to 30 mins were optimal for extraction yield while prolonged duration could result in re-adsorption of certain metals. Regardless, all durations of the sonication gave better TCLP leaching results and positive correlation could be seen between duration and stabilization of FA. The use of alkaline agent gave the lowest extraction potential due to the high pH condition and only capable of leaching Pb while acidic agent such as citric and nitrate acid showed much higher extractability with citric acid > nitric acid with higher yield %. However, the usage of acidic leaching agents came with negative consequences as the natural buffering mineral phases in the FA were consumed and thus the FA after acidic sonication showed increased mobility of Zn and Pb. The best extracting agent was EDTA, a chelating agent that showed high extraction yield for most metal without altering the pH condition at 0.10 M concentration. Variation in the EDTA concentrations also showed that a higher amount of EDTA could increase the extraction yield, the ionic abundance was found to be a dominant factor over the EDTA-metal complex stability values as ions with higher abundance and lower stability experience enhanced extraction using EDTA.

Chapter 6 utilized the sonicated FA in partial replacement of cement and achieved higher than 75% of the control's compressive strength of 36.2 MPa by 28 days. Images of the hardened FA Raw and FA Wash samples suggested that large air void due to hydrogen gas generation could be the main cause in lower compressive strength. The FA Raw replacement showed lesser voids but had higher salt crystal contents which resulted in more weakness in the hardened product and an even lower compressive strength of only 23.3 MPa after 28 days. The ultrasound treatment was found to reduce the number of air voids to give higher strength through the reduction of reactive aluminum and accelerated the formation of ettringite to mitigate delayed ettringite formation that could cause long term durability issues. The long-term environmental impacts of FA concrete were also evaluated and the leaching of Cd, Cr, Pb and Zn were found to be of the negligible amount with the majority due to surface leaching.

In conclusion, proper characterization and ultrasound treatment of FA enabled the utilization of FA as a suitable construction material replacement. This study showed that ultrasound treatment can serve as an alternative solution to turn a disposal problem into a construction material. These findings can also help divert the FA away and extend the life span of the expensive offshore landfill in Singapore and provide durable construction material for utilization.

8.2 Recommendation

This study had shown that ultrasound treatment of 15 mins could treat FA by enhancing metal extraction, accelerated formation of stabilizing mineral ettringite and reduction of metallic aluminum from the FA. Since the focus of this study was to understand the enhanced extraction effects and suitability as used for construction material, the mechanism of the mineral formation and the ultrasonic mechanism were discussed based on existing literature but not verified experimentally.

Some recommendations for future studies could be the usage of other chelating agents or combinations of the chelating and acidic agents to get the best extraction outcome while reducing the negative environmental impact. For example, the use of other more chelating agents such as EDDS and DTPA with a combination of acids to adjust the pH for better yield. Also, the study of chelating agent stability under ultrasound condition can be investigated to find out if ultrasound will affect the binding efficiency of chelating agents due to the constant acoustic agitation.

The use of probe sonication device in this study was for maximum power and efficiency but faced the limitation of scaling up while bath sonication devices showed potential in terms of large scale treatment but did not have sufficient intensity to generate transient cavitation. Therefore, the use of multi-frequency ultrasound within a single system can be studied to scale up the current setup for more commercial purposes. Also, due to the lack of proper instrumentation, the study of the effects of different intensity and different frequencies from the same device is not possible for fair comparison and such studies can be further used to optimize the ultrasonic process.

Finally, the formation of various mechanisms and intermediate steps of mineral formation and other adsorption processes can also be studied for a better understanding of the extraction and stabilization effect of the ultrasound process.

APPENDIX

SEM images for 5 mins, 15 mins, 30 mins and 60 mins

SEM Images for different leaching agent

SEM images for Different EDTA concentrations

Metal leaching under variable pH for Mixed Ash

2-way ANOVA of pH level and ash types effects for the total amount of metal leached for As, Ba, Cd, Cr, Cu, Fe, Mg, Ni, Pb

Factor	Type	Levels	Values
pH	fixed	3	high, low, neutral
ash type	fixed	3	APC, FA, mix

Analysis of Variance for As leach

Source	DF	SS	MS	F	P
pH	2	28.224	14.112	12.02	0.020
ash type	2	1.920	0.960	0.82	0.504
Error	4	4.698	1.174		
Total	8	34.842			

S = 1.08373 R-Sq = 86.52% R-Sq(adj) = 73.03%

Analysis of Variance for Ba leach

Source	DF	SS	MS	F	P
pH	2	0.9478	0.4739	3.00	0.160
ash type	2	4.2085	2.1043	13.31	0.017
Error	4	0.6322	0.1580		
Total	8	5.7885			

S = 0.397550 R-Sq = 89.08% R-Sq(adj) = 78.16%

Analysis of Variance for Cd leach

Source	DF	SS	MS	F	P
pH	2	57.959	28.980	8.66	0.035
ash type	2	18.825	9.412	2.81	0.173
Error	4	13.383	3.346		
Total	8	90.166			

S = 1.82913 R-Sq = 85.16% R-Sq(adj) = 70.32%

Analysis of Variance for Cr leach

Source	DF	SS	MS	F	P
pH	2	12.622	6.311	3.67	0.125
ash type	2	9.237	4.619	2.68	0.182
Error	4	6.883	1.721		
Total	8	28.743			

S = 1.31182 R-Sq = 76.05% R-Sq(adj) = 52.10%

Analysis of Variance for Cu leach

Source	DF	SS	MS	F	P
pH	2	3295.4	1647.7	4.59	0.092
ash type	2	641.4	320.7	0.89	0.478
Error	4	1436.3	359.1		
Total	8	5373.0			

S = 18.9490 R-Sq = 73.27% R-Sq(adj) = 46.54%

Analysis of Variance for Fe leach

Source	DF	SS	MS	F	P
pH	2	16352.3	8176.1	9.39	0.031
ash type	2	1740.6	870.3	1.00	0.445
Error	4	3483.7	870.9		
Total	8	21576.6			

S = 29.5116 R-Sq = 83.85% R-Sq(adj) = 67.71%

Analysis of Variance for Mg leach

Source	DF	SS	MS	F	P
pH	2	101176	50588	404.70	0.000
ash type	2	46	23	0.19	0.837
Error	4	500	125		
Total	8	101723			

S = 11.1804 R-Sq = 99.51% R-Sq(adj) = 99.02%

Analysis of Variance for Ni Leach

Source	DF	SS	MS	F	P
pH	2	0.98381	0.49191	5.09	0.080
ash type	2	0.38282	0.19141	1.98	0.253
Error	4	0.38667	0.09667		
Total	8	1.75330			

S = 0.310914 R-Sq = 77.95% R-Sq(adj) = 55.89%

Analysis of Variance for Pb Leach

Source	DF	SS	MS	F	P
pH	2	4793.9	2397.0	11.35	0.022
ash type	2	201.3	100.7	0.48	0.652
Error	4	844.9	211.2		
Total	8	5840.2			

S = 14.5336 R-Sq = 85.53% R-Sq(adj) = 71.07%

Elemental metal composition for 5 mins, 15 mins, 30 mins and 60 mins sonication

Duration	5 mins	15 mins	30 mins	60 mins
Elements	(mg/kg)			
Al	49980	48500	50600	60520
Ba	1998	2144	2216	2560
Cd	320	308	308	354
Cr	364	342	346	428
Cu	2288	2208	2226	2626
Fe	26720	27660	28760	35440
Mg	24340	23220	23940	28060
Mn	1148	1160	1186	1470
Ni	154	160	156	196
Pb	6422	6256	6350	7228
Ti	0	0	0	0
Zn	26700	25320	25600	29900

Elemental Metal composition for different leaching agent

Leaching agent	NaOH 0.1M	Citrate Acid 0.1M	Nitric Acid 0.1M	EDTA 0.1M
Elements	(mg/kg)			
Al	34199	32065	29216	53300
Ba	1431	1538	1577	2336
Cd	195	87	235	94
Cr	247	210	252	390
Cu	1429	739	1409	997
Fe	18942	19360	15730	27540
Mg	15202	11627	13310	24120
Mn	755	822	769	780
Ni	103	125	101	111
Pb	3098	3397	4084	2668
Ti	306	677	313	311
Zn	14240	11132	16456	25540

Photo images of expansion due to hydrogen gas generation

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