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BENEFICIAL UTILIZATION OF MUNICIPAL SOLID WASTE INCINERATION ASHES
AS SUSTAINABLE ROAD CONSTRUCTION MATERIALS

by

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A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Civil, Environmental, and Construction Engineering
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at the University of Central Florida
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2014

Major Professor: BooHyun Nam

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ABSTRACT

Incineration of municipal solid waste (MSW) is common for energy recovery, and management of municipal solid waste incineration (MSWI) ashes has received a growing attention around the world. In the U.S., generation of MSW has increased up to 65% since 1980, to the current level of 251 million tons per year with 53.8% landfilled, 34.5% recycled and composted, and 11.7% incinerated with energy recovery. In the process of incineration, MSWI ash is being produced as byproducts; about 80 to 90% of the MSWI ash is bottom ash (BA) and 10 to 20% is fly ash (FA) by weight. The current practice of the U.S. is to combine both BA and FA to meet the criteria to qualify as non-hazardous, and all combined ashes are disposed in landfills.

European countries have utilized MSWI BA as beneficial construction materials by separating it from FA. The FA is mostly limited to landfill disposal as hazardous material due to its high content of toxic elements and salts. BA has been actively recycled in the areas of roadbed, asphalt paving, and concrete products in many of European and Asian countries. In those countries, recycling programs (including required physical properties and environmental criteria) of ash residue management have been developed so as to encourage and enforce the reuse of MSWI ashes instead of landfill disposal. Moreover, many studies have demonstrated the beneficial use of MSWI ashes as engineering materials with minimum environmental impacts.

On the other hand, the U.S. has shown a lack of consistent and effective management plans, as well as environmental regulations for the use of MSWI ashes., Due to persistent uncertainty of engineering properties and inconsistency in the Federal and State regulations in

the U.S., however, the recycling of the MSWI ashes has been hindered and they are mostly disposed in landfills.

In this research work, current management practice, existing regulations, and environmental consequences of MSWI ashes utilization are comprehensively reviewed worldwide and nationwide with an emphasis of the potential area of its utilization in asphalt paving and concrete product. This research also entails a detailed chemical and microstructural characterization of MSWI BA and FA produced from a Refuse Derived Fuel (RDF) facility in Florida so that the MSWI ash is well characterized for its beneficial uses as construction materials.

The material characterization includes Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray Diffraction (XRD) techniques. In addition, leaching experiments have been conducted to investigate the environmental properties (e.g. leachate concentration) of BA and ash-mixed hot mix asphalt (HMA) and Portland cement concrete (PCC). Leaching results reveals the reduced leaching potential of toxic material from MSWI ashes while incorporated in HMA and PCC. Lastly, a preliminary experimental approach has been devised for the vitrification of FA which is a promising thermal process of transferring material into glassy state with higher physical and chemical integrity to reduce toxicity so that utilization of FA can be possible.

Dedicated to my loving family

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LIST OF ABBREVIATION

APC	-	Air Pollution Control
BA	-	Bottom Ash
BSE	-	Back-Scattered Electron
BUD	-	Beneficial Use Demonstrations
CEN	-	European Committee for Standardization
CEWEP	-	Confederation of European Waste-to-Energy Plants
CFR	-	Code of Federal Regulation
CTL	-	Cleanup Target Level
DSC	-	Differential Scanning Calorimetry
DSPA	-	Dutch Soil Protection Act
DTA	-	Differential Thermal Analysis
EDS	-	Energy Dispersive X-ray Spectroscopy
EPA	-	Environmental Protection Agency
FA	-	Fly Ash
FAC	-	Florida Administrative Code
FDEP	-	Florida Department of Environmental Protection
FDOT	-	Florida Department of Transportation
FHWA	-	Federal Highway Administration
FIT	-	Florida Institute of Technology
GWCTL	-	Groundwater Cleanup Target Levels
HMA	-	Hot-Mix Asphalt
HDPE	-	High Density Polyethylene
ICP-OES	-	Inductively Coupled Plasma Optical Emission Spectrometer
ISWA	-	International Solid Waste Association

JCPDS	-	Joint Committee on Powder Diffraction Standards
LAGA	-	Board of German States of Ministers
LAP	-	Landelijk Afvalbeheer Plan
LEAF	-	Leaching Environmental Assessment Framework
LOI	-	Loss of Ignition
MB	-	Mass Burn
MCL	-	Maximum Contaminants Level
MSGP	-	Multi-Sector General Permit
MSW	-	Municipal Solid Waste
MSWI	-	Municipal Solid Waste Incineration
NF	-	Network Former
NM	-	Network Modifier
NPDES	-	National Pollutant Discharge Elimination System
PCC	-	Portland Cement Concrete
RCRA	-	Resource Conservation and Recovery Act
RDF	-	Refuse-Derived Fuel
RTL	-	Reuse Target Level
SE	-	Secondary Electrons
SEM	-	Scanning Electron Microscopy
SMCL	-	Secondary Maximum Contaminants Level
SPLP	-	Synthetic Precipitation Leaching Procedure
SWANA	-	Solid Waste Association of North America
TCLP	-	Toxicity Characteristic Leaching Procedure
TDS	-	Total Dissolved Solid
T _c	-	Crystallization Temperature
T _g	-	Glass Transition Temperature

T _m	-	Melting Temperature
WET	-	Waste Extraction Test
WTE	-	Waste to Energy
XRD	-	X-ray Diffraction
ZHE	-	Zero-Head Extractor

CHAPTER 1 INTRODUCTION

1.1 Problem Statement

Incineration of municipal solid waste (MSW) with energy recovery and management of municipal solid waste incineration (MSWI) ashes have been receiving a growing attention over the world. Many countries have addressed the issue of beneficial utilization of MSWI ashes by establishing and executing strategic management plans and regulations [1-7]. For example, many European countries have beneficially utilized MSWI bottom ash as a sustainable transportation material with environmental criteria set by their strategic regulations [2-4, 8].

In the U.S., higher amount of MSW are being produced than any other country in the world; however, the recycling rate is considerably low [9]. The total MSW generation in the U.S. has increased up to 65% since 1980, to the current level of 251 million tons per year with 53.8% landfilled, 34.5% recycled and composted, and 11.7% incinerated with energy recovery [10]. The total of 86 MSW Waste to Energy (WTE) plants are being operated in 24 states of the U.S. as of 2010 [11], where major users of MSWI plants are Connecticut, New York, New Jersey, Pennsylvania, and Virginia [6]. Typical residue produced from these incineration plants are MSWI bottom ash (BA) and fly ash (FA), and those are mostly combined to be disposed in lined landfill in the U.S. [7].

In spite of successful demonstration on the application of MSWI ashes in a number of construction projects [3], disposal of ashes has remained a common practice in the U.S. which leads to negative environmental impact associated with landfilling. Therefore, efforts are required to be taken to identify the potential area of beneficial utilization of MSWI ashes such as Hot-Mix Asphalt (HMA) and Portland cement concrete (PCC). Chemical and

environmental properties associated with those applications are also needed to be addressed so that sustainable utilization of MSWI ash can be ensured.

1.2 Objectives and Overview

In this study, the current practices and environmental consequences of MSWI ash management were comprehensively reviewed, emphasizing the potential area of its utilization in asphalt paving and concrete product. In order to find out the appropriate applications of MSWI ashes utilization, characterization of chemical and microstructural properties were conducted with MSWI ashes from one of the incineration facilities in Florida, U.S. Florida owns the largest number of MSW WTE plants (11 facilities) in the U.S. [6]. This Thesis presents: (1) a comprehensive review on the MSWI ash regarding environmental and engineering properties, (2) MSW management practices in the U.S. and other countries, (3) characterization of MSWI bottom and fly ashes by spectroscopic techniques and microanalyses, and (4) leaching properties and behaviors of HMA and PCC containing MSWI BA. Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray Diffraction (XRD) techniques were employed. The expected outcomes of this research study are:

1. Comprehensive review of current management practice, existing regulations, and environmental consequences of MSWI ashes utilization;
2. Detailed chemical and microstructural characterization of MSWI BA and FA produced in Florida, U.S. using SEM, EDS, and XRD techniques;
3. Environmental properties and impacts (such as leachate concentration) of BA and ash-mixed HMA and PCC using Synthetic Precipitation Leaching Procedure (SPLP);

4. Preliminary study of MSWI FA vitrification technology and recommendation for future research on optimization of composition compatible to glass and glass ceramic formation from MSWI FA.

1.3 Organization of the Thesis

Apart from this chapter, the remainder of the thesis has been divided into six chapters. Chapter 2 represents the overview of the incineration technologies, brief discussion on the properties of MSWI ashes and extensive review on the management practice of MSWI ash utilization and environmental regulations in different countries.

Chapter 3 presents extension of review on the beneficial utilization of MSWI ashes in concrete, asphalt, road paving applications. In this regard, innovative vitrification technology was also introduced. Later section in this chapter includes the review on the leaching test procedure commonly practiced in the U.S. and the leaching of MSWI ashes while using as road construction materials.

Chapter 4 includes the microstructural evaluation of MSWI ashes using SEM, compositional analysis using EDS, and mineralogical analysis using XRD techniques. Furthermore, it covers the chemical characterization of MSWI ashes by conducting laboratory chemistry experiment.

Chapter 5 discusses the leaching evaluation of MSWI BA in HMA and PCC. Leaching characteristics of inorganic constituents from MSWI ashes while using in HMA and PCC have been investigated by using the SPLP test conducted in the laboratory.

Chapter 6 presents the scientific concepts of energy-saving vitrification techniques for MSWI FA. Preliminary data from initial laboratory works and future research plan on vitrification are also presented.

Finally, chapter 7 presents the major conclusion of the study and also provides recommendations for the further study. Attempts are made to draw conclusions from various findings of the study and recommendations provide a basis of further study.

CHAPTER 2 LITERATURE REVIEW- MANAGEMENT PRACTICE OF MSWI ASHES

2.1 Introduction

As the volume of waste generation in the U.S. has continued to raise, the emerging concern of the management of MSW tend to adopt incineration technology that reduces waste to ash by about 75% and also generate energy during the combustion process. Thus produced ash is referred to as MSWI ash, which is different from coal FA. The coal FA is a byproduct of pulverized coal combustion in electric power plants and widely known as supplementary cementitious material in concrete manufacture. Most of the modern incinerators, however, are equipped with an energy recovery scheme; thus, also known as WTE plant. In the process of incineration, about 80 to 90% of the MSW by weight are BA and 10 to 20% are FA [2].

Many European and Asian countries have addressed the issue of potential reuse of MSWI ashes by executing strategic management plans, and especially, utilizing BA as sustainable transportation material based on environmental criteria set by their strategic regulations. On the other hand, the U.S. is limited to the disposal of MSWI ashes into landfill which is third largest sources of greenhouse gas emission in the U.S. [12]. Both BA and FA are combined mostly in the U.S. to meet the criteria to qualify as non-hazardous, and most of them are disposed in landfills.

In this chapter, relevant literature on incineration of MSW, incineration technologies, and chemical and physical properties of MSWI ashes have been thoroughly reviewed. This chapter also provides extensive review of management practice and environmental regulations of MSWI ashes in European and Asian countries, and the U.S.

2.2 Municipal Solid Waste Incineration Ashes

Broadly, BA, FA, and air pollution control (APC) residue are the main products of MSWI. BA is referred to as grate ash discharged from the furnace grate and collected in the water quenching tank. During the process, the BA is combined with grate shifting (fine particles falling through the furnace) and heat recovery ash (particulate matter collected from the heat recovery system). FA is fine particles carried over the furnace and separated prior injecting sorbents to treat the gaseous effluent. Gas condensate and reaction products are produced from APC devices, such as electrostatic precipitator, scrubber, etc. APC residue is then produced by combining the FA, sorbents, gas condensates, and reaction products together in APC devices. In the U.S., most MSWI plants combine BA and FA from APC devices in one stream [3, 13] referred to as combined ash, unlike European countries where ashes are separately managed.

In the past, the major concern with the MSWI was associated with air pollution by dioxin ($C_4H_4O_2$), furan (C_4H_4O), and heavy metals originated from MSW [13]. Later, the emission was reduced drastically by implementing APC devices to treat toxic flue gases with sorbents using dry/semi dry and wet scrubber systems [2, 5, 13]. The employment of APC devices, therefore, shifted the concern from air pollution to the leachate from disposal of MSWI ashes into landfill.

2.3 Overview of Incineration Technology

Solid waste has been converted to beneficial material over 100 years. Incineration of municipal solid waste with energy recovery (now known as WTE) has been accepted as safe, effective, and environmentally sound technology. The established large-scale waste processing technologies are, in general:

1. Mass Burn (MB) Incinerator
2. Modular Incinerators
3. Refuse-Derived Fuel (RDF) Incinerator
4. Fluidized Bed Incinerator

2.3.1 Mass Burn (MB) Incinerators

A mass burn technique is the incineration of MSW without prior processing or separation scheme. Most mass burn plants, however, separate the non-combustible steel and iron for recycling using magnetic separation processes before the incineration [2, 8].

In a typical massburn incineration (Figure 2.1), MSW to be incinerated is collected onto a tipping floor or storage pit so that sufficient waste input is ensured for continuous operation of incineration. The storage pit also facilitates the removal of large non-combustible materials from the waste and uniform mixing of waste. The fairly mixed waste is then transferred to charging hopper which is used for maintaining a continuous feeding of waste into the incinerator. Waste is then undergoes gravity fall onto the moving stoker (also referred to as grate system) at the bottom of incineration chamber where incineration takes place.

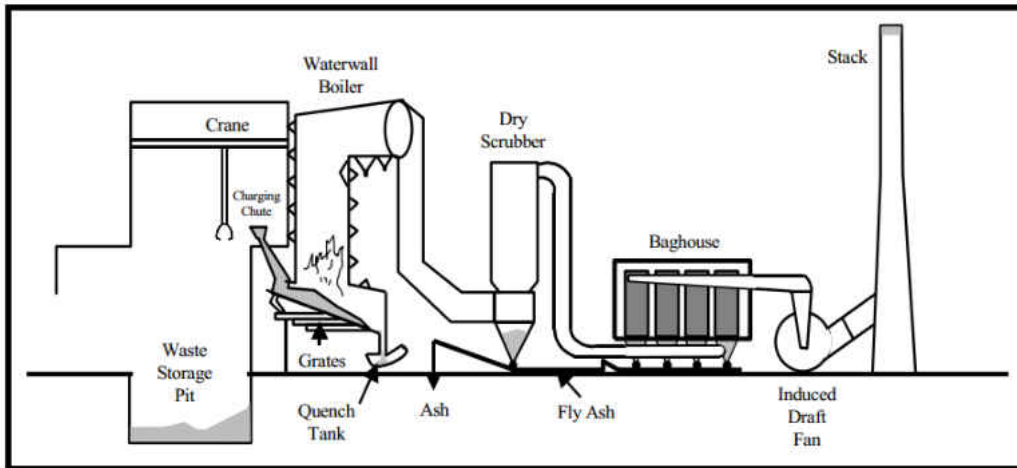


Figure 2.1: Key feature of a massburn incinerator system [14]

A stoker is a grate system that allows the solid fuel to move through the incineration chamber [2, 14]. In general, the system of grates in large-scale massburn incinerators are movable (vibrating, rocking, reciprocating, or rotating) to provide agitation to the wastes, thereby promoting combustion as seen in the Figure 2.2. The movement also facilitates the removal of the residue from the incineration chamber.

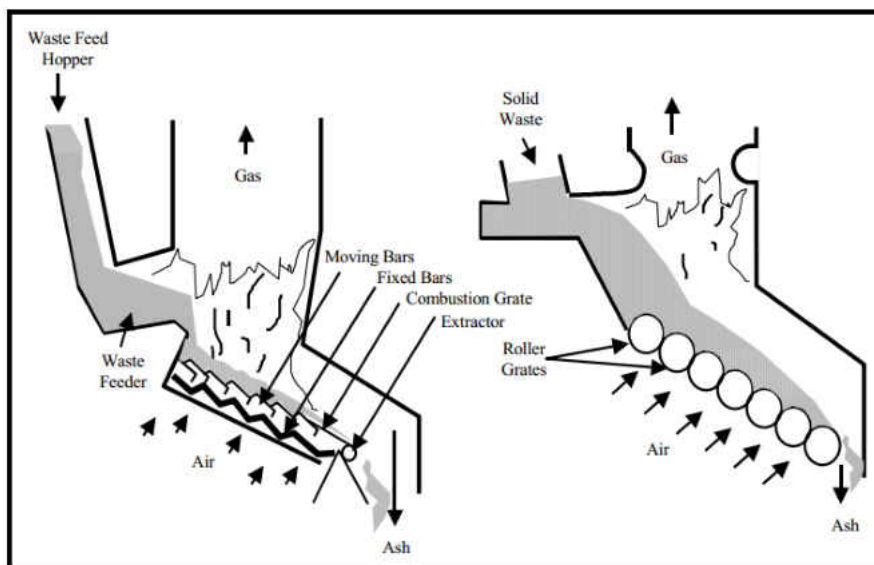


Figure 2.2: Moving grate systems used in massburn MSW incinerators [14]

2.3.2 Modular Incinerators

Modular incinerators are the small scale mass burn facility with a capacity of 15 to 100 tons of waste incineration per day [2]. Modular incineration facilitates two combustion chambers where gases generated in the primary chamber are transferred to the secondary chamber in order to ensure complete incineration [2].

2.3.3 Refuse-Derived Fuel (RDF) Incinerators

Over one-fifth of the U.S. municipal solid waste incinerators use RDF [14]. RDF incineration process offers extensive preprocessing of solid waste before its incineration. Pre-processing includes removal of non-combustible items, such as glass, metals and other recyclable materials. The residual solid waste is then shredded into smaller pieces for incineration. Sometimes RDF materials are compacted at high pressure to produce fuel pellets. Therefore, the unique feature of RDF systems is in the pre-processing of waste as seen in the following diagram of a typical RDF processing facility in Figure 2.3. Entering MSW passes through pre-trommel, followed by passing through secondary trammel, and then going to the shredder. A magnetic separator removes ferrous metals and the balance of the material is fired in the furnace. Due to the processing of waste input, RDF process entails the reduced potential of the heavy metal emissions from the incinerators. These may reduce the heavy metal content of MSW as follows: lead 52%, cadmium 73%, chromium 63% [15].

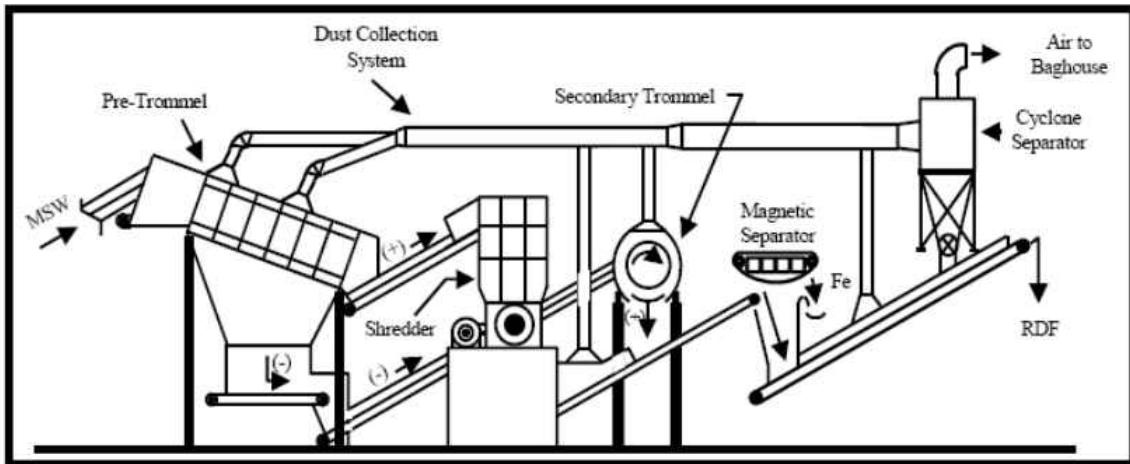


Figure 2.3: Typical RDF processing facility [14]

RDF incineration process design is similar to the massburn facility. There is, however, some key distinctions between the designs [2, 14]. RDF incinerators usually have a travelling grate at the bottom of the incinerator in order to allow continuous travel of finer feed particles, as opposed to the moving or agitating grates incorporated in massburn incinerators. Besides, pneumatic or high velocity mechanical injection type feeding system is associated with RDF combustion systems whereas massburn facilities use gravity driven charging hopper. RDF incineration schematic is presented in Figure 2.4.

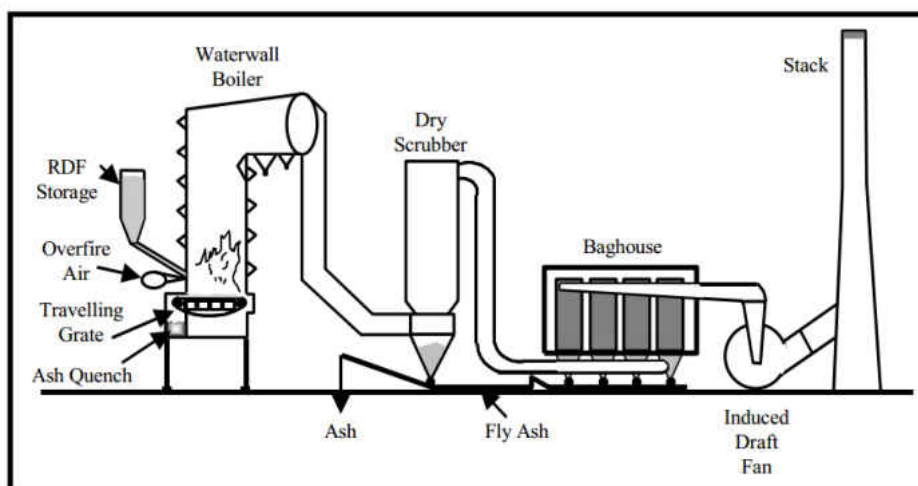


Figure 2.4: Key features of RDF incineration system [14]

The stoker commonly employed stoker system in large RDF incinerators is a travelling grate which consists of a set of hinged grate sections, configured as a conveyor belt as shown in Figure 2.5.

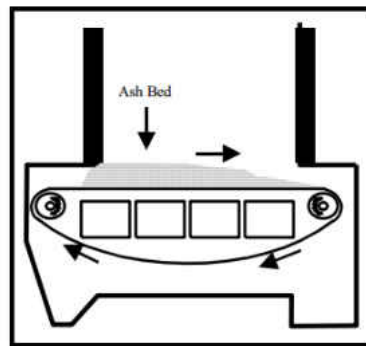


Figure 2.5: Travelling grate system used in RDF-fired incinerators [14]

2.3.4 Fluidized Bed Incinerators

In a fluidized bed incinerator, solid waste is incinerated within a chamber containing a high temperature bed of a fluidized, granular, noncombustible medium, such as sand. This technique offers almost complete incineration of solid waste by providing intimate contact with hot bed medium in the incineration chamber which results in little residual unburned carbon. Design concept for fluidized bed incineration requires particulate type feed input. Thus, RDF is the typical form of solid waste that is supplied to fluidize bed combustion units as shown in Figure 2.6.

Although fluidized bed incinerator is associated with higher cost than massburn units, it certainly offers few advantages over the latter in terms of higher thermal efficiency, lower unburned residual ash and low emission of air pollutants [2, 14].

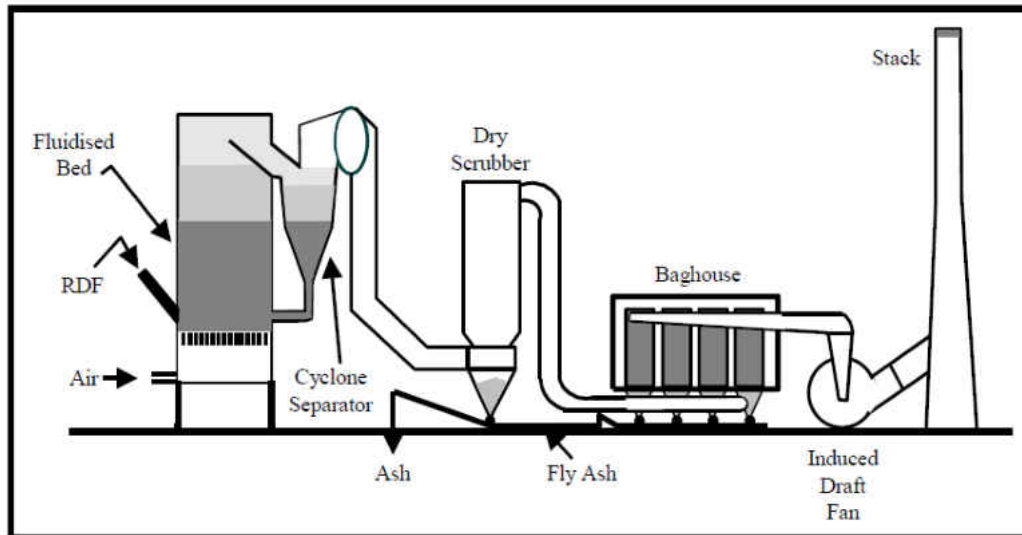


Figure 2.6: Key features of RDF-fired circulating fluidized bed combustion system [14]

2.4 Properties of MSWI ashes

Based on historical data [1, 2], different elemental compositions of MSWI ash products, BA, FA, and APC residues, were investigated and they are summarized in Table 2.1.

2.4.1 MSWI Bottom Ash

MWSI BA is the major by-product residue of the MSWI process (85-95 wt. %) and is a porous, grayish, and coarse gravel material, containing primarily glasses, ceramics, minerals, ferrous and non-ferrous materials with small contents of unburned materials, and organic carbon [2, 3]. Major forms of compounds are oxides, hydroxides, and carbonates. According to research studies using different spectroscopic analyses [16-19], the main compounds (> 10 wt. %) of BA are SiO_2 , CaO , Fe_2O_3 , and Al_2O_3 , whereas Na_2O , K_2O , MgO , and TiO_2 are found in minor concentrations (0.4-5.0 wt. %), as predominant form of oxides. SiO_2 is found to be predominant compound in BA, which constitutes up to 49% [20]. Ba, Zn,

Cl, Mn, and Pb are trace elements (< 1 wt. %) as shown in Table 1. S is found in minor concentrations in the fine fractions (< 1 mm) [16]. The presence of trace and minor elements (Pb, Cl, and S) in smaller particles is reported to be attributed to the deposition of such elements onto particles with higher surface area [2]. The BA has a pH ranging from 10.5 to 12.2, partly due to the presence of hydroxide formation of CaO [2].

Table 2.1: Elemental compositions of MSWI Ash residues (mg/kg) [1, 2]

Element	BA	FA	APC residue (dry/semi dry system)	Wet APC residue (excluding FA)
Ag	0.29-37	2.3-100	0.9-60	-
Al	22,000-73,000	49,000-90,000	12,000-83,000	21,000-39,000
As	0.12-190	37-320	18-530	41-210
B	38-310	-	-	-
Ba	400-3,000	330-3,100	51-14,000	55-1,600
C	10,000-60,000	-	-	-
Ca	37,000-120,000	74,000-130,000	110,000-350,000	87,000-200,000
Cd	0.3-71	50-450	140-300	150-1,400
Cl	800-4,200	29,000-210,000	62,000-380,000	17,000-51,000
Co	6-350	13-87	4-300	0.5-20
Cr	23-3,200	140-1,100	73-570	80-560
Cu	190-8,200	600-3,200	16-1,700	440-2,400
Fe	4,100-150,000	12,000-4,4000	2,600-71,000	20,000-97,000
Hg	0.02-7.8	0.7-30	0.1-51	2.2-2,300
K	750-16,000	22,000-62,000	5,900-40,000	810-8,600
Mg	400-26,000	11,000-19,000	5,100-14,000	19,000-17,0000
Mn	83-2,400	800-1,900	200-900	5,000-12,000
Mo	2.5-280	15-150	9.3-29	1.8-44
N	110-900	-	-	1,600
Na	2,900-42,000	15,000-57,000	7,600-29,000	720-3,400
Ni	7-4,300	60-260	19-710	20-310
O	400,000-500,000	-	-	-
P	1,400-6,400	4,800-9,600	1,700-4,600	-
Pb	98-14,000	5,300-26,000	2,500-1,0000	3,300-22,000
S	1,000-5,000	11,000-45,000	1,400-2,5000	2,700-6,000
Sb	10-430	260-1,100	300-1,100	80-200
Se	0.05-10	0.4-31	0.7-29	-
Si	91,000-310,000	95,000-210,000	36,000-120,000	78,000
Sn	2-380	550-2,000	620-1,400	340-450
Sr	85-1,000	40-640	400-500	5-300
Ti	2,600-9,500	6,800-14,000	700-5,700	1,400-4,300
V	20-120	29-150	8-62	25-86
Zn	610-7,800	9,000-70,000	7,000-20,000	8,100-53,000

With respect to the utilization of BA, important properties of BA are loss on ignition (LOI) and presence of metallic Al. A study in Denmark [2] reported that the mean value of

BA LOI varies from 1.9 to 6.3% based on the efficiency of the incineration process. Modern MSWI plants facilitate proper incineration that results in lower LOI, where the LOI less than 3% is indicative to satisfactory burn out [2]. On the other hand, the presence of metallic Al is one of the biggest hindrances of BA utilization in PCC due to the evolution of hydrogen gas originated from the reaction of metallic Al [2, 8, 21-25]. However, it has been reported that if the BA ash is separated from grate shifting that contains more metallic Al content, the problem of metallic Al can be greatly reduced [2].

Despite of the fact that the BA has considerable amount of heavy metals, due to the relatively low level of leaching potential, the BA is often considered as a benign material. The aging and weathering processes of BA can further reduce the reactivity and potential of heavy metal release by the reaction between CO₂ and water, which form stable complex compounds in BA [26-30]. Aging is also known to transform metallic Al to stable Al₂O₃, thereby reduce the potential of hydrogen gas formation [2, 31]. Therefore, the aging and weathering of BA can eventually improve the quality of BA, making its recycling a viable option in the area of road construction material.

2.4.2 MSWI Fly Ash

In general, MSWI FA is referred to as the entire ash residues from the APC devices. Hence, properties of FA greatly vary with different APC systems, such as dry/semi-dry or wet scrubber equipped with electrostatic precipitator or fabric filter [2]. The FA is characterized with fine particulate matters, dusty appearance with gray to dark gray color [2, 32]. The FA mostly contains oxide form of calcium, different metal salts, chloride compounds, and heavy metals [2, 20]. The major elements found in FA are O, Cl, Ca, Fe, Al, Na, K, Ph, Zn, and S, whereas trace elements are Hg, Cd, Cr, Ni, As, and Co as listed in

Table 1. CaO is found to be predominant compound in FA, which constitutes up to 46% [20]. When FA is subjected to a treatment with lime (CaO) scrubber, Ca(OH)₂ is obtained as end product [2].

FA is generally considered more toxic material than BA, because the FA comprises higher concentration of heavy metals, salts, and organic micro-pollutants due to the volatilization and condensation of different elements during the incineration [20, 33, 34]. Due to the presence of highly soluble salts, Cl, and heavy metals, the FA is not considered for direct utilization as transportation materials [2, 3, 5, 20]. Especially, high content of Cl in FA may increase corrosion probability of reinforced concrete structure when mixed with cement. In addition, when the FA with lime scrubber treatment is incorporated in construction materials, the workability is considerably reduced due to the high water absorption characteristic of hygroscopic CaCl₂ [2]. Moreover, similar to the BA, large content of metallic Al in FA makes the utilization of FA uncertain [35-37].

The presence of readily soluble salt, such as Cl and Na in FA can significantly contaminate drinking water system [20, 33]. Although dioxin and furan do not leach easily, high potential of heavy metals and trace metals is another concern that can pose a threat to human health [5, 7, 20]. In order to reduce the adverse effect of FA, different treatment techniques are being practiced. These treatments are (1) extraction and separation using water or acid [5], (2) chemical stabilization using carbon dioxide/phosphoric acid (CO₂/H₃PO₄), ferrous sulphate (FeSO₄) [5], sodium sulfide (Na₂S) [5], and orthophosphate (PO₄³⁻) [2], (3) solidification using lime, cement, asphalt, and gypsum [5, 8], and (4) thermal treatment, such as vitrification and pyrolysis [2, 5].

2.5 Management Practices of MSWI ashes

Confederation of European Waste-to-Energy Plants (CEWEP) [38] reported that around 371 WTE plants treated approximately 85% of the total MSW in Europe during 2001 to 2011. As a result, incineration and recycling were increased by 7% and 12%, respectively, and landfilling was reduced by 19% [38]. Figure 2.7 shows MSW production and recycling in European countries in 2003 [4] and in the U.S. [10, 39]. Compared with other European countries, the U.S. is the highest waste-generation country [9] but has very low recycling in terms of ferrous and non-ferrous metal removal only. Most countries consider the separation of BA from FA and APC residue, and employ separate treatment schemes for utilization of BA and for environmentally safe landfill of FA and APC residue with least leachability [3-5]. In the U.S., on the contrary, most MSWI plants combine BA and FA in one stream and disposed in landfills [3, 13].

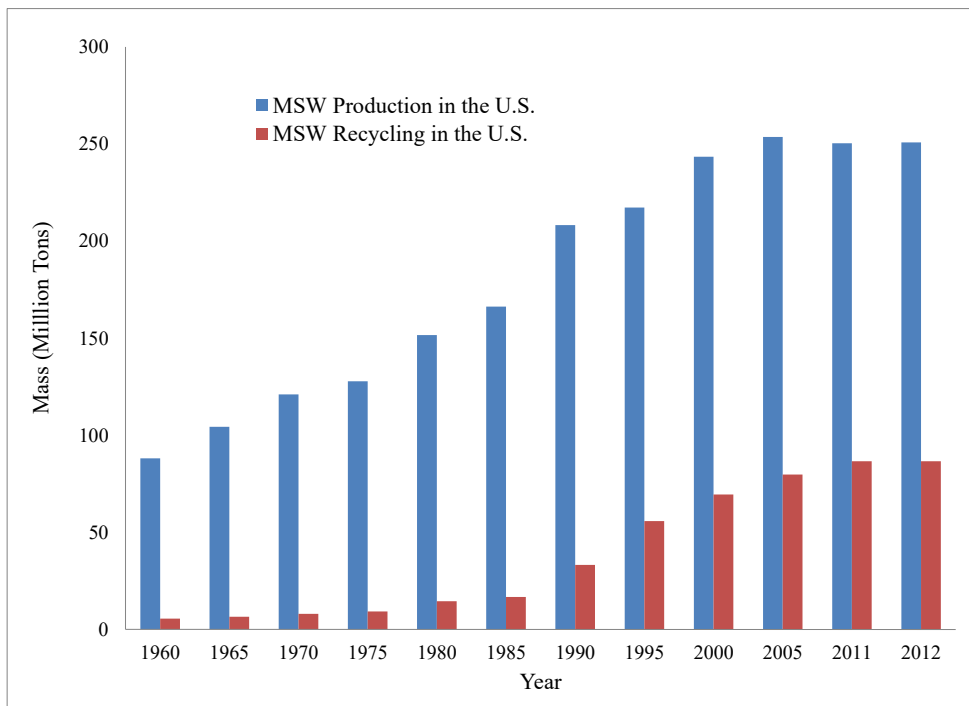
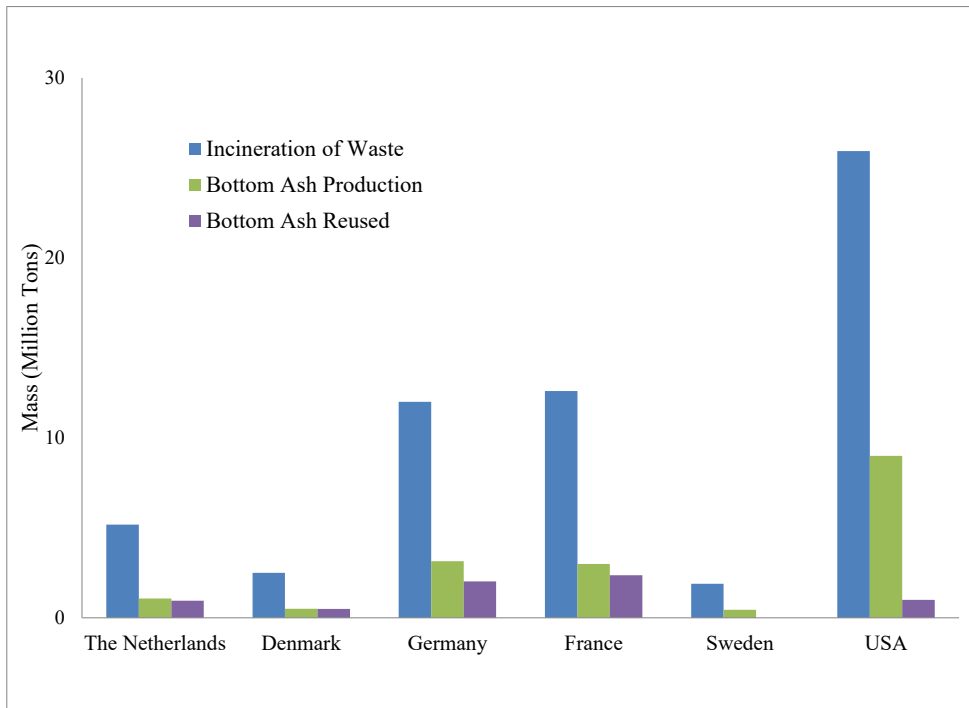


Figure 2.7: MSW management in European countries in 2003 and in the U.S. [4, 39] (top) and in the U.S. [10] (bottom)

The managements of MSWI ash in several countries, including European countries, Japan, and U.S. are summarized below.

2.5.1 The Netherlands

Approximately 80% of the BA produced is recycled in civil engineering purpose after certain treatment scheme, such as ferrous and non-ferrous metal recovery and size reduction [4]. It is encouraged to use BA, considering it as a special category for the application as embankment fill, road base, and disposal into landfill [4]. Only the Netherlands among European countries utilizes FA in a small extent [3, 5]. About 30% of FA and APC residue are used as filler material in asphalt as the alternative of limestone [5]. Significant part of these residues has been exported to German and used as backfilled material in coal and salt mines [5].

2.5.2 Denmark

BA is considered as a suitable gravel substitute as subbase material when used with asphalt or concrete cover to avoid a direct contact with soil and water [4]. Denmark aimed at recycling 98% of BA into building and road construction and embankment fill after screening, crushing, and ferrous metal recovery [4]. APC residues, including FA and acid cleaning end product are considered as special hazardous waste, required to landfill after treatments [5]. Denmark exports APC residue to Norway for the use in neutralizing acid waste or to Germany in order to use as backfill in salt mines [5].

2.5.3 Germany

Germany recycles BA about 65%, while landfills 28% after the reduction of salt content by water quenching, followed by ferrous and non-ferrous metal recovery and 3-

month maturation [2, 4]. A reduction in leaching potential makes BA suitable for the utilization as road construction and secondary building materials [3, 8]. Salt content of ash and dry scrubber residues are subjected to backfill in the old mines to prevent subsidence [3, 5]. Small quantity of APC residue is disposed into landfill after stabilization [5].

2.5.4 France

France recycles 79% of BA produced in the civil constructions [4]. BA treatments involve ferrous and non-ferrous metal removal, size reduction, and sometimes cement stabilization [4]. APC residue management is mostly done by cement and chemical stabilization using NaHCO_3 , and disposal into landfill designated for hazardous waste [5]. Thermal treatment is also considered as a new option for ash treatment, which is not very common, yet [5].

2.5.5 Sweden

Having enough natural resources accompanied by less incentive of ash utilization, BA and FA are collected separately, and BA is disposed into the landfills without any treatment [4]. On the other hand, FA is disposed in the special lined landfill or cell after treatments [3]. Sweden exports their APC residues to Norway for neutralization of acid waste and landfilling after solidification and stabilization [5].

2.5.6 Japan

Due to a very large number of incinerators, a great amount of ashes is being producing, and lack of land space for landfilling makes Japan to predominantly practice thermal and melting treatment of MSWI combined ashes [40-42]. FA is permitted to be disposed in landfill after melting, followed by solidification or stabilization with cement or

chemicals and acid or solvent extraction [5]. Molten slag produced from the melting processes are considered for civil engineering application, such as filler material, interlocking blocks, roadbeds, and aggregate for asphalt paving [3].

2.5.7 United States

Combined ash (mixed BA and FA) are mostly disposed in landfills. Predominant method for the management of combined ash is disposal in monofill, lined with clay, synthetic liners, or a combinations of those methods that is associated with the facility for leachate collection and treatment scheme [3]. Currently, there is no recycling of MSWI ash; instead, ash management only involves with preprocessing, such as recovery of ferrous metals using magnetic separators and non-ferrous metals using an eddy current in facilities incorporated with incineration plants [1, 3, 7].

Although currently there is no recycling of combined ash or BA as a road construction materials, field research and demonstration projects for the beneficial use of ash have been conducted over 25 years in the U.S. [3]: (1) geotechnical applications, including base and subbase, embankment [43, 44], (2) hot-mix asphalt [45, 46], and (3) Portland cement concrete [3, 46]. BA and combined ash used as asphalt pavement aggregate, Portland cement concrete, block aggregate, structural fill, landfill cover, and road base as gravel replacement in the U.S. are summarized in Table 2.2 [3, 43].

Table 2.2: Research projects on MSWI ash as road construction materials in the U.S. [3, 43].

Utilization area	Location	Description	Report	
Hot Mix Asphalt	Houston, TX	300 feet of test section, 6 inch base course contained 100% ash aggregate, 9% binder, 2% lime	Excellent	
	Philadelphia, PA	900 feet test section, 1 ½ inch surface course contained 50% replacement of rock with ash, 7.4% binder, lime 2.5%	Acceptable	
	Delaware County, PA	60 feet test section, 1 ½ inch surface course contained 50% replacement of rock with ash, binder content 7%, lime 2.5%	Acceptable	
	Harrisburg, PA	test road section 220 feet long		Poor
		1 ½ inch surface course, vitrified ash 100% aggregate, binder content 6.7%, no lime addition		Vitrified ash, excellent
	Washington, DC	400 feet of 4 ½ inch base course with ash as 70% and 100% aggregate, binder content 9%, lime 2%	Good	
	Albany, NY	Replacement of gravel as subbase in a parking lot, 2 ½ inch wearing course of asphalt concrete, 12 inches BA after ferrous recovery placed on geotextile filter membrane	Good physical condition, Environmental: groundwater testing, no hazard found	
	Tampa, FL	McKaynite, proprietary aggregate processed by crushing, screening and chemically stabilizing the combined ash, 5%, 10%, 15% replacement in sand component in 500 feet test section each	Up to 10% replacement was satisfactory, beyond this mix proportion it introduced some wear	
	Shelton, CT	BA passing ¾ inch screening and 50% mixed with gravel as structural fill of 3 meter depth	BA acted satisfactorily as structural fill and bituminous pavement	
	Laconia, NH	BA replaced 50% of natural aggregate in asphalt pavement binder course	No environmental hazard	
Concrete	Honolulu, HI	Combined ash placed on an up ramp	Ash was too wet for bitumen, but with reduced ash content, suitable mixture can be obtained	
	Albany, NY	After ferrous removal and size reduction at smaller than ¾ inch, BA replaced all coarse and partial fine aggregate in concrete block foundation	Excellent, no ground, water and air pollution	
	Rochester, MA	Boiler Aggregate, BA processed by ferrous removal and screening, used in concrete block for building frontage and concrete curbing	No environmental risk	
	Long Island, NY	Processed after ferrous recovery and screened to size, stabilized BA and combined ash (85% ash and 15% type II portland cement) used in masonry blocks and artificial reef	Blocks were stronger than original concrete blocks. No ground/water pollution	
	Montgomery County, OH	BA, before and after ferrous removal, used as aggregate in building blocks. Spalling was observed due the ferrous metal for the former condition	Ferrous metal recovery is effective before use of BA in block manufacturing	
	Los Angeles, CA	90% ash, smaller than 1 inch, mixed with 10% type II portland cement. Cured blocks were crushed to gravel size aggregate to use as road surface	Satisfactorily acceptable	
	Ruskin, FL	Ash used as partial replacement of coarse aggregate in portland cement mix	Acceptable	
	Islip, NY	Combined ash treated with portland cement in a patented process, named as Rolite, used as gas venting layer at landfill and lightweight fill in closed area	Acceptable	
	Palm Beach, FL	waste tire-clad and concrete log with ash aggregate content, named as Tirelog, used as reef barrier and highway guard rail	Feasible	
	Landfill Cover	Honolulu, HI	Combined ash used as landfill cover at landfill	Very well performance
Blydenburgh, NY		portland cement treated combined ash, Rolite was used as landfill cover	Feasible	
Embankment Fill	Pinellas County, FL	Phosphate treated (WES-PHix process) combined ash was used as embankment fill	Acceptable	

2.6 Environmental Regulations of MSWI Ashes

European countries have implemented more strategic and scientific regulations for MSWI ash management compared to those of U.S. Environmental regulations in European countries are based on leaching criteria set by standard test procedures [4] for beneficial utilization of BA and disposal of FA after treatments. In the U.S., on the contrary, BA and FA are combined to be disposed as combined ash. Environmental regulations of MSWI ashes in European countries and U.S. are summarized below.

2.6.1 The Netherlands

It is encouraged to use BA as embankment fill and road base with ensuring minimum rain water infiltration [4]. The regulatory framework, Federal Waste Management Plan (Landelijk Afvalbeheer Plan, LAP) does not permit mixing of BA and FA [3, 4] and Dutch Waste Incineration Directive requires the LOI to be less than 5% [4]. Based on the standard column leaching test (NEN 7343, liquid/solid ratio (L/S) = 1-10) [47], two utilization categories (1 and 2) are distinguished for the BA application of maximum 15-m layer [4]:

- There is no restriction for category 1 with allowed filtration of 300 mm/year.
- Utilization is restricted for category 2 with allowed filtration of 6 mm/year through the liners.

Since high leaching of Cu and Mo from BA hardly meets the leaching criteria for the category 2 utilization, Dutch Ministry of Environment consider MSWI BA as special category with less stringent leaching criteria for Cu, Mo, and Sb, in order for the continuous utilization of BA [4].

2.6.2 Denmark

European Committee for Standardization (CEN) sets three categories, 1 to 3, based on the leaching criteria using the compliance standard batch leaching test (CEN prEN 12457, L/S = 2,) [48]. Categories 1 and 2 have the strict leaching criteria, while category 3 has lenient criteria. MSW ash is categorized as soil and inorganic residue; BA mostly falls under category 3 and never falls under category 1 due to the high inorganic constituent. Some of the details of the regulations are as follow [3, 4]:

- Category 2 BA can be utilized in roads, paths, cable graves, floors and foundations, parking lots, noise banks, and ramps.
- Category 3 BA is not allowed to utilize in parking lots, noise banks, and ramps.
- Ash residue can be applied to dikes, dams, and embankments with the approval from Danish Environmental Protection Act [4].
- All MSWI ash application should be covered with liner.
- Utilization site has to be remote from drinking water well over 30 m.
- BA should be placed above the ground water table.
- The average thickness of the BA layer should be 1 m, while thickness requirements for the specific applications are: 0.3 m for path, 4 m for ramps, and 5 m for noise bank.

Danish Highway Department also set some performance criteria for BA use as subbase in road construction:

- Maximum particle size should be 50 mm.
- Fine contents should be less than 9% below 0.075 mm and less than 8% below 0.063 mm.

- Water content range should be between 17 and 25 %.

However, according to Danish Soil Pollution Act [4], it is recognized that BA utilization area was determined as contaminated land that pose obstacle for BA beneficial use.

2.6.3 Germany

Despite having state wide variation in regulations, Germany encourages the research and development in an effort to improve treatment techniques, separation schemes, and beneficial utilization of MSWI ash [3, 4]. Based on the German regulation set by Board of German States of Ministers (LAGA) [4], BA is required some treatment schemes before utilization as road construction:

- Reduction of salt content by water quenching.
- Ferrous and non-ferrous metal recovery.
- 3-month maturation.
- Meeting the standard leaching criteria based on batch leaching test (DEV S4, L/S = 10) [49]
- Total organic carbon content should be less than 1.0 wt. %.

In addition, ash beneficial use as secondary building material is required to meet additional standard for mechanical properties [4, 8], including density, mechanical strength, grain size distribution, and freeze-thaw-stability.

2.6.4 France

Standard batch leaching test (NF X31-210, L/S = 20) [50] has been designed to classify BA in three categories, V, M, and L, for the utilization in civil application.

- Category V: BA with low leaching potential for immediate use as road base.
- Category M: after 12-month maturation, BA should be tested to confirm if the material is eligible for reuse.
- Category L: must be landfilled.

It has been reported that after 9 months of maturation, BA mostly meet category V, exhibiting least leaching potential [4]. In order to utilize those BA with 9-month maturation, however, additional requirements must be met [4]:

- Physical and chemical data of aged BA must be documented.
- Embankment thickness should be less than 3 m.
- Application should be limited in area with less potential of inundation.
- Distant from drinking water well should be no less than 30 m.

2.6.5 Sweden

There is no national regulation on the use of BA, thus the rules on its use significantly vary regionally regulated by local environmental authority. However, Denmark enforces higher landfill tax in order to encourage the alternative beneficial use option for BA [4, 5].

2.6.6 United States

Despite of having many studies regarding successful demonstration projects of MSWI ash utilization in transportation applications [3, 43, 44], acceptance of ash is still under debate. Absence of proper Federal regulation and guidance and their variable applicability in different states hinder the implementation of the beneficial use of MSWI ash.

2.6.6.1 Federal Regulation

In the U.S., BA and FA are mixed together and disposed in landfill as combined ash [13]. According to Resource Conservation and Recovery Act (RCRA), MSWI ashes are required to pass the Toxicity Characteristic Leaching Procedure (TCLP) (SW-846 EPA Method 1311) [51, 52] to be considered as non-hazardous waste. FA often fails TCLP; however, BA with lower in hazardous constituents generally passes. Hence, in the U.S. the two are combined and disposed in order to avoid the high cost and negative stigma that requires special disposal technique for hazardous waste.

Without considering the field leaching scenario, Environmental Protection Agency (EPA) devised the TCLP leaching test using acetic acid to classify simply whether ash is hazardous or non-hazardous. Hence, TCLP leaching test results often overestimate leaching potential as compared to field condition [3]. For this reason, alternative leaching tests method has been developed to better simulate the field performance. The Synthetic Precipitation Leaching Procedure (SPLP) (EPA Method 1312) [3] has been practiced using sulfuric/nitric acid of 40/60 by weight and EPA has been working with Leaching Environmental Assessment Framework (LEAF) to characterize leachates and run off from the field [53]. LEAF tests are designed to understand the dependence of pH and mass transfer rate on batch or column leaching test with varied liquid to solid ratio [53]. In addition to the environmental criteria set by EPA, Federal Highway Administration (FHWA) provided guideline for the use of MSWI BA and combined ash in pavement construction [54], such as granular base and asphalt concrete application.

2.6.6.2 State Regulation

Several states have been considering MSWI ash for beneficial use by implementing some state rules and regulations. One extensive survey [55] revealed that 28 states require TCLP tests, while 9 states have their substitute testing procedures. 20 states permit ash utilization, but 9 states do not permit [3, 55]. Disposal as ash monofill with daily cover is a typical practice for ash management with limited application in asphalt paving and concrete [3, 7].

Few states, including New Hampshire and Massachusetts permit demonstration research projects [3]. Some states have their own administrative codes that include groundwater, surface water, soil, or air quality [3]. For example, Washington DC and California enforce leaching test, Waste Extraction Test (WET) [3, 56, 57] with more stringent threshold limit for inorganic substance than those of TCLP test. Similarly, New York has comprehensive waste management regulations requires TCLP test and SW-924 extraction test [3] using distilled water as a leachant. Some states, including Pennsylvania and Illinois only recognize ash as special waste [3, 57, 58].

Having the highest number of MSWI plants and aiming at 75% recycling by 2020 [59], Florida Administrative Code (FAC) includes chapter intended to the extensive ash management strategy for landfill and recycling to meet TCLP and drinking water standard, respectively [53, 60]. Reuse Target Levels (RTLs) are also recommended by Florida Department of Environmental Protection (FDEP) as describes in the document of Guidance for Preparing Municipal Waste-to-Energy Ash Beneficial Use Demonstration [61]. This document provides the guidance for the Department and the WTE ash generator to prepare the acceptable Beneficial Use Demonstrations (BUDs).

2.7 Comparison of Leaching Regulation among Different Countries

Different countries implemented their own leaching test procedure depending on the regulatory and environmental perspective that results in wide variation in threshold values for particular chemical constituent for the MSWI ash utilization. In order to compare the variation among different country standards, an effort was made to compile the legislative limit values and they are summarized in Table 2.3.

Table 2.3: Summary of leaching criteria for different constituents from MSWI BA residue for utilization in various countries (mg/L) [4, 62, 63]

Element	The Netherlands Column (L/S = 1-10) 2005	Denmark Batch (L/S = 2) 2000	Germany Batch (L/S = 5) 1994	France Batch (L/S = 5) 1994	US EPA Toxicity Criteria ^b 1987	US Drinking Water Standard 2009
Cl	440	300	125			
F	14.4					4
SO ₄	3,250	400	300	500		
Na		150				
As	0.35	0.005		0.1	5	0.01
Ba	7.75	0.4			100	2
Pb	0.41	0.01	0.025	0.5	5	0.015
Cd	0.00305	0.004	0.0025	0.05	1	0.005
Cr	0.06	0.05	0.1	0.05	5	0.1
Cu	0.165/1.15 ^a	0.2	0.15			1 ^c
Hg	0.00375	0.0001	0.00005	0.01	0.2	0.002
Mn		0.1				
Ni	0.175	0.007	0.02			0.1
Zn	0.7	0.15	0.15			5 ^c
Co	0.115					
Mo	0.13/1.15 ^a					
Sb	0.06/0.1 ^a					0.006
Se	0.0135				1	0.05
Sn	0.115					
V	4.8					
Ag					5	0.1 ^c
Tl						0.001

^a The Netherlands consider BA to fall under special category with less strict leaching criteria for Cu, Mo, and Sb [4]

^b Code of Federal Regulation (CFR) 40-261.24 [62]

^c Secondary drinking water standards [64]

2.8 Summary

In the process of incineration, about 80 to 90% of the MSW by weight are BA and 10 to 20% are FA. In the U.S., both bottom and FA are combined mostly to meet the criteria to qualify as non-hazardous, and most of them are disposed in landfills. The current practice of the U.S. combines MSWI BA and FA, and the combined ashes are being disposed in landfills. This may be due to the state-wide inconsistency in ash management, regulations, and standard leaching test procedures. In addition, debates regarding highly soluble salt content and heavy metal concentration in MSWI ashes further discourage its utilization.

In the contrary, many of European and Asian countries have already successfully implemented systematic approach towards the beneficial utilization of MSWI ashes. European countries aim at utilizing MSWI BA as beneficial construction materials by separating it from FA. The FA is mostly limited to landfill disposal as hazardous material due to its high content of toxic elements and salts. FA can be utilized by vitrification technology which is a thermal process of transferring material into glassy state with higher physical and chemical integrity to reduce toxicity.

CHAPTER 3 LITERATURE REVIEW- TREATMENT, UTILIZATION AND LEACHING OF MSWI ASHES

3.1 Introduction

Beneficial utilization of MSWI ashes are growing interest due to the limited space requirement and cost associated with landfill disposal, natural resource recovery, and environmental pollution perspective. Common utilization of the MSWI ashes has included PCC, HMA, base and subbase layer, and embankment. Chemically reactive MSWI ashes are required to be pretreated prior the utilization in order to reduce the vulnerability of toxic release. However, utilization of MSWI ashes such cement and asphalt stabilization can render further encapsulation of toxic elements so that environmental exposure can be minimized. Due to the high soluble salt and heavy metals contained in MSWI ashes, the risk of toxic leaching associated with ash beneficial utilization can be a concern. Therefore, assessment of leaching potential using proper leaching tests is required prior to the utilization in the field so that environmental safety is confirmed.

3.2 Treatment of MSWI Ashes

Treatment of MSWI ashes by means of stabilization is considered to be a viable option for the beneficial utilization of MSWI ashes because the treatments can improve environmental and structural properties of the MSWI ashes. Prior to the utilization, treatment such as carbonation and weathering, water washing, and/or washing and chemical treatments with lime, phosphoric acid, etc. [2, 5, 55] are required to stabilize MSWI ashes in order to make it feasible in construction application with minimum environmental risk. Additives used as stabilizer includes the combination of hydraulic binder, lime, pozzolans gypsum, and silicates [2, 3, 5, 8]. Stabilizing agent such as cement and asphalt can be used as a means to

transform the chemical properties of MSWI ashes, and reduce the solubility of trace elements contained in ashes [2, 20]. Addition of these additives can limit the metal release; thus, offer better suitability of MSWI ash for the purpose of manufacturing construction aggregate. Chemical treatment and water washing can lead to the removal of high soluble salts and chloride contents [2].

Innovative thermal technique has also been introduced to treat MSWI FA by means of transferring toxic material into glassy matrix so that glass derived product can be utilized beneficially [40, 65, 66]. Currently, this technology has been adopted to vitrify MSWI ash to obtain physically and chemically highly durable product that can be further utilized as a secondary building material. A detail discussion on vitrification technology is presented below.

3.2.1 Vitrification Technology

MSWI BA has been successfully utilized in civil engineering applications [2, 4], but in contrast, final destination of MSWI FA is still, mostly, limited to landfill disposal as hazardous material [5]. In this regard, Japan, Korea, Taiwan have been implementing the unique vitrification technique to treat MSWI FA due to their limited land availability for disposal option and in order to produce inert glassy product with least leachability and reuse potential of MSWI FA bearing glassy materials [40, 65-67].

Vitrification is a thermal process of transferring material into glassy state with higher physical integrity and chemical durability. This is an attractive and promising technique of the treatment of MSWI FA by integrating its inorganic elements in glass network or by encapsulating them into the final glass product. Although, vitrification is highly energy intensive thermal process, it reduces the waste volume and produces durable waste glass with

limited leachability that can be considered as aggregate. Also, devitrification or recrystallization technique can be associated with it in order to improve the physical integrity of the final waste glass ceramic product. Vitrification of waste material results in high quality glass product which has fundamentally important feature of chemical stability with the incorporation of toxic elements into its matrix. Therefore, not only landfilling of MSWI ash can be made without further concern, but also secondary reuse of the material is possible.

Vitrification has been considered a promising option for MSWI ashes (BA and FA) treatment in Asian countries such as Korea and Japan due to the lacking of land requirement for disposal [40, 41, 65, 67] and China also has been demonstrated research study on vitrification technology to handle large quantity of residue ashes [68]. Environment Protection Administration policy enforces Taiwan to reuse the FA that leads to the vitrification of FA to make inert material [69]. As another treatment method such as cement solidification and chemical treatments are appeared to be less effective in Korea due to their FA containing higher quantity of chlorine. Therefore, Korea is more likely to adopt the thermal treatment technology [65].

Among different treatment techniques for MSWI FA, vitrification offers the highest quality of product with least leaching results. Therefore, this technique can be utilized extensively if innovative approach can be made to reduce the temperature of melting process which involves the high cost in terms of energy consumption required for vitrification. Melting technology can be classified as follows: fuel burning melting systems and electric melting systems [40]. However, plasma torch electric melting system has gained attention due to the superior treatment quality, but improvement in thermal efficiency is warranted to make it a viable alternative [70, 71].

Mostly reported MSWI FA compositions are, in general, deficient of silica content which is considered as glass former. Hence, addition of other materials (MSWI BA, glass cullet, silica sand, feldspar waste, iron slag, clay by-product) with FA has been demonstrated by researchers [72-75]. Based on the average composition, MSWI FA is pertinent to SiO₂-CaO-Al₂O₃ system. Additionally, due to the presence of Fe₂O₃ or TiO₂, phase separation and heterogeneous nucleation and crystallization occurs during the vitrification of FA which results in the formation of glass-ceramics though controlled heat treatment scheme [76-79]. Attempts also has been made to reduce the melting point of vitrification of FA with lime addition [80].

The FA vitrified at around 1500 °C with the addition of other materials to improve the melt quality for glass formation and glass ceramic formation by subsequent heat treatment followed by crystallization has been reported to offer excellent leaching resistance against cadmium, chromium, copper and other potential heavy metals [65, 68, 73, 77, 81, 82]. However, glass product shows slightly superior leaching resistance compared to glass ceramic which contains crystalline phases bearing toxic heavy metals [83]. Several potential applications of the vitrified FA are road base material, embankments, blasting grit, partial substitution of fine aggregate in concrete, ceramic tiles, pavement blocks [84].

3.3 Utilization of MSWI Ashes

The European countries have developed the successful practice of reusing the MSWI ashes and the ashes are now commonly used in road construction as a gravel material in compacted base layers [84-86]. It was also demonstrated that MSWI BA is classifiable as adequate soil for embankment and landfill, and a proper material for granular layers (bases and sub-bases) [84]. Applications of MSWI ashes as partial replacement of fine or coarse

aggregate in asphalt paving and concrete formulation have been also employed [2-4, 7, 8]. These applications are promising and effective from environmental safety perspective. In the ash utilization into concrete, cement matrix captures the heavy metals in physical and chemical manner and they are transformed into more stable and insoluble compounds, making it less vulnerable to potential contamination [87]. Leaching potential from the ash in HMA can be reduced significantly by being physically encapsulated in asphalt binder [45, 88].

3.3.1 Asphalt and Road Paving Application

MSWI ashes can be utilized as a substitute of crushed rock and gravel in many civil engineering applications, such as base course and sub-base. These are widely used in European countries in road construction as compacted road base, structural fill in wind barrier, highway ramps, sound barriers, and in asphalt application [2, 7, 8].

Sweden successfully used MSWI BA as sub-base material instead of gravel in the test road which demonstrated no effect of heavy metal release to the environment [20]. In France, three-year study has been conducted for the utilization of MSWI BA in road pavement where leachate concentrations of heavy metals were below the authorized limit of potable water, indicating environmentally safe utilization of MSWI BA [20]. Approximately half of MSWI ashes produced in Germany have been utilized beneficially in road construction.

The Netherland, having many years of experience in handling of MSWI FA, has implemented the use of FA in asphalt application as a substitute of natural aggregate without imposing environmental impact by toxic leaching [3, 7, 8]. One of the possible utilization of MSWI FA is soil stabilization as a replacement of lime or cement due to having pozzolanic reactivity [23]. Researcher also reported the potential use of MSWI FA as substitute for filler

material [23, 89]. Environmental concern regarding leaching of contaminants into soil and groundwater can be mitigated by pre-treatment of washing of ash which can greatly reduce the leaching and eventually increase the potential of utilization of MSWI ashes [84].

In the U.S., MSWI ashes was investigated showing satisfactory performance in demonstration projects for more than 20 years [3]. Unbound ashes by asphalt or cement were used as gravel and aggregate substitute in road base layer. In asphalt concrete, substitution of rock aggregate by MSWI ashes with reduced particle size smaller than $\frac{3}{4}$ inches demonstrated potential utilization option for MSWI ashes in several projects in the U.S. without any environmental effect. [3]. MSWI ashes are desirably applicable as base and filler material due to having high stability and low density with some consideration of low durability [3].

FHWA provides an extensive set of guidelines for using MSWI BA and combined ashes in pavement construction [54]. According to FHWA, after removal of metal, ash passing $\frac{3}{4}$ inch screen can be used as a replacement of 10% to 25% of natural aggregate in bituminous surface courses and up to 50% in base and binder course. Addition of hydrated lime by 2% by weight with MSWI ash has also been suggested in order to prevent striping problem of asphalt binder from the ash [54]. Ash storing for maturation for 30 days are required until 20% of replacement of pavement material in order to stabilize potentially reaction ingredients. In granular base application, use of the ash passing $\frac{1}{2}$ inch screening after 1 to 3 months of maturation has been suggested [3, 54].

3.3.2 Concrete Application

MSWI ashes are assumed to cause pozzolanic reactivity when Ca component is retained from APC devices in the ash and then the ash can act as a partial replacement of

Portland cement and also MSWI BA can substitute as rock aggregate in PCC [3, 23, 84]. In European countries, several studies used the MSWI BA and FA as partial replacement of cement in order to investigate their effect on the cement paste and PCC [21, 86, 90-94]. MSWI ashes has been also utilized as substitute of rock aggregate in concrete blocks in several states in the U.S. [3]. MSWI ashes in PCC appeared to be promising, however, metals, glass, and soluble salts removal prior utilization is necessary which comprise the strength of the final product [3].

However, some of side effects in PCC applications have been reported. Although sometimes MSWI FA is considered to have similar properties with cement [20, 95, 96], experimental observation reveals that both ashes contain considerable amount of metallic Al that can generate hydrogen gas , resulting in volume expansion, cracks and voids in cement paste specimens [21, 22, 36, 92, 97]. In addition, the FA contains significant amount of Cl, which may increase corrosion probability of reinforcing steel in reinforced concrete structure.

Due to the swelling originated from hydrogen gas evolution, cement pastes containing MSWI BA exhibit inferior mechanical properties compared to those of control specimen of cement paste [21]. On the other hand, the compressive strength of the cement paste containing the FA is sometimes similar or higher than those of control specimens [94]. Unlike the addition of MSWI BA, the FA addition in concrete reduces the workability because of smaller particles of MSWI FA [21]. Washing of FA is effective to reduce the soluble salt and Cl content in the FA and wet grinding of the BA would be viable option to facilitate gas production before its addition as cement replacement in concrete production [21, 90-92, 96]. According to the findings through the literature study, the concrete application for the MSWI BA and FA is promising to minimize potential of environmental

leachate but material treatments would be necessary to remove deleterious chemical components and to improve the structural properties of ash-combined concrete products.

3.4 Leaching of MSWI Ashes

Due to the presence of heavy soluble salt and heavy metals in MSWI ashes, leaching properties of MSWI BA, FA, and combined ash have been considered as one of the most critical parameters for years in order to utilize MSWI ashes without impairing the environment, [30, 98]. Different countries implemented their own standard procedure of leaching test and set threshold limit for toxic elements to evaluate the leaching potential of heavy metals and soluble salts when the MSWI ashes are either landfilled or exposed to soil and water [1-5].

3.4.1 Leaching Test Procedures

In the U.S., TCLP is the federal regulatory leaching test using acetic acid to determine if the waste is hazardous or non-hazardous [51]. TCLP test, however, is associated with overestimation of leaching potential in compared to field condition. Thus, the SPLP (EPA Method 1312) using sulfuric/nitric acid of 40/60 by weight has been devised for more realistic assessment of leaching scenario of MSWI ashes [3]. Brief description of TCLP and SPLP are summarized below.

3.4.1.1 Toxicity Characteristic Leaching Procedure

The TCLP is designed to determine the leachability of inorganic and organic constituent of waste material. TCLP is EPA method 1311 [99] which involves agitated extraction of contaminants from waste sample passing through 9.5 mm standard sieve using acetic acid as extraction fluid with 20:1 liquid to solid ratio by weight in a zero-head extractor

(ZHE) or High Density Polyethylene (HDPE) extraction vessel. ZHE vessel facilitates the separation liquid and solid which is important for the analysis of volatile component. After agitation in a rotary tumbler at 30 rpm for 18 hours (see Figure 3.1), the intimate mixture of waste sample and extraction fluid is filtered through glass fiber filter under 50 psi pressure. The collected filtrate is then analyzed for the constituent of interest.

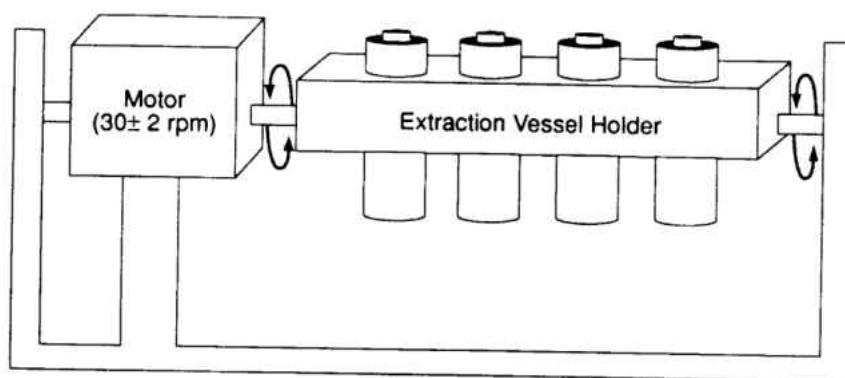


Figure 3.1: Rotary agitation apparatus with extraction vessels containing waste sample [99, 100]

Prior to the sample extraction, percent of solid is determined for the liquid waste. The sample which has less than 5% of solid undergoes filtration through a 0.6 to 0.8 μm glass fiber filter. Thus, the extract collected is referred to as TCLP extract and constituents of interest are analyzed without extraction. Waste containing greater than or equal to 0.5% of solids are required to necessary size reduction and be extracted from the liquid according to the above mentioned extraction procedure.

3.4.1.2 Synthetic Precipitation Leaching Procedure

The SPLP [100] is EPA 1312 method which is a single batch agitated extraction process to determine leaching potential of inorganic and organic constituents of waste material. This leaching procedure is similar to that of TCLP except for the use of extraction fluid which comprises sulfuric/nitric acid of 40/60 by weight instead of acetic acid in the case

of TCLP. TCLP is intended to simulate the landfill leaching scenario, whereas, SPLP is devised to simulate the leachate scenario due to the rainfall [3]. For the solid waste material, extraction fluid pH is maintained at 4.2 [100]. SPLP test, in fact, appears more realistic to assess the leaching potential of waste material while used in application site exposed to rainwater percolation.

Determination of percent of solids is also done for SPLP and particle size of waste sample is maintained at passing 9.5 mm sieve, if necessary. Sample extraction is conducted with 20:1 liquid to solid by weight in extraction vessel for 18 hours of agitation period in a rotary agitation apparatus (see Figure 3.1). Agitation followed by filtration through glass filter fiber under 50 psi pressure, and thus derived SPLP extract are collected for further analysis is done for organic and/or inorganic components of interest in order to compare with drinking water standards [63] and toxicity standards [62].

3.4.2 Assessment of Leaching of MSWI Ashes

Evaluation of leachate from MSWI ashes run off from landfill and application sites have been performed mostly in European countries [2-4, 8], but also at small extent in the U.S. [3, 7]. Leaching test results reveal that MSWI FA contains significantly higher soluble salt content (i.e., Na, K, Ca, Cl) and toxic elements (i.e., Pb, Zn, Cr, Ni, Cu) with compared to MSWI BA [101, 102]. Oxyanions, such as Zn and Pb are termed as amphoteric, are characterized with high leaching potential at both high and low pH. Release of such amphoteric heavy metals from the FA can be significantly increased due to the high pH of FA originated from APC devices which contain scrubber lime solution [103]. Substantial Pb leaching has also been confirmed by the researchers in Korea and Japan [104]. Danish researchers [105] evaluated MSWI BA and FA from 25 MSWI plants from 1998 to 2010 and

reported that the FA is likely to exceed the leaching limit values for Cl, SO₄, Cd, Cr, Hg, Mo, Pb, and Zn whereas the BA is likely to exceed limit values for Cl, SO₄, Cu, Mo, Sb, and Se.

Weathering and carbonation of MSWI BA [29, 106-109] and FA [110] may decrease the pH of the ashes and reduce toxic metal release. Although carbonation technique is less effective in the leaching of Mo and Sb, it is effective for the release of Cu [111]. Although Cu in the leachate is immobile in neutral and basic condition; in acidic condition, Cu exists as highly mobile ions that substantially increase its leaching [112, 113]; thus, Cu release is considered to be a critical concern. Dissolved organic carbon is believed to be responsible for Cu and Ni release due to the potential complexation of these metals [114, 115]. Similarly, Zn leaching also follows the same characteristics of Cu when the BA is in acidic condition [116].

Leaching tests have been conducted to evaluate toxic elements release from the leachate of MSWI BA, FA, and combined ash when used as base or sub-base course in asphalt pavement [84, 86, 117-125], PCC product [21, 36, 92, 93, 97, 98], and embankment fill [43, 126, 127]. The U.S. studies reported that heavy metal concentration in leachate mostly meets the leaching requirements [51] and often meets the U.S. drinking water standard [63]. It was also reported that the concentration of dioxin and furan, especially in the FA, does not pose any threat in regard of the environment and health [13]. However, although heavy metal concentrations in the ash leachate are found mostly below the threshold limits in the U.S., salt concentration was reported to be much higher than the limit of the drinking water standard [7, 105].

3.4.2.1 Leaching Potential of MSWI Ashes in Asphalt and Paving Application

Significant reduction of leachability in MSWI ashes has been observed while beneficially utilized as aggregate substitute in asphalt and road paving application [32, 88,

120-125, 128-130]. Asphalt is a hydrophobic material that can form an immobile barrier to encapsulate toxic heavy metals, acting as a more effective stabilization and solidification agent for MSWI ashes compared to cement stabilization [88, 129].

In France, researchers used MSWI BA in test road section [121] BA was screened to remove particle larger than 33 mm and matured for 3 months, and has been utilized as 25 cm thick subbase layer. Long term leaching behavior has been investigated for 10 years. Leachate pH and concentration of major elements (Na, Al, Ca, Cl) and heavy metals (Pd, Zn, Cu) were found to decrease eventually over 2 years and obtain a minimum value within 10 years. Only SO₄ concentration is the exception in comparison to natural calcareous aggregate as subbase. Due to the interaction with CO₂, MSWI BA mineralogy changes to a more stable form that reduces the leaching potential significantly with time [121]. MSWI BA was also utilized as subbase material in Greenland's road construction [120]. It was found to be in compliance with Danish regulation for the application of BA as road construction material. Leaching test results indicated that Cu and Cr release rate was higher for smaller grain size of BA which problem can be minimized by removing smaller size particle to improve the potential use of BA.

Leaching behavior of BA as aggregate substitute in unbound pavement layer has been investigated [123]. After quenching, air drying, removal of metallic fraction and unburned material, and several months of maturation, MSWI BA was prepared to use in test road section. 0.5 m BA layer used as unbound granular road base, covered with limestone aggregate layer. Field leaching test results shows higher concentration of Cl and SO₄. Pb, Cd, Zn were found to be highly immobile, whereas Cu release was much higher due to the organic compounds in the ash. Complete combustion would be an approach to reduce the potential release of elements.

Road site built with MSWI un-weathered combined ash has been investigated for leaching potential of toxic elements [124]. Leaching test result indicates major elements are Al, Ca, Na, K, Cl, SO₄, and trace elements are As, Cd, Cr, Pb, Cu. Results implies that weathering or maturation of ash would give improved leaching potential. However, metal release did not exceed the Dutch Soil Protection Act (DSPA) threshold limit and leachate percolation to the soil was also found to be insignificant.

In the U.S., field demonstration project was conducted by Florida Department of Transportation (FDOT) with Florida Institute of Technology (FIT) for the beneficial utilization of MSWI combined ash as embankment fill material [43]. The concentration of heavy metals was investigated for comparison with U.S. drinking water standard [63] and toxicity standard [62]. Combined ash was collected used for embankment construction was obtained from Pinellas County's RDF incinerator facility. After metal recovery, ashes were intended to beneficial use for embankment fill. The concentration of metals in leachate, runoff and rain water was collected over one year from the embankment fill and environmental characteristics of ash (combined ash) have been evaluated suggesting its potential for using as highway construction material [43] With few exception, the concentration of metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver) was observed to be lower than the limit of drinking water standard and toxicity characteristic.

MSWI BA used as aggregate substitute in asphalt concrete formulation with 10, 20, 30, and 40% of replacement [88]. Taiwan TCLP test results for MSWI BA showed that leachate concentration of Cd, Cu, Cr, Pb, As, Hg were below the Taiwan TCLP regulatory standard, whereas, MSWI BA mixed asphalt concrete resulted in non-detectable heavy metal concentration. For large scale application of MSWI BA, certain period time storing has been advised by researchers [88] which can stabilize the toxic heavy metals prior using as

construction material. MSWI FA has been used as a partial replacement of fine aggregate in stone matrix asphalt mixture [129]. TCLP test results indicated that asphalt effectively limits the leaching of Cu, Cd, Pb, Zn and Cr. Stabilization of Ni, however, appeared to be less effective [129].

Using column test, leaching potential has also been investigated for manufactured hot-mix asphalt with MSWI combined ash with 25% replacement of natural aggregate [128]. Hardened asphalt concrete samples were screened to 9.5 mm particle size for the leaching test in order to assess the risk potential if MSWI ash containing asphalt gets exposed to the environment after in the road [128]. Leaching test was intended to compare the metal concentrations of elements of interest with Florida Groundwater Cleanup Target Levels (GWCTL) criteria [131]. Leaching results (see Table 3.1) revealed that the concentration of Cl and total dissolved solid (TDS) exceeded the target level initially which eventually decreased below the limit during 75 days of experiments. Aluminum concentration, originated from MSWI ash, however, found to exceed the standard.

Table 3.1: Leaching test for MSWI combined ash and asphalt formulated with combined ash (mg/L) [128]

Element	SPLP ^a leachate concentration		Florida GWCTL ^c
	MSWI combined ash	Asphalt formulation with MSWI ash ^b	
Al	10.3 ± 1.8	1.28 ± 0.5	0.2
As	< 0.012	< 0.012	0.05
Ba	0.15 ± 0.01	0.15 ± 0.03	2.0
Cd	< 0.001	< 0.001	0.005
Cl	890 ± 25	385 ± 200	250
Cr	0.02 ± 0.003	0.01 ± 0.004	0.1
Pb	0.014 ± 0.002	< 0.005	0.015
TDS ^d	2340	1001 ± 470	500

^a SPLP = Synthetic Precipitation Leaching Procedure [100]

^b Leachate collected on day 5 within 75 days long column experiment [128]

^c GWCTL = Groundwater Cleanup Target Levels [131]

3.4.2.2 Leaching Potential of MSWI Ashes in Concrete

Several researchers confirmed significant reduction of leaching potential of MSWI BA, FA, and combined ash when they are incorporated into cement and concrete [84, 93, 98, 119]. Researchers used MSWI FA in concrete production as a replacement of cement. Initially, leaching toxicity was higher, but over time, heavy metal release was greatly reduced, even far below the Chinese national standard [98].

Spanish researchers formulated granulated material with combined ash and cement to use as secondary building material [119]. In this research study, batch leaching tests were performed to evaluate leaching behavior of BA, APC, and combined ash containing concrete. Concrete mixtures were prepared with 10% cement, 10% APC, and 80% BA by weight. The test results are provided in Table 3.2 with threshold values established by utilization criteria [132] and three categories of landfill criteria [133] set by Spanish Government for MSWI BA utilization as secondary building material. It is indicated that a significant reduction of leaching was observed for the combined ash mixed concrete formulation and heavy metal concentrations were below the criteria of utilization. A considerable reduction in leaching of heavy metals from MSWI ashes by chemically encapsulating within concrete has also been confirmed by many other researchers [84, 93, 98, 117].

Another researcher [118] suggested the use of weathered MSWI BA rather than “fresh” one as secondary building material. As a replacement of aggregate, BA combined with FA at the proportion of 90:10 and 95:5 BA: FA and used for concrete formulation with cement to aggregate ratio of 1:4 which can be utilized as non-structured concrete application. These combinations of BA and FA utilization were found to exhibit highest compressive strength above 15 MPa and lowest leaching potential. Washing off the ash prior to the application also leads to improved leaching potential.

Table 3.2: Leaching results for MSWI BA, APC residue, and formulated concrete mixture (mg/kg) [119].

Element	BA	APC	Combined Ash	Concrete with Combined Ash	Criteria for Utilization ^b	Criteria for Landfill ^c		
						Inert	Non-hazardous	Hazardous
As	0.003	0.004	0.003	0.001	1.0	0.50	2	25
Ba	0.504	43.682	5.302	15.04	-	20.0	100	300
Cd	0.043	0.040	0.043	0.026	1.0	0.04	1	5
Cr	0.390	3.643	0.751	0.050	5.0	0.50	10	70
Cu	0.989	4.999	1.435	0.938	20	2.00	50	100
Hg	<0.01	<0.01	0.010	<0.010	0.2	0.01	0.2	2
Mo	0.401	2.611	0.647	0.117	-	0.50	10	30
Ni	0.060	1.290	0.197	0.170	5.0	0.40	10	40
Pb	0.079	138.284	15.435	2.139	5.0	0.50	10	50
Sb	0.460	0.040	0.413	0.079	-	0.06	0.7	5
Se	0.007	0.092	0.016	<LOD ^a	-	0.10	0.5	7
Zn	0.818	35.083	4.625	1.008	20.0	4.00	50	200

^a LOD = limit of detection

^b Spanish utilization criteria [133]

^c Spanish landfill criteria [132]

3.4.2.3 *Leaching Potential of vitrified MSWI Fly Ash*

Major environmental concern comes from FA (residue from APC devices) which is significantly rich in readily soluble salt, such as Cl and Na that significantly contaminate drinking water system. High potential of heavy metals and trace metals are of another concern that pose threat to human health risk has gained attention. Although dioxin and furan does not leach easily, these are of importance due to their toxicity. In this regard, vitrification appears to be the most credible technique for the treatment of FA with least leachability. Researchers [72-75] demonstrated the feasibility of the vitrification of MSWI FA and investigated the chemical properties of the vitrified FA [80, 134-136].

Taiwan researchers conducted TCLP in order to investigate the leaching potential of vitrified MSWI FA [134]. FA was premixed with glass cullet at 3:1 mass ratio has been undergone vitrification treatment at 1450 °C. TCLP extracts were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Leaching test results (see Table

3.3) reveals excellent leaching resistance of vitrified FA in compared to as received FA based on Taiwan regulated standard [134].

Table 3.3: Leaching test results for MSWI FA and vitrified FA (mg/L) [134]

Element	TCLP ^a leachate concentration		Taiwan Standard ^b
	MSWI FA	Vitrified MSWI ash ^b	
Al	50.7	0.001	-
Cd	100.0	0.001	1.0
Co	100.0	0.004	-
Cr	66.1	0.003	5.0
Cu	98.3	0.001	15.0
Fe	93.8	0.003	-
Mn	98.3	0.001	-
Ni	97.4	0.010	-
Pb	99.9	0.004	5.0
Zn	97.9	0.001	-

^a TCLP = Toxicity Characteristic Leaching Procedure [99]

^b Taiwan Environmental Protection Administration Standards [134]

FA contains higher amount of chlorine which appears to be less soluble into glassy matrix [137]. Still research is underway to better predict the behavior of chlorine stability in glass material. However, water washing prior to vitrification and sintering technique would be effective as suggested by researchers [69, 74, 82, 138].

3.5 Summary

Beneficial utilization of MSWI ashes has been practiced for years as road construction material in concrete and asphalt formulation, and road paving. Although MSWI BA, in general, has been employed for the civil engineering applications, MSWI FA is mostly destined to landfill disposal due to toxicity. With the consideration of large landfill space requirement, innovative vitrification technology has been devised in order to produce glass or glass ceramic from FA with superior physical and chemical property. Vitrified ash also offer excellent toxicity resistance.

Since heavy metal content and highly soluble salts in MSWI ashes are the hindrance for their application, different countries adopted different leaching methods with distinguished limit standard to investigate the environmental risk associated with their beneficial application. Leaching test results appears to be promising indicating the significant reduction of leachability of MSWI ashes while using in asphalt and concrete due to stabilization by physical and chemical encapsulation.

CHAPTER 4 CHARACTERIZATION OF MSWI ASHES

4.1 Introduction

In an effort to address the potential utilization of MSWI ash as transportation material applications, BA and FA (Figure 4.1) were collected from one of RDF incineration facilities in Florida, U.S., and chemical and microstructural characterization of the MSWI BA and FA have been carried out. The RDF facility preprocesses MSWs with shredding and metal removal prior to the incineration in order to make the feeding wastes more effective for combustion. After the combustion, the BA is water quenched, while the FA is lime-scrubber treated in an APC device for reducing the acid gases. Thus, the FA characterized in this study is technically APC residues but referred as FA as a general term.

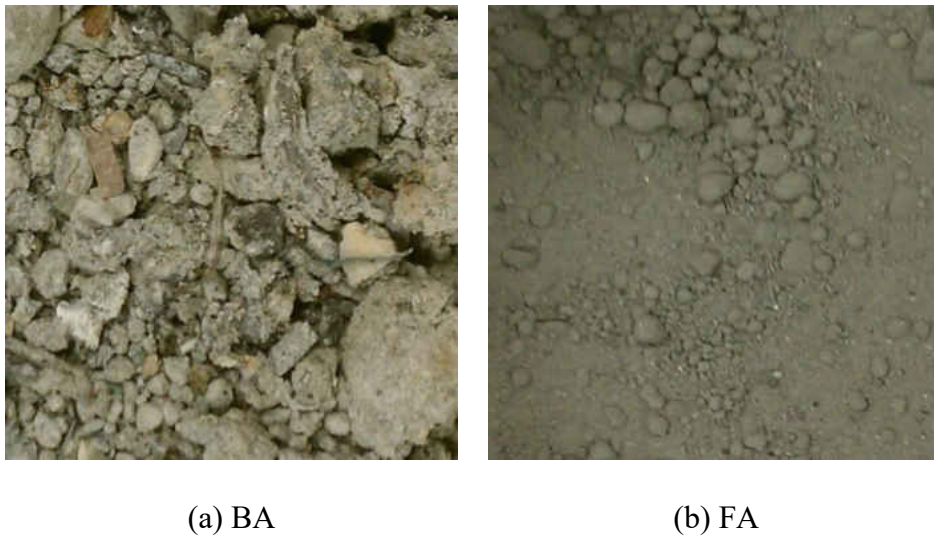


Figure 4.1: Photos of MSWI ashes

The MSWI ashes were oven dried at 110 °C for 2 hours. The microstructure, morphology, chemical composition, and mineralogy of the BA and FA specimens were then characterized by utilizing SEM, EDS, and XRD. Finally, a laboratory chemistry experiment was conducted to measure the hydrogen gas evolution from the BA and FA and to back calculate the amount of metallic aluminum in the BA.

4.2 Instrumental Techniques

The utilized microscopic analysis tools were SEM and EDS. The SEM analysis utilized the Zeiss Ultra-55 SEM Spectrometer with acceleration voltage of 5 to 20 kV, equipped with Ultra-Dry silicon drift EDS detector as shown in the Figure 4.2. Two different modes of detection utilized in this study are secondary electrons (SE) and back-scattered electron (BSE). In the secondary electron imaging, a primary electron beam collides with electrons from the sample atom and results in low energy electrons that gives near surface images of the sample. In the back-scattered imaging, high energy beam electrons are scattered by the sample. Heavier elements with higher atomic number produce stronger BSE than lighter elements having lower atomic number; thus, they appear brighter in the image. Therefore, the BSE are commonly used to identify the prominent contrast between areas with different phase and chemical compositions [139].



Figure 4.2: Zeiss SEM equipped with EDS Detector [140]

The EDS provides chemical compositions of the sample at a particular spot either point or area. In EDS, a high electron beam is bombarded with sample and produces X-ray

spectrums that are detected by an energy dispersive detector. This technique produces a set of peaks on a continuous background where every peak is the chemical information of particular elements, and thus the position of peaks and corresponding relative intensity enables the identification of different elements within the sample [139].

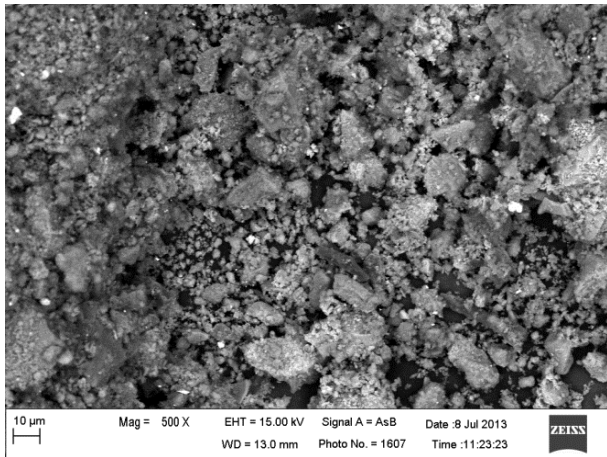
The mineralogical analysis was carried out using Rigaku X-ray diffractometer (Figure 4.3) which is equipped with 40KV Copper X-ray tube, 2 Theta Goniometer. It is facilitated with Datascan 4 Acquisition Software and, Jade 7 Analysis Software with JCPDS (Joint Committee on Powder Diffraction Standards) Database. X-Ray diffraction is a technique that measures the characteristic intensity of X-rays, diffracted by a sample specimen which corresponds to crystallographic information from that particular material [141]. XRD analysis offers the determination of the crystal structure and lattice parameters of crystalline materials using the JCPDS database for phase identification of unknown samples [141].



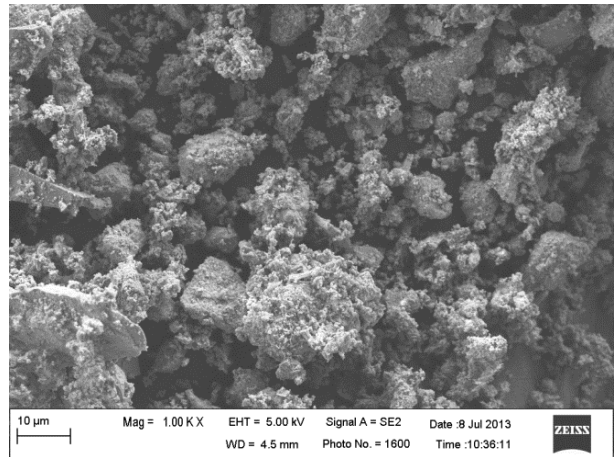
Figure 4.3: Rigaku X-ray Diffractometer [142]

4.3 Microstructure Analysis by SEM

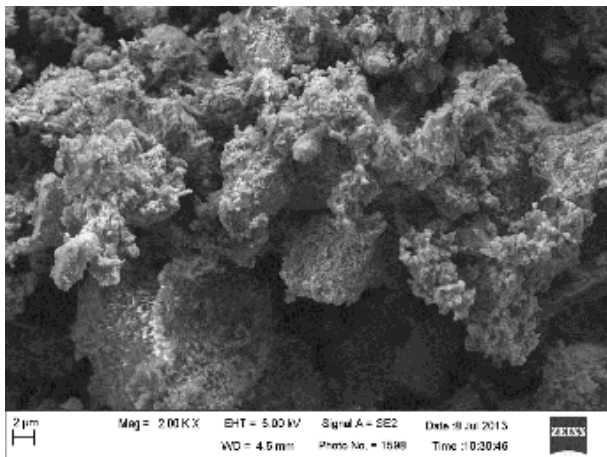
Surface morphology and texture of the ash samples were investigated using Zeiss Ultra-55 SEM Spectrometer with acceleration voltage of 5 to 20 kV. Thin sections of sample were coated with Gold-Palladium using a sputter coater. Figure 4.4 and 4.5 show the SEM images of BA and FA at different magnifications. It is observed that the BA exhibits poor crystalline structure. The FA, on the other hand, exhibits more angular shape than the BA; therefore, it is expected that mixing FA with cement will cause a lower workability. BA particles are mostly rounded, with no distinguishable crystal structures due to having amorphous phase, while FA exhibits planar, cylindrical, and spherical particles on sintered clusters with highly crystalline phase [87]. It can be assessed from Figure 4.1 that the particle size of FA appears to be smaller than that of BA. Therefore, FA with smaller particle size is likely to render an intense filling effect by incorporating into the cement grain when used in cement paste.



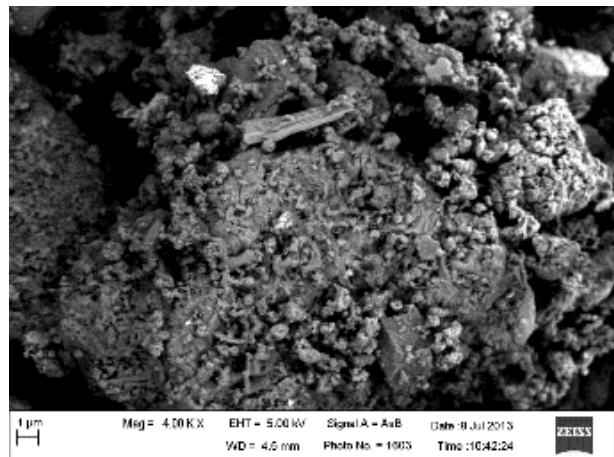
(a) 500X



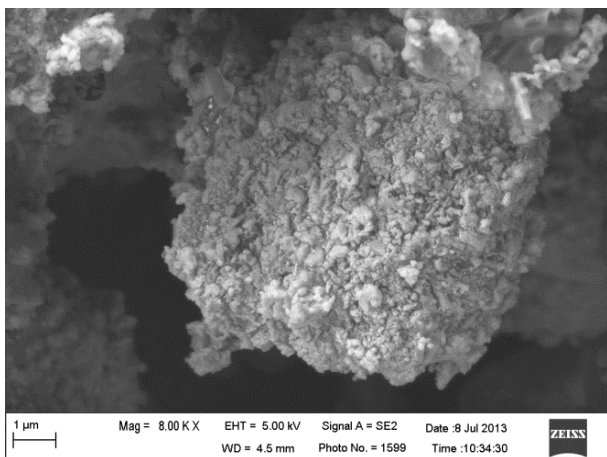
(b) 1,000X



(c) 2,000X

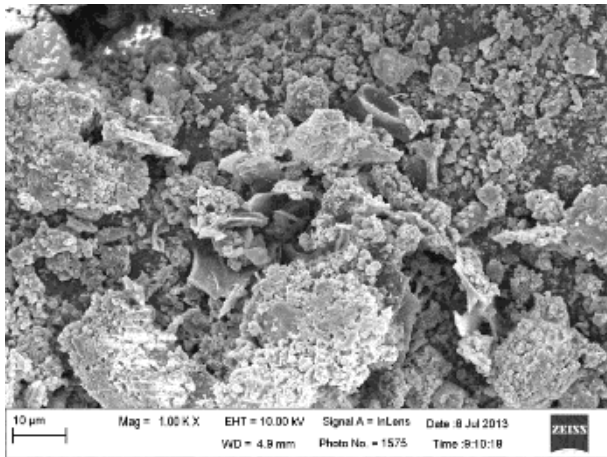


(d) 4,000X

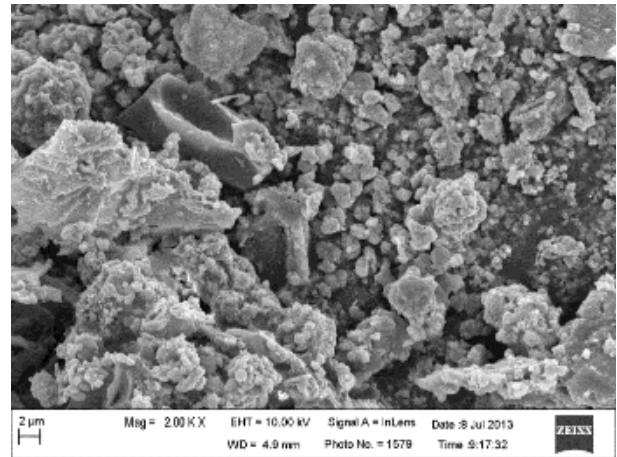


(e) 8,000X

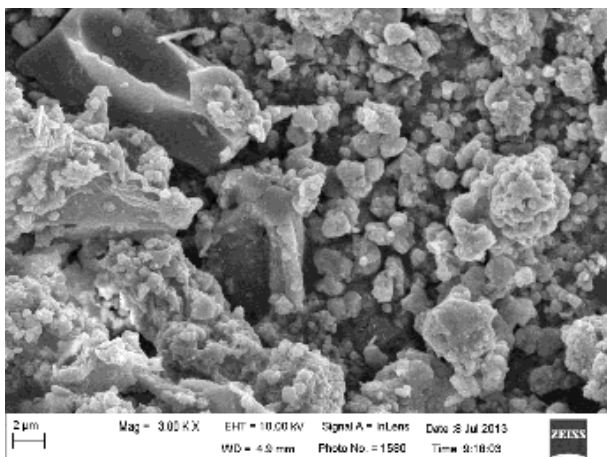
Figure 4.4: SEM images of MSWI BA with varied magnifications.



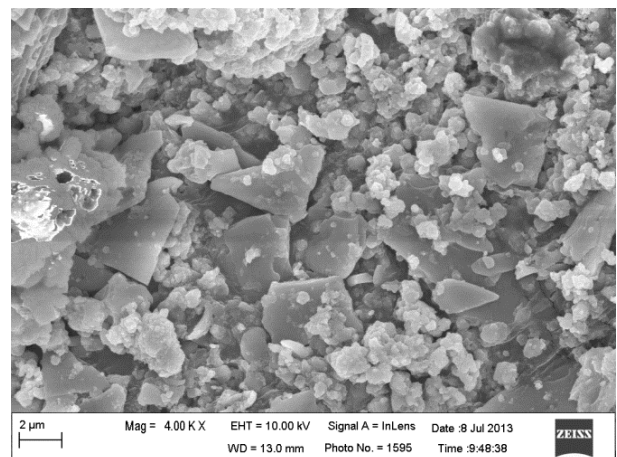
(a) 1,000X



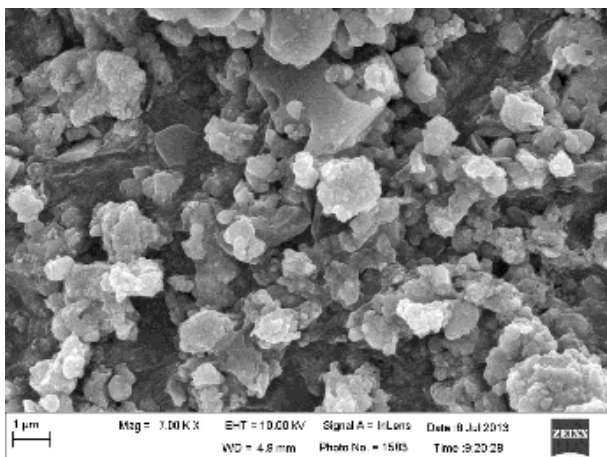
(b) 2,000X



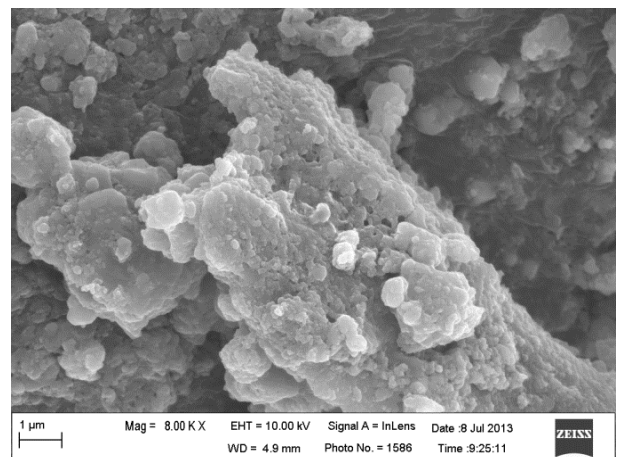
(c) 3,000X



(d) 4,000X



(e) 7,000X



(f) 8,000X

Figure 4.5: SEM images of MSWI FA with varied magnifications.

4.4 Compositional Analysis by EDS

Chemical elemental analysis was carried out for the BA and FA using the EDS. Average chemical compositions (elemental and oxide form) are listed in Table 4.1. The EDS results show that the major elements of the BA are Ca, Si, and Al and the minor elements are Na, Mg, Fe, and Ti with small amount of K, Cl, and Zn. It is apparent that oxygen is the predominant element; thus, it can be assumed that most chemical elements exist in oxide form. On the other hand, higher amount of Cl and Hg (highly volatile element) are observed in the FA. Major elements of the FA are Cl, Ca, K, Na, and Hg and minor elements are Si, Al, Cu, and Co. Due to the lime scrubber treatment that absorbs acid gases and produces different salts, higher amount of Ca than what expected is observed in the FA.

Table 4.1: Average chemical composition of BA and FA (wt. %)

Element	BA	FA	Oxide form	BA	FA
O	45.19	6.83			
Na	3.90	3.09	Na ₂ O	5.74	4.35
Mg	1.70	0.21	MgO	3.12	0.40
Al	4.60	1.00	Al ₂ O ₃	9.50	1.96
Si	8.00	1.07	SiO ₂	18.81	2.39
P	0.90	-	P ₂ O ₅	2.28	-
S	3.70	0.43	SO ₃	10.16	1.12
Cl	2.00	32.24	Cl	2.25	33.70
K	0.87	11.02	K ₂ O	1.15	13.89
Ca	25.30	25.25	CaO	38.92	18.50
Ti	1.38	-	TiO ₂	2.52	-
Cr	-	0.08	Cr ₂ O ₃	-	0.12
Mn	-	0.14	MnO	-	0.18
Fe	1.10	1.76	Fe ₂ O ₃	3.68	2.63
Co	-	0.29	CoO	-	0.38
Ni	-	1.68	NiO	-	2.23
Cu	0.80	0.93	CuO	1.10	1.21
Zn	0.56	6.81	ZnO	0.77	8.85
Hg	-	7.17	HgO	-	8.09
Total	100	100	Total	100	100

4.5 Mineralogy Analysis by XRD

Rigaku X-ray diffractometer with $\text{CuK}\alpha$ radiation, 2θ scanning from 5 to 80° with 0.02° step size and 1 second per step was employed for the mineralogical analysis of the BA and FA samples. The XRD results for the BA and the FA are presented in Figure 4.6 and 4.7, respectively. The XRD result for the BA appears to have relatively less crystal peaks compared to those of FA due to poor crystallinity in BA. This is in agreement with the observation from the SEM images (Figure 4.4) that BA has amorphous phase without distinguishable crystal structures. On the contrary, the FA exhibits highly crystalline phase as seen in Figure 4.5 that is in good agreement with the X-ray diffraction results with numerous peaks of crystals.

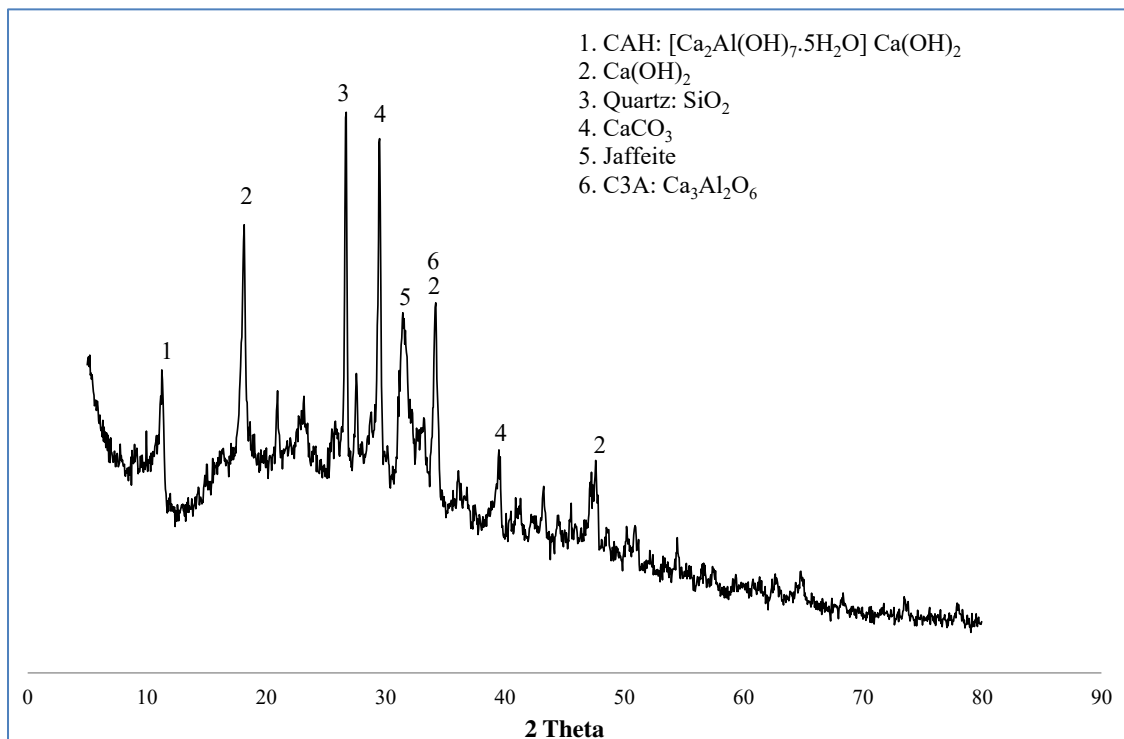


Figure 4.6: X-ray diffraction pattern for MSWI BA

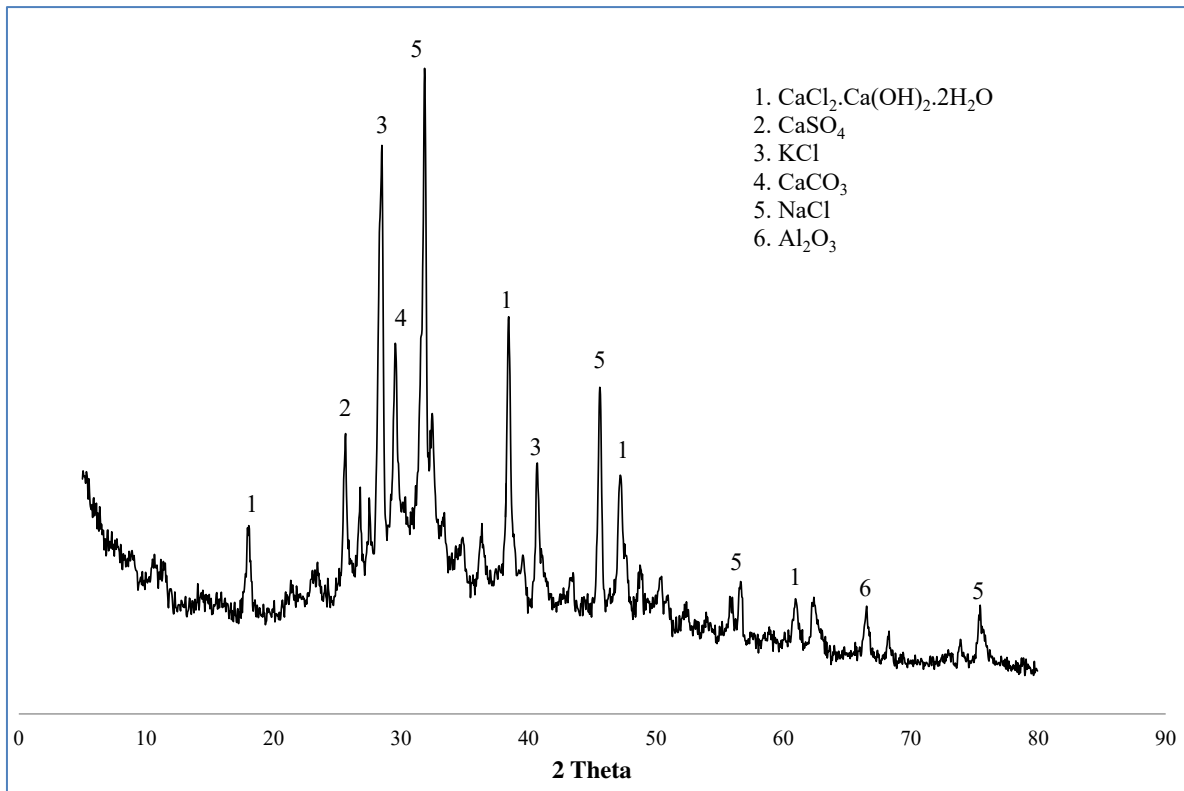


Figure 4.7: X-ray diffraction pattern for MSWI FA

XRD pattern shows major mineral phases in the BA, such as portlandite ($\text{Ca}(\text{OH})_2$), quartz (SiO_2), and calcite (CaCO_3) and minor compounds are calcium aluminum hydrate ($\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 5\text{H}_2\text{O}$), jaffeite ($\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$), and tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$). Very minor peak appears to be xonolite ($\text{Ca}_6\text{Si}_6\text{O}_{17} \cdot (\text{OH})_2$). In the BA, oxide and hydrated phases are present: jaffeite, poorly crystalline calcium silicate hydrate in high temperature [143] which is relevant to the high temperature incineration of MSW; $\text{Ca}_3\text{Al}_2\text{O}_6$, an integrated component of cement grain [144]; and xonolite, a natural equivalent to tricalcium silicate hydrate that happened to be cement constituent [145]. Jaffeite, which is produced at high temperature during the incineration process, is known to be a strength building component, contributing to the strength development when used in concrete [143]. Presence of several

strength building hydrated phases from the BA XRD analyses are in agreement with the findings by other researchers [16, 17].

XRD pattern of the FA results in numerous peaks. Major phases are halite (NaCl), sylvite (KCl) and calcium chloride hydroxide hydrate ($\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$). Minor phases are calcium sulphate (CaSO_4), calcite (CaCO_3), and Alumina (Al_2O_3). XRD analysis supports the chemical composition analysis (Table 5) that the prevalence of Cl in FA and the presence of several salts of K and Na with comparative abundance of Ca and Cl compounds. These findings of presence of highly soluble Na and K salts are in good agreement with the results addressed by fellow researchers [66, 87, 135, 136, 146, 147]. Compound $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ appears to be originated from FA treatment with lime scrubber. CaCl_2 is believed to be hardened and filled the gap between FA particles, thus the presence of $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is expected to indirectly improve the mechanical strength of FA [2].

4.6 Hydrogen Gas Evolution Experiment

Hydrogen gas generation problem is associated with the beneficial use of MSWI BA and FA in construction materials [2, 8], especially in cement paste and concrete due to the hydrolysis of metallic Al which is present in MSWI BA and FA as confirmed by material characterization [24, 25, 35]. In order to investigate the hydrogen (H_2) gas generation from MSWI BA and FA and to estimate the relative amount of metallic Al in total Al content in the MSWI ashes, both the BA and the FA were treated with an excess amount of 1, 2 and 3 M NaOH solution and reaction product H_2 gas was collected in an inverted cylinder over water as shown in the Figure 4.8.

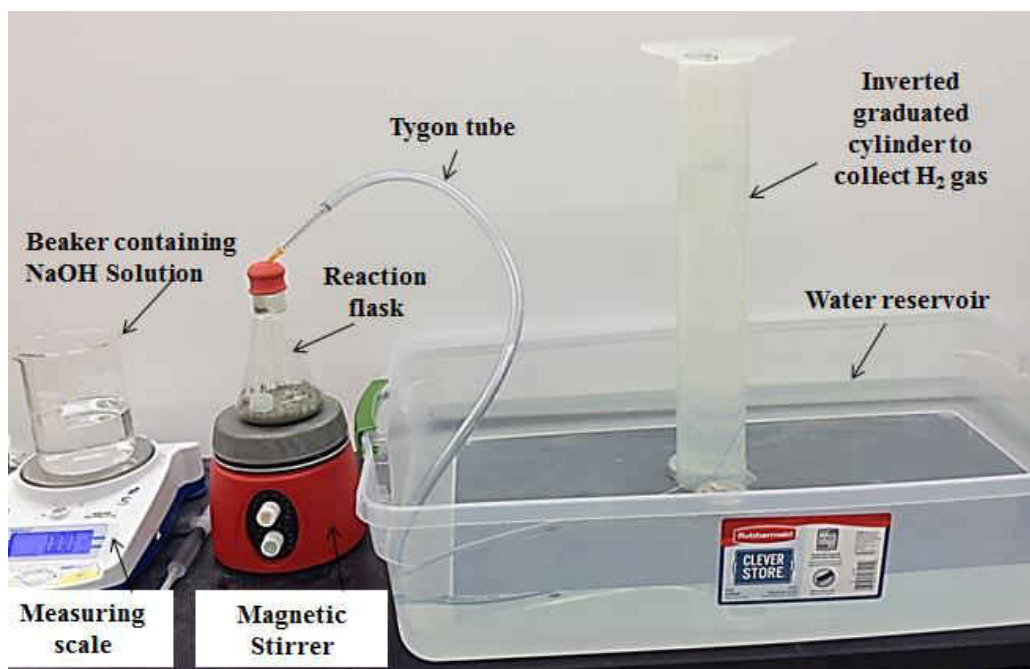


Figure 4.8: Ash experiment for measuring the H₂ gas evolved from metallic Al within the BA and FA samples

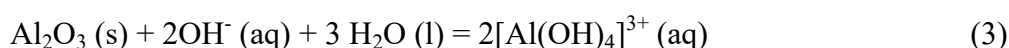
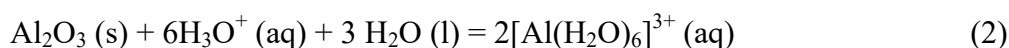
Experiments were carried out to measure the hydrogen gas by using varied amount of Al, Al₂O₃, BA and FA samples (with same particle size of 90 μm) in NaOH aqueous solution at different volume and concentration. Aluminum and aluminum oxide powders used in this test were obtained from Alcoa, Inc., Rockdale, TX and N.T. Ruddock Company, Cleveland, OH, respectively. According to the material data sheet provided by each manufacturer, both powders have particle sizes of 90 μm (0.0035 in.) and over 99% of purity. Molecular biology grade sodium hydroxide beads were ordered from Fisher Scientific, Hanover Park, IL. All reaction materials used in this test were prepared their particle size smaller than or equal to 90 μm (0.0035 in.).

In separate experimental trials, pure Al, Al₂O₃, BA and FA samples were added in Erlenmeyer flask and the flask was facilitated with magnetic stirrer for proper mixing. NaOH

solution was added from the top of the flask through septum in order to prevent any gas produced to vent from the system. Gas evolved due to the reaction of sample with NaOH solution was collected through Tygon tubing from the flask and collected in an inverted graduated cylinder over water. Since H₂ gas is sparingly soluble in water, the water over which H₂ gas collected did not require pre-saturation with H₂ gas. However, the graduation marks in the cylinder were recorded before and after the reaction for 24 hours; the volume changes within the cylinder correspond to the production of H₂ gas. Theoretical amount of H₂ gas produced from metallic Al [148]:



On the contrary, Al₂O₃ does not produce H₂ gas as shown in following reaction scheme [149]:



In all separate experimental setup (shown in Figure 4.8) for Al, BA, and FA, H₂ gas evolution has been observed in the inverted graduated cylinder according to Eq. (1). However, as expected from Eq.s (2) and (3), no H₂ gas production was observed from Al₂O₃. The experimental data are summarized in Table 4.2.

Table 4.2: Data collection for hydrogen gas evolution from Al, Al₂O₃, BA and FA

Material (g)	Solution (NaOH)		Gas Production (ml)	Mass Difference (g)	Gas Production per (ml/g)	Avg. Production gm(ml/g)	Gas Theoretical production (ml/g)	Backcalculated Al content (g/g) wt%
	(M)	(ml)						
Al	0.29	1	10	390	0.19	1344.82	1344.82	1350
Al ₂ O ₃	1.05	1	10	0	0.78	0	0	-
	150	3	400	0	1.4	0	0	-
FA	20	1	150	0	0	0	0	-
	40	3	100	0	0.97	0	0	-
	80	3	200	20	1.57	0.25	0.383	0.028
	100	2	400	50	0.93	0.5	0	-
	150	3	400	60	1.31	0.4	0	-
BA	10	1	30	0	0.2	0	0	-
	50	1	100	10	1.13	0.2	0.333	0.025
	100	2	400	40	1.17	0.4	0	-
	150	3	400	60	1.3	0.4	0	-

In Table 4.2, theoretical volume of hydrogen gas evolution per unit mass of metallic Al is 1,350 ml/g at temperature of 23 °C and atmospheric pressure and experimental hydrogen gas volume was 1,344.8 ml/g; thus, the calculated metallic aluminum content of the aluminum powder used in this test is 99.62% by weight. As expected, no development of hydrogen gas was detected as a result of the hydrolysis reaction of Al₂O₃ in alkaline sodium hydroxide solution even when the concentration of solution was increased to 3 M. When a small quantity of ashes was used with low sodium hydroxide concentration, the reaction rate appeared to be significantly reduced and therefore, hydrogen gas was not detected during 24 hours. Except for the initial two cases for both ashes when small quantities were used in low concentrated solution, the calculated aluminum contents in both ashes were approximately 0.03% by weight. Aluminum content in the BA and the FA as observed by the chemical experimentation appears considerably small; thus, they are not evident from the XRD analyses (shown in Figure 4.6, and 4.7).

4.7 Summary

In order to investigate the potential beneficial utilization of MSWI ashes as construction material, extensive material and chemical characterization have been conducted. According to the microstructural analyses, the FA particles exhibit more irregular, angular morphology and internal porosity compared to the BA; thus, it may cause the reduced workability and high leaching potential from FA while using in cement and asphalt. Based on the chemical composition and phase analyses using EDS and XRD, respectively, beneficial components are present in both MSWI BA and FA. Hydrogen gas evolution test, however, shows evolution of hydrogen gas even from significantly small amount of metallic Al which appears to present in MSWI BA and FA eventually will lead to inferior mechanical performance of the ash-mixed concrete. High content of soluble salts, Cl, and heavy metals were also observed in the FA that is attributed to potential leaching from FA application site.

CHAPTER 5 LEACHING EVALUATION OF MSWI BOTTOM ASHES IN HMA AND PCC

5.1 Introduction

Significant reduction of toxic element leaching has been observed due to the physical and chemical encapsulation while MSWI ashes are incorporated into HMA and PCC. Environmental impacts of the MSWI BA used as a partial replacement of fine aggregate in HMA and PCC were evaluated. Leaching properties and behaviors of those HMA and PCC containing varied amount of the BA have been investigated by conducting a number of SPLP batch tests. Details of leaching tests are presented in this chapter.

5.2 Leaching Characteristics of MSWI Bottom Ash in HMA

In this section, the leaching characteristics of major and minor inorganic elements from HMA containing different amount of BA were investigated.

5.2.1 Material and Methods

BA-combined HMA specimens were prepared by replacing fine aggregate with 0 (control specimen), 10, 20, 30, and 40% of BA. The BA with particle size smaller than sieve No. 4 (4.45 mm) was used as replacement of fine aggregate in HMA. Marshall Mix Design was employed for the specimen preparation. 4-in. diameter HMA specimens were prepared with the optimum binder content of 5.7% based on the mix design. Compacted (hardened) HMA specimens containing the BA were then crushed to obtain sample size greater than 9.5 mm which were subject to standard SPLP tests as shown in Figure 5.1.



Figure 5.1: HMA specimen containing BA with particle size greater than 9.5 mm

After the samples were prepared, leaching tests were outsourced because of incapacity of testing facility in the laboratory. Batch SPLP tests [100] has been devised in the laboratory (see Figure 5.2) in order to simulate leaching scenario from BA application site due to the rain water percolation. Extraction fluid was prepared by mixing sulfuric and nitric acids to obtain solution with pH 4.2 to simulate rain at the east of the Mississippi river. BA-mixed HMA specimens with particle size greater than 9.5 mm were subject to the leaching experiment in 2 L High Density Polyethylene (HDPE) extraction vessel at solid-to-liquid ratio of 1:20 by mixing 1.5 L of synthetic rain and 75 g of HMA with BA. The HDPE vessels containing leaching solution and sample were agitated in a rotary tumbler at 30 rpm for 18 hours. All SPLP extracts were then filtered out by using a 0.25- μm filter paper under 50 psi pressure, preserved with nitric acid, and stored at 4 °C. Leaching tests were conducted in triplicate.



a) Extraction vessels and samples



b) Preparation of extraction fluid



c) Vessels placed in tumbler



d) Rotary tumbler at 30 rpm

Figure 5.2: SPLP leaching test set up for HMA sample containing BA

Major alkaline elements and trace heavy metal concentrations in the eluate were determined with inductively coupled plasma optical emission spectrometry (ICP-OES, Vista-MPX CCD Simultaneous ICP-OES, Varian Inc., CA, US). Total ten elements, Al, Ca, Na, Si, and K (major elements) and Cu, Fe, Mg, Ti, and Zn (minor element) were chosen to be evaluated in this study. Major elements including Al, Ca, Na, Si and K have too high concentration to detect with minor elements. Sampling solution was diluted at 1:50 and reanalyzed the concentration of the major elements.

5.2.2 Leachate Analysis for HMA Containing Bottom Ash

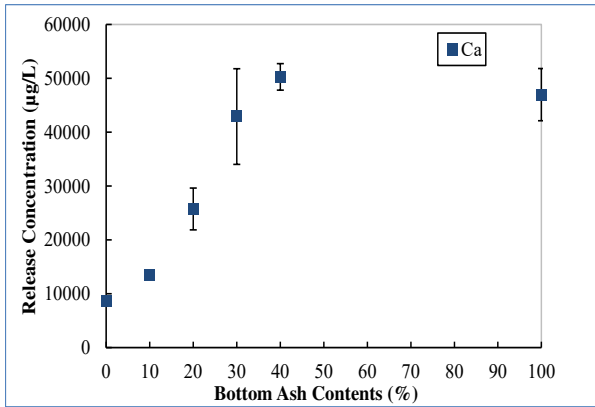
5.2.2.1 *Effect of the Bottom Ash Contents*

Batch leaching tests for HMA containing different amount of BA from 0, 10, 20, 30, and 40% were conducted to investigate the effect of BA content on leaching behavior. As a control specimen, the case of BA without HMA also was tested.

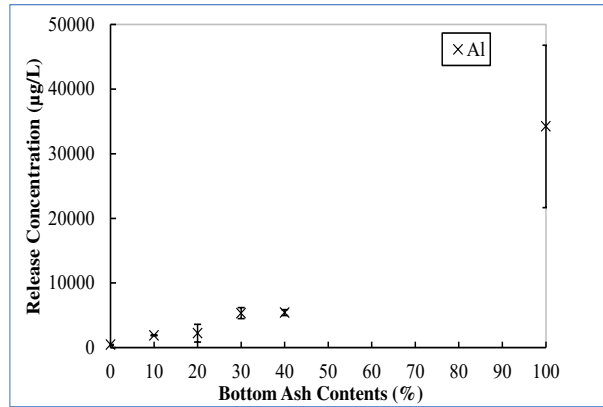
For major element such as Ca, Al, Si, Na, and K which are large portion of component in HMA with BA in terms of weight, release concentration increases with increasing the BA content as shown in Figure 5.3. With increasing BA contents, the major elements are more exposed to synthetic rain solution and cause more leachates. Since these elements are more abundant in the BA than the HMA, the leachate of the elements from HMA containing the BA is similar or less than those from the BA without HMA.

However, minor elements such as Cu, Fe, Mg, Ti, and Zn show different leaching behavior from the major elements. Generally, minor elements are slightly reduced in lower contents of the BA (e.g., 10 and 20% of BA) and then increase again in higher contents of the BA (e.g., 30 and 40%) as shown in Figure 5.4. Significantly reduced leaching of heavy metals (except Zn) with time are observed for BA combined HMA with compare to BA itself.

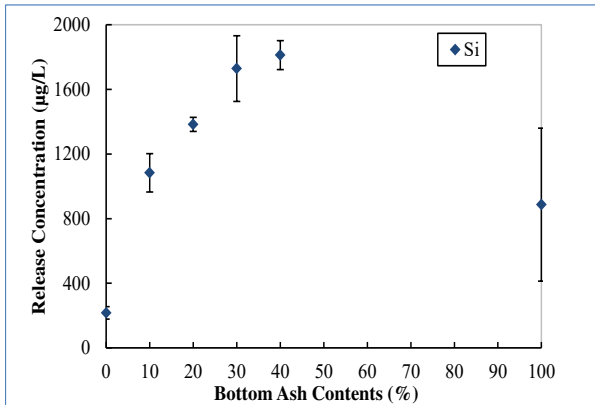
Zn is believed to be originated from HMA itself thus higher leaching of Zn is the results of adding HMA with BA. One of potential reasons of this trend is attributed to the adhesiveness of the HMA that can capture the minor elements to impede release into the solution, as also observed by other researchers [2, 88, 129]. In comparison with the control specimen, the concentration of release from HMA containing BA is similar or less than those from BA without HMA (see Figure 5.3 and 5.4) for major and minor components.



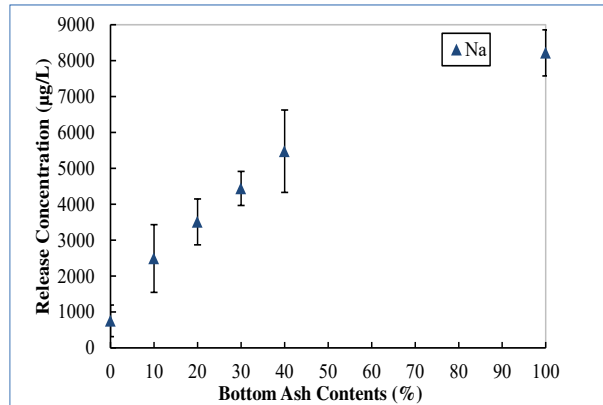
a) leaching of Ca



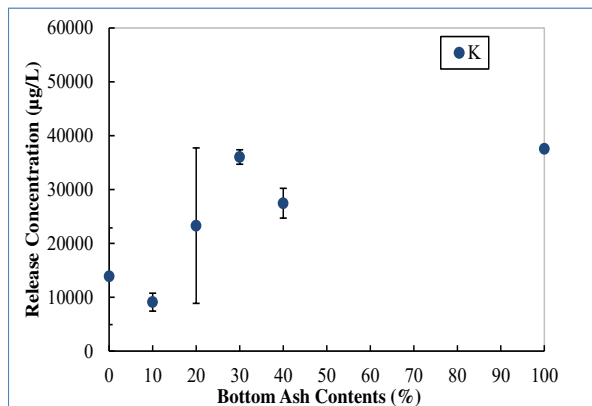
b) leaching of Al



c) leaching of Si

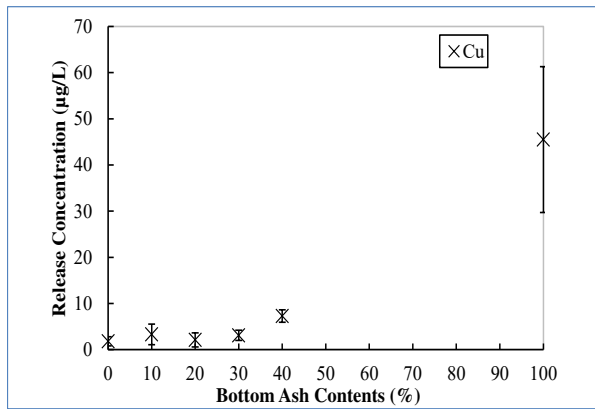


d) leaching of Na

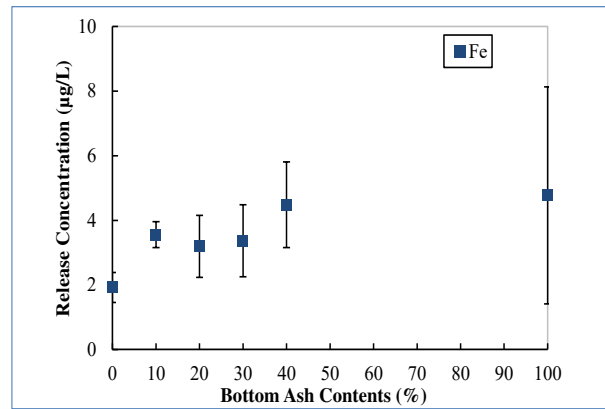


e) leaching of K

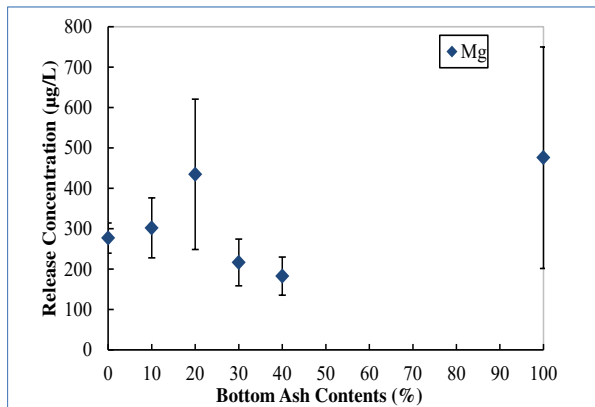
Figure 5.3: Effect of BA contents for releasing major elements in 1 day from HMA with BA



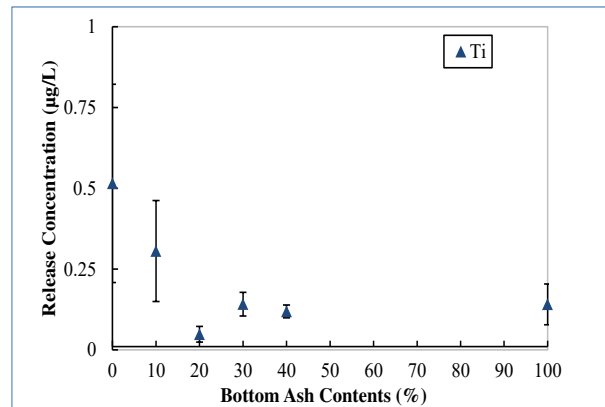
a) leaching of Cu



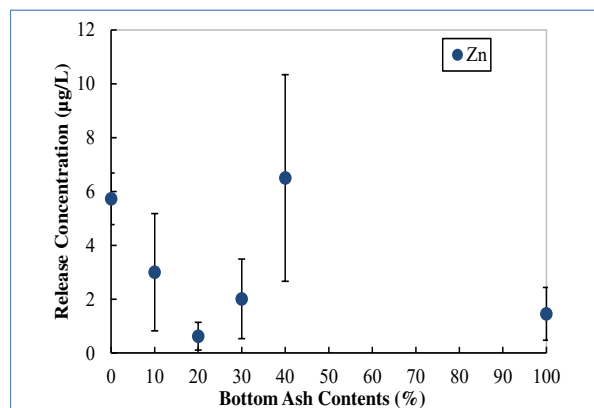
b) leaching of Fe



c) leaching of Mg



d) leaching of Ti



e) leaching of Zn

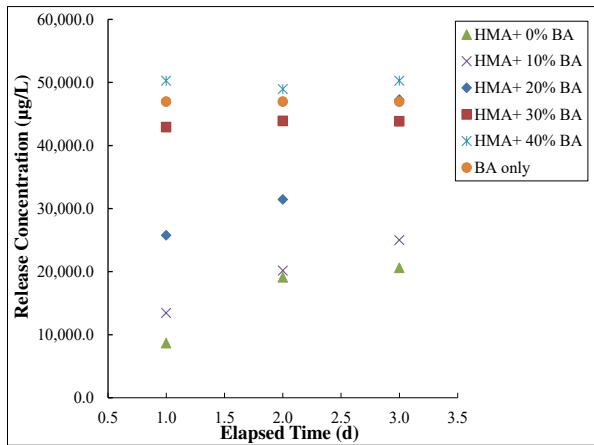
Figure 5.4: Effect of BA contents for releasing minor elements in 1 day from HMA with BA

5.2.2.2 Effect of Elapsed Time Exposed to Synthetic Rain Solution

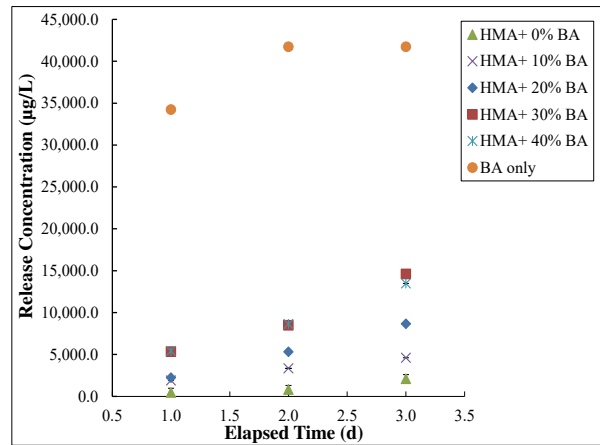
Typically, the concentration of major elements increases with increasing time except Ca. However, the concentration of minor elements is stable or reduced with increasing time (see Figure 5.5) which appears to be the characteristics of availability control leaching [2, 33] where leaching of elements is a function of “availability of leaching”. However, the source of Ca, Al, Na are from BA itself, whereas, both BA and HMA contribute to the concentration of K. In addition, higher leaching of Al at low pH condition with the progress of time is attributed to the characteristics of amphoteric element [2, 33] which exhibits high release concentration of element both at low and high pH condition.

Ca is out-ranged from detection limit, which shows approximate 50000 µg/L regardless high contents of BA. High concentration of Ca is believed to be partially originated from limestone which was used in HMA as coarse aggregate, is predominantly CaCO₃. Limestone disintegrated during the crushing of HMA as the sample preparation for the leaching test; thus broken limestone aggregate particles were exposed to the acidic extraction fluid which leads to the high content of Ca leaching with time.

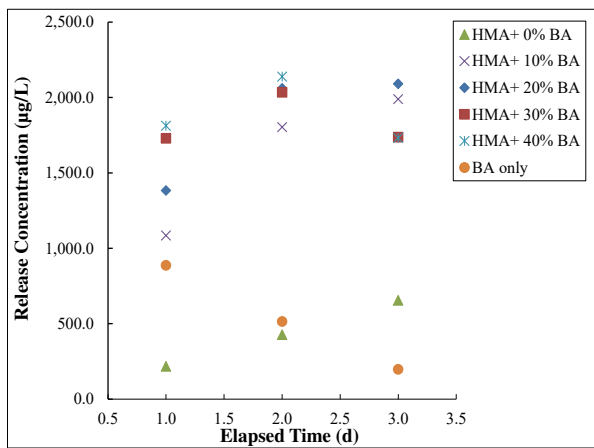
The concentration of minor elements exhibit steady or even reduced leaching trends with time for the HMA specimens containing 10 and 20% BA (see Figure 5.6). Higher proportion of BA provides higher content of minor elements available for acid leaching; thus, with elapsed time minor element leaching increased for the specimens containing 30 and 40 % BA. Acidic pH of the synthetic rain solution over 3 day period cause to lower the pH of the leachate, thus available elements in the specimens were subject to release over the elapsed time.



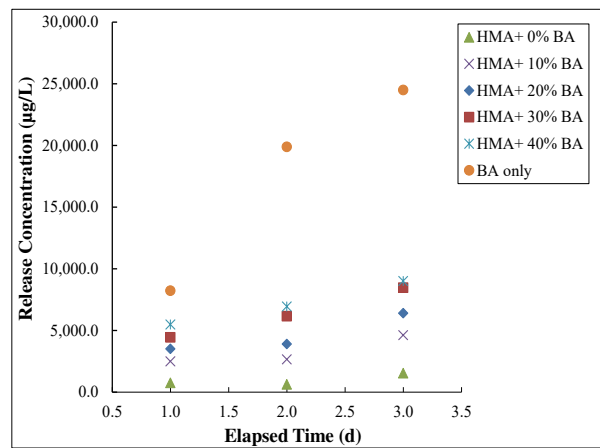
a) leaching of Ca



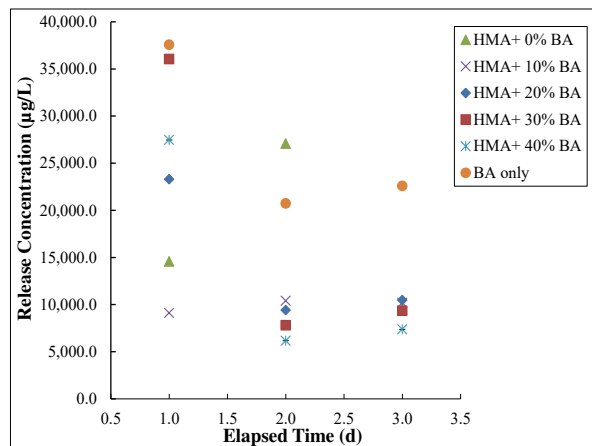
b) leaching of Al



c) leaching of Si

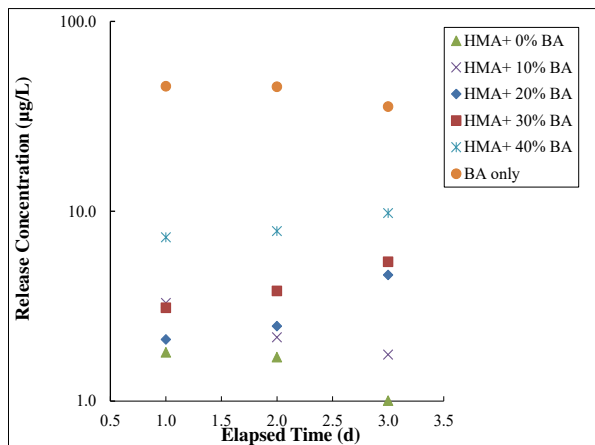


d) leaching of Na

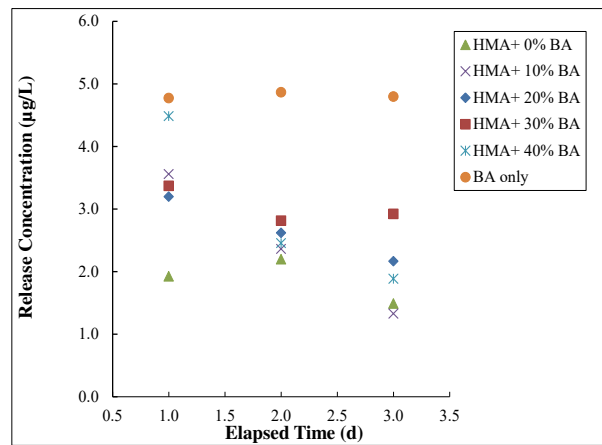


e) Leaching of K

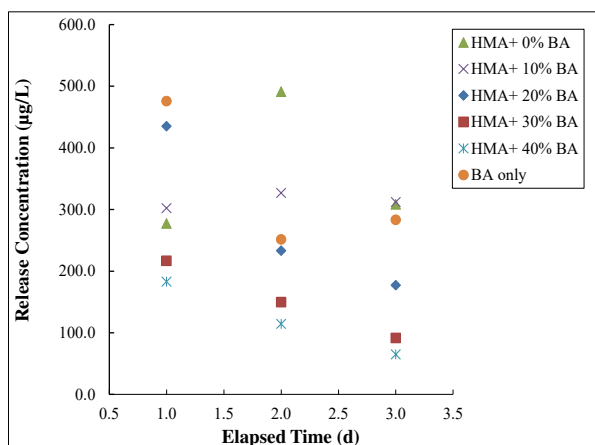
Figure 5.5: Leaching concentration for major elements from BA mixed HMA with respect to elapsed time



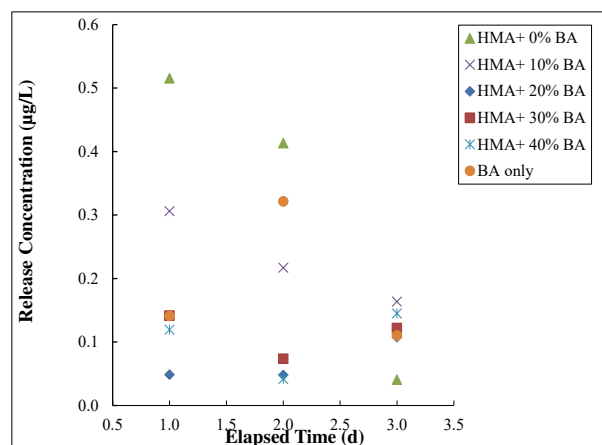
a) leaching of Cu



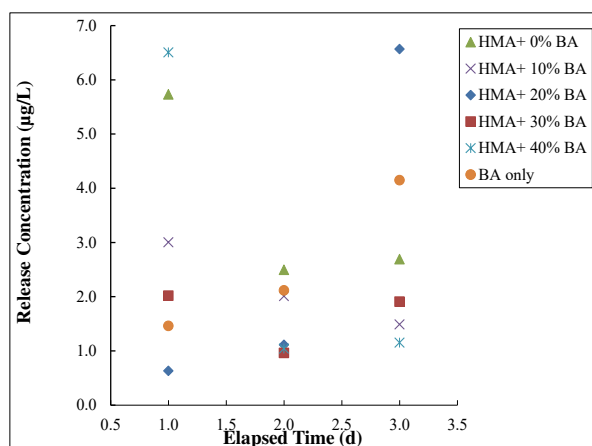
b) leaching of Fe



c) leaching of Mg



d) leaching of Ti



e) leaching of Zn

Figure 5.6: Leaching concentration for minor elements from BA mixed HMA with respect to elapsed time

5.2.2.3 Comparison with Water Quality Regulation

In order to address the potential of contamination from reuse of MSWI ashes, leaching concentration of elements of interest were compared with the stringent drinking water standards [63] and more pragmatic Multi-Sector General Permit for Stormwater Discharges Associated with Industrial Activity, the “2008 MSGP” [150], both of which are regulated by the U.S. Environmental Protection Agency (U.S. EPA).

Leachate originated from the waste utilization site, can infiltrate in the groundwater and contaminate the drinking water sources. Drinking water standard includes Maximum Contaminants Level (MCL) and Secondary Maximum Contaminants Level (SMCL) [63, 64]. MCLs are enforceable standards for the elements directly toxic for health and SMCL are the non-mandatory standards limiting the elements for aesthetic concern.

Due to the stormwater percolation through the waste application site, runoff can carry the pollutants from the application site to the receiving water; thereby, contaminate the nearby waterbodies via storm-sewer system. Therefore, U.S. EPA classified waste management as an activity at industrial facilities which can be considered as a major source of pollutants in stormwater [151] and enforced 2008 Multi-Sector General Permit (MSGP) to regulate the stormwater discharge [150].

MCLs, SMCLs and MSGP benchmarks for different elements of interest are summarized in Table 5.1. Release concentration of Fe, Zn and Al were compared with SMCLs and MSGP benchmarks. Although Cu has both MCL and SMCL, more stringent SMCL and MSGP benchmark value were considered to compare with the leachate concentration of Cu.

Table 5.1: Drinking water standard for elements of interest ($\mu\text{g/L}$) [63, 64, 150]

Element	MCL ^a	SMCL ^b	MSGP ^c
Cu	1300	1000	14000
Fe	-	300	1000000
Zn	-	5000	120000
Al	-	200	750000

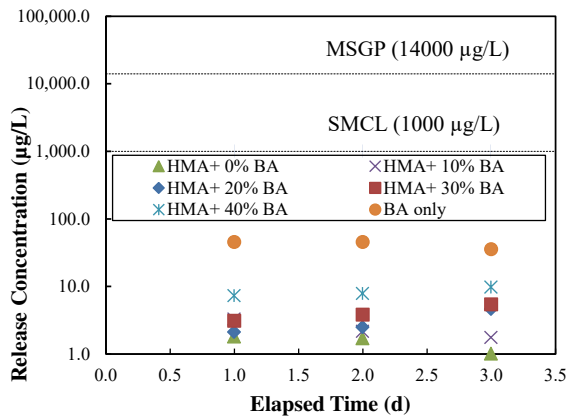
^aMCL = Maximum Contaminants Level

^bSMCL = Secondary Maximum Contaminants Level

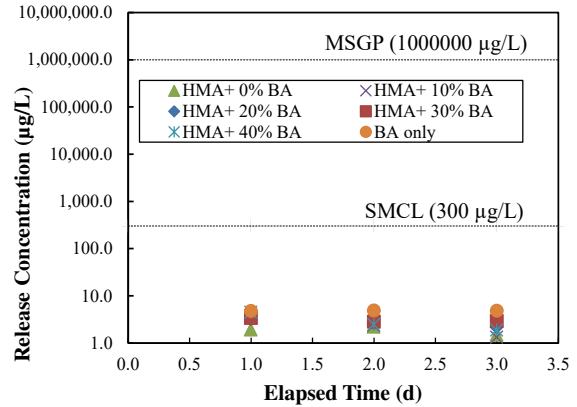
^cMSGP = Multi-Sector General Permit

The average concentration of Cu, Fe, and Zn from BA and BA-mixed HMA were far below their corresponding SMCLs (see Figure 5.7. a, b, c). Highest concentration of Cu found in the BA was in the range of 35 – 45 $\mu\text{g/L}$ which is insignificant compared to SMCL (1000 $\mu\text{g/L}$) and MSGP (14000 $\mu\text{g/L}$). Similarly, Fe concentration was found to be highest in the only BA specimens. The maximum concentration of Fe did not exceed 6 $\mu\text{g/L}$ whereas SMCL and MSGP values are 300 $\mu\text{g/L}$ and 1000000 $\mu\text{g/L}$, respectively. Although the leaching of Zn from BA is minimal, HMA containing 20% of BA exhibited comparatively higher extent of leaching in the range of 0.63 – 6.5 $\mu\text{g/L}$ which is well below the SMCL of 5000 $\mu\text{g/L}$ and MSGP of 120000 $\mu\text{g/L}$.

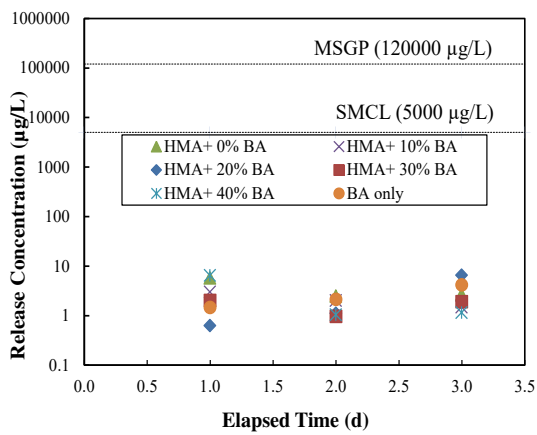
On the contrary, large amount of Al leaching resulted from BA and HMA containing BA specimens compared to the SMCL value of 200 $\mu\text{g/L}$ (see Figure 5.7. d). However, Al leaching is considerably below the MSGP benchmark value of 750000 $\mu\text{g/L}$. Leaching results obtained from control specimen (0 % BA) also gives higher Al concentration than the SMCL, but lower than MSGP limit. The concentration of Al in BA (more than 40000 $\mu\text{g/L}$) is almost 2 to 3 times higher than those of BA mixed HMA samples (range of 5000 – 14600 $\mu\text{g/L}$ from HMA containing 30 % BA). However, it is evident that such higher concentration of Al mostly originated from BA, although HMA contribute to the high leaching of Al.



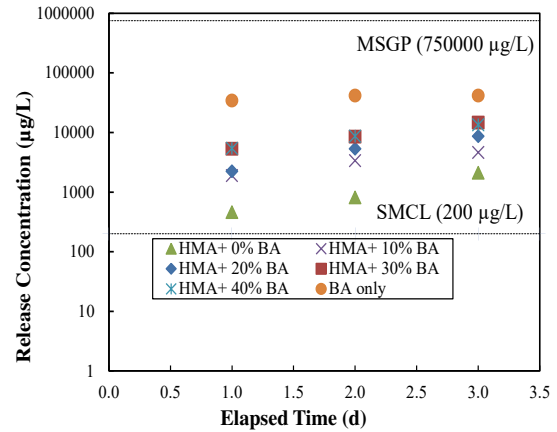
a) leaching of Cu



b) leaching of Fe



c) leaching of Zn



d) leaching of Al

Figure 5.7: Leaching concentration of priority elements from BA mixed HMA compared to SMCL and MSGP

5.3 Leaching Characteristics of MSWI Bottom Ash in PCC

In this section, leaching behavior has been investigated for concrete specimens containing different proportion of MSWI BA as partial substitute of fine aggregate. Leaching concentrations were obtained for the inorganic constituents originated from BA incorporated in concrete specimen with a different range of particle size.

5.3.1 Material and Methods

MSWI BA obtained from RDF incineration plant in Florida, U.S., were oven dried at 110 °C for 2 hours. BA was then screened to particle size range passing 4.75 mm up to 75 µm to meet the requirement for the fine aggregate replacement in concrete formulation. Sand acquired from Florida Department of Transportation (FDOT) with particle size passing 4.75 mm was used as fine aggregate and limestone sourced from CEMEX with nominal maximum size of 19 mm was used as coarse aggregate. With water to cement ratio of 0.5, five different sets of concretes specimens (100 × 200 mm²) were casted with 10, 20, 30, and 50% fine aggregate replacement with BA. The specimens were then demolded and air-cured for 28 days. Hardened concrete specimens were crushed to obtain particle size range from 20 to 40 mm in order to investigate leaching potential of major and minor constituents using SPLP test [100]. After the sample preparation (see Figure 5.8), leaching tests were outsourced due to the unavailability of the testing facility in the laboratory. SPLP tests were devised according to the same procedure discussed in Section 5.2.1. (see Figure 5.2). The concentrations of major and minor elements were analyzed using with ICP-OES as discussed earlier.



Figure 5.8: PCC specimen containing BA with particle size greater than 20 mm

5.3.2 Leachate Analysis for PCC Containing Bottom Ash

5.3.2.1 *Effect of Bottom Ash contents*

Batch leaching tests for PCC combined with 10, 20, 30, and 50% of BA were conducted to examine the effect of BA content on leaching performance. BA without HMA was also tested as a control specimen to evaluate the leaching potentials from the reuse of BA in PCC.

For most major element such as Ca, Al, K and Na, which are large portion of component in PCC with BA in terms of weight, release concentration increases with increasing BA contents except Si as shown in Figure 5.9. With increasing BA contents, the major element of BA is more exposed to synthetic rain solution and leachates more. Significant reduction of the release of Al, Si, and Na were observed due to the incorporation of BA in PCC as compared to the BA control specimen (see Figure 5.9. b, c, d). Since Ca(OH)_2 is major composition in PCC itself [119, 143], both PCC and BA were responsible for the Ca release.

However, minor (metal) elements shows different leaching behavior from the major elements. Generally, minor elements increase with increasing the amount of BA as shown in Figure 5.10. Unlike the case of the HMA, the PCC impede releasing the element from the BA in lesser extent. Ca bearing minerals are believed to encapsulate heavy metals into the PCC, PCC itself contains Fe as an integrated component in the strength building cement matrix [143], thus higher leaching of Fe from BA-mixed PCC has been observed with compared to the BA control specimen (see Figure 5.10. b). The leaching concentrations of elements from PCC containing BA, however, appeared to be lower than the control BA specimen (see

Figure 5.9 and 5.10). Replacement of 50% of BA in PCC resulted in significantly increased leaching for most of the heavy metals.

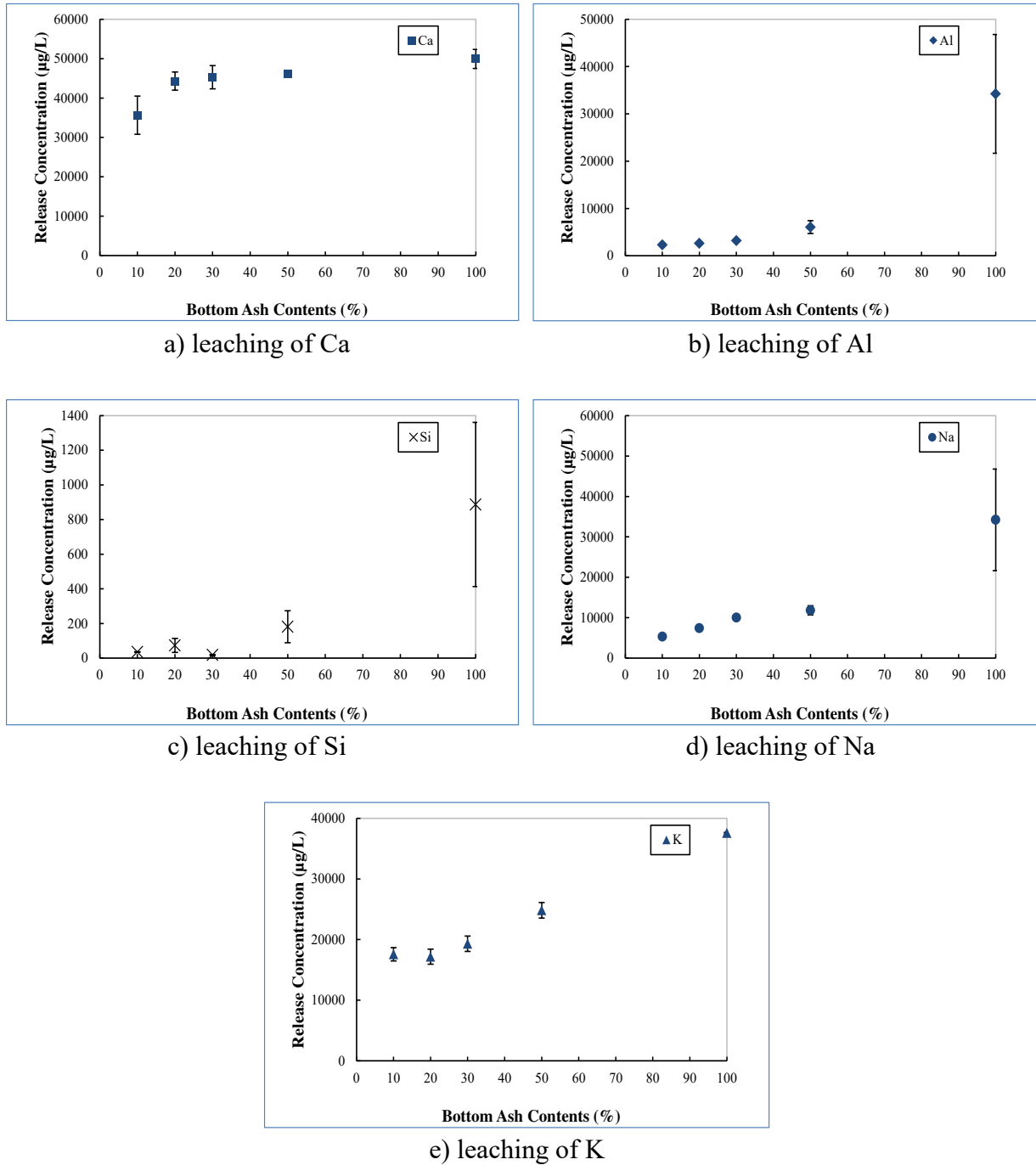
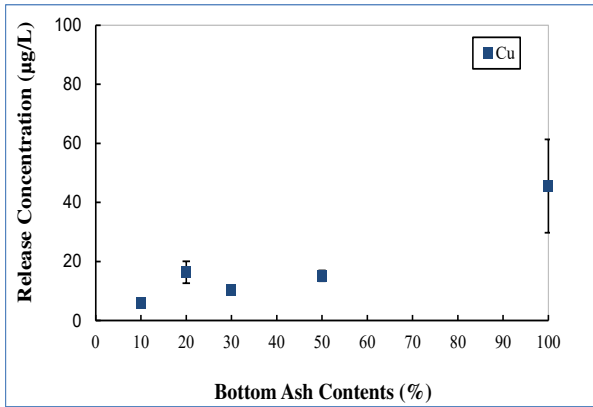
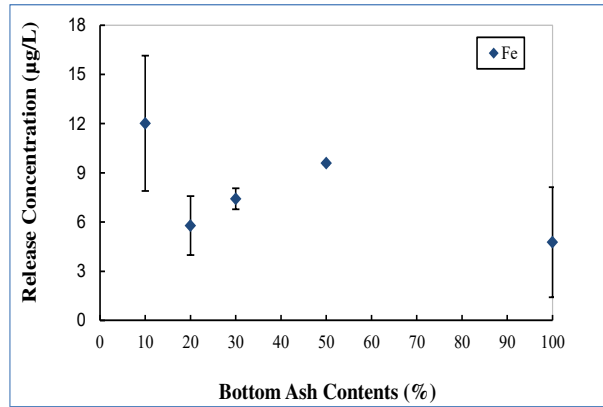


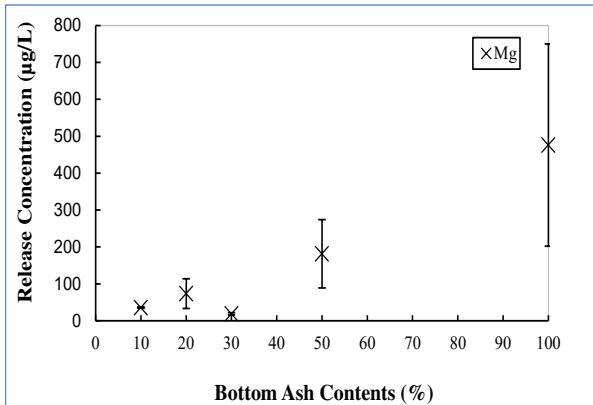
Figure 5.9: Effect of BA contents for releasing major elements in 1 day from PCC with BA



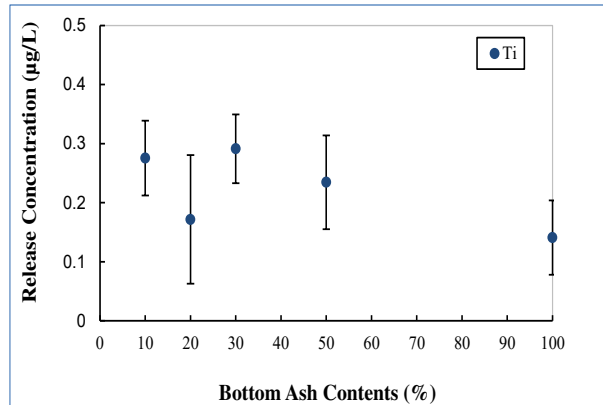
a) leaching of Cu



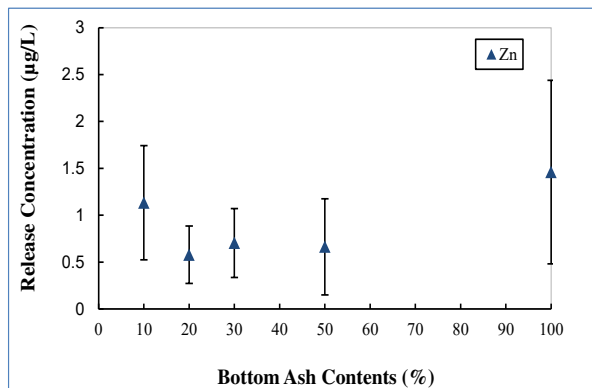
b) leaching of Fe



c) leaching of Mg



d) leaching of Ti



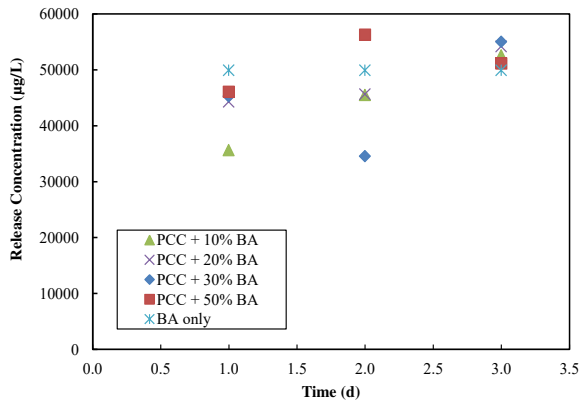
e) leaching of Zn

Figure 5.10: Effect of BA contents for releasing minor elements in 1 day from PCC with BA

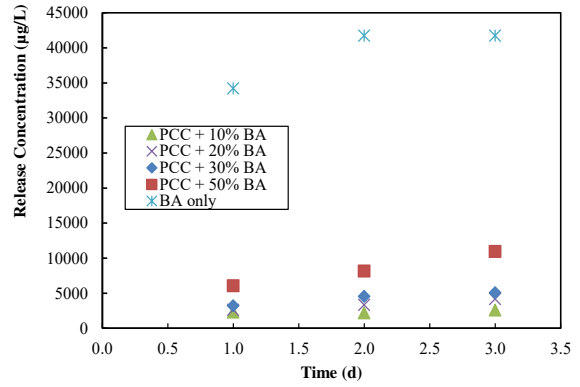
5.3.2.2 Effect of Elapsed Time Exposed to Synthetic Rain Water

Typically, the concentration of major elements such as Al and Na increases with increasing time (see Figure 5.11). These elements were available to leach due to the exposure to the synthetic rain water. Increasing release of Ca with time from the BA-mixed PCC was attributed to the Ca(OH)_2 dissolution [119] from the PCC matrix due to the acidic pH condition (Figure 5.11. a). Si showed reduced leaching with the passage of time (Figure 5.11 c). K release appears to be stable with the increasing exposure to acidic rain water (Figure 5.11 e).

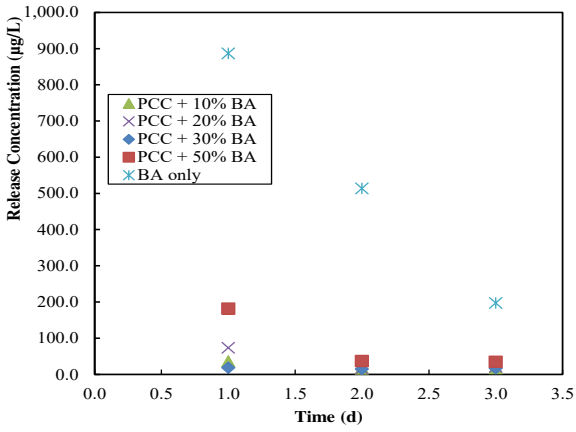
Among the minor elements, Cu, Fe, and Zn exhibit significant increase in leaching with time. Due to the acidic extraction, such increasing trend is observed. The concentrations of Fe and Zn increase rapidly in 3days due the characteristic feature of amphoteric elements exposed to acidic synthetic rain water (Figure 5.12. b and e). On the other hand, the concentrations of Mg and Ti are reduced or fluctuated with time (see Figure 5.12. c and d).



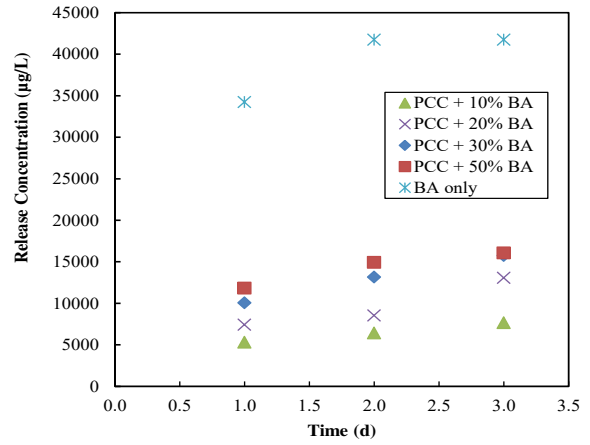
a) leaching of Ca



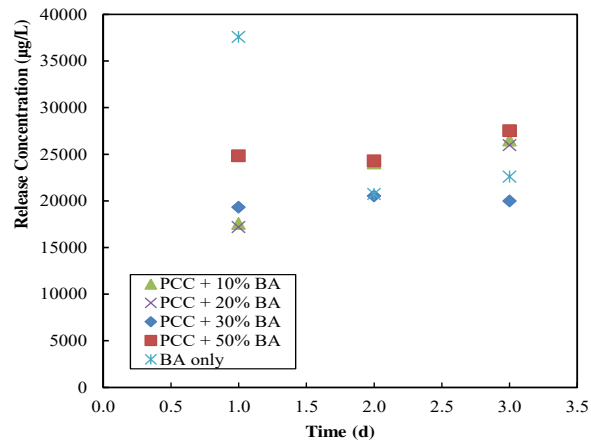
b) leaching of Al



c) leaching of Si

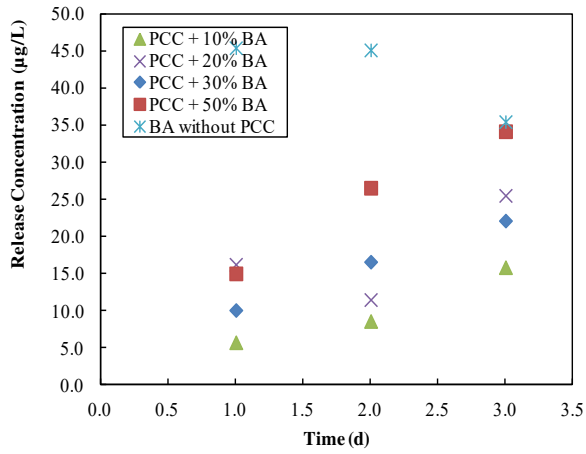


d) leaching of Na

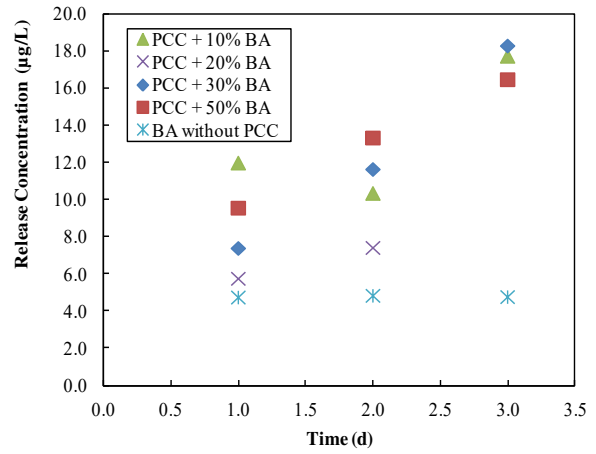


e) Leaching of K

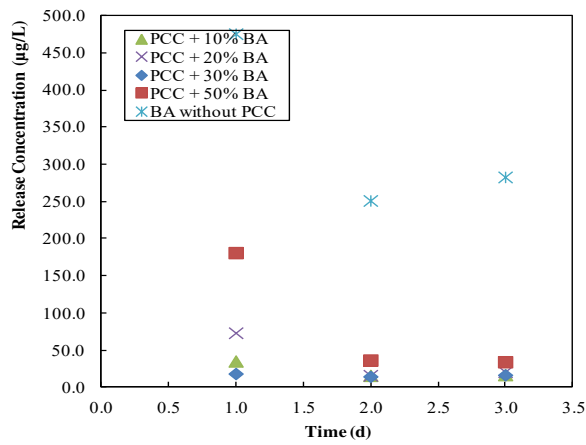
Figure 5.11: Leaching concentration for major elements from BA mixed PCC with respect to elapsed time



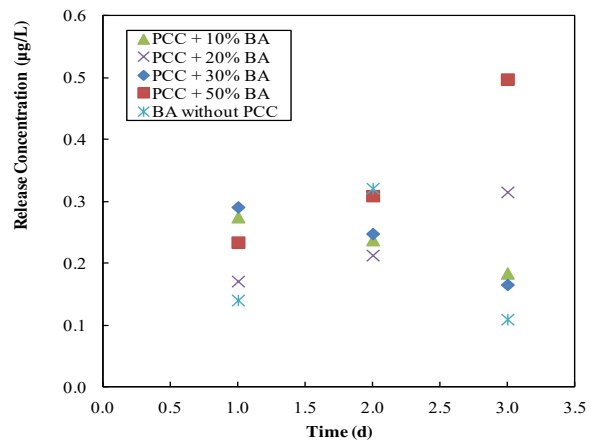
a) leaching of Cu



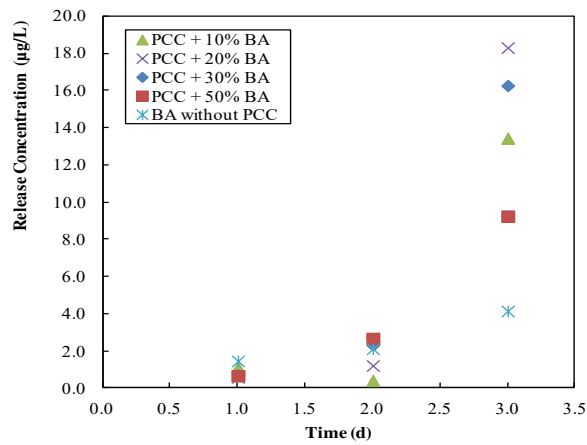
b) leaching of Fe



c) leaching of Mg



d) leaching of Ti



e) leaching of Zn

Figure 5.12: Leaching concentration for minor elements from BA mixed PCC with respect to elapsed time

5.3.2.3 Comparison with Water Quality Regulation

To investigate the environmental risk associated with application of BA in PCC, leaching concentration of priority elements from BA-mixed PCC were compared with the drinking water standards, particularly SMCLs, and stormwater discharge limit, named as MSGP benchmarks as discussed in Section 5.2.2.3. Leachate concentration of Cu, Fe, Zn and Al were compared with the corresponding SMCLs and MSGPs (see Figure 5.13).

The average concentration of Cu, Fe, and Zn (except Al) from BA and BA-mixed PCC were far below the SMCLs (see Figure 5.13). However, release concentration of these elements (including Al) remains considerably below the MSGPs. Maximum Cu concentration, found in BA, was in the range of 70.1 - 22.9 µg/L which is minor compared to the SMCL (1000 µg/L) and MSGP (14000 µg/L). Unlike BA-mixed HMA specimens, BA combined with PCC, however, did not show significant reduction of Cu and Zn leaching. Over 3 day period, PCC combined with 50% BA was found to leach 35.56 µg/L of Cu with compared to 32.26 µg/L of Cu from BA itself.

Leaching of Fe did not improve by the application of BA in PCC, rather leaching of Fe increased with the addition of PCC. With elapsed time, release of Zn increased significantly such that BA-combined PCC specimens resulted in higher leaching of Zn compared to BA specimen. Highest concentration of Zn leaching from 20% BA-mixed PCC found to be 18.3 µg/L. which is considerably below the SMCL value of 5000 µg/L and MSGP value of 120000 µg/L. Maximum concentration of Fe was found to be 16.5 µg/L from the specimen of PCC with 50% BA which is still well below the SMCL (300 µg/L) and appears insignificant compared to MSGP benchmark value of 1000000 µg/L.

Release of Al from all the specimens including BA itself exceeded the SMCL (200 µg/L), meets the criteria for MSGP limit (750000 µg/L). Unlike the HMA specimens,

significant reduction of Al was observed due to the application of BA in PCC, although they did not meet the drinking water standards. Maximum release of Al from BA was found to be 41727.5 $\mu\text{g/L}$ which was reduced to 10935.6 $\mu\text{g/L}$ in the case of 50% addition of BA into PCC.

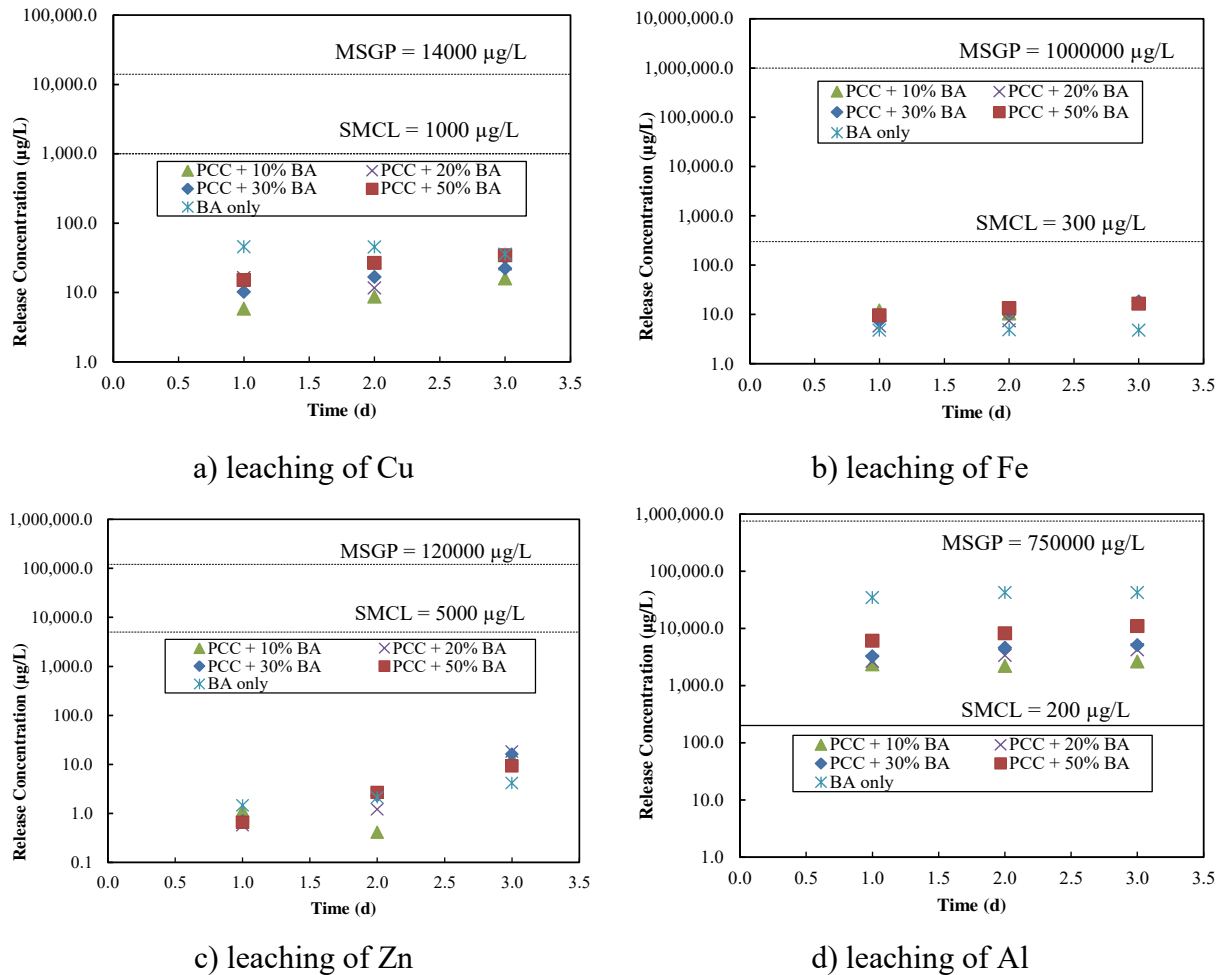


Figure 5.13: Leaching concentration of priority elements from BA mixed PCC compared to SMCL and MSGP

5.4 Summary

BA reuse in the HMA matrix appears likely for the significant reduction of heavy metal release, except for the release of Al. 10 to 20% addition of BA into HMA shows satisfactory performance to limit the release of heavy metals. HMA facilitates adhesiveness that aid to encapsulate the trace elements within the HMA. On the other hand, BA incorporation in PCC appears to be less promising to encapsulate the heavy metals. PCC specimens, however, demonstrate significant reduction of major elements except Al. Ineffectiveness to capture heavy metals into PCC matrix can be attributed to the dissolution of $\text{Ca}(\text{OH})_2$ due to the acidic synthetic rain water extraction. Ca bearing such mineral phases is believed to provide adsorption sites of encapsulation of heavy metals in PCC [33, 118].

SMCLs are associated with aesthetic concern of drinking water quality, thus this limit criteria appears to be stringent in the context of Al concentration release from the reuse of BA in HMA and PCC. Moreover, results from acid leaching do not necessarily simulate the field area of application, especially for this large amount of Al and Ca leaching. Contamination induced by stormwater infiltration through the waste application site can be considered as appropriate practical scenario of MSWI utilization. Thus, stormwater discharge limit of MSGP for the priority pollutants would be more reasonable for utilization of BA. Based on the latter criteria, leaching from BA-mixed HMA and PCC meets the stormwater discharge limits. Further leaching investigation is recommended to better simulate the field scenario. Extensive research study should be warranted for the stabilization and/or removal of major and minor elements so that BA in HMA and PCC application can be viable with least leaching potential of heavy metals.

CHAPTER 6 PRELIMINARY STUDY OF VITRIFICATION OF MSWI FLY ASH

6.1 Introduction

Vitrification is one of the most effective techniques to treat hazardous waste materials to encapsulate toxics into an amorphous glassy matrix. In particular, vitrification of MSWI FA has been extensively investigated throughout the world [152]. As MSWI ash, in general, contains significant amount of SiO_2 , Al_2O_3 and CaO which are the major ingredient of glass; thus, it has glass forming capability. It can offer a large reduction in volume up to 80 to 90% and also provide more environmentally stable and chemically resistant glassy slag which can be used as secondary material such as road base material, blasting grit, embankments, pavement bricks and water-permeable blocks [20]. It is demonstrated that dioxin, furan other toxic compounds are destructed during vitrification above $1400\text{ }^\circ\text{C}$. However, high melting temperature requires high cost associated with vitrification process and release of contaminants during melting can be an another potential concern [20]. Therefore, further air pollution control scheme may be required.

In spite of the reliability of vitrification technology, high cost due to high vitrification temperature allows this technique only for high toxic waste materials with which environment is the highest priority [152]. In this chapter, efforts have been made to develop a concept of an energy-saving vitrification technique of MSWI FA. This chapter summarizes the scientific background of vitrification, experimental works for MSWI FA vitrification and future direction for successful vitrification technique with the proof of theoretical concept.

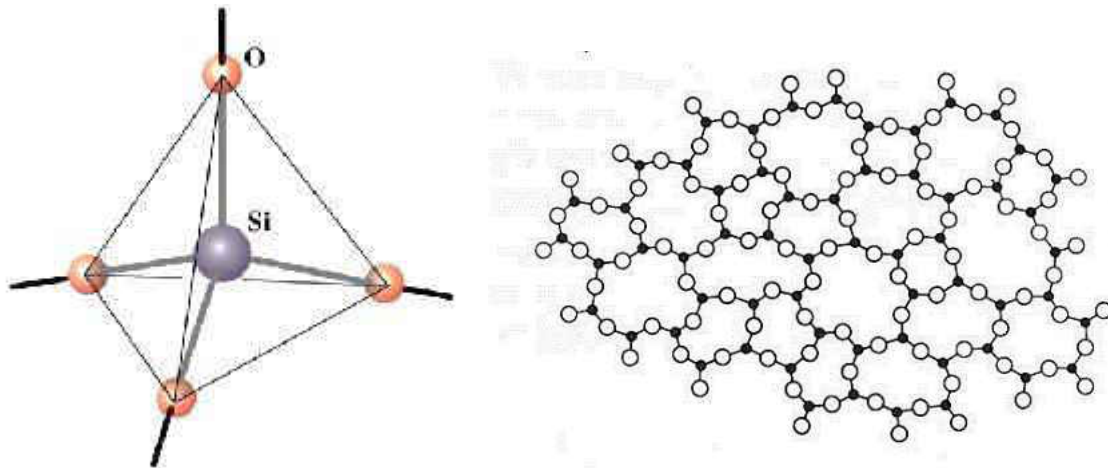
6.2 Theoretical Background

Theoretical aspects encompass glass structure, their stabilization mechanism, recrystallization, heat treatment of glassy material, and fundamental of phase diagrams of different oxide forms which are described below.

6.2.1 Structure of Glass

Vitrification can be defined as the transformation of material into amorphous glassy state. Glass is predominantly inorganic material with short range order and characteristic feature of glass transition temperature at which, upon rapid cooling, non-crystalline materials transform from super-cooled liquid to amorphous glass [153]. Vitrification technique comprises of two steps: (1) the formation of liquid phase above its melting point in the presence of glass forming oxide such as SiO_2 and (2) subsequent rapid quenching to prevent the formation crystalline phase in order to obtain glass.

Glass structure predominantly contains inorganic silica (SiO_2). The basic silicate structure comprise of silicon-oxygen tetrahedron as shown in Figure 6.1a, where a silicon (Si) atom is bonded with four oxygen (O) atoms. Oxygen atoms can be shared between tetrahedra to form three dimensional networks (Figure 6.1b). Irregular and random Si-O-Si bonds in network prevents the formation of ordered crystal structure [153].



a) Silicon-Oxygen Tetrahedron

b) Silicate Network

Figure 6.1: Glass Structure. a) Si-O tetrahedron [154], b) random 3D network structure of glass [155]

In the glass structure, the oxygen covalently bonded with Si is termed as bridging oxygen while the bond is between Si and O. When other elements are present in the glassy structure, for instance, sodium making bond with O ionically, interrupts the network continuity. Oxygen thus bonded ionically with other elements is called non-bridging oxygen. Some elements can replace Si in the glass network and make covalent bond with O are denoted as Network Former (NF) and elements those create ionic bond with O are known as Network Modifier (NM). Here is a list of elements acting as NF and NM in the Table 6.1. Alkali metals typically act as modifier. Aluminum may be a network former and sometimes modifier depending upon the alkali contents in the glass, thus is called intermediate. The role of iron depends on redox condition or oxygen availability on the molten material. For example, Fe(III) is a network former [156].

Table 6.1: Role of different elements in glassy structure [156]

Glass Former	Intermediates	Glass Modifier
Boron (B)	Aluminum (Al)	Zinc (Zn)
Silicon (Si)	Lead (Pb)	Barium (Ba)
Phosphorus (P)	Zinc (Zn)	Calcium (Ca)
Vanadium (V)	Beryllium (Be)	Sodium (Na)
Arsenic (As)		Potassium (K)
Antimony (Sb)		
Germanium (Ge)		

6.2.2 Stabilization Mechanisms

Stabilization mechanism for different elements in glassy network can be accomplished by chemical bonding: a) covalent bond, replace silicon, network former and b) ionic bond, bond with oxygen, network modifier; and another mechanism is encapsulation of the inorganic materials by surrounding molten phase and then cooled to glassy phase. In order to keep the integrity of the glass structure, network former is more involved rather than network modifier. To reduce the melting temperature of silica, alkali oxides are added which is again associated with the problem of decreasing durability and increasing leaching potential [2]. Presence of alkali and earth alkali metals oxides increases the O to NF ratio produced singly bonded oxygen, breaks up glass network that result in less durable glassy phase with slightly inferior leaching potential. In order to compensate the structural integrity issue, Al_2O_3 , Fe_2O_3 addition would be beneficial to increase durability along with an increase with melting temperature of material and crystal formation in glassy matrix. Thus, proper understanding and knowledge of the roles of different oxides in the glass formation is warranted. It is necessary to optimize the addition of materials for the vitrification of MSWI FA so that reasonable decrease in melting temperature with increased strength of the product and improved leaching behavior can be obtained. Table 6.2 shows a list of different oxides and their roles in glass processing [156].

Table 6.2: Effect of oxide addition in glassy matrix [156]

oxides	Roles in glass processing			
	viscosity	waste solubility	tendency to crystallize	durability
SiO ₂	increase greatly	reduces		increase
B ₂ O ₃	reduce	increase		slightly increase
Na ₂ O	reduce	increase		reduce
Li ₂ O	reduce greatly		increase	slightly reduce
K ₂ O	reduce	increase	increase	reduce greatly
CaO	increase then reduce			increase then reduce
MgO	increase then reduce		increase	increase then reduce
TiO ₂	slightly reduce	increase then reduce	increase	increase
Al ₂ O ₃	increase		increase	increase
Fe ₂ O ₃	reduce	reduce greatly		increase
NiO		reduce greatly	increase	increase
MnO		reduce greatly		increase

6.2.3 Devitrification/Recrystallization: Heat Treatment Analysis

In general, vitrification is followed by crystallization, either by cooling from the melt or by controlled secondary heat treatment for the formation of crystalline phases within glassy matrix. Controlled crystallization involves two stages of heat treatment, such as, nucleation and crystallization stages, within a certain glass composition range [147, 157, 158]. Small nuclei are formed during the nucleation stage and after the stabilization of nuclei, growth of crystalline phase results in crystallization in latter stage. Proper understanding of nucleation and crystallization is necessary to achieve desired microstructure and properties of derived glass-ceramic. During the formation of glass ceramic from MSWI FA, nucleating agents (Fe₂O₃, TiO₂) are present and sometimes reported to be added in the initially formed glass systems [73, 147] to facilitate crystallization.

Controlled recrystallization or divitrification are employed for the production of glass-ceramics which are characterized with better physical, mechanical and chemical durability. Glass-ceramic are fine grained polycrystalline materials derived when glasses at suitable

composition are undergone heat treatment to obtain controlled crystallization with lower stable energy state. Formation of long range ordered crystals from liquid or solid phase following two steps nucleation and crystal growth is termed as crystallization [153, 157]. During nucleation, structural lattice of atoms, ions or molecules spontaneously organize themselves as cluster of a characteristic crystal structure. Being thermodynamically stable by reaching a critical cluster size of few nanometers, nuclei start to growth as a subsequent stage of crystal growth with a definite order. This technique of crystallization is termed as heat treatment. Another means of densification of glass –ceramic is sintering which involves the heating of powdered glass below the melting point to allow the diffusion across grain boundary and fusing to each other to facilitate denser product with improved properties. Sintering process is governed by surface crystallization whereas heat treatment is mostly by bulk crystallization [72, 157].

Based on the composition of raw material, nucleation and crystal growth are associated with characteristic temperatures which are required to obtain precisely using Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC). Key terminology of those temperatures is described below.

- T_g (glass transition temperature): It is a temperature below which the physical properties of amorphous materials behave like glassy state, and above which amorphous materials behave like liquids. It is also the mid-point of a temperature range (usually at 600–700 °C) in which the materials gradually become more viscous and change from being liquid to solid.
- T_c (crystallization temperature): Above this temperature, a crystallization process consisting nucleation followed by crystal growth. During this process, a sharp

exothermic peak (usually between 700 and 800 °C) on the DSC figure could be clearly observed.

- T_m (melting temperature): Liquid temperature is the temperature at which the specimen changes from solid to liquid state. It represents the temperature for the dissolution or melting of crystals, and is usually above 1200 °C.

Typical DSC or DTA analysis is shown in Figure 6.2, the plot of heat flow of the material against the temperature that produces characteristic exothermic peaks of crystallization and endothermic peak of glass transition and melting temperature. In general, there is another exothermic peak (not sharp) that correspond to nucleation temperature in between T_g and T_c .

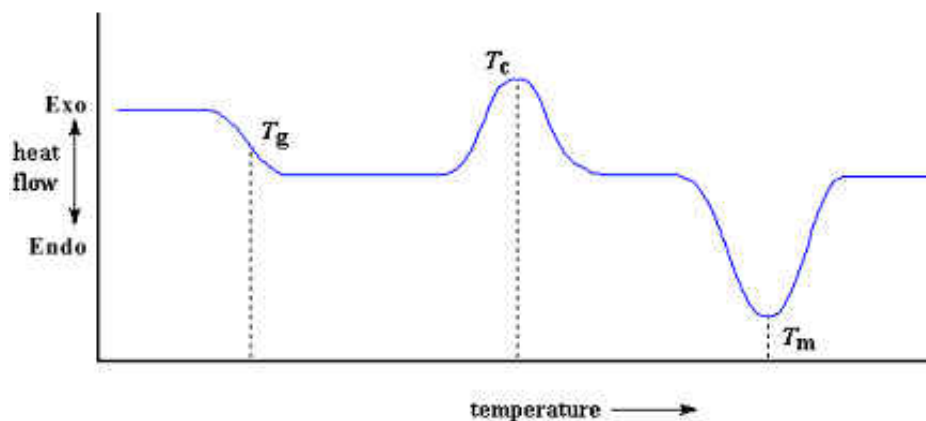


Figure 6.2: Typical heat flow pattern obtained from DSC analysis showing characteristic peaks of glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) [159]

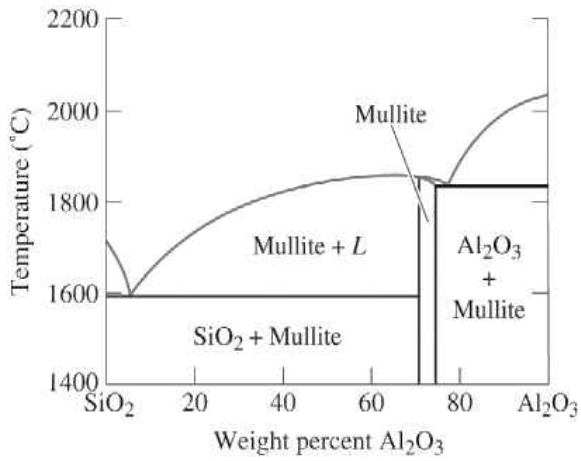
According to the DSC or DTA analysis, the parent glass is then heated at the maximum nucleation temperature and then heated to a higher temperature which refers to

crystallization temperature for a certain time for each step, and finally it is allowed to cool to develop glass ceramic. Microcrystalline glass-ceramics are produced by extensive nucleation containing higher number of nuclei are significantly mechanically superior [76]. In the case devitrified MSWI FA, most crystalline phases appears after heat treatment and sintering are reported to be gehlenite ($2\text{CaO}\cdot\text{SiO}_2\cdot\text{Al}_2\text{O}_3$), wollastonite (CaSiO_3), and other silicate and alumino-silicate phases (pyroxen groups) as observed by previous researchers [66, 72, 74, 76, 79, 80].

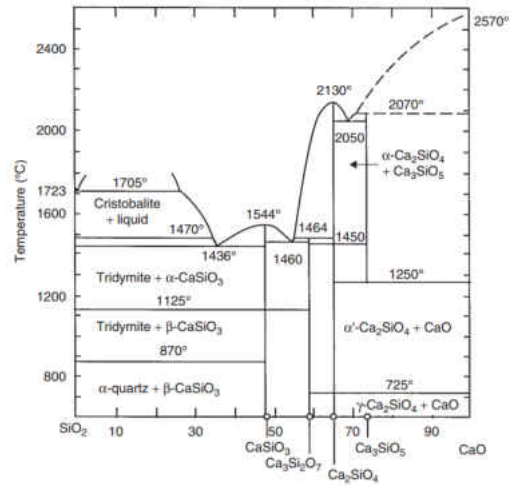
6.2.4 Phases Diagrams in Glass Formation of MSWI Fly Ash

MSWI FA, in general, belongs to $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ system based on its compositions. This chemical system is termed as ternary phase diagram which is originated and constructed from three binary phase diagram systems [153] as shown in the Figure 6.3. These phase diagrams facilitate information regarding relative composition of components in a particular phase at a certain temperature.

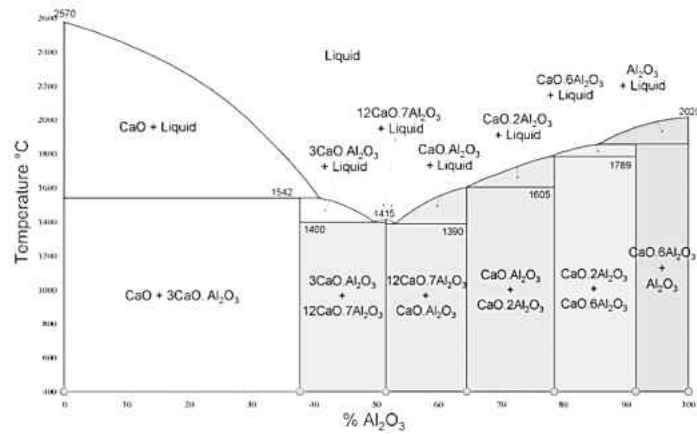
Another important feature of phase diagram is Eutectic point. A eutectic system is a mixture of chemical compounds or elements that has a single chemical composition that solidifies at a lower temperature than any other composition. This composition is known as the eutectic composition and the temperature is known as the eutectic temperature. The eutectic point can be seen in the Figure 6.4 for a hypothetical A-B binary phase system.



a. SiO₂-Al₂O₃ phase diagram [160]



b. SiO₂-CaO phase diagram [161]



c. Al₂O₃-CaO phase diagram [162]

Figure 6.3: Binary phase diagrams correspond to glass and glass ceramic from MSWI FA

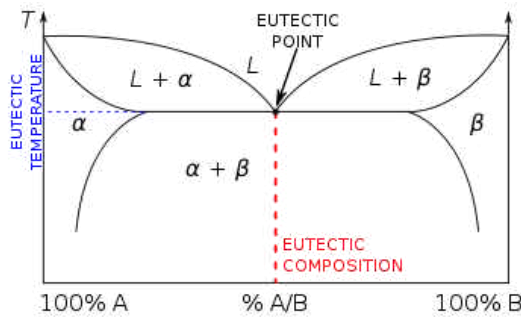


Figure 6.4: Hypothetical binary phase diagram showing eutectic point

SiO₂-Al₂O₃, SiO₂-CaO, and Al₂O₃-CaO binary systems (Figure 6.3) can be utilized to form ternary phase of SiO₂-CaO-Al₂O₃ system as shown in Figure 6.5. This represents the phases present during the glass transformation of MSWI FA, in general. In the Figure 6.5, the eutectic composition in the ternary system has been found to be 23.25 wt% CaO, 14.75 wt% Al₂O₃, 62 wt% SiO₂ at lowest melting temperature of 1170 °C.

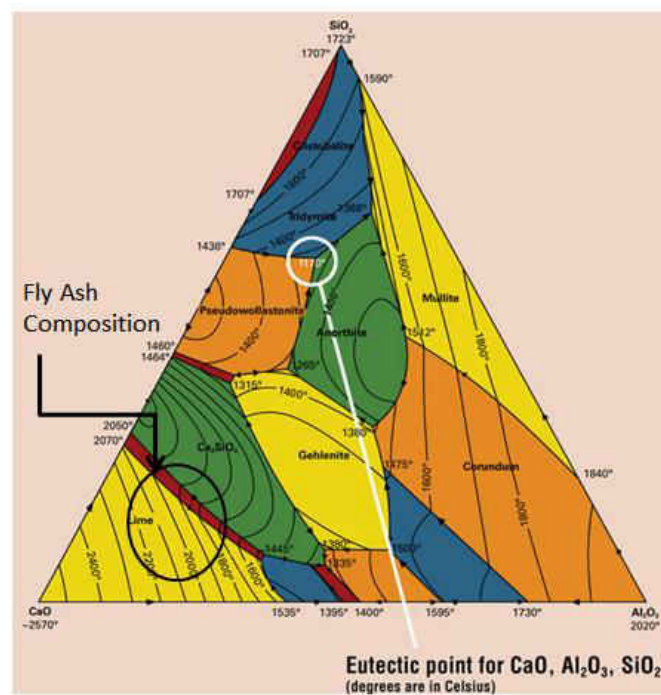


Figure 6.5: SiO₂-CaO-Al₂O₃ ternary phase diagram [163]

Figure 6.5 shows that, of all possible mixtures of minerals made only of calcium, aluminum, silicon and oxygen: anorthite (calcium feldspar), quartz and wollastonite, will melt at precisely 1170°C. MSWI FA composition falls under the dark circle zone of the Figure 6.5. Therefore, it is required to add other oxides in proper proportion with FA to obtain theoretical eutectic composition that correspond to minimum melting temperature at eutectic point.

Based on the waste composition of SiO_2 , CaO and Al_2O_3 of particular MSWI FA and melting temperature obtained from DTA or DSC analysis, it is possible to locate the position of that sample within this ternary diagram that will further give the idea about the crystalline characteristics and microstructure of resultant glass derived ceramics. This theoretical information can further be investigated for the thorough characterization of vitrified ash in terms of their chemical durability which is closely tied with the improved leaching behavior. This is an important issue for the use of vitrified ash in the context of environmental point of view.

6.3 Experimental Works

Experimental strategies have been devised for the vitrification of MSWI FA based on the theoretical aspects of glass structure, their stabilization mechanisms, and heat treatment scheme along with the aid of fundamental phase diagrams of different oxide compounds which are discussed below.

As discussed in Chapter 4, MSWI FA was obtained from a RDF plant in Florida. The RDF facility preprocesses raw MSWs with shredding and metal removal prior to the combustion; thus, feeding wastes become smaller size and more homogeneous for more effective combustion. After the combustion, FA goes to an APC device where lime-scrubber treatments are applied to the FA for reducing the acid gases. Thus, the FA characterized in this study is technically APC residues but referred as FA as a general term.

The experimental work focused on characterization of derived glass and crystallized glass-ceramic phases. Previous researchers have utilized glass-forming materials such as, silica, iron waste, alumina waste, and glass cullet for the MSWI FA to obtain desired and suitable composition for making glass [72-74]. During the glass formation, quenching was

conducted to derive glass from the melt. Either air quenching or water quenching or the combination can be used to observe the effect of quenching on the formation of glass as discussed by Kuo et al. [75].

The aim was to vitrify the MSWI FA within the eutectic composition to obtain the lowest melting temperature based on Figure 6.5. Chemical elemental composition of the MSWI FA was analyzed to identify the material to be added for obtaining the eutectic composition of FA. EDS detector equipped with SEM, discussed in Section 4.2, was used for the chemical composition analysis. The chemical compositions in oxide forms are shown in Table 6.3.

Table 6.3: Chemical composition of FA as oxide form

Oxides	FA (Weight %)
Na ₂ O	4.35
MgO	0.40
Al ₂ O ₃	1.96
SiO ₂	2.39
SO ₃	1.12
Cl	33.70
K ₂ O	13.89
CaO	18.50
Cr ₂ O ₃	0.12
MnO	0.18
Fe ₂ O ₃	2.63
CoO	0.38
NiO	2.23
CuO	1.21
ZnO	8.85
HgO	8.09
Total	100

The EDS results show that major oxides of FA are Na_2O , K_2O , CaO and HgO and Cl , and minor compounds are SiO_2 , and Al_2O_3 . Higher amount of Cl and Hg (highly volatile element) were observed in the FA. Due to the lime scrubber treatment that absorbs acid gases and produces different salts, higher amount of calcium was observed in FA. The chemical analysis demonstrates the presence of SiO_2 and Al_2O_3 (glass former) are deficient in the MSWI FA (see Table 6.3); thus, it required adding silica to obtain desired and suitable composition for glass formation.

With the aim at demonstrating the scientific concept of the vitrification technology with low melting temperature, which eventually reduces the energy consumption associated with vitrification, the first task was to obtain glass by adding glass forming oxide with the FA in an alumina crucible within a furnace (Figure 6.6). An alumina cylindrical crucible with covering lid was used with the dimension of 40 mm OD, 34 mm ID, and 40 mm height.



a. Furnace Chamber containing crucible



b. Cylindrical Alumina Crucible in the
Measuring Scale

Figure 6.6: Experimental equipment. a) laboratory furnace chamber, b) alumina crucible

In the laboratory furnace, 5 gram of the FA was placed in the alumina crucible with the lid and it was mixed with 2.3 gram of amorphous silica powder as shown in Figure 6.7 a. Amorphous silica powder with 0.2- μm particle size was purchased from Geltech, Inc. The amount of silica to be added was determined in order to meet the requirement for the eutectic composition as discussed in Figure 6.5. The mixed powder was then placed in the alumina crucible with the lid, and heat-treated at 800 $^{\circ}\text{C}$ for 1 hour, followed by melting in a laboratory furnace at 1200 $^{\circ}\text{C}$ for 1 hour. After air quenching, the final product appeared to be glassy as seen in the Figure 6.7 b.



a) FA with silica before melting



b) FA with silica after melting

Figure 6.7: Vitrification of FA. a) FA mixed with silica before melting, and b) FA with silica melting at 1200 $^{\circ}\text{C}$ with 1 hour holding time.

In order to determine the mass loss, weight before and after the vitrification was measured. Mass loss calculation is summarized in Table 6.4. Mass loss due to evaporation appeared to be negligible.

Table 6.4: Mass loss calculation for vitrification of FA

	Initial mass: Crucible + lid + 5 gram of FA + 2.3 gm of Silica	Intermediate mass: After 800 °C heating with 1 hour holding time	Final mass: After melting at 1200 °C with 1 hour holding time
Mass, gm	91.5149	90.3023	89.3081
Mass loss, %	-	1.33	2.4

6.4 XRD Analysis

Rigaku X-ray diffractometer with CuK α radiation, 2 θ scanning from 5 to 80° with 0.05° step size and 3 second dwell time per step was conducted for the vitrified silica-mixed FA sample. The XRD result for the vitrified FA is presented in Figure 6.8 and major phases in as received FA and vitrified FA from XRD results are summarized in Table 6.5.

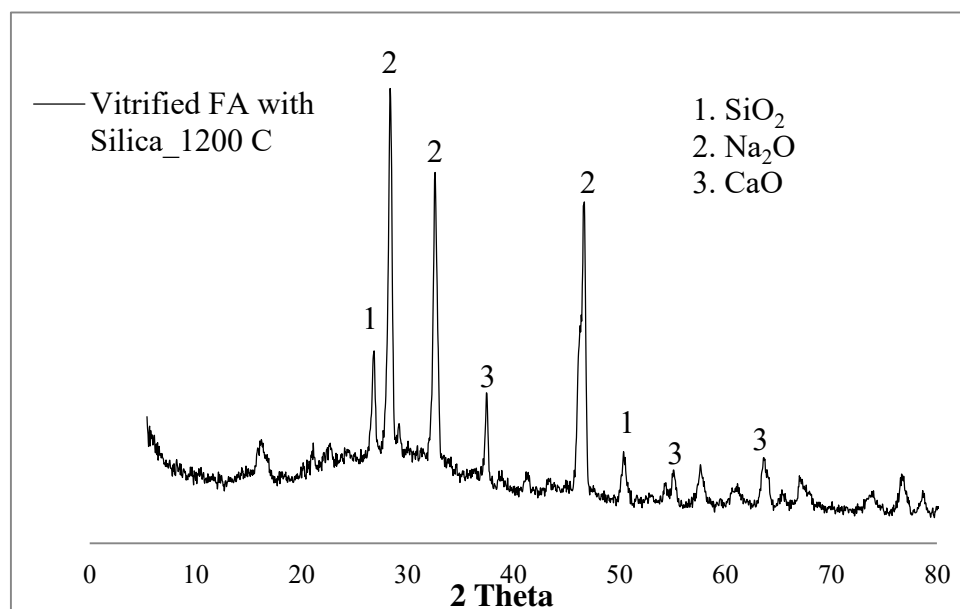


Figure 6.8: X-ray diffraction pattern for the vitrified MSWI FA

Table 6.5: Major phases in the ‘as received’ FA and the vitrified FA

Major Phases in as received FA	Major Phases in vitrified FA
Halite (NaCl)	Sodium oxide (Na ₂ O)
Sylvite (KCl)	Silica (SiO ₂)
Calcium Chloride Hydroxide Hydrate (CaCl ₂ .Ca(OH) ₂ .2H ₂ O)	Calcium Oxide (CaO)
Calcium Sulphate (CaSO ₄)	
Calcite (CaCO ₃)	

In spite of the exhibiting characteristic amorphous structure of glass, XRD pattern of the vitrified FA (Figure 6.8) shows major crystalline peaks which are associated with mostly stable oxide forms; Sodium oxide (Na_2O), Silica (SiO_2) and Calcium Oxide (CaO). In contrast, major phases in the XRD pattern of 'as received' FA are Halite (NaCl), Sylvite (KCl) and Calcium Chloride Hydroxide Hydrate ($\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$) as discussed in Section 4.5 (Figure 4.7) and Table 6.5. During melting, unstable compounds in the FA have been transformed into chemically more stable oxide forms and there were the evaporation of NaCl and KCl and dissociation of $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ at high temperature. This is in agreement with other researcher's work which revealed that NaCl and KCl in FA are evaporated at 804 and 779 °C and $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ is dissociated to remove chlorides at 689 °C [66]. The XRD analysis also supports the EDS results as shown in Table 6.3. Since Mercury oxide (HgO) transform to highly volatile elemental mercury (Hg) at high temperature [148], any significant peak was not evident in XRD data of the vitrified FA. Although, this preliminary experimentation did not result in effective glass formation of MSWI FA, it appeared to be promising by the evidence of the formation of more stable chemical forms of FA after vitrification with the aid of glass forming oxide of silica.

6.5 Recommended Future Research

Future work for the successful vitrification of MSWI FA is recommended, which is further investigations of making glass with FA and corresponding temperature behavior with the addition of other oxides using thermal analysis tool, such as, DTA or DSC as described in the previous section. A proof-of-concept test is proposed and each task is presented as followed.

1) Pure oxides to form glass

MSWI FA, in general, possesses SiO₂-CaO-Al₂O₃ system as discussed in the previous section. From the ternary phase diagram (Figure 6.5), an eutectic point refers to the lowest melting temperature of 1170 °C with composition of 23.25 wt. % CaO, 14.75 wt. % Al₂O₃, 62 wt. % SiO₂. Glass will be prepared using these compositions of glass forming oxides. Prior to the vitrification, ball milling may be necessary to reduce and control the particle size distribution throughout the sample. This is widely practiced in glass-ceramic industry to make more homogeneous material for further vitrification and processing [164]. The thermal analysis can be conducted by using the DSC or DTA to obtain featured temperatures associated with vitrification and subsequent crystallization; thus, the theoretical melting temperature shown in the ternary phase diagram (see Figure 6.5) is confirmed.

2) Adding other oxides to lower the melting points

Secondly, the research work will be aimed at reducing the melting temperature of glass. Table 6.2 demonstrates the effect of presence of different oxides within the glassy matrix. From this perspective, alkali oxide, for instance, K₂O can be added with the glass forming oxide powders to form glass. The DSC analysis can be then conducted to determine the effect of addition of alkali oxide regarding the melting temperature of the sample.

3) Adding oxides to make it more durable

Since addition of alkali oxide reduces the durability of glass (see Table 6.2), the proposed third task is associated with further addition of other oxide that can improve the durability of glass. In this case, Fe₂O₃ can be added to enhance the durability of vitrified glass; however,

addition of Fe_2O_3 may slightly increase the melting temperature of the sample which can be observed by DSC analysis.

CHAPTER 7 CONCLUSION AND RECOMMENDATION

7.1 Conclusion

Many countries, especially European and Asian countries, have already successfully implemented systematic approach towards beneficial utilization of municipal solid waste incineration (MSWI) ashes in civil construction sectors. MSWI bottom ash (BA), in general, has been utilized in the area of asphalt, road paving, and concrete products. Due to higher content of deleterious elements, MSWI fly ash (FA) is mostly disposed in the landfill after stabilization treatments. Successful recycling programs are being enforced in different countries so as to encourage the beneficial use of MSWI ashes with minimum environmental consequence.

Although research and demonstration projects ensure the beneficial utilization of MSWI ashes as a feasible option, currently there is no recycling of the ashes in the U.S. The current practice of the U.S. combines MSWI BA and FA, and the combined ashes are being disposed in landfills. This may be due to the statewide inconsistency in ash management, regulations, and standard leaching test procedures of the MSWI ash. In addition, debates regarding highly soluble salt content and heavy metal concentration in MSWI ashes further discourage its utilization.

Microstructural evaluation of MSWI ashes through SEM analysis reveals that FA possess more internal porosity and exhibits irregular and angular morphology in comparison to those of BA. This can be attributed to reduced workability of FA being used in asphalt and concrete mixtures and also increase of leaching susceptibility.

Based on compositional and mineralogical analysis by EDS and XRD, respectively, BA appears to contain higher amount of strength-building components (e.g. silica rich) than

FA, and FA mostly contains highly soluble salts, Cl, and heavy metals, which needed to be treated prior to utilization.

Metallic Al appears to be present in BA and FA based on the chemistry laboratory experiment. It demonstrates the evolution of hydrogen gas due to the metallic Al in both ashes, which is very small amount and was not detected in the XRD analysis. According to the back-calculation from the hydrogen gas measurement, both BA and FA contain approximately 0.03% of Al by weight. The presence of Al leads to the inferior performance of concrete product due to the hydrogen gas evolution produced as a result of hydrolysis of Al in highly alkaline environment.

Since highly soluble inorganic salts, Cl compounds, and heavy metals were mostly found from MSWI FA, the utilization of MSWI BA or combined ash (mixture of BA and FA) might be a potential candidate with reduced probability of deterioration. Among several options to reuse MSWI ashes, incorporating the MSWI bottom and combined ashes into hot-mix asphalt (HMA) and Portland cement concrete (PCC) are appears to be encouraging option because these can result in significant reduction of the release of toxic elements as well as sufficient level of structural integrity.

Standard leaching experiments have been conducted to investigate the environmental properties (e.g. leachate concentration of inorganic major and minor elements) of BA and ash-mixed HMA and PCC. Leaching results reveals the reduced leaching potential of toxic material from MSWI ashes while being incorporated into asphalt and concrete formulation. Release of most of the toxic elements of interest (except Al) meets the drinking water standards. However, leaching of all of the priority elements (including Al) are well below the stormwater runoff discharge limit.

As a means of advance technique to stabilize FA, vitrification appears to be a promising technique in terms of encapsulating toxic elements in glassy matrix. Preliminary study on FA vitrification demonstrates the formation of more stable form of mineral phases in fly while vitrified with the aid of glass forming compounds.

7.2 Recommendation

Weathering and proper pretreatment are highly advised prior to the utilization of MSWI ashes that can reduce the deleterious substances. Extensive research efforts should be made for the development of material processing technology to make the utilization of treated MSWI ashes as a promising option for a sustainable transportation material.

In order to utilize MSWI BA as aggregate replacement in concrete application, appropriate chemical treatment is warranted to eliminate metallic Al which produces hydrogen gas causing inferior properties of MSWI ash amended products.

Mechanical and environmental properties are required to be investigated thoroughly to obtain the optimum % replacement of MSWI ashes in asphalt and concrete in order to ensure desirable engineering performance and minimum environmental impact.

Further leaching experiments which can better represent the field condition is the context of release of Al should be devised. Effective technique of the stabilization or removal of the major and minor elements of concern is also essential in order to make BA utilization a sustainable one from environmental perspective. Besides, more relevant limit criteria should be designed that can appropriately represent the environmental consequences of BA utilization.

Extensive research needs to be conducted for the further study on vitrification of FA which demonstrates excellent leaching reduction. Since vitrification is a cost intensive and

energy consuming thermal technology, efforts are required to make this technique more economic by lowering the melting temperature by adding appropriate compounds based on glass chemistry. Glass ceramic products are merited with higher physical integrity, thus, experimental works should be planned to make glass ceramic from FA vitrification which will eventually enhance the potential of utilization of vitrified FA.

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