2015

Characterization of Waste-To-Energy (WTE) Bottom and Fly Ashes in Cementitious Materials

Jin Woo An
University of Central Florida

University of
Central
Florida

STARS
Showcase of Text, Archives, Research & Scholarship

CHARACTERIZATION OF WASTE-TO-ENERGY (WTE)

BOTTOM AND FLY ASHES IN CEMENTITIOUS

MATERIALS

by

JINWOO AN

B.S. Dankook University, 2007
M.S. Yonsei University, 2010
M.S. University of Texas at Austin, 2012

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Civil, Environmental and Construction Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Fall Term
2015

Major Professor: Boo Hyun Nam

ABSTRACT

Waste-to-Energy (WTE) ashes (or called as municipal solid waste incineration ashes) have been recycled in the areas of road bed, asphalt paving, and concrete products in many 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 for WTE ashes instead of landfill disposal. However, the U.S. has shown a lack of consistent and effective management plans as well as environmental regulations for the use of WTE ashes. Many previous studies demonstrated the potential beneficial use of WTE ash as an engineering material with minimum environmental impacts. Due to persistent uncertainty of engineering properties and inconsistency in the Federal and State regulations in the U.S., the recycling of WTE ash has been hindered, and they are mostly disposed of in landfills.

The goal of this study is to identify beneficial use of WTE ashes as construction materials; thus, the recycling program of WTE ashes will become more active in the U.S. One of potential applications for the WTE ashes can be cement-based materials because the ashes contain good chemical components such as calcium and silicon. Moreover, toxics (heavy metals) can be bound or encapsulated in cement matrix; thus, the leaching potential can be reduced. The specific objectives are: (1) to understand the current practice of the reuse of WTE ashes as construction materials, (2) to physically and chemically characterize WTE bottom and fly ashes, (3) to investigate the effects of WTE bottom and fly ashes in cementitious materials (e.g. cement paste

and concrete) as replacement of either cement of fine aggregate with emphasis on cement hydration, and (4) to investigate the environmental impacts of WTE bottom ash on leaching when used in cement-based materials.

Fundamental properties of MSWI bottom ash and fly ash were studied by conducting physical, microstructural, and chemical tests. Petrographic examinations, such as scanning electron microscopy (SEM), energy dispersive x-ray (EDX), and x-ray diffraction (XRD) were performed in order to identify chemical composition of the ash and to determine their contents. To evaluate the main side effect of ash when used in concrete, the creation of a network of bubbles due to the presence of aluminum, ashes and aluminum powder were submerged in high pH solution, and the evolution of hydrogen gas was measured.

Efforts were made to investigate the influence of WTE ashes on engineering properties of cement paste and concrete specimens when part of Portland cement and fine aggregate are replaced with ground and sieved WTE ashes. Cement paste and concrete cylinders were cast with various amounts of mineral and fine aggregate additions, respectively, and their strength and durability were investigated. Subsequently, optimum mix proportioning of the WTE ashes was investigated when they are used in cement paste and concrete specimens. In addition, the leaching characteristics of major alkaline and trace elements from concrete containing varied amounts (10%-50%) of BA were investigated by Synthetic Precipitation Leaching Procedure (SPLP) batch testing.

This work is dedicated to my mother and wife
Without their support, this work would have not been possible.

ACKNOWLEDGMENTS

I would like to express my profound gratitude to my supervisor Professor. Boo Hyun Nam for the guidance and support I received. At every stage help was available to deal with obstacles both large and small. Appreciation is also extended to my thesis committee, Professor. Manoj Chopra, Professor. Hae-Bum Yun, and Professor. Linan An for their valuable time and contributions.

I would also like to thank Dr. Jinyoung Kim for his guidance, valuable comments and profound suggestions he offered towards my research and this dissertation.

Special thanks to Behnam Golestani, Baig Abdullah Al Muhit and Kazi M. Tasneem, HoBum Lee, IlHwan Lee for their friendship and support; I truly enjoyed the time we spent together. I'd like to express my gratitude to Mr. Juan Cruz who is a lab manager and my friend, Gerald Hornik.

Most importantly, my deepest gratitude goes to my mother, ChunPyo Hong, and my wife, Dana Choi, and my sister, JinHee An who always proactively have supported me through all aspects in life, especially for the pursuit of this degree. Without my family these accomplishments would not have been possible. I also extend my thanks to my son, Abel.

PREFACE

This dissertation is the result of a Ph.D. study carried out at the department of Civil, Environment and Construction Engineering (CECE). The study was partly funded by Florida Department of Transportation (FDOT). Professor Dr. BooHyun Nam and Ph.D. Jinyung Kim acted as supervisors.

Technical report was issued during the FDOT project and is referred to in the dissertation

I.   **J. W. An**, J. Y. Kim, B. Golestani, K. M. Tasneem, B. H. Nam , A. H. Behzadan, "Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials", FDOT technical report, Grant No. BDK78-977-20, Feb 2014.

Journal manuscripts prepared during the course of the study have been accomplished during the study but some of them are not enclosed:

I.   J. Y. Kim, B. H. Nam**,** B. A. Al Muhit, K. M. Tasneem, **J. W. An**, "Effect of chemical treatment of MSWI bottom ash for its use in concrete," *Magazine of Concrete Research, 2015, 67(4), 179-186*.

II. J. Y. Kim, **J. W. An**, B. H. Nam*, K. M. Tasneem, "Investigation on the side effects of municipal solid waste incineration ashes when used as mineral addition in cement-based material," Road Materials and Pavement Design (In printing).

III.   **J. W. An**, B. H. Nam.*, and J. Y. Kim, "Investigation on the impacts of municipal solid waste incineration (MSWI) bottom ash on cement hydration", ACI materials journal (under 2nd review).

IV.   **Jinwoo An**, Jongwan Eun, and BooHyun Nam*, Effects of Cement Hydration on Leaching Behavior of Cement mixed Municipal Solid Waste Incineration Bottom Ash, Journal of cleaner production, (In preparation).

The above manuscripts are referred to in the dissertation by their roman numerals. In addition to these, two publications in proceedings are enclosed:

I.   **J.-W. An**, B. H. Nam*, J. Y. Kim, "Investigation on chemical and physical effects of municipal solid waste incineration (MSWI) ashes in cement hydration," Transportation Research Board 94th Annual Meeting, Jan 11-15, 2015, Washington DC.

II.   **J.-W. An**, B. Golestani, B. H. Nam*, Jeffrey L. Lee "Sustainable utilization of MSWI bottom ash as road construction materials, Part I: physical and mechanical evaluation," ASCE/T&DI Airfield, Highway Pavement Conference 2015, June 7-10, 2015, Miami, FL, USA.

UNIT CONVERSION

To convert from	To	Multiply by
mm	cm	0.1
	m	0.01
	in.	0.03937
	ft.	0.003281
mg	g	0.001
	kg	$1e^{-6}$
	oz	0.000035
	lb	$2.2046e^{-6}$
ml	l	0.001
	cm^3	1
	m^3	$1e^{-6}$
	$in.^3$	0.061024
	$ft.^3$	0.000035
	gal	0.000264
	oz	0.033814
Pa	hPa	0.01
	kPa	0.001
	MPa	$1e^{-6}$
	kgf/cm^2	0.00001
	psi	0.000145

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION[1]

1.1 Problem Statement

Traditionally, the most common method of disposal of waste-to-energy (WTE) ash residues is landfilling. The motivation to pursue "Florida's 75 Percent Recycling Goal" was, in part, the Energy, Climate Change, and Economic Security Act of 2008 (HB 7135, 2008). The statute requires that 75 percent of generated municipal solid waste (MSW) be diverted from disposal in landfills. Converting trash into energy in municipal waste combustor (MWC) facilities significantly reduces the waste volume (by nearly 90 percent). The remaining 10 percent is composed of fly ash and bottom ashes which can be deposed of in lined landfills.

In the U.S., bottom ash and fly ash at WTE plants are mixed together and not segregated. In many other countries, especially in Europe, the WTE fly ash is not mixed with bottom ash but rather handled as "special" waste. In these instances, the bottom ash is often recycled and used as an ingredient in paving materials, construction field materials and other similar products. In order to accomplish the best management in recycling WTE ash in Florida, there are still questions to be answered. If operators did not mix the bottom ash and the fly ash at the WTE plants:

- Would they be able to recycle the WTE ash into useful products, such as road construction materials and other infrastructure materials (Portland cement based materials)?

---

[1] An, J., Kim, J., Golestani, B., Tasneem, K.M., Al Muhit, B.A., Nam, B.H., and Behzadan, A.H., Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials.(2014)
Using the paper as a chapter of this study is **with Courtesy of the Florida Department of Transportation (please see the appendix).**

- Would using the WTE bottom ash as an ingredient in Portland cement based materials cause significant environmental problems?

One important factor hindering the accepted use of WTE ash as a construction material is its variability in physical and chemical properties due to different plants' processes and feeding materials. In addition, without consistent use of the ash in engineering applications, reuse of this material might not be economical. For these reasons, the long-range goals for ash management are to: (1) ensure a consistent and uniform production of the bottom ash by controlling the plant processes and the material which goes into the process; (2) safely increase recycling or reuse of these products; and (3) develop specific uses for WTE bottom ash as a construction material (i.e., Portland cement based materials).

1.2   Research Objectives

In Florida, since Cosentino et al. [P. J. Cosentino], any further study on the WTE bottom ash (BA) as road construction materials has not been conducted. In particular, Cosentino et al. [P. J. Cosentino] characterized only the physical properties of the WTE BA not the mechanical properties of ash mixed PCC. The objectives of this research are:

- To understand the current characteristics of WTE BA in Florida, including quantity, composition, and material variability;

- To conduct a review on the environmental properties and impacts (such as leachate concentration) of bottom ash and ash-mixed PCC;

- To characterize the physical and engineering properties of Florida's WTE BA; and

- To evaluate the mechanical performance of the WTE BA-mixed PCC with emphasis on construction field applications.

- To investigate the impacts of WTE bottom ash regarding cement hydration and leaching when used cement-based materials.

CHAPTER 2: LITERATURE REVIEW[2]

2.1   Introduction

Incineration of municipal solid waste (MSW) with energy recovery and management of municipal solid waste incineration (MSWI) ashes have been receiving a growing attention around the world. Many countries have addressed the issue of beneficial utilization of MSWI ashes by executing strategic management plans and regulations [Carlton C. Wiles, A.J. Chandler, C. Wiles, C. S. Psomopoulos, Floyd Hasselriis]. For example, many European countries beneficially utilize MSWI bottom ash as a sustainable transportation material with environmental criteria set by their strategic regulations [A.J. Chandler, C. Wiles, Juergen Vehlow]. In the U.S., MSW are being produced more than any other country in the world; however, the recycling rate is considerably low [OECD, 2007]. The total MSW generation in the U.S. has increased up to 65% since 1980, to the current level of 250 million tons per year with 53.6% landfilled, 34.7% recycled and composted, and 11.7% incinerated with energy recovery [U.S. EPA, 2011]. The total of 86 MSW Waste to Energy (WTE) plants are being operated in 24 states of the U.S. as of 2010 [T Michaels], where major users of MSWI plants are Connecticut, New York, New Jersey, Pennsylvania, and Virginia [C. S. Psomopoulos]. Typical residue produced from these incineration plants are MSWI bottom

---

[2] The content of this chapter also appeared in:
An, J., Kim, J., Golestani, B., Tasneem, K.M., Al Muhit, B.A., Nam, B.H., and Behzadan, A.H., Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials.(2014)
Using the paper as a chapter of this study is **with Courtesy of the Florida Department of Transportation (please see the appendix).**

ash (BA) and fly ash (FA), and those are mostly combined to be disposed of in sanitary landfill in the U.S. [Floyd Hasselriis].

2.2 Incineration of Municipal Solid Waste (MSW)

As the volume of waste generation is continued to raise, the emerging concern of the management of MSW tends to adopt incineration technology that reduces to about 60% by weight and 90% by volume [A.J. Chandler]. Produced ash is referred to as MSWI ash; unlike the coal fly ash, which is a byproduct of pulverized coal combustion in electric power plants. Most modern incinerators are equipped with energy recovery schemes; thus, also known as WTE MSWI ash. There are three major types of MSWI process: mass burn (MB), refuse derived fuel (RDF), and fluidized bed combustion (FBC) [A.J. Chandler]. Most MSWI facilities are MB plants that burn the MSW as received, after the recovery of metals for recycling. RDF plants facilitate preprocessing of MSW to remove non-combustibles and to shred into a more uniform fuel pellet. FBC plants incinerate RDF into a hot fluidized bed of noncombustible granule like sand within the furnace.

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 [D.A. Tillman, K. Millrath] referred to as combined ash, unlike European countries where ashes are separately managed.

In the past, the major concern with MSWI was associated with air pollution by dioxin ($C_4H_4O_2$), furan (C_4H_4O), and heavy metals originated from MSW [K. Millrath]. 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 [A.J. Chandler, K. Millrath]. The employment of APC devices, therefore, shifted the concern from air pollution to the leachate from disposal of MSWI ashes into landfill. It has been reported that RDF processes provide a significant control over the release of heavy metals, reducing Pb to 52%, Cd to 73%, and Cr to 63% [D.A. Tillman].

2.3   Properties of Waste-to-Energy (WTE) Ashes

Based on historical data [Carlton C. Wiles, A.J. Chandler], different elemental compositions of MSWI products, BA, FA, and APC residues, were investigated and they are summarized in Table 2-1.

2.3.1   *WTE Bottom Ash*

BA is the major by-product residue of the MSWI process (85-95 wt. %) consisting of grate ash and sometimes grate shifting. The BA 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 [A.J. Chandler, C. Wiles]. Major forms of compounds are oxides, hydroxides, and carbonates. According to research studies using different spectroscopic

analyses [C. Speiser, X. C. Qiao, A. P. Bayuseno], 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% [G.H. K. Lam]. Ba, Zn, Cl, Mn, and Pb are trace elements (< 1 wt. %) as shown in Table 2-1. S is found in minor concentrations in the fine fractions (< 1 mm) [C. Speiser]. 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 [A.J. Chandler]. The BA has a pH ranging from 10.5 to 12.2, partly due to the presence of hydroxide formation of CaO [A.J. Chandler].

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 [A.J. Chandler] 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 [A.J. Chandler]. On the other hand, the presence of metallic Al is one of the biggest hindrances of BA utilization in Portland cement concrete (PCC) due to the evolution of hydrogen gas originated from the reaction of metallic Al [A.J. Chandler, A.J. Chandler, Luca Bertolini]. 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 [A.J. Chandler].

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

7

weathering processes of BA can further reduce the reactivity and potential of heavy metal release by the reaction between CO_2 and water, which form stable complex compounds in BA [S. Arickx, Eva Rendek, R. Baciocchi]. Aging is also known to transform metallic Al to stable Al_2O_3, thereby reduce the potential of hydrogen gas formation [A.J. Chandler]. Therefore, the aging and weathering of BA can eventually improve the quality of BA, making its recycling a viable option in transportation application.

Table 2-1. Elemental compositions of MSWI ash residues (mg/kg)

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

2.3.2 *WTE Fly Ash*

In general, 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 [A.J. Chandler]. The FA is characterized with fine particulate matters, dusty appearance with gray to dark gray color [A.J. Chandler, H.M Alhassan]. The FA mostly contains oxide form of calcium, different metal salts, chloride compounds, and heavy metals [A.J. Chandler, G.H. K. Lam]. 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 2-1. CaO is found to be predominant compound in FA, which constitutes up to 46% [G.H. K. Lam]. When FA is subjected to a treatment with lime (CaO) scrubber, $Ca(OH)_2$ is obtained as end product [A.J. Chandler].

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 [G.H. K. Lam, T. Sabbas]. Due to the presence of highly soluble salts, Cl, and heavy metals, the FA is not considered for direct utilization as transportation materials [A.J. Chandler, C. Wiles, G.H. K. Lam]. 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 $CaCl_2$ [A.J. Chandler]. Moreover, similar to the BA, large content of metallic Al in

FA makes the utilization of FA uncertain [J. E. Aubert 2004, 2006, 2007].

The presence of readily soluble salt, such as Cl and Na in FA can significantly contaminate drinking water system [G.H. K. Lam, T. Sabbas]. 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 [6, 8, G.H. K. Lam]. 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 [ISWA 2008], (2) chemical stabilization using carbon dioxide/phosphoric acid (CO_2/H_3PO_4), ferrous sulfate ($FeSO_4$) [ISWA 2008], sodium sulfide (Na_2S) [ISWA 2008], and orthophosphate (PO_4^{3-}) [A.J. Chandler], (3) solidification using lime, cement, asphalt, and gypsum, and (4) thermal treatment, such as vitrification and pyrolysis [A.J. Chandler, ISWA 2008].

2.4   Leaching of WTE Ashes

Due to the presence of heavy soluble salt and heavy metals in MSWI ashes, leaching properties of 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, [Rafael M. Santos, Hui Sheng Shi]. 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 in contact with soil and water [Carlton C. Wiles, A.J. Chandler, C. Wiles].

Evaluation of leaching from MSWI ashes, leachate, and run off from landfill and application sites have been performed mostly in European countries [A.J. Chandler, Juergen Vehlow], but also at

11

small extent in the U.S. [C. Wiles, Floyd Hasselriis]. Leaching test results reveals that 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 BA [Margarida J. Quina, Akiko Kida]. Oxyanions, such as Zn and Pb are termed as amphoteric, which are characterized with high leaching potential at both high and low pH. Release of such amphoteric heavy metals from FA can be significantly increased due to the high pH of FA originated from APC devices containing lime solution [A. Polettini]. Substantial Pb leaching has also been confirmed by the researchers in Korea and Japan [Young Sook Shim]. Danish researchers [O.   Hjelmar] evaluated 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, SO_4, Cd, Cr, Hg, Mo, Pb, and Zn whereas the BA is likely to exceed limit values for Cl, SO_4, Cu, Mo, Sb, and Se.

Weathering and carbonation of BA [R. Baciocchi, Thomas Astrup] and FA [Xiaomin Li] are beneficial for the application of the ashes, because these treatments reduce the pH of the ashes and toxic metal release. Although carbonation technique is less effective in the leaching of Mo and Sb, it is effective for the Cu release [T. Van Gerven]. Although Cu in the leachate is bound in neutral and basic condition; in acidic condition, Cu exists as highly mobile ions that substantially increase its leaching [Jun Yao, H. A. van der Sloot]. Therefore, 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 [S. Olsson, Jiri Hyks]. Similarly, Zn leaching also follows the same characteristics of Cu when BA is in acidic condition [Jun Yao].

Leaching tests have been conducted to evaluate toxic elements release from the leachate of BA, FA, and combined ash when used as base or sub-base course in asphalt pavement [M. A.

Sørensen, R. Forteza, O. Ginés], PCC product [J. E. Aubert, Xiang Guo Li], and embankment fill [C.A. Andrews, H. Roffman]. The U.S. studies reported that heavy metal concentration in leachate mostly meets the leaching requirements [U.S. EPA 1995] and often meets the U.S. drinking water standard [U.S. EPA 2009]. It was also reported that the concentration of dioxin and furan, especially in FA, does not pose any threat in regard of the environment and health [K. Millrath]. However, although heavy metal concentrations in 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 [Floyd Hasselriis, O. Hjelmar].

Researchers confirmed significant reduction of leaching potential of BA, FA, and combined ash when incorporated with cement and concrete [R. Forteza, R. del Valle-Zermeño]. Spanish researchers formulated granulated material with combined ash and cement to use as secondary building material [R. del Valle-Zermeño]. 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 2-2 with threshold values established by utilization criteria [Dogc 2009] and three categories of landfill criteria [Dogc 1996] 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 [R. Forteza, Xiang Guo Li].

Table 2-2. Leaching results for MSWI BA, APC residue, and formulated concrete mixture (mg/kg)

Element	BA	APC	Combined ash	Concrete with combined ash	Criteria for utilization[a]	Criteria for landfill[b]		
						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[c]	-	0.10	0.5	7
Zn	0.818	35.083	4.625	1.008	20.0	4.00	50	200

[a] Spanish utilization criteria [Dogc 1996]
[b] Spanish landfill criteria [Dogc 2009]
[c] LOD = limit of detection

2.5   Utilizations of WTE Ashes

MSWI BA and FA have been used as partial replacement of cement in order to investigate their effect on the cement paste and PCC [Jill R. Pan, Carlo Collivignarelli, Z. Cai]. Although sometimes FA is considered to have similar properties with cement [G.H. K. Lam, Wu Jang Huang, C. Ferreira], experimental observation reveals that both ashes contain considerable amount of metallic Al that results in hydrogen gas evolution, cracks, and voids in cement paste specimens [J. E. Aubert]. In addition, 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, BA containing cement pastes exhibit

inferior mechanical properties with compared to those of controlled cement paste specimens [Luca Bertolini]. On the other hand, compressive strength of FA containing cement pastes is sometimes similar or higher than control specimens that makes FA suitable for the application as base layer in road construction [Z. Cai]. Unlike the addition of BA, the FA addition in concrete reduces the workability [Luca Bertolini]. Washing of FA is believed to be effective to reduce the soluble salt and Cl content in FA and wet grinding of BA would be viable option to facilitate gas production before its addition as cement replacement in concrete production [Luca Bertolini, Carlo Collivignarelli, C. Ferreira].

2.6   Management Practices of WTE Ashes

Beneficial utilization of MSWI ash has been well established in European countries. Applications of MSWI ashes as road construction material in asphalt paving and PCC have been common practice [A.J. Chandler, C. Wiles, ISWA 2006]. These applications are not only promising from structural integrity standpoint, but also effective from environmental safety perspective. In the ash utilization into concrete, concrete 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 [M Rachakornkij]. Leaching potential from ash residue can be reduced significantly by being physically encapsulated in asphalt [S.P. Lucido].

Confederation of European Waste-to-Energy Plants (CEWEP) 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

15

reduced by 19%. Figure 2-1 shows MSW production and recycling in European countries in 2003 [ISWA 2006] and in the U.S. [U.S. EPA 2011]. Compared with other European countries, the U.S. is the highest waste-generation country [OECD 2007] but has very low recycling. 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 [C. Wiles, ISWA 2006, 2008]. In the U.S., on the contrary, most MSWI plants combine BA and FA in one stream and disposed of in landfills [C. Wiles, K. Millrath].

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

2.6.1 *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 [ISWA 2006]. It is encouraged to use BA, considering it as a special category for the application as embankment fill, road base, and disposal into landfill [ISWA 2006]. Only the Netherlands among European countries utilizes FA in a small extent [ISWA 2008]. About 30% of FA and APC residue are used as filler material in asphalt as the alternative of limestone [ISWA 2008]. Significant part of these residues has been exported to German and used as backfilled material in coal and salt mines [ISWA 2008].

16
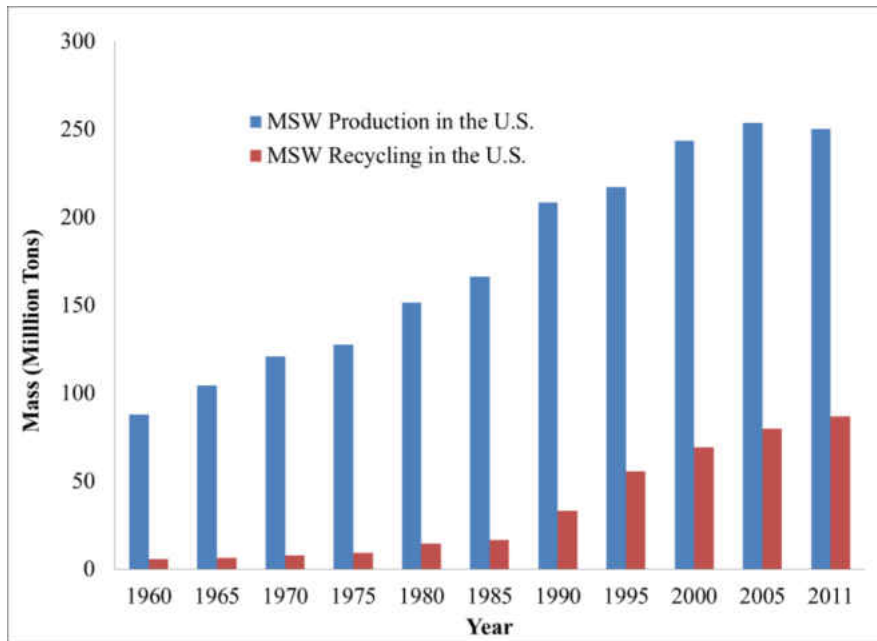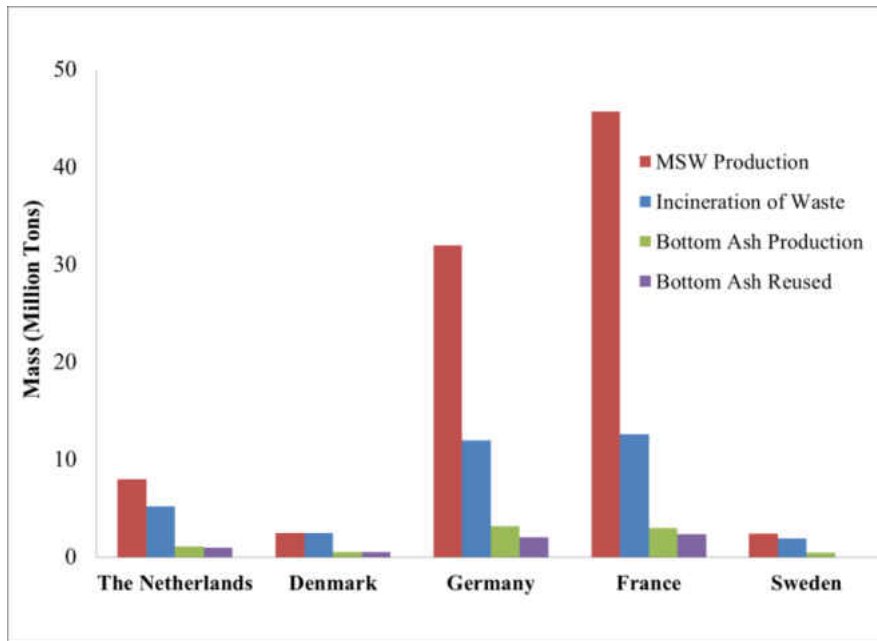
Figure 2-1. MSW management in European countries in 2003 [ISWA, 2008] (top) and in the U.S. (bottom) [U.S. EPA, 2011]

2.6.2 *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 [ISWA 2006]. Denmark aimed at recycling 98% of BA into building and road construction and embankment fill after screening, crushing, and ferrous metal recovery [ISWA 2006]. APC residues, including FA and acid cleaning end product, are considered as special hazardous waste, required to landfill after treatments [ISWA 2008]. 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 [ISWA 2008].

2.6.3 *Germany*

Germany recycles about 65% of BA, while landfilling 28% after the reduction of salt content by water quenching, followed by ferrous and non-ferrous metal recovery and 3-month maturation [A.J. Chandler, ISWA 2006]. A reduction in leaching potential makes BA suitable for the utilization as road construction and secondary building materials [C. Wiles]. Salt content of ash and dry scrubber residues are subjected to backfill in the old mines to prevent subsidence [4, ISWA 2008]. A small quantity of APC residue is disposed of in a landfill after stabilization [ISWA 2008].

2.6.4 *France*

France recycles 79% of BA produced in the civil constructions [ISWA 2006]. BA treatments involve ferrous and non-ferrous metal removal, size reduction, and sometimes cement stabilization [ISWA 2006]. APC residue is managed mostly by stabilization with either cement or treatment

with NaHCO$_3$; it is then disposed of in a landfill designated for hazardous waste [ISWA 2008].

Thermal treatment is also considered as a new option for ash treatment, which is not very common, yet [ISWA 2008].

2.6.5 Sweden

Having enough natural resources accompanied by less incentive for ash utilization, BA and FA are collected separately, and BA is disposed of in landfills without any treatment [ISWA 2006]. On the other hand, FA is disposed of in the special lined landfill or cell after treatments [4]. Sweden exports their APC residues to Norway for neutralization of acid waste and landfilling after solidification and stabilization [ISWA 2008].

2.6.6 Japan

Due to a very large number of incinerators, a great amount of ash is being produced, and lack of land space for landfilling causes Japan to predominantly practice thermal and melting treatment of MSWI combined ashes [82-84]. Landfill disposal of FA is permitted after melting, followed by solidification or stabilization with cement or chemicals and acid or solvent extraction [ISWA 2008]. 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 [C. Wiles].

2.6.7 United States

Combined ash (mixed BA and FA) are mostly disposed of 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 [C. Wiles]. 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 [Carlton C. Wiles, C. Wiles].

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. [C. Wiles]: (1) geotechnical applications, including base and subbase, embankment [P.J. Cosentino, C.D. Shieh], (2) hot-mix asphalt [S.P. Lucido, D.E. Sawyers], and (3) Portland cement concrete [C. Wiles, D.E. Sawyers]. 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 2-3 [C. Wiles, P.J. Cosentino].

Table 2-3. Research projects on MSWI ash as road construction materials in the U.S. [C. Wiles, P.J. Cosentino]

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
	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

Table 2.3: Research projects on MSWI ash as road construction materials in the U.S., continued

Utilization area	Location	Description	Report
Concrete	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 or 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

CHAPTER 3: MATERIAL CHARACTERIZATION OF WTE ASHES[3]

3.1   Introduction

According to a recent research work [C. S. Psomopoulos], the total municipal solid waste (MSW) generation in the US is about 250 million tons per year, which was increased approximately 65% since 1980. Moreover, only about 35% of the total waste is recycled and the rest is incinerated or landfilled. Global trends for the MSW generation are similar [Carlton C. Wiles] and the quantities are ever increasing. Therefore, the utilization of municipal solid waste incineration (MSWI) ashes from waste-to-energy (WTE) facilities has been receiving increasing attention around the globe. Owing to the large quantity consumptions and relatively low quality requirements, the use of MSWI ashes as construction materials would be a very attractive option. In fact, many research works have addressed the utilization of MSWI ashes as a gravel material in road base layers [R. Forteza, G. Pecqueur] as well as aggregate for reinforced concrete structures [Urs Müller, K. Rubner, S. Sorlini]. One of the important factors hindering the accepted use of the ashes as construction materials, however, is their uncertain physical and chemical properties due to their heterogeneous characteristics. Thereby, in order to expand the utilization of MSWI ashes in construction, understanding of the physical and chemical properties is critical.

---

[3] The partial content of this chapter also appeared in:
An, J., Kim, J., Golestani, B., Tasneem, K.M., Al Muhit, B.A., Nam, B.H., and Behzadan, A.H., Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials.(2014)
Using the paper as a chapter of this study is **with Courtesy of the Florida Department of Transportation (please see the appendix).**

A typical waste treatment process involves a thermal treatment, in which waste materials are combusted at a temperature of approximately 1,000 ºC. During the thermal treatment, the quantity of the waste is reduced by 65-80% in mass and 85-90% in volume [Luca Bertolini]. As a result of this incineration, two types of ashes are produced: fly ash, which is typically considered a more hazardous material due to the presence of heavy metals and dioxins [Luca Bertolini, J. E. Aubert 2004] and bottom ash, large agglomerated residue.

In this chapter, efforts were made to physically and chemically characterize MSWI fly ash and bottom ash in order to assess the feasibility of the reuse of the ashes as road construction materials. Basic physical properties of the bottom ash were studied in accordance with American Standard Testing Methods (ASTM). Petrographic examinations, including scanning electron microscopy (SEM), energy dispersive x-ray (EDX), and x-ray diffraction (XRD) were carried out in order to identify the chemical and microstructural properties of the ashes. To evaluate the main side effect of ashes when used in cement, the creation of a network of bubbles due to the presence of aluminum, ashes and aluminum powder were submerged in high pH solution and the evolution of hydrogen gas was measured.

3.2   Materials and Experiments

MSWI fly ash and bottom ash (Figure 3-1) were sourced from a refuse-derived fuel (RDF) WTE facility in Florida, US in April, 2013. The maximum particle size of the ashes were 0.1 mm and 50 mm for the fly ash and bottom ash, respectively. Previous to a series of experimental investigations, both ashes were oven dried at 110 ºC for 2 hours in order to remove moisture from

the quenching process in the WTE facility.
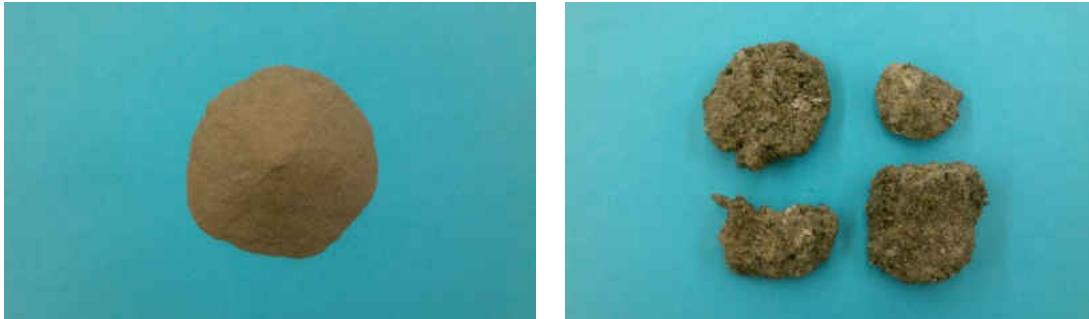
Figure 3-1. Photographs of MSWI fly ash (left) and bottom ash (right)

Basic physical properties of the ashes, including specific gravity, absorption capacity, unit weight, void content, and L.A. abrasion mass loss were evaluated in accordance with ASTM guidelines. Microstructural morphology and chemical element compositions of both ashes were determined by SEM and EDX analyses, respectively, using the Zeiss Ultra-55 SEM equipped with UltraDry silicon drift x-ray detector. Phase compositions of the ashes were examined by XRD analysis using the Rigaku D/MAX-II XRD with copper K-α radiation.

3.3   Physical Properties

Averaged test results of the basic physical properties and corresponding test methods are listed in Table 3-1. Note that the absorption capacity and L.A. abrasion tests for the fly ash were not conducted in this study due to its fine particle size. As expected, low specific gravity and unit weight for both ashes were observed compared to those of natural aggregates (typical specific gravity and unit weight of 2.60 and 2,600 kg/m^3, respectively [ACI E1-07]). In addition, high

absorption capacity was obtained from the bottom ash compared to that of typical natural aggregate, 0.5 to 4% [ACI E1-07]. The measured specific gravity and unit weight of the fly ash were slightly lower than those of the bottom ash. The L.A. abrasion test determines the ability of aggregate to resist being worn away by friction impact and is generally considered as a measure of degradation due to handling, stockpiling, and mixing. According to an ASTM specification [ASTM C33], the allowable upper limit on the mass loss is 50%. Thus, the L.A. abrasion mass loss obtained from the bottom ash complies with the ASTM requirement for aggregate.

Table 3-1. Averaged physical properties of MSWI fly ash and bottom ash, and corresponding standard test methods

Properties	Fly ash	Bottom ash	Test methods
Specific gravity (oven dry)	2.11	2.20	ASTM C127
Absorption capacity, %	N/A	12.8	ASTM C127
Unit weight (oven dry), kg/m^3	2,104	2,195	ASTM C29
L.A. abrasion mass loss, %	N/A	43	ASTM C535

3.4 Microstructural and Chemical Properties

The microstructural morphology of each ash obtained from SEM is shown in Figure 3-2 and Figure 3-3. Compared with the bottom ash, the fly ash particles exhibit irregular and angular morphology and smoother surface texture. In addition, fly ash particles have a high internal porosity than the bottom ash. It has been reported that the surface morphology and particle texture can provide essential information on leaching behavior and mechanical properties. The high porosity of the fly ash provides not only a higher potential for a leaching due to a highly reactive surface but also

higher absorption rate. Moreover, porosity is closely related to the specific gravity and unit weight. Therefore, the higher porosity of the fly ash may explain the lower specific gravity and unit weight measured from the physical tests discussed above (Table 3-1). The irregular and angular shape of the fly ash will cause low workability when incorporated with cement or asphalt.

Chemical element compositions for both ashes obtained by EDX analysis are listed in Table 3-2. The major elements present within the fly ash are Ca, Cl, and Hg, while Ca, Si, and Al are the major elements found from the bottom ash. It is obvious that the oxygen content is predominant for the bottom ash and therefore, most chemical elements in the bottom ash are likely to exist as an oxide form. One of the major concerns when the fly ash is used in reinforced concrete structures is the high content of Cl, which will most probably induce a corrosion of embedded reinforcement. Another side effect is attributed to the considerably high Al contents in both ashes. The high concentration of metallic aluminum can cause an evolution of hydrogen gas in the high alkaline environment created during the early hydration process of Portland cement [S. Sorlini]:

$$2Al + 4OH^- + 2H_2O \rightarrow 2Al(OH)_3 + H_2\uparrow \qquad (3.1)$$
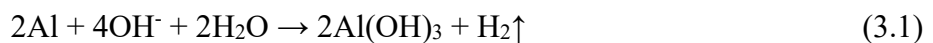
As a result, a network of bubbles are entrapped inside a concrete and the strength and durability of the entire structure can be greatly reduced [K. Rubner]. It is important to note that high Ca contents were observed from the both ashes. Therefore, it may be possible to use the ashes for supplementary cementitious materials (SCMs) if the negative effects, high concentration of Cl and development of hydrogen gas can be eliminated by proper treatments.

27
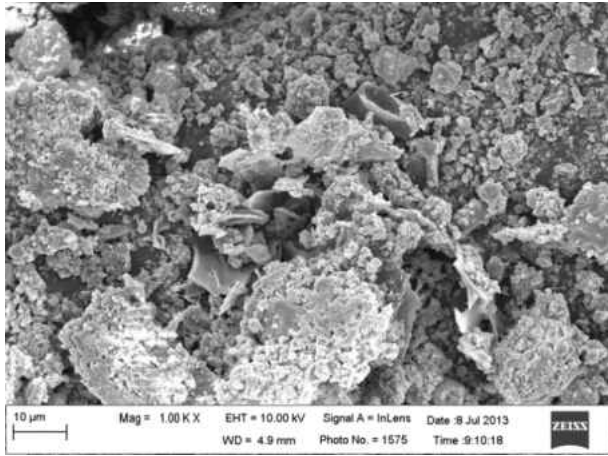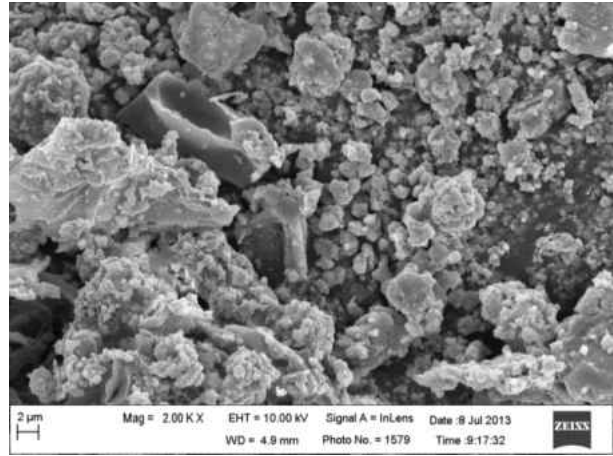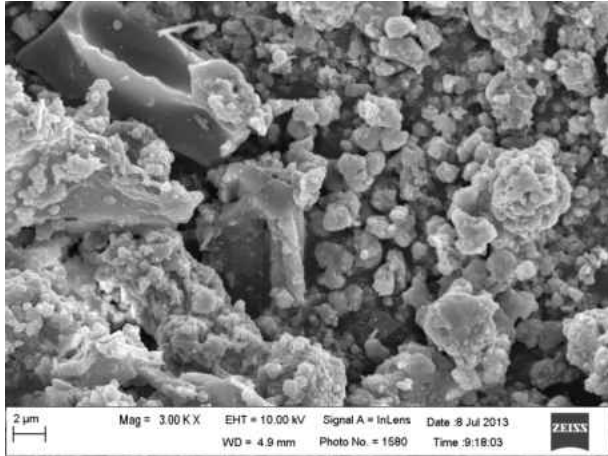
(a) 1,000X

(b) 2,000X

(c) 3,000X
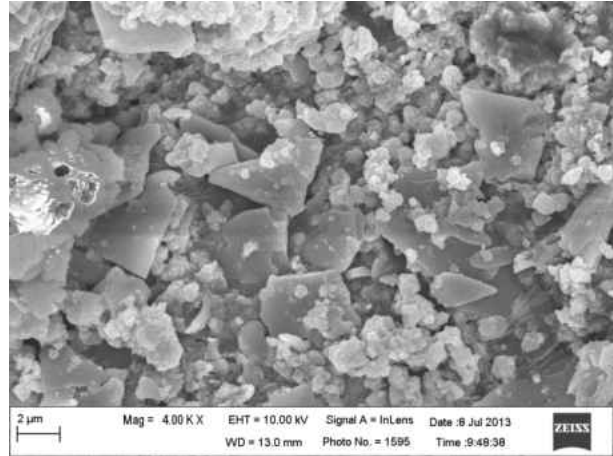
(d) 4,000X
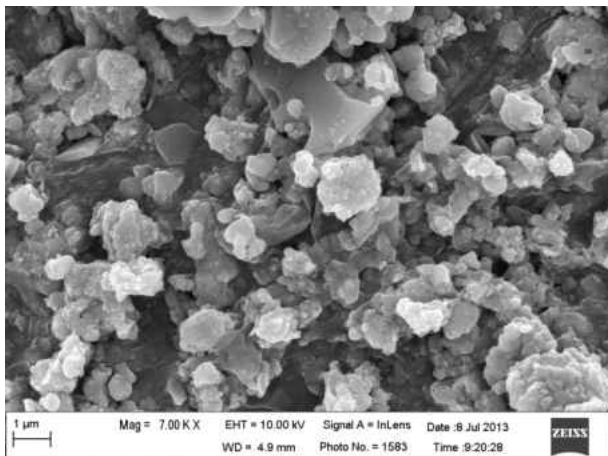
(e) 7,000X
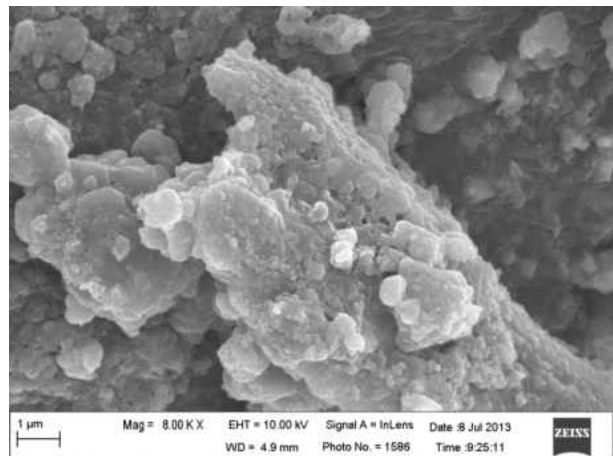
(f) 8,000X

Figure 3-2. SEM images of MSWI FA with varied magnifications

28
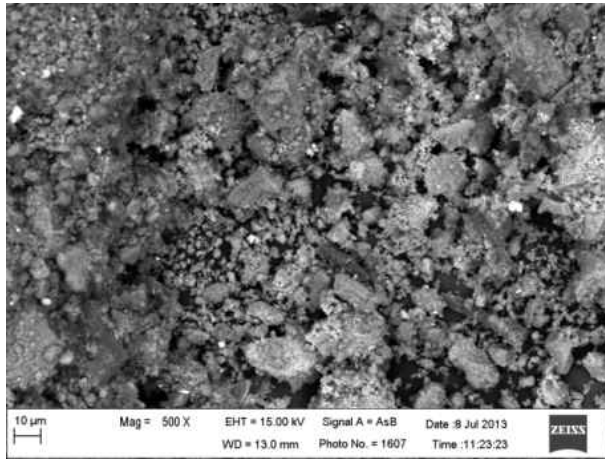
(a) 500X
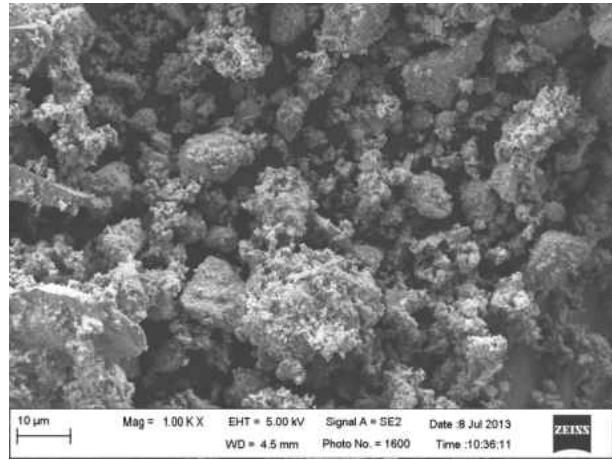
(b) 1,000X
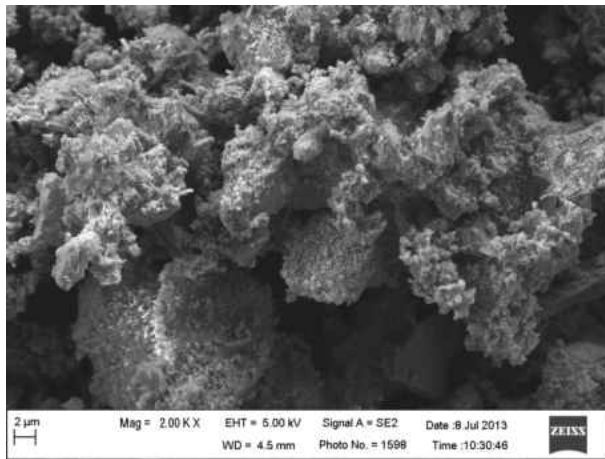
(c) 2,000X
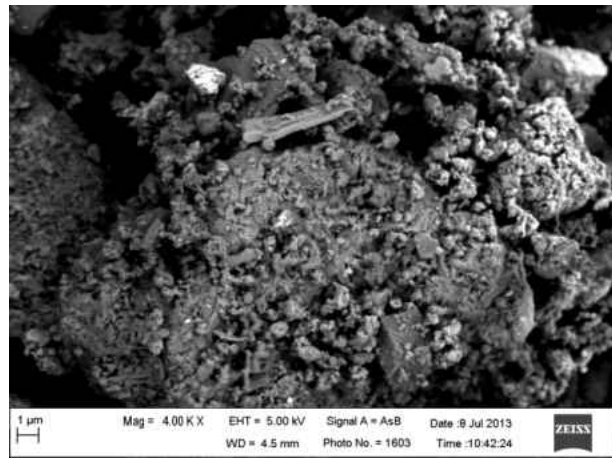
(d) 4,000X
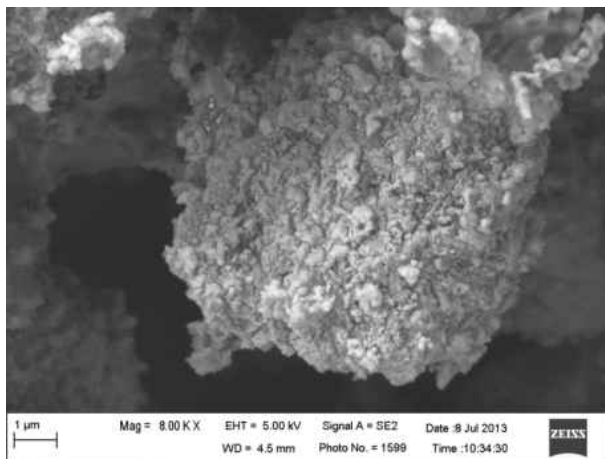
(e) 8,000X

Figure 3-3. SEM images of MSWI BA with varied magnifications

Figure 3-4 shows the XRD analyses of the both ashes. The major mineral components of the fly ash are lawsonite ($CaAl_2Si_2O_7(OH)_2H_2O$), calcite ($CaCO_3$), and $CaCl_2Ca(OH)_2H_2O$, while quartz (SiO_2), calcite, and portlandite ($Ca(OH)_2$) are the main elements found from the bottom ash. In addition to the mineral components listed, many other minor minerals were detected with low amounts due to the intrinsic heterogeneous characteristics of the ashes. The analysis of the XRD data shows a good agreement with the findings from the EDX results.

Table 3-2. Element contents in MSWI fly ash and bottom ash

Element	Fly ash (wt. %)	Bottom ash (wt. %)
Al	1.20	5.01
Ca	34.59	23.40
Cl	30.46	1.88
Cr	0.32	-
Cu	1.19	0.83
Fe	2.75	0.82
Hg	8.16	-
K	1.22	0.91
Mg	0.73	1.53
Na	4.69	4.15
Ni	2.99	-
O	7.10	46.54
S	-	3.58
Si	2.26	9.50
Ti	-	1.50
Zn	2.34	0.36
Total	100.00	100.01
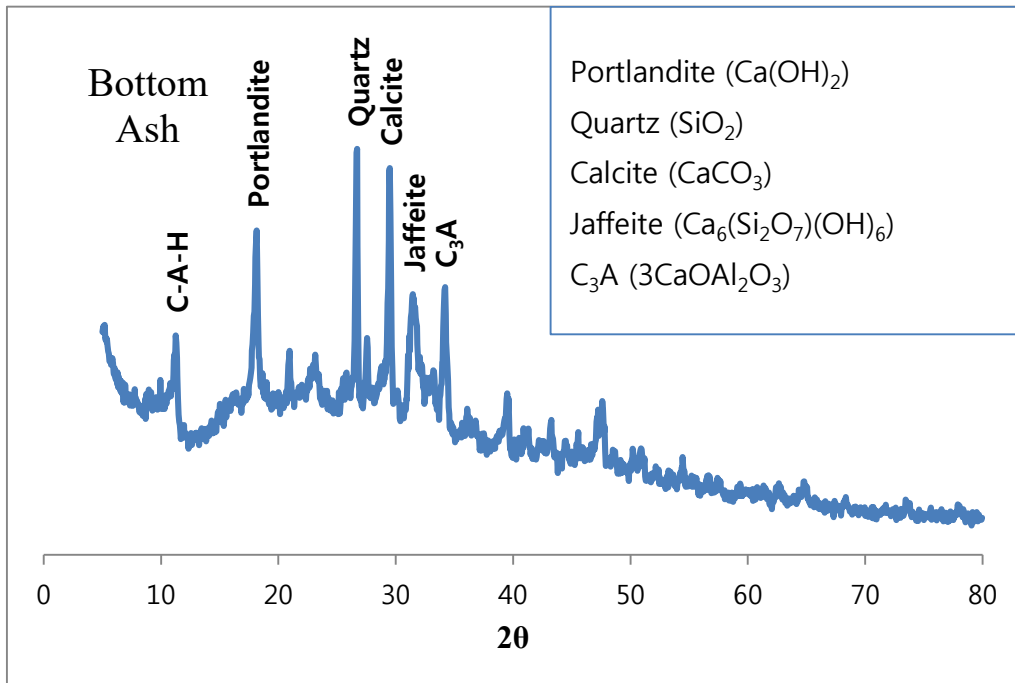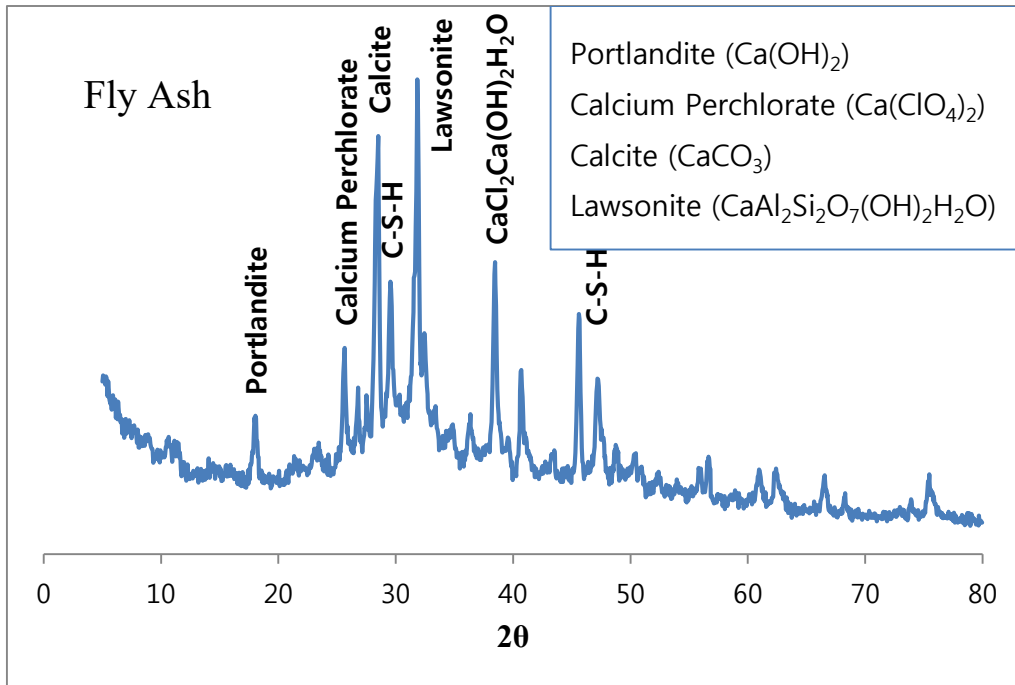
Figure 3-4. XRD of MSWI fly ash (top) and bottom ash (bottom)

3.5   Summary

The potential of the reuse of the MSWI ashes as road construction materials was evaluated through a series of experimental investigations. From the analyses of the test data, the following conclusions can be drawn:

- Both ashes have slightly low specific gravity and unit weight compared to those of typical natural aggregate. For the bottom ash, the L.A. abrasion mass loss complies with the ASTM requirements, but a considerably high absorption capacity was obtained.

- According to the microstructural evaluation using SEM, the fly ash particles exhibit irregular and angular morphology and a high internal porosity compared with the bottom ash. This can cause reduced workability when mixed with cement or asphalt as well as a high absorption rate and leaching for the fly ash.

- Based on the chemical components analyses by EDX and XRD, the presence of high concentration of aluminum was observed from both ashes. This can reduce the strength and durability of a concrete structure due to the development of hydrogen gas. In addition, high content of Cl found from the fly ash has a high potential for corrosion of embedded reinforcement.

- Based on the experimental investigation, both MSWI ashes contain considerable amount of metallic aluminum, which release large amount of hydrogen gas. This may eventually lead to a significant reduction of the overall concrete properties when the ashes are incorporated in concrete.

CHAPTER 4: EVALUATION OF WTE ASHES WHEN USED AS CEMENT REPLACEMENT[4]

4.1   Introduction

The main focus of this chapter is the characterization of the municipal solid waste incineration (MSWI) ashes and their influence on engineering properties of cement paste when part of Portland cement is replaced with ground MSWI ashes. There have been several studies on the beneficial use of MSWI ash in cementitious materials. MSWI bottom ash was evaluated as a potential mineral addition (Bertolini et al., 2004; Filipponi et al., 2003; Polettini et al., 2005) as well as partial replacement of fine aggregate in cement products (Ampadu & Torii, 2001; Sikalidis et al., 2002; Torii et al., 2003). Chemical and physical properties of fresh and hardened concrete containing MSWI bottom ash were investigated and the results demonstrated the potential use of bottom ash as an aggregate. Some of studies reported that the bottom ash can replace up to 50% without sacrificing durability and strength of concrete (Pera et al., 1997; Rashid & Frantz, 1992). Juric et al. (Jurič et al., 2006) investigated the reuse of bottom ash as a cement replacement and concluded that up to 15% substitution is considered acceptable; however, freshly quenched bottom ash tends to create swelling problems. Giampaolo et al. (Giampaolo et al., 2002) and Filipponi et

---

[4] The partial content of this chapter also appeared in:
J. Y. Kim, J. W. An, B. H. Nam*, K. M. Tasneem, "Investigation on the Side Effects of Municipal Solid Waste Incineration Ashes when Used as Mineral Additions in Cement-Based Materials," Road Materials and Pavement Design (2015). Using the paper as a chapter of this study is **with Courtesy of Road Materials and Pavement Design (please see the appendix).**

al. (Filipponi et al., 2003) have shown potential pozzolanic reaction of the bottom ash in cement-based materials, but the compressive strength of bottom ash-cement mixtures was lower than the control sample. Other researchers studied MSWI fly ash as replacement of cement (Alba et al., 2001; Saikia et al., 2007) and addressed that cement can be replaced by up to 30–40% of the fly ash. However, some studies (Aubert et al., 2006; Polettini et al., 2001) have found that cement only maintains its strength with a maximum of 20% fly ash, although this depends on the nature and the technology involved in fly ash production. A potential reuse of fly ash as aggregate for concrete was demonstrated by Collivignarelli and Sorlini (Collivignarelli & Sorlini, 2002) that the concrete compressive strength of over 15 MPa was achieved by replacing chemically stabilized fly ash with natural aggregate in concrete.

Nevertheless, the utilization of MSWI ashes in concrete still faces a number of challenges to achieve their potential as a replacement of aggregate or cement. The presence of aluminum can generate the hydrogen gas, which is one of critical side effects of the MSWI ashes in cement-based materials (Aubert et al., 2004; Bertolini et al., 2004; Müller & Rübner, 2006; Rubner et al., 2008). MSWI ashes, byproducts of an incineration process, are mostly formed by the inorganic substances as an oxide form. In the case that an entire aluminum is oxidized, no metallic aluminum contents would be found in the ashes and the side effect when used in concrete is expected to be negligible. This is because aluminum oxide (Al_2O_3) is known to be a very stable chemical compound (Patnaik, 2003) under typical condition expected during cement hydration and therefore, the reaction or decomposition of Al_2O_3 is hardly expected. However, although waste material is incinerated at high temperature, not all inorganic substances are expected to be oxidized; some metals would

remain as unoxidized form (Wiles, 1996). For this reason, although the concentration varies with waste source, location of incineration facility, and quality of incineration process, typical MSWI ashes are known to have relatively high concentration of metallic aluminum (Chandler, 1997; Sorlini et al., 2011). The main side effect due to the presence of high concentration of metallic aluminum is the evolution of hydrogen gas (Aubert et al., 2004; Müller & Rübner, 2006; Sorlini et al., 2011). In the high alkaline environment created during the hydration reaction of cement (pH 12-13), corrosion of some metals, especially aluminum, occurs and reacts to form aluminate that releases a great amount of hydrogen gas (Müller & Rübner, 2006):

$$2Al + 4OH^- + 2H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow \qquad (4.1)$$
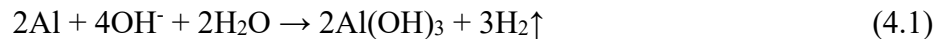
The production of hydrogen gas due to the reaction of aluminum is entrapped in the fresh concrete, creating a network of bubbles that significantly reduces the strength and durability of the hardened concrete (Aubert et al., 2004; Bertolini et al., 2004; Müller & Rübner, 2006; Rubner et al., 2008).

In the US, to date, no recycling of the MSWI ashes has been made and a lack of research on the MSWI ash has been conducted; thus, transportation authorities have sought for performance data and proper mix designs for the use of MSWI ash in cement and concrete products. The scope of this work is to characterize the MSWI bottom and fly ashes produced from a refuse-derived fuel (RDF) facility in the US and to evaluate their influence on cement paste properties when a portion of Portland cement is replaced by both MSWI bottom and fly ashes. Petrographic examinations were performed in order to identify chemical composition of MSWI ashes and to determine their

contents. To evaluate the main side effect of MSWI ashes when used in cement, various materials, including MSWI ashes, and pure aluminum and aluminum oxide powders were submerged in lye solution and the volume of hydrogen gas evolution was measured. Cement paste cylinders were cast with various types and amounts of mineral additions and their strength and durability were investigated.

4.2   Experimental Procedure

4.2.1   *Materials*

MSWI ash samples (Figure 4-1) were collected from an RDF waste-to-energy (WTE) facility in Florida, US on April, 2013. The ashes involve a wide range of particles size: fly and bottom ash in the particle range approximately up to 0.1 mm and 50 mm, respectively. The ashes contain moisture that has been a result of quenching process in the incineration facility and therefore, the ashes were oven dried. The oven dried density (ASTM C188 (ASTM, 2009)) of ASTM C150 Type I ordinary Portland cement, fly ash, and ground bottom ash were measured, and the measured densities were 2.9, 2.2, and 2.1, respectively. In order to assure similar particle sizes for all the materials and also to make these materials to be suitable as mineral additions, bottom ash was ground under dry conditions in a ball mill machine. The ground bottom ash and fly ash were then sieved through a No. 170 sieve (opening size of 90 μm). The ashes were further sieved out with two more sieves; No. 200 and No. 400 (opening sizes of 75 and 37 μm, respectively) in order to assess their particle size distribution, and the results are shown in Figure 4-2. In regard of aluminum and aluminum oxide powders, both powders have particle sizes of 90 μm and over 99%

of purity, as specified in the material data sheet.
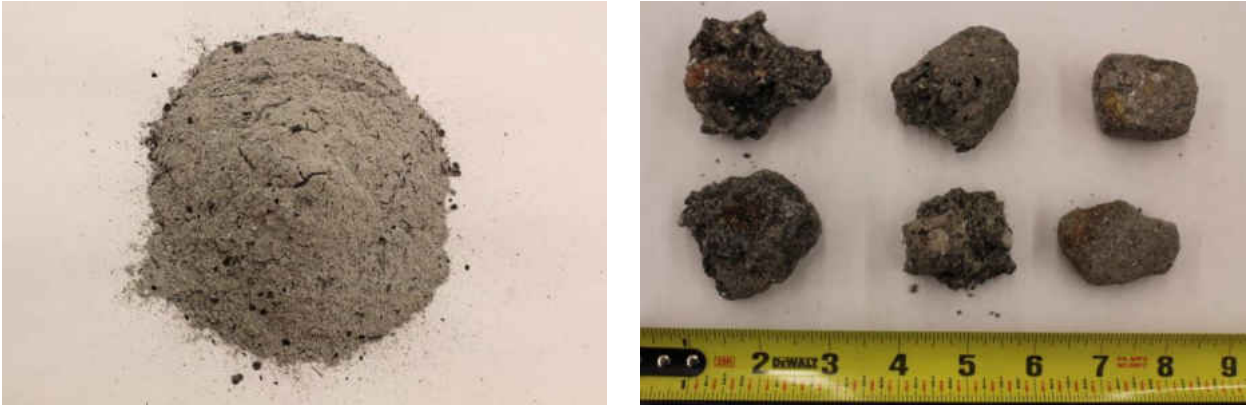
Figure 4-1. Photographs of MSWI fly ash (left) and bottom ash (right).
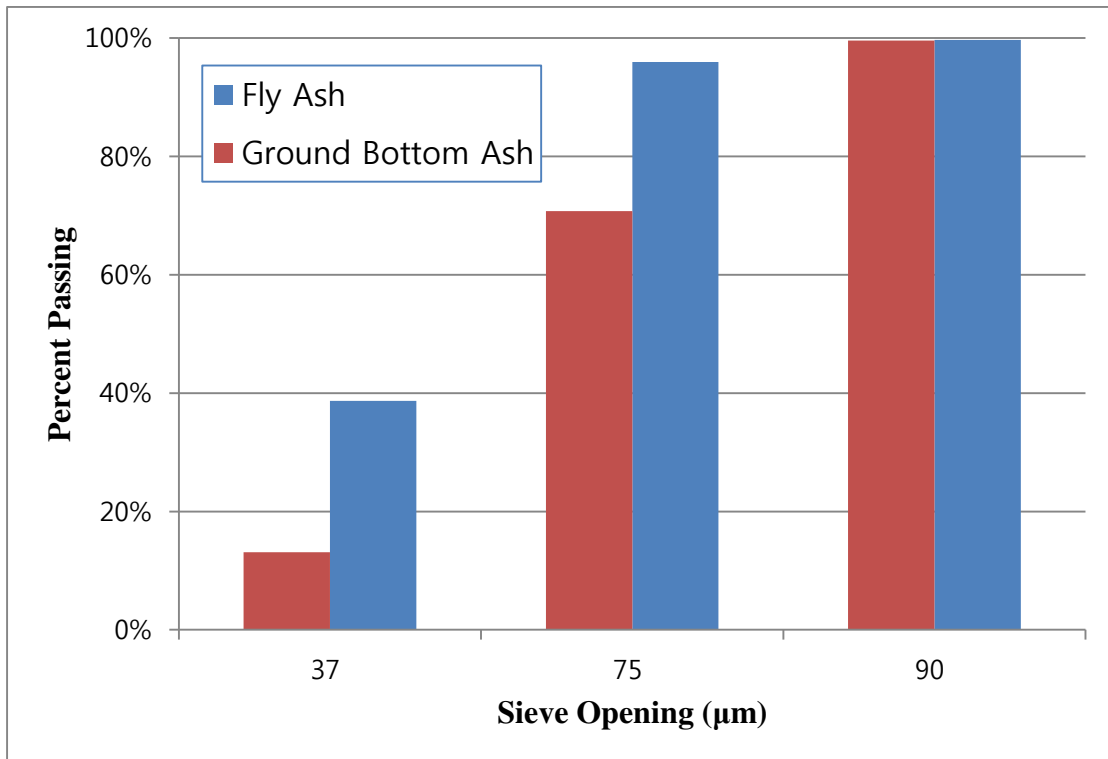
Figure 4-2. Particle size distribution of MSWI ashes.

4.2.2 *Chemical characteristics*

Chemical compositions and morphology of both MSWI ashes were determined by microscopic and spectroscopic methods, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX), according to ASTM C295 (ASTM, 2012a). Additional information regarding the phase compositions of the ashes were obtained by X-ray diffraction (XRD) analysis. Equipment used for the petrographic microscopy analyses in this study is located in the Advanced Materials Processing and Analysis Center of University of Central Florida.

4.2.3 *Measured volume of hydrogen gas*

In order to evaluate the emission of hydrogen gas by the oxidation reaction of metallic aluminum given by Equation (1), both the metallic aluminum content in the ashes and the amount of hydrogen gas released should be provided. Until recent, however, no rapid and direct methods for detecting metallic aluminum content in MSWI ashes have been reported. Spectroscopy techniques have limited accuracy in determining such minor chemical elements and only provide total quantity of aluminum with chemical forms and oxidation states (Aubert et al., 2004). Thus, in this study, an indirect measurement was employed to describe the oxidation reaction of metallic aluminum; the metallic aluminum content was indirectly determined by the measured volume of hydrogen gas due to the reaction of metallic aluminum under high pH environment. According to the chemical formula in Equation (1), for every two atoms of aluminum consumed, one molecule of hydrogen is produced. Therefore, a linear relationship between the amount of aluminum and the volume of

hydrogen gas produced is expected from the chemical experiment.

Fly ash, ground bottom ash, aluminum powder, and aluminum oxide powder were submerged in sodium hydroxide (NaOH) solution. All reaction materials used in this test were prepared their particle size smaller than or equal to 90 μm. A schematic illustration of the experimental setup to measure the volume of hydrogen gas is shown in Figure 4-3. The reaction vessel is attached to hydrogen collection burette through a tube and is facilitated with magnetic stirrer for proper mixing. Hydrogen gas produced during the chemical reaction is trapped in the burette and the volume of gas is determined by reading the water level. The measurement of the volume of hydrogen gas was conducted for 24 hours. The weight variation of the reaction vessel was measured on an hourly basis to check the reaction progress of each material and to make sure weight of each reaction vessel becomes constant during the test period. The entire test setup was stored in an indoor environment at all times with an ambient temperature of 23 ºC at atmospheric pressure.
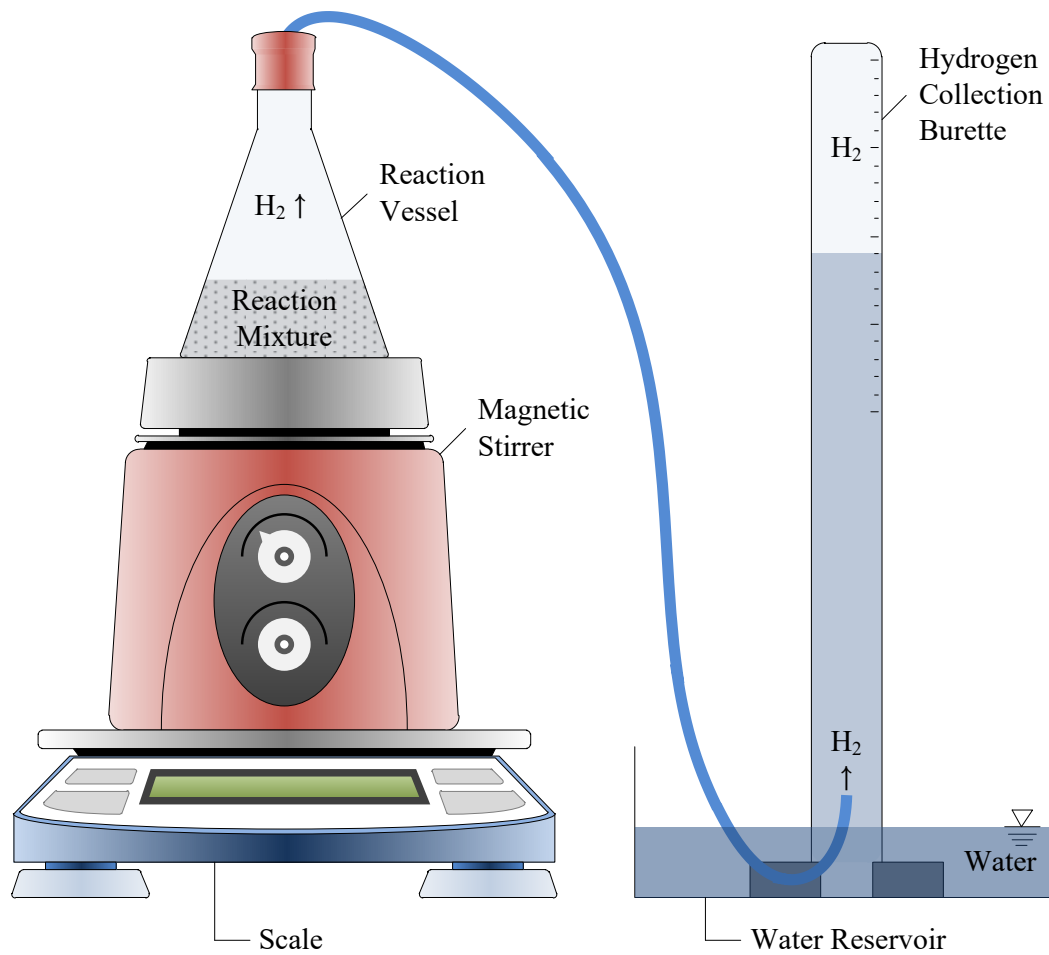
Figure 4-3. Test setup for volume of hydrogen gas measurement.

4.2.4 *Cement paste cylinder test*

The mixture proportions of the cement paste specimens are listed in Table 4-1. Each mixture was prepared in 30-liter (0.03-m^3) batches and three types of cylinders having different height were cast for each batch: four cylinders with the diameter of 100 mm and height of 200 mm, one cylinder with both the diameter and height of 100 mm, and two cylinders with the diameter of

100 mm and height of 50 mm. The water-to-cementitious materials ratio was constant (0.5) for all mixtures. With the exception of control mixture (C) other mixtures contained fly ash (F) and ground bottom ash (B) as replacing materials. The amount of cement replaced by fly and ground bottom ashes was varied from 10% to 30% by weight of cement. Note that the ashes utilized in this study may not comply with all requirements specified in the standards for coal fly ash or calcined natural pozzolan to be used as a cement replacement (i.e. fineness or chemical compositions). Due to the less pozzolanic efficiency expected from the ashes, the actual water-to-cementitious materials ratio may be higher than 0.5, which may have negative influences on the cement paste, especially for the specimens with 30% ash addition. Quantitative evaluation of the pozzolanic efficiency of the ashes, and reflecting this influence in the mixture design would be very complex. For practical purpose, therefore, the amount of the ash addition is assumed to be the same as the cement replacement. All test specimens were stored in an indoor environment at all times with an ambient temperature of 21 ± 1 ºC and relative humidity of $70 \pm 3\%$, and removed from the cylinder molds three days after casting.

Table 4-1. . Mixture proportions of cement paste specimens per cubic meter (kg/m^3)

Paste ID	W/C	Water	Cement	Fly ash	Ground bottom ash
C	0.5	180	360		
F10		180	324	36	
F20		180	288	72	
F30		180	252	108	
B10		180	324		36
B20		180	288		72
B30		180	252		108

In order to evaluate the influence of replacing materials on time of setting of cement paste, mixtures of C, F30, and B30 were prepared and their setting time was measured according to ASTM C191 (ASTM, 2008). A Vicat consistency apparatus was used and all mixtures were remained in the hard-rubber conical mold (60-mm diameter at the top, 70-mm diameter at the bottom, and 40-mm height) throughout the test period.

Cement paste specimens with presence of metallic aluminum are expected to experience swelling during setting due to the development of hydrogen gas. Therefore, four cylinders with 100-mm diameter and 200-mm height for each mixture were prepared and their density was measured in accordance with ASTM C1688 (ASTM, 2013a) when freshly mixed and ASTM C1754 (ASTM, 2012c) when hardened.

Expansion of cement paste would eventually leads to a significant increase in the permeability as well as porosity of the hardened cement paste. Thus, permeability and porosity tests were conducted on each cement paste specimen in accordance with ASTM C1585 (ASTM, 2013b) and ASTM C1754 (ASTM, 2012c), respectively. For the permeability test, two disc specimens with 100-mm diameter and 50-mm height were prepared for each Past ID listed in Table 4-1. The rate of one-dimensional water absorption into the specimens from a water reservoir was measured with other surfaces sealed with Latex based water proof paint. As illustrated in Figure 4-4, a water reservoir was installed beneath each cement paste cylinder and the height of water level was controlled to be approximately 2 mm from the bottom of cylinder specimens as specified in the standard method. The weight variation of each specimen was recorded at regular time intervals. For the porosity test, each type of cylinder specimens with 100-mm diameter and height

were prepared, and dry and submerged mass of each specimen were measured until the submerged mass becomes constant.
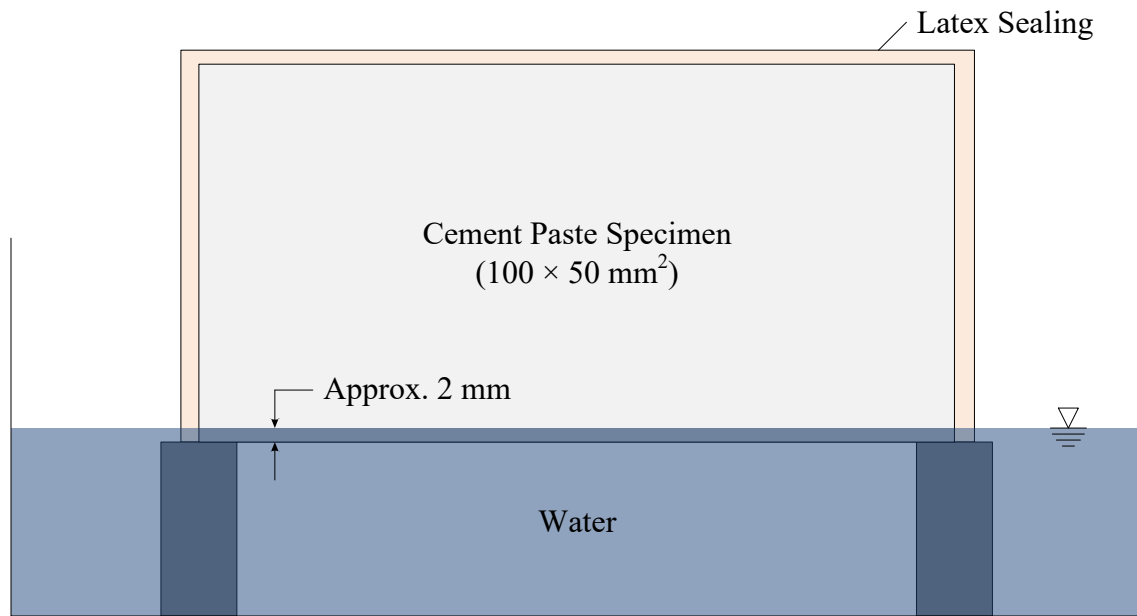
Figure 4-4. Configuration of one-dimensional water absorption test setup.

In order to evaluate the influence of replacing materials on mechanical property of cementitious materials, three replicate cement paste cylinders (diameter of 100 mm and height of 200-mm) were prepared for each mixture and their compressive strength were determined at 28 days of curing according to ASTM C39 (ASTM, 2012b).

4.3   Results and discussion

4.3.1   *Chemical characteristics*

SEM images of fly ash and ground bottom ash at 8.0 kX magnification are shown in Figure 4-5. The surface of fly ash particles appears to be smoother than that of ground bottom ash. The rough surface of bottom ash is most likely due to dry grinding process.
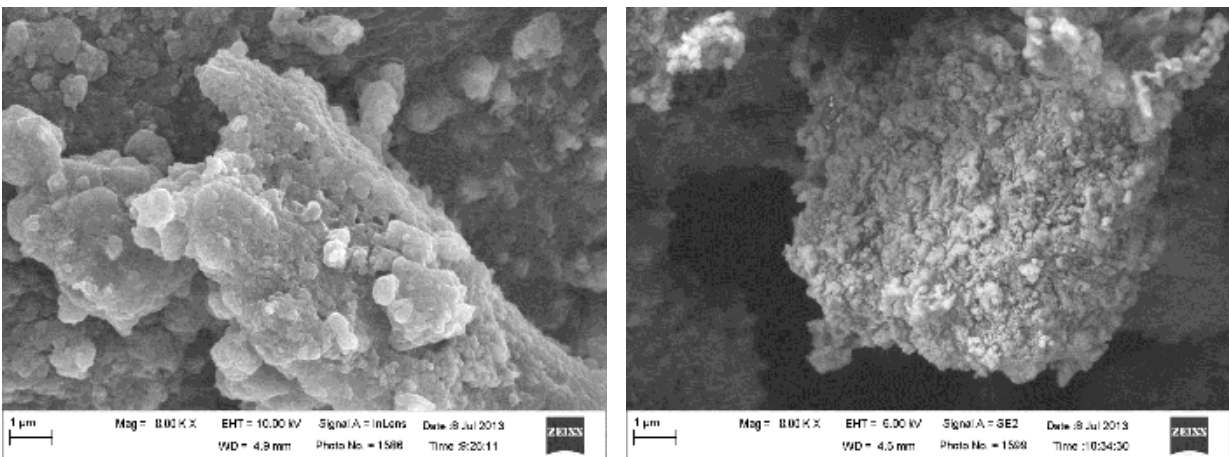
Figure 4-5. SEM images of fly ash (left) and ground bottom ash (right).

The elementary compositions of fly and bottom ashes obtained by EDX are listed in Table 4-2. Total aluminum (Al) contents of fly and bottom ashes were 2.47 and 4.43% by weight, respectively. More than 70% by weight of the fly ash consists of calcium (Ca), oxygen (O), chlorine (Cl), mercury (Hg), and potassium (K). The Cl contents in fly ash is considerably high (15% wt.), which may induce the corrosion of embedded steel reinforcement when fly ash is incorporated in the reinforced concrete structure. The major components of bottom ash, O, Ca, and

silicon (Si) account for approximately 80% wt. High Ca and Si contents of bottom ash may have beneficial influence on the properties of cement-based materials through hydraulic and pozzolanic activity when used as mineral addition.

Table 4-2. Chemical compositions of fly and bottom ashes

Element	Fly ash (% wt.)	Ground bottom ash (% wt.)
Al	2.47	4.43
Au	-	-
Ca	23.03	21.46
Cl	15.33	2.32
Co	1.03	-
Cr	0.29	
Cu	0.90	0.69
Fe	1.79	1.29
Hg	6.41	-
K	5.31	1.09
Mg	1.06	1.24
Mn	0.50	-
Na	3.61	3.30
Ni	2.99	-
O	22.99	38.24
P	0.79	0.90
S	2.54	3.68
Si	3.81	19.23
Ti	1.28	1.60
V	0.06	-

Figure 4-6 shows the XRD analyses of ashes. The main mineral components are lawsonite ($CaAl_2Si_2O_7(OH)_2H_2O$), calcite ($CaCO_3$), and $CaCl_2Ca(OH)_2H_2O$ for fly ash and quartz (SiO_2), calcite, and portlandite ($Ca(OH)_2$) for bottom ash that are consistent with the EDX results. In addition to the minerals listed in the figure, many others were also detected with low amounts. This may explain the heterogeneous characteristic of MSWI ashes.
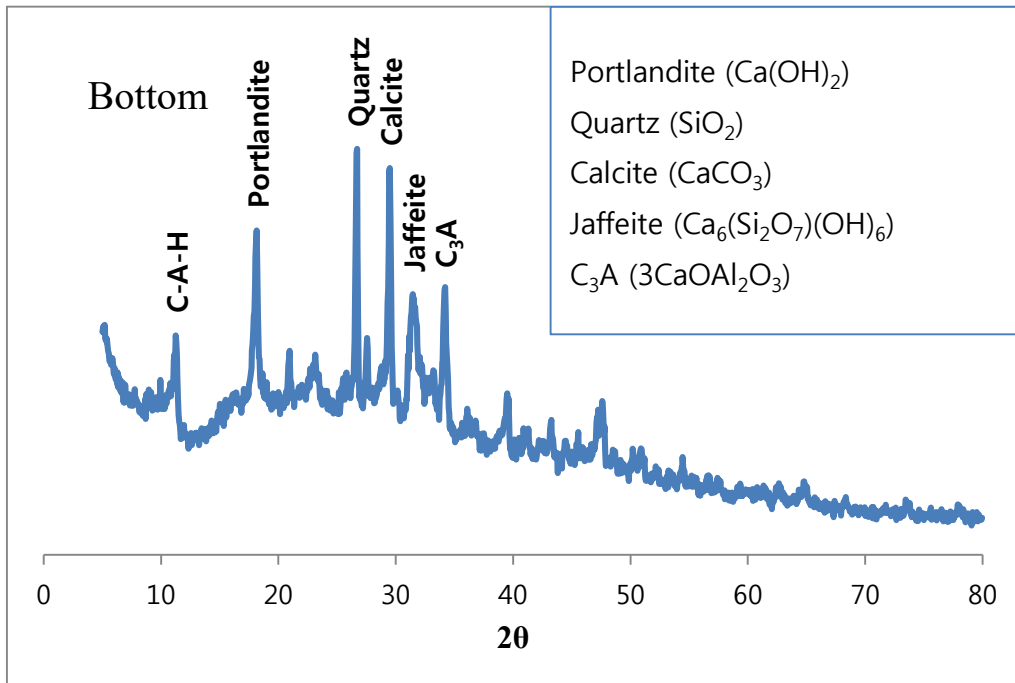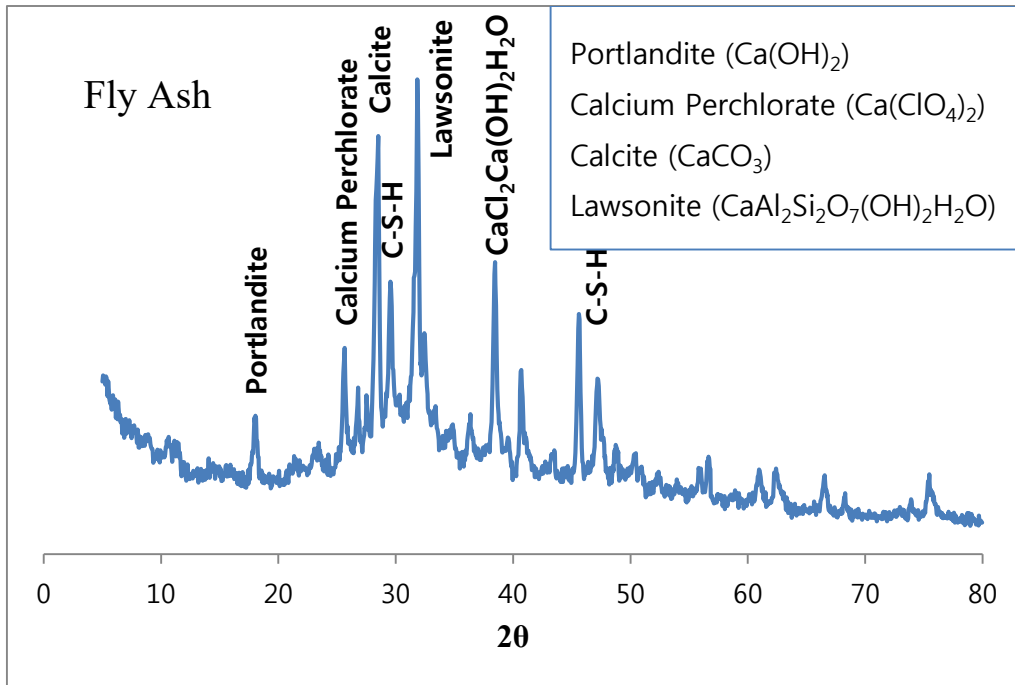
Figure 4-6. XRD analyses of fly ash (top) and bottom ash (bottom)

4.3.2 *Measured volume of hydrogen gas*

The measured volume of hydrogen gas and calculated metallic aluminum content are presented in Table 4-3. Metallic aluminum content of each material was calculated using the assumption of perfect gas with consideration of the testing conditions, temperature and pressure. For pure metallic aluminum, theoretical volume of hydrogen gas evolution per unit mass is 1,350 ml/g at temperature of 23 ºC and atmospheric pressure. The obtained 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 aluminum oxide reaction in 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 seems to be considerably reduced and therefore, hydrogen gas was not detected during the 24-hour test period. 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.

Table 4-3. Measured volume of hydrogen gas and calculated metallic aluminum content of each material

Material	Mass (g)	NaOH solution		H_2 gas volume (ml)	Gas vol. / unit mass (ml/g)	Calculated Al content	
		Concent-ration (M)	Volume (ml)			Mass (g)	Weight ratio (%)
Al	0.29	1	10	390	1,344.8	0.29	99.62
Al_2O_3	1	1	10	0	0	0	0
	150	3	400	0	0	0	0
Fly ash	20	1	150	0	0	0	0
	100	2	400	50	0.5	0.04	0.04
	150	3	400	60	0.4	0.04	0.03
Ground bottom ash	10	1	30	0	0	0	0
	100	2	400	40	0.4	0.03	0.03
	150	3	400	60	0.4	0.04	0.03

Based on the test results, the maximum volume of hydrogen gas release per one cylinder specimen (100-mm diameter by 200-mm height) for each mixture was calculated and the results are presented in Table 4-4. Theoretical values of hydrogen gas evolution from the specimens with 30% addition of both ashes are 4 to 5% of the volume of cement paste specimen (1,570 ml).

Table 4-4. Calculated metallic aluminum contents and maximum volume of hydrogen gas evolution per one cylinder specimen (100-mm diameter by 200-mm height)

Paste ID	Ash content (g/cyl)	Calculated metallic Al content (g/cyl)	Calculated hydrogen gas release	
			Volume (ml/cyl)	Gas / cylinder volume ratio (%)
F10	56.52	0.02	25.4	1.6
F20	113.04	0.04	50.9	3.2
F30	169.56	0.06	76.3	4.9
B10	56.52	0.02	22.6	1.4
B20	113.04	0.03	45.2	2.9
B30	169.56	0.05	67.8	4.3

4.3.3 *Cement paste cylinder test*

A visual inspection was conducted to detect surface defects of cement paste cylinder specimens after removing from cylinder molds. Figure 4-7 shows the surface condition of each specimen observed one week after the casting. The control specimen had smooth and clean surface condition with no surface defects such as crack or void, while other specimens showed visible surface defects. Some minor longitudinal cracks were observed on the surface of the specimen with the 10% addition of fly ash. No further cracks were found from the specimens with increasing amount of fly ash addition; however, their surface was dominated by air voids. The void size increases with increasing the added ash proportions. On the other hand, longitudinal and transverse cracks were found from the bottom ash specimens, and the number of surface cracks increased with increasing bottom ash addition. Some surface defects with dense air voids were also found from the upper part of the bottom ash specimens. Expansion of cement paste cylinders was evident for all specimens containing the ashes. Using a high proportion of fly ash addition made the cement paste darker in color while the color of other specimens remained unchanged.

(a) C

No cracks or voids

(b) F10

Minor longitudinal cracks

(c) F20

Small air voids

(d) F30

Large air voids

(e) B10   (f) B20   (g) B30

Minor longitudinal cracks   Minor longitudinal and   Moderate longitudinal and

                                transverse cracks   transverse cracks

Figure 4-7. Photographs of cement paste cylinder specimens and their surface conditions.

The measured initial and final setting times for control mixture, and mixtures with 30% addition of fly ash and bottom ash are provided in Table 4-5. The control cement paste exhibited initial and final setting times that were 5.4 and 9.2 hours, respectively. For B30, both setting times were increased to 6.9 and 12.0 for the initial and final, respectively, which are increase of about 28% in the initial set and 30% in the final set compared to those of the control mixture. This delay in setting time is most likely attributed to an increased water-to-cement ratio of the mixtures with a large amount of ash replacement. According to the EDX and XRD results shown in Table 4-2 and Figure 4-6, respectively, MSWI ashes contain several beneficial chemical elements and minerals. However, these components are present in much smaller quantities compared to the

51

cement; thus, hydraulic behavior of the ashes would be considerably less. For this reason, large amount of cement replacement with ground bottom ash could results in an increased water-to-cement ratio and delayed hydration of cement. For the mixture F30, on the contrary, both initial and final setting times were significantly decreased to 2.1 and 5.2 hours, respectively, which are reduction of approximately 61% in the initial set and 43% in the final set compared to those of the control mixture. This is due to the high contents of Cl as shown in the elementary compositions of fly ash obtained by EDX (Table 4-2). Chloride-based chemical admixture, especially Calcium chloride ($CaCl_2$), has long been known as an excellent accelerator and its accelerating effect has been studied by many researchers (Bortoluzzi et al., 2009; Rapp, 1935; Rosskopf et al., 1975) . Although the 30% of cement replacement with fly ash would have an increased water-to-cement ratio, the considerably high content of Cl in fly ash dominated the early hydration behavior of cement paste and consequently accelerated the time of settings.

Table 4-5. Averaged properties of the fresh and hardened cement paste specimens

Paste ID	Setting time (hour)		Density (kg/m³)		Void content of hardened cement paste (%)	28-day compressive strength (MPa)
	Initial	Finial	Fresh	28-day		
C	5.4	9.2	1,878	1,825	22.8	28.3
F10			1,839	1,748	26.0	26.5
F20			1,815	1,705	17.9	43.2
F30	2.1	5.2	1,803	1,681	12.3	27.1
B10			1,790	1,699	23.6	15.4
B20			1,739	1,634	25.2	26.8
B30	6.9	12.0	1,718	1,607	25.3	15.1

Measured average densities of the fresh and hardened cement paste are provided in Table 4-5 and the ratios of average hardened density-to-fresh density for all mixtures are compared in Figure 4-8. As seen in Table 4-5, the fresh and hardened density of cement paste incorporating the ashes decreased with increasing the replacement proportions due to lower density of the ashes compared to that of cement. Owing to the volume expansion during setting as a result of hydrogen gas evolution, density of the hardened cement paste decreased for all specimens with the ashes. The trends are similar for cement paste with fly and bottom ashes and the density ratio decreased with increasing ash addition for both ashes. Hardened-to-fresh density ratio of each mixture is in good agreement with calculated hydrogen gas-to-cylinder volume ratio given in Table 4-4.
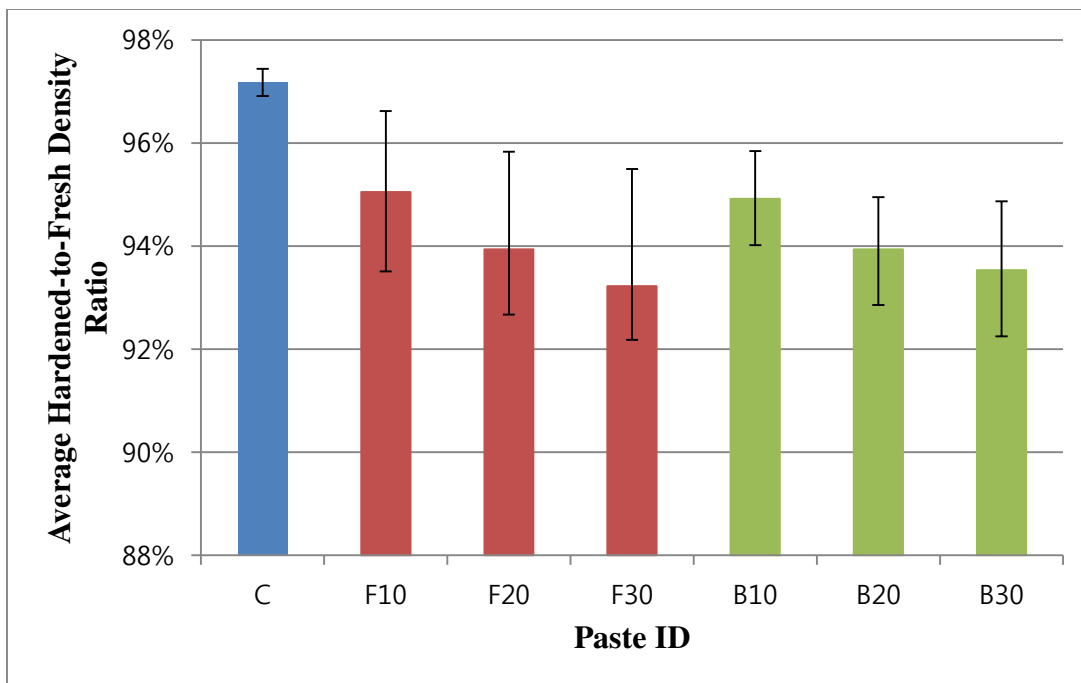
Figure 4-8. Average density ratios (hardened density / fresh density) for all mixtures.

Figure 4-9 shows the absorbed water in cement paste cylinders measured for over 60 days. The most rapid change in the water absorption occurred within the initial three days for the control specimen and the rate of change in the absorption decreased significantly thereafter. For the specimens with bottom ash, no significant difference in the absorption was found compared to that of the control specimen. The absorption for all bottom ash specimens was slightly lower than the absorption measured from the control specimen until day 3, but it became higher thereafter. For the fly ash specimens, F10 and F20 specimens exhibited much higher absorption than that of the control specimen. The F30 specimen, on the other hand, the absorption was lower than the control specimen until day 21 and the absorption increased with much slower rate; thus, the saturation behavior was observed much later than other specimens. Clear trend with increasing amount of ash addition was not found for both ashes.
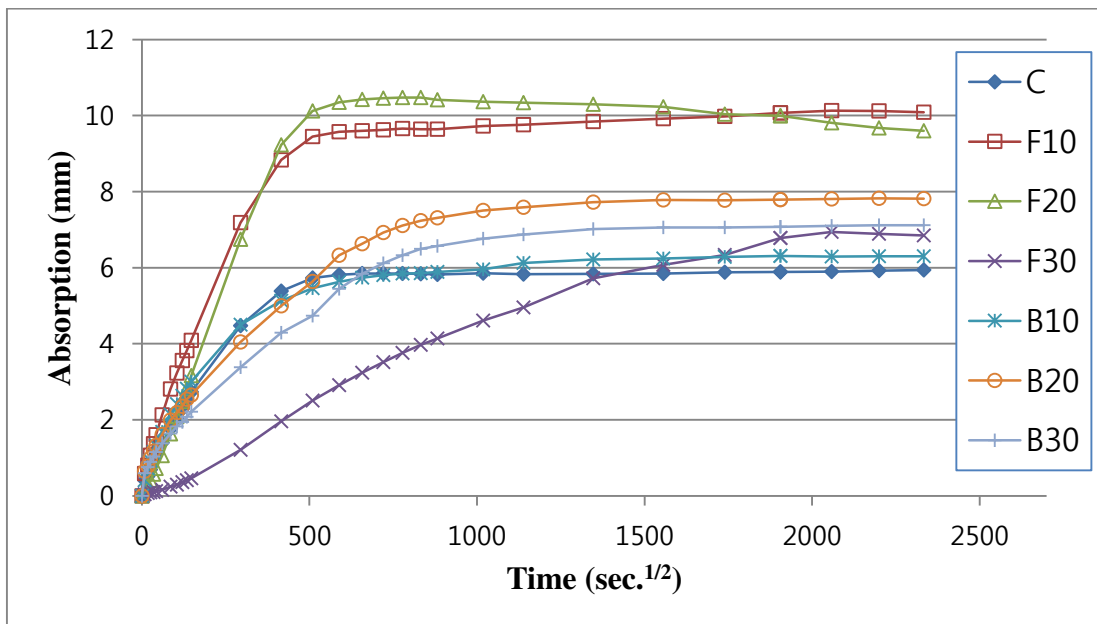
Figure 4-9. Water absorption for all cement paste cylinders.

Measured void content of hardened cement paste are provided in Table 4-5. The void content of all bottom ash specimens was higher than that of the control specimen and increased with increasing the ash addition. For the fly ash specimens, on the other hand, 10% addition of fly ash increased the void content of cement paste, but the void content decreased with further increasing replacement proportions. The void content of F20 and F30 specimen was approximately 21% and 46% lower than that of the control specimen, respectively.

The results found from the absorption and porosity tests were unexpected. Because an increase in the permeability of the cement paste was expected for both ashes based on the surface defects observed from the visual inspection (Figure 4-7) and the reduced density (Figure 4-8). Therefore, although a negative effect due to the development of hydrogen gas is evident, the use of ashes as mineral addition in cement paste must also include a positive effect to describe the unexpected findings from the absorption and porosity tests. It is suggested that these results are closely related to the filler effect by the fine particles of ashes. Numerous experimental investigations indicated that fillers have a profound effect on cement-based materials in both the fresh and hardened states (Cordeiro et al., 2008; Gutteridge & Dalziel, 1990; Moosberg-Bustnes et al., 2004; Soroka & Setter, 1977). When fine particles with a maximum size of 125 μm are incorporated in cement, these particles fill the intergranular voids between cement particles (Moosberg-Bustnes et al., 2004) and consequently increases the compressive strength as well as the durability (Mehta & Monteiro, 2006; Mindess et al., 2003). Therefore, it can be considered that the use of ashes in cement paste has both detrimental and beneficial effects caused by the hydrogen gas development and filler effect, respectively and both effects increases with higher ash

proportions. More specifically, while the development of hydrogen gas increases with increasing amount of metallic aluminum, the filler effect is influenced not only by the amount of filler, but also the particle size and their morphology. Based on the volume of hydrogen gas measurements (Table 4-3), both ashes released similar amount of gas, approximately 0.4 ml/g; however, filler effect is considered to be stronger for fly ash than bottom ash because the particle size of fly ash appears to be smaller (Figure 4-2) and their particle surface is smoother as seen in the SEM images (Figure 4-5). As results, F20 and F30 specimens exhibited lower void content compared to that of the control and the bottom ash specimens as presented in Table 4-5. In spite of the apparent surface air voids observed for F20 and F30 specimens in Figure 4-7, the fine particle of fly ash likely causes an increase in the packing density of cement paste and consequently reduced the absorption and void content.

Trends attributed to the surface defects shown in Figure 4-7 may also be explained with consideration of both hydrogen gas development and filler effect. A strong filler network formed in the cement paste containing fly ash and therefore, the air bubbles are pushed out and moves to the surface by the dense cement matrix. As a result, air voids were formed on the surface of the fly ash specimens without having visual cracks. For the bottom ash specimens, on the other hand, hydrogen gas became trapped inside the pores and further development of hydrogen gas may induce an expansion of pores. Internal pores were then connected each other and created pore passages. Consequently, longitudinal and transverse cracks were developed and observed on the surface of cement paste specimens with bottom ash addition.

In order to confirm the hypothesis that both development of hydrogen gas and filler effect are coupled to influence the overall performance of the cement paste, specimens were split and fractured surface of each cement paste was examined. Figure 4-10 shows the condition of cement paste section of each specimen. For the bottom ash specimens, higher amounts of entrapped air were observed with increasing addition ratio. For the fly ash specimens, on the other hand, the pore concentration appears to decrease with increasing the replacing ratio. Considering the fact that both ashes release similar amount of hydrogen gas (Table 4-3), this can be interpreted as due to the stronger filler effect owing to finer particle size of fly ash.
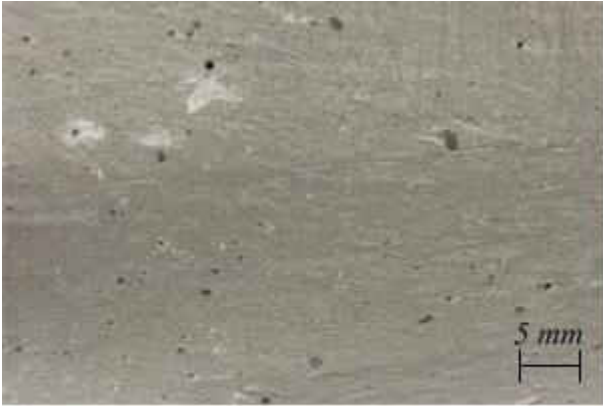
(a) C

(b) F10

(c) B10

(d) F20

(e) B20

(f) F30   (g) B30
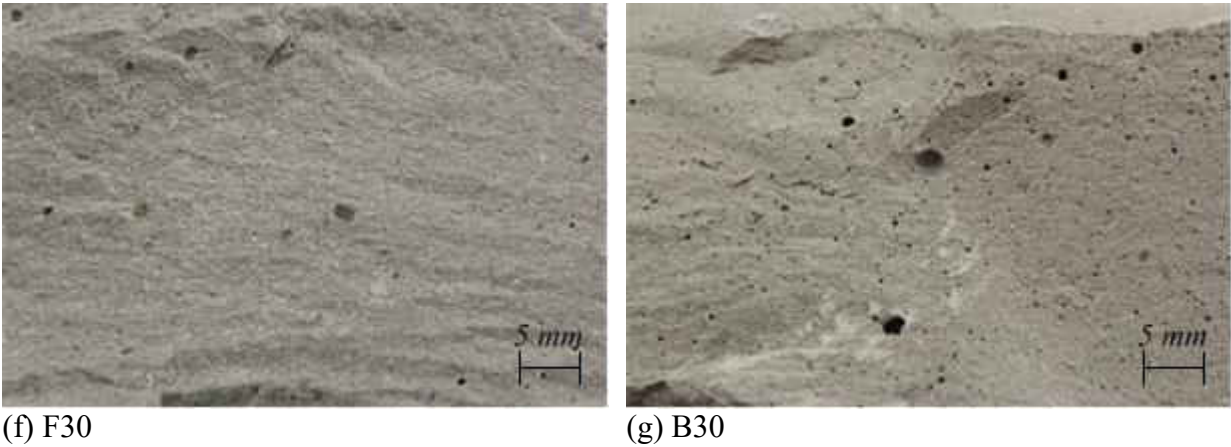
Figure 4-10. Photographs of cement paste section.

The average compressive strength of cement pastes measured at 28 days is plotted in Figure 4-11 and the values are given in Table 4-5. As expected, overall compressive strength of fly ash specimens were higher than that of the bottom ash specimens. When compared to the control specimen, the strength measurements of the fly ash specimens were similar or higher, while those of the bottom ash specimens were lower. For both ashes, specimens with 10% and 30% replacement ratios exhibited about the same strength; however, exceptionally high compressive strength was observed for the specimens with 20% ash addition. The compressive strength of F20 specimen is approximately 60% higher than that of F10 and F30 specimens and even 50% higher than that of the control specimen. Similarly, the compressive strength of B20 specimen is approximately 75% higher than that of B10 and B30 specimens.

59
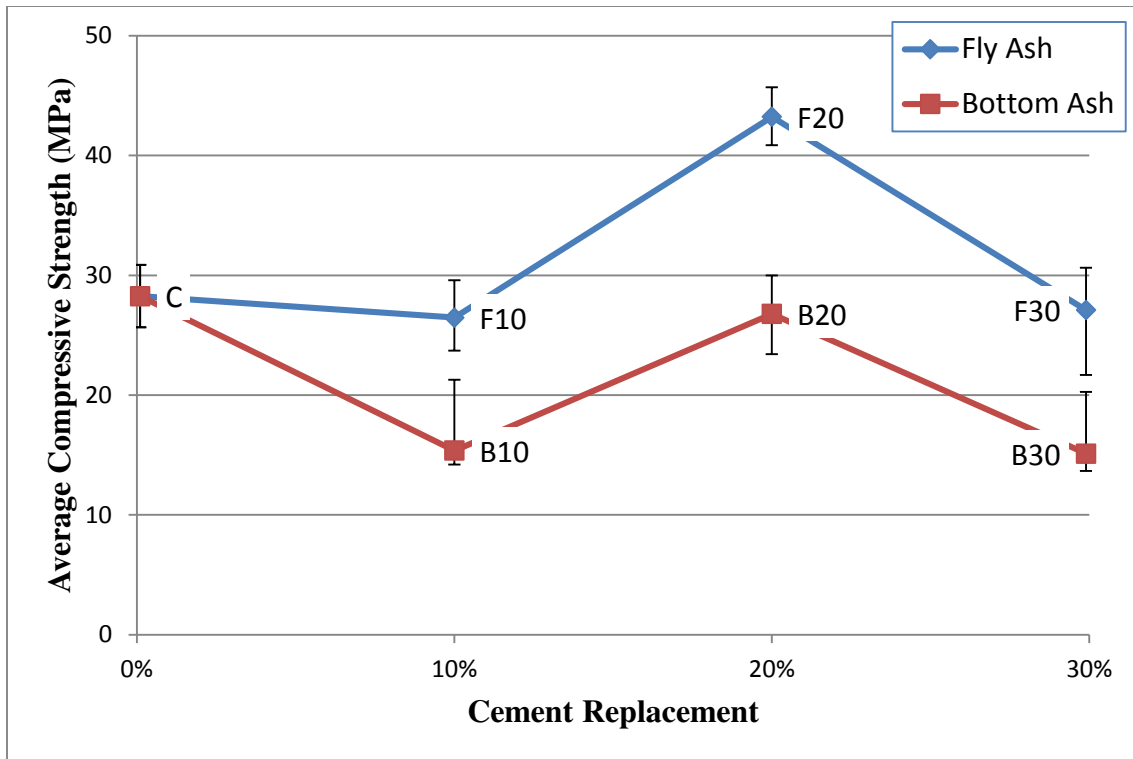
Figure 4-11. Average compressive strength measured at 28 days for all cement paste cylinders.

In the same way as other properties, both development of hydrogen gas and filler effect are coupled to influence the compressive strength of the cement paste cylinders. An increase of strength is attributed to the fine particles of ashes acting as fillers, while the production of hydrogen gas due to the reaction of metallic aluminum causes a decrease in strength. Another source of strength decrease is the reduced amount of hydration product with increasing ash addition. Although it is obvious that influence of these three combined effects increases with increasing percentage of ash incorporation, these effects are difficult to be generalized due to a trade-off between the effects. Similar compressive strength measured from the specimens with 10% and 30% replacements is mostly likely due to the trade-off of the factors that simultaneously influence the

compressive strength. The notable increases in the compressive strength for 20% replacements for both ashes, on the other hand, are likely to be attributed to the prevalence of the beneficial filler effect. A visual inspection of the cracked surface was conducted after the compressive strength test and the observations were in agreement with those presented in Figure 4-10.

4.4   Conclusions

In this chapter, municipal solid waste incineration (MSWI) fly ash and ground bottom ash were used as partial replacement of cement in cement paste specimens to investigate the possible use as a pavement or other road material. Based on the experimental investigation, both ashes contain considerable amount of metallic aluminum, which release large amount of hydrogen gas and eventually leads to a significant reduction of the overall cement paste properties. Cracks and air voids were observed from all specimens containing ashes, and their volume expansion was evident.

For the specimens incorporating ground bottom ash, mechanical and durability characteristics were inferior compared to those of the ordinary cement paste. This is mainly attributed to the swelling of cement paste due to the development of hydrogen gas. For the fly ash specimens, on the contrary, the compressive strength was similar or higher than the control specimen. For the specimens with 20% and 30% fly ash addition, much lower void content was observed compared to that of the control specimen. This is due to the fact that the fine particle of fly ash caused an increase in the packing density of cement paste and consequently increased compressive strength and reduced void content. Based on the petrographic analyses, however, considerably high quantity of chlorine was detected from fly ash, which would induce an

accelerated corrosion of embedded reinforcement when fly ash is used in reinforced concrete structure.

In spite of the fact that replacing cement with MSWI ashes in concrete is environmental friendly and cost effective, based on the tests results, the use of the ashes as mineral addition is hardly expected unless those detrimental influences are eliminated. Thus, ashes are required to be properly treated to deplete the high metallic aluminum and chlorine contents prior to mixing with cement. Thereby, MSWI ashes could be used as supplementary cementitious materials contributing to the enhanced properties of the hardened cementitious materials through hydraulic and pozzolanic activity with micro-filler effect.

CHAPTER 5: WTE BOTTOM ASH AS FINE AGGREGATE REPLACEMENT IN PCC[5]

5.1 Introduction

The objective of this chapter is to evaluate the impacts of MSWI BA as replacement of fine aggregate on cement hydration from the multiple performance perspectives such as physical, chemical, mechanical properties and behaviors. The focus was placed on the MSWI BA produced in the U.S. Unlike European and Asian countries, the U.S. has made no recycling of MSWI BA and conducted only limited studies on the use of MSWI BA in concrete a long time ago (Rosmadi Abdul Rashid, 1991; Berg, E., and Neal, J, 1998). Although several studies regarding the use of MSWI BA in concrete, different geographical locations having different solid wastes will cause significant variation if physical and chemical properties of MSWI BA (Bruder-Hubscher et al., 2001; Forteza et al., 2004).

This chapter focuses on the effects of MSWI BA as partial replacement of fine aggregate in concrete. Basic physical properties of MSWI BA were investigated by multiple standard testing methods such as fineness modulus, specific gravity and absorption capacity (American Society for Testing and Materials (ASTM) C33, C127, and C128). Petrographic examinations, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray

---

[5] The partial content of this chapter also will be appeared in:
J. W. An, B. H. Nam*, J. Y. Kim, "Investigation on the impacts of municipal solid waste incineration (MSWI) bottom ash on cement hydration," ACI Materials Journal.

diffraction (XRD) were also performed in order to identify the chemical and microstructural properties of the ashes in compliance with ASTM standard methods. Concrete cylinder specimens were cast with various amounts of fine aggregate replacement with MSWI BA. The overall performances of BA-combined concrete were investigated in accordance with ASTM standards.

5.2 Materials

Ordinary Portland cement Type I conforming to the ASTM C150 was used in the concrete. Limestone with nominal maximum size of 19 mm was used as coarse aggregate and Florida Department of Transportation certified sand passing 4.75 mm was used as fine aggregate. The detailed particle size distributions of the coarse and fine aggregates obtained by sieving are plotted in Figure 5-1 and Figure 5-2 and , respectively with corresponding ASTM grading requirements (ASTM, 2011). As shown in the figures, both aggregate types met the ASTM requirements. The calculated fineness moduli of the coarse and fine aggregates were 3.81 and 2.36, respectively.
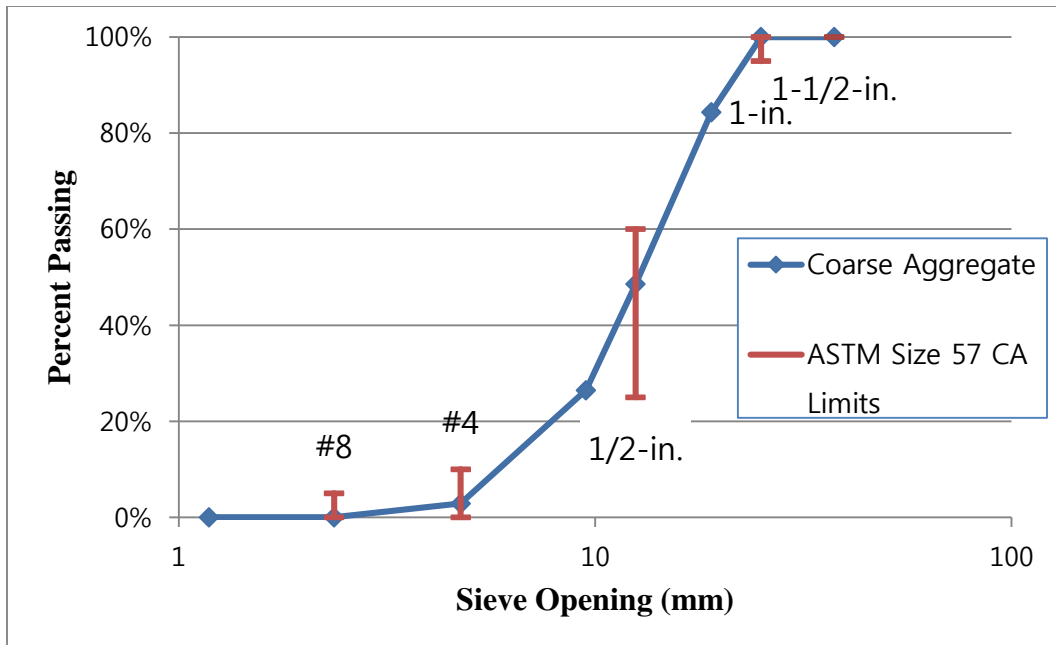
Figure 5-1. Gradation curves for coarse aggregates and ASTM C33 (ASTM, 2011) grading requirements for No. 57 aggregate
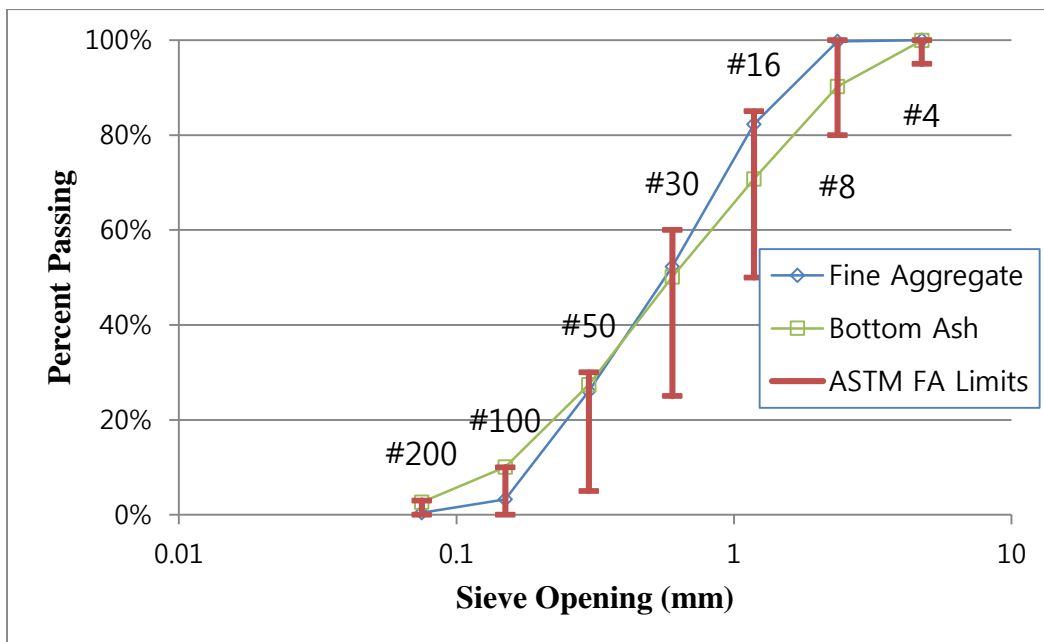
Figure 5-2. Gradation curves for fine aggregate and MSWI bottom ash, and ASTM C33 (ASTM, 2011) grading requirements for fine aggregate

MSWI bottom ash (Figure 5-3) was sourced from a refuse-derived fuel waste-to-energy facility in Florida, US in April, 2013. The maximum particle size of the ash was approximately 50 mm. Initially, bottom ash was oven dried at 105 ºC for 24 hours and then sieved to obtain the particle size similar to that of the fine aggregate. The particle size distribution curve of the sieved bottom ash showed a similar gradation as the sand and met the ASTM C33 standard as seen in Figure 5-2. Fineness modulus of the ash was 2.52, which indicates that the bottom ash contains coarser particles in comparison with the natural sand.

Figure 5-3. Photographs of MSWI bottom ash

5.3   Experimental procedures

Five different batches of the concrete specimens were cast with 0%, 10%, 20%, 30%, and 50% replacement of the fine aggregate with MSWI BA by weight. The mixture proportions for all five

batches are summarized in Table 5-1. Water-to-cement (w/c) ratio was kept constant at 0.5 for all specimens. Three specimens (100-mm diameter and 200-mm height) for the compressive strength tests (ASTM, 2012), four specimens (100-mm diameter and 100-mm height) for the density change (ASTM, 2012, ASTM, 2013), and three specimens (100-mm diameter and 50-mm height) for the absorption test (ASTM, 2013) were prepared for each of the five batches of the concrete mixture listed in Table 5-1. Mixing was carried out according to the ASTM C192 (ASTM, 2013) in a rotary drum mixer and all specimens were vibration compacted using a shaking table. During the mixing, the slump test (ASTM, 2012) of each mixture was conducted to evaluate the workability of the concrete. All test specimens were demolded three days after casting, and properly cured over 28 days. Concrete specimens were tested for the compressive strengths at day 28. The specimens for the absorption test were coated with the UGL Latex Base DryLok on three surfaces exposing the bottom surface as the source through which water can percolate in the vertical direction from a water reservoir.

Table 5-1. Mixture proportions of concrete specimens per cubic meter (kg/m^3)

Mixture ID	w/c	Water	Cement	Fine agg.	Bottom ash	Coarse agg.
C	0.5	180	360	761	-	949
B10		180	360	685	76	949
B20		180	360	609	152	949
B30		180	360	533	228	949
B50		180	360	381	381	949

5.4   Results and discussion

5.4.1   *Physical Properties of MSWI Bottom Ash*

Averaged test results of the basic physical properties and corresponding standard test methods are

listed in Table 5-2. MSWI bottom ash exhibited lower specific gravity compared to that of the

natural aggregates, indicating that the bottom ash is a lighter aggregate. In addition, considerably

high absorption capacity was obtained from the bottom ash, over three times greater absorption of

the natural aggregates. The lower specific gravity and higher absorption capacity of the bottom

ash suggest that the ash is a highly porous material (Izquierdo, Vazquez, Querol, Barra, Lopez and

Plana, 2001). Therefore, it can be assumed that the fine aggregate replacement in concrete with

bottom ash is expected to result in a loss of workability of fresh concrete and slump reduction.

Table 5-2. Basic physical properties of materials and standard test methods

Properties	Cement	Fine agg.	MSWI bottom ash	Coarse agg.	Test methods
Fineness modulus	-	2.36	2.52	3.81	ASTM C33 (ASTM, 2011)
Specific gravity (OD)	3.15	2.66	2.20	2.60	ASTM C127(ASTM, 2012), C128 (ASTM, 2012)
Absorption capacity, %	-	2.0	12.8	3.9	ASTM C127(ASTM, 2012), C128 (ASTM, 2012)

5.4.2   *Microstructural and Chemical Properties of MSWI Bottom Ash*

The microstructural morphology of MSWI bottom ash obtained from SEM at 500 X and 8,000 X

magnifications is shown in Figure 3-3 in the chapter 3. It can be observed from the figure that the

ash particle exhibits high internal porosity, which appears to be the main cause of the lower specific gravity and higher absorption capacity compared to those of the natural aggregates as listed in Table 5-2. Moreover, the high porosity may result in a highly reactive surface available for the leaching (Izquierdo, Vazquez, Querol, Barra, Lopez and Plana, 2001), which is found to be a common characteristic of MSWI ashes (Chandler, 1997, Forteza, Far, Seguí and Cerdá, 2004, Hyks and Astrup, 2009). In addition to the high porosity, the irregular and rough surface of the bottom ash observed from the SEM images is another possible cause of reducing the workability of concrete (Cheng, 2012).

Chemical elemental compositions of MSWI bottom ash obtained by the EDX analysis are listed in Table 3-2 in the chapter 3. Oxygen (O), calcium (Ca), silicon (Si), and aluminum (Al) are the major elements found from the bottom ash, which together form over 80% of the total elemental compositions of the ash by weight. It is obvious that the oxygen content is predominant (46.5 %); therefore, most chemical elements in the bottom ash are likely to exist in oxide forms. High Ca and Si contents may indicate a possible utilization of MSWI bottom ash as a supplementary cementitious material, once the ash is ground into a finer particle size.

Figure 3-4 shows the XRD analysis of MSWI bottom ash. The major mineral components found from the bottom ash are quartz (SiO_2), calcite ($CaCO_3$), and portlandite ($Ca(OH)_2$). In addition to the mineral components listed, many other minor minerals were detected with low amounts, indicating the intrinsic heterogeneous characteristics of MSWI ash. The analysis of the XRD data shows a good agreement with the findings from the EDX result.

5.4.3 *Workability of Fresh Concrete*

Measured slumps of the concrete specimens are presented in Table 5-3. The control specimen exhibited the highest slump of 25 mm and the slump decreases with increasing the replacement ratio of MSWI BA. These results support the previous assumption that the workability of concrete decreases with increasing the BA due to high absorption capacity of MSWI BA (Table 5-2).

Table 5-3. Measured properties of fresh and hardened concrete (conversions: 1 mm = 0.0394 inch; 1 kg/m^3 = 0.0624 lb/ft^3; 1 MPa = 145.038 psi)

Specimen ID	Slump (mm)	Density (kg/m^3)		28-day compressive strength (MPa)	
		Fresh	28-day	Average	STDEV
C	25	2,421	2,262	50.7	0.61
B10	13	2,395	2,223	48.5	1.26
B20	7	2,390	2,212	43.7	1.06
B30	4	2,376	2,183	38.7	2.77
B50	2	2,174	1,989	21.8	3.12

(note: STDEV = standard deviation)

5.4.4 *Fresh and Hardened Density of the Concrete*

Measured average densities of concrete specimens when freshly mixed and at 28-day curing are also presented in Table 5-3. As expected, a decrease in the density of the fresh concrete was observed as the BA addition increases. A similar decreasing trend was also observed for the hardened density of the concrete. The density decreases with time due to the loss of internal moisture content which led to a slight reduction in weight (Mindess, Young and Darwin, 2003); however, a greater reduction in the density was observed with increasing fine aggregate

replacement over the 28 days of curing. In order to compare the reduction ratio of density, the fresh-to-hardened density ratio was calculated and is plotted in Figure 5-4 as a function of fine aggregate replacement. The measured density decreased by 6.6% over the test period for the control concrete specimen. The density reduction ratio increased almost linearly with increasing fine aggregate replacement. In order to provide the variability of the measured data, error bars were added indicating the minimum and maximum values for each specimen. It is observed that the variability in the hardened-to-fresh density ratio increases as the aggregate replacement ratio increases. As discussed earlier, an increase in the measured fresh-to-hardened density ratio with increasing MSWI BA replacement percentage is most likely attributed to the volume expansion due to the hydrogen gas evolution.
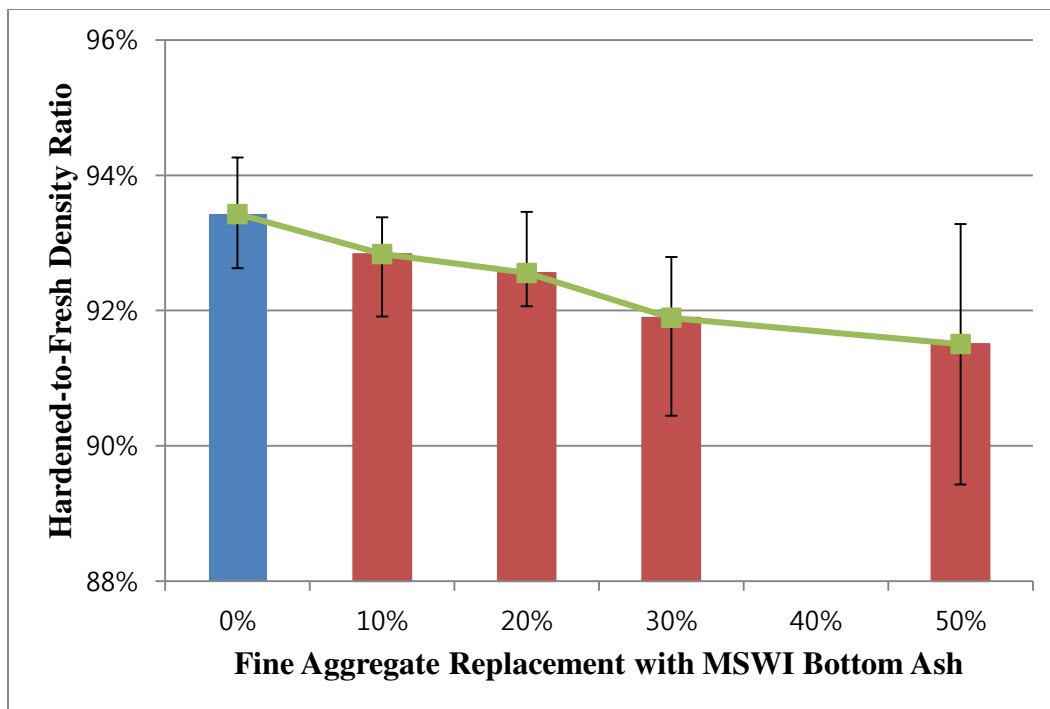
Figure 5-4. Density ratio (fresh / hardened density) as a function of fine aggregate replacement

The absorption of the concrete specimens measured over 35 days is shown in Figure 5-5. Within the initial four days, the most rapid change in the water absorption was observed for all specimens and the rate of change in the absorption decreased drastically thereafter. The control specimen exhibited the lowest amount of the absorption, indicating that the control specimen is least permeable. The measured absorption of the concrete specimen with 30% fine aggregate replacement exhibited the highest absorption capacity, demonstrating approximately 47% increased absorption compared to that of the control specimen at the end of the test. The difference in the absorption measurements among the specimens with 10%, 20%, and 50% replacement ratios were modest exhibiting about 28-33% increased absorption over the control specimen.
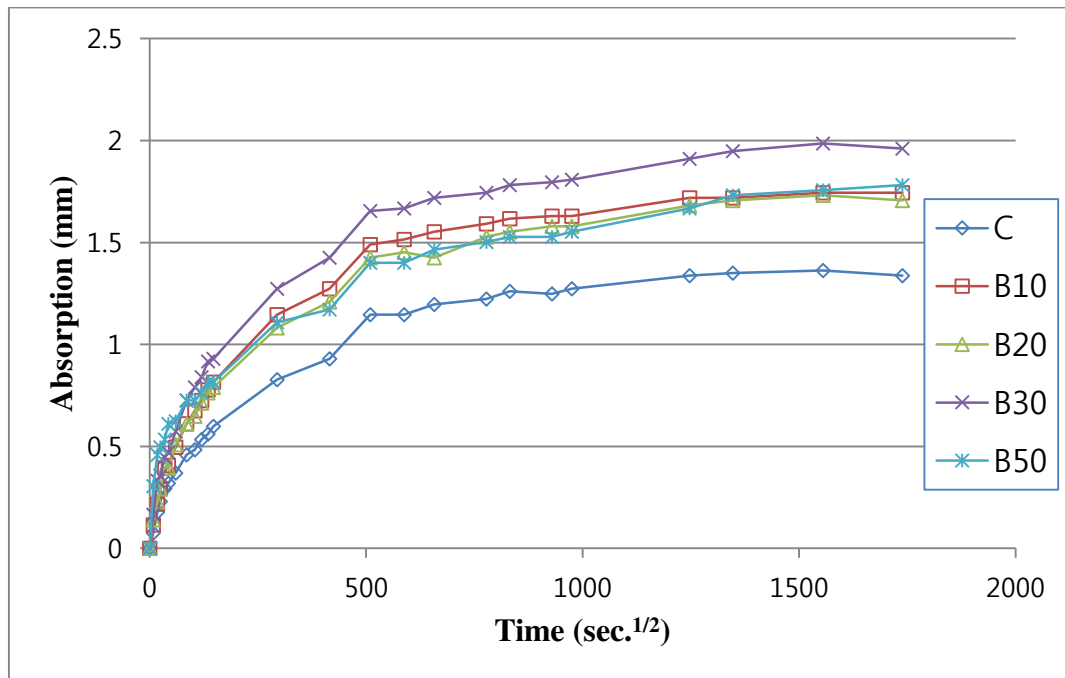
Figure 5-5. Measured absorption of all concrete specimens as a function of square root of time

72

The absorption capacity of concrete is known to be influenced by various factors, such as size and type of aggregate, quantity of cement and mixing water, curing condition, etc. (Walker, 1922, Verbeck, 1956, Pitroda and Umrigar, 2013) The main cause of the increased absorption for the concrete specimens with MSWI BA addition is most likely due to a significantly higher absorption capacity of the ash than the natural aggregate as compared in Table 5-2. The decrease in the absorption, on the other hand, seems to be attributed to increased tortuous path for the water migration due to the voids generated by the hydrogen gas as a result of the chemical reaction of metallic Al in a highly alkaline environment. It is important to note that according to the previous studies (Walker, 1922, Nambiar and Ramamurthy, 2007), density of the concrete does not have a general relation with the absorption capacity. For these reasons, the inconsistent absorption trends with increasing the fine-aggregate replacement ratio observed in Figure 5-5 appears to be because of the above mentioned positive and negative factors influencing simultaneously on the concrete absorption capacity.

5.4.6 *Compressive Strength*

The compressive strength measured at day 28 for all concrete specimens are compared in Figure 5-6 as a function of fine-aggregate replacement ratio. The average compressive strength of the control specimen was approximately 51 MPa. The strength measurements exhibited a decreasing trend with an increase in MSWI BA content. When 10% of the fine aggregate was replaced with the BA, the average compressive strength decreased about 4% from the control concrete specimen. As the BA replacement increased to 20%, 30%, and 50%, the average compression strength

decreased rapidly by 14%, 24%, and 57%, respectively of the compressive strength of the control specimen. The variability in the compressive strength measurements increased with increasing fine aggregate replacement ratio.
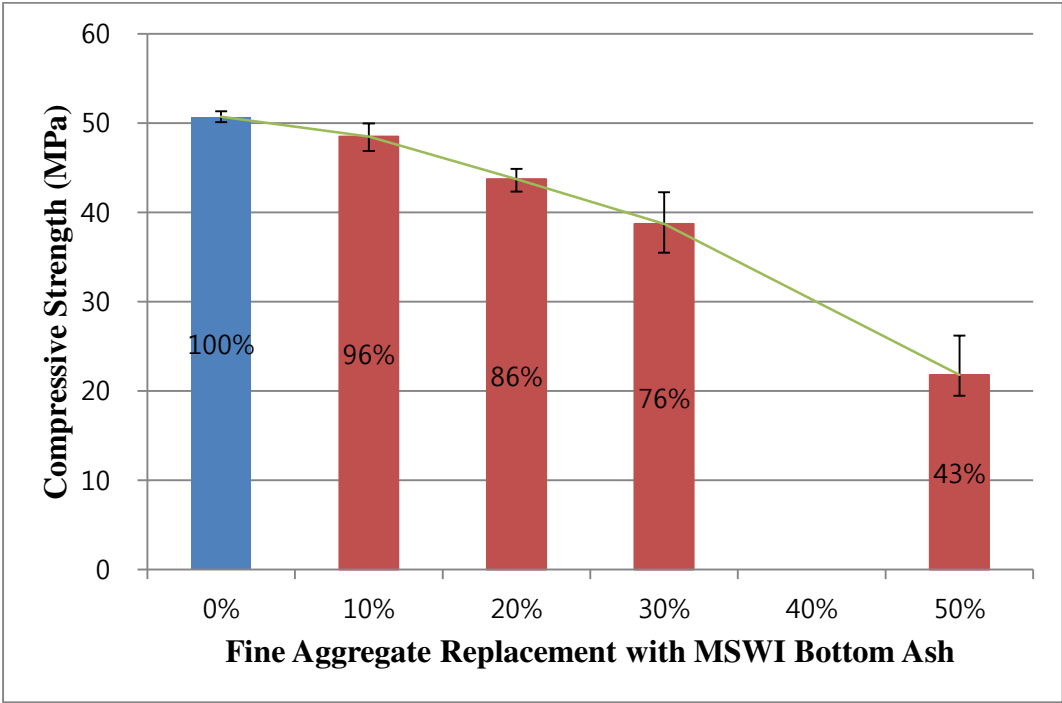
Figure 5-6. Measured compressive strength of all concrete specimens and their strength ratio compared to the control specimen as a function of fine aggregate replacement

5.5   Conclusions

The potential of the utilization of municipal solid waste incineration (MSWI) bottom ash as a partial replacement of fine aggregate in concrete was evaluated through a series of experimental investigations. From the analyses of the test data, the following conclusions can be drawn:

MSWI bottom ash exhibited lower specific gravity and considerably higher absorption capacity compared to those of natural aggregate. Therefore, bottom ash can be classified as a highly porous material and thus the concrete workability was largely reduced for the specimen with increased fine aggregate replacement ratio.

High volume of internal porosity was observed from the microstructural evaluation of MSWI bottom ash using scanning electron microscopy, and the bottom ash exhibited irregular and rough surface morphology. Based on the chemical component analyses by energy dispersive X-ray spectroscopy and X-ray diffraction methods, the presence of aluminum was observed in the ash. The existence of metallic aluminum in the ash was then further investigated by measuring the volume of hydrogen gas release from the bottom ash submerged in sodium hydroxide solution in the chapter 4.

The presence of metallic aluminum in MSWI bottom ash seems to reduce the strength and durability performance of the concrete specimens. As a result of the chemical reaction of metallic aluminum in high pH environment during the early hydration of concrete, a network of bubbles may be entrapped inside the concrete. Consequently, the overall concrete performance was decreased as the fine aggregate replacement with the bottom ash increased.

Based on the test results, in order to utilize MSWI bottom ash as sustainable civil material, it is essential to develop proper material processing techniques to remove metallic aluminum from the ashes. Thereby, overall concrete structural and durability properties can be enhanced. In addition, it is recommended to use a plasticizer when utilizing bottom ash in concrete to increase its workability. Moreover, leaching tests are needed to determine the potential environmental impacts when the ash is used in concrete.

CHAPTER 6: EFFECT OF CHEMICALLY TREATED WTE BOTTOM ASH ON PCC[6]

6.1   Introduction

In this chapter, municipal solid waste incineration (MSWI) bottom ash was characterized before and after the chemical treatment, and the effect of the ash addition on the performance of concrete as a partial replacement of fine aggregate was evaluated. The chemical treatment aimed at eliminating the side effect of MSWI ash, creation of network of bubbles, which can eventually lead to a significant reduction of the overall performance of concrete. Petrographic examinations, EDX and XRD, were carried out to chemically characterize MSWI bottom ash. Mechanical performance of the ash-combined concrete was evaluated by measuring the compressive strength. Analysis on measured data demonstrated that the chemical treatment successfully transformed metallic aluminum in the ash into a stable form; hence, expansion of concrete due to the hydrogen gas evolution was no longer detected from the concrete with the treated ash. Consequently, an increased performance was observed from the concrete specimens with the treated bottom ash compared to the specimens with the untreated ash.

In spite of the increased global efforts to prevent, reduce, and recycle the use of natural resources,

---

humans are producing an ever-increasing amount of waste. The total amount of solid waste produced in the US during 2010, for example, was approximately 250 million tons, according to a recent US government report (2010), and is increasing continuously each year. In the last few decades, great efforts were thus made to reduce the amount of waste produced; however, only a small percentage of solid waste has been recycled or composed, and a large amount of waste has still been combusted or dumped at landfills. Therefore, public agencies are investing significant portions of their budgets to improve the recycling rate of solid waste and to reduce the requirements for the construction of landfills.

To reduce the volume and weight for disposal, a waste treatment process generally involves a thermal treatment; combusting organic substances contained in waste materials at temperature of approximately 1,000 ºC (Chandler, 1997, Bertolini et al., 2004). The quantity of waste is typically reduced to 65-80% in mass and 85-90% in volume by the incineration process (Bertolini et al., 2004). Ashes, as a result of a municipal solid waste incineration (MSWI), can be categorized as: (1) fly ash, which is a fine particle, rises with the gaseous by-products, and (2) bottom ash, which is a large agglomerated residue, collected at the bottom of an incinerator. Fly ash is generally categorized as a hazardous waste material due to the presence of considerably high levels of heavy metals, chloride, dioxins, etc. (Aubert et al., 2004, Bertolini et al., 2004). Bottom ash, on the other hand, contains much less heavy metals, persistent organic pollutants (POPs), and chloride (Chandler, 1997). From the environmental point of view, therefore, a less intensive treatment is often adopted for bottom ash (Keppert et al., 2012).

Due to a relatively minor environmental impact expected when MSWI bottom ash is used with construction materials, a number of research studies have been conducted on the use of bottom ash in road construction (Lucido and Wilson, 2002, Forteza et al., 2004, Izquierdo et al., 2001, Bruder-Hubscher et al., 2001) and in concrete (Müller and Rübner, 2006, Bertolini et al., 2004, Keppert et al., 2012, Rubner et al., 2008, Jurič et al., 2006). Efforts have been focused on the use of bottom ash as a replacement for aggregate or cement. Unlike successful applications of other recycled materials in concrete and their active research works, such as recycled aggregate concrete (Gökçe and Şimşek, 2013, Saravanakumar and Dhinakaran, 2014), coal fly ash (Gao et al., 2013, Wang, 2013), and others (Ahmadi et al., 2014, Ferreira et al., 2014, Kwan et al., 2013), not many successful use of ash addition has been reported. This is mainly due to the side effect caused by the chemical reaction of aluminum in a high alkaline environment (Aubert et al., 2004, Bertolini et al., 2004, Müller and Rübner, 2006, Rubner et al., 2008). The presence of metallic aluminum in bottom ash causes an evolution of hydrogen gas, and the gas is entrapped within concrete by the following chemical reaction (Aubert et al., 2004, Müller and Rübner, 2006, Sorlini et al., 2011):

$$2Al + 4OH^- + 2H_2O \rightarrow 2Al(OH)_3 + H_2\uparrow \qquad (6.1)$$
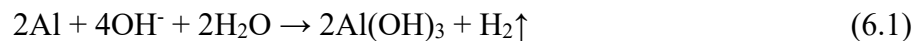
In addition, concrete expands due to an undesirable increase in volume of aluminates by the formation of aluminum hydroxide as described below (Müller and Rübner, 2006):

$$Al(OH)_3 + OH^- \rightarrow (Al(OH)_4)^- \qquad (6.2)$$

$$2(Al(OH)_4)^- + 3Ca^{2+} + 4OH^- \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O\downarrow \qquad (6.3)$$

These reactions cause cracking and spalling of concrete (Bertolini et al., 2004) and eventually leads to a significant increase in permeability and a reduction in strength of hardened concrete. In order for an appropriate utilization of MSWI bottom ash as a sustainable construction material, therefore, it is essential to develop proper treatment techniques to remove metallic aluminum in the ash.

This paper reports experimental investigations on the concrete incorporating MSWI bottom ash as a partial replacement of fine aggregate. The two primary experimental parameters are: (1) two types of MSWI bottom ashes, treated and untreated, and (2) five different ratios of fine aggregate replacement, 0, 10, 20, 30, and 50%. In order to eliminate the undesirable effect of MSWI ash addition in concrete, metallic aluminum in bottom ash was converted into a stable form by performing a chemical treatment using the sodium hydroxide (NaOH) solution. Basic physical properties of natural aggregates and treated and untreated bottom ashes were analyzed in accordance with ASTM standards. Petrographic examinations were performed to chemically characterize MSWI bottom ash before and after the treatment. Mechanical performance of the ash-combined concrete was evaluated by measuring the compressive strength.

6.2   Experimental procedure

6.2.1   *Materials*

The ASTM C150 Type I ordinary Portland cement was used in this study. Natural aggregates used were river sand and crushed lime stone for fine and coarse aggregates, respectively. MSWI bottom

ash was sourced from a refuse-derived fuel waste-to-energy facility in Florida, US (Figure 6-1). Particle size of the bottom ash was ranged approximately from 0.2 mm to 50 mm. Initially, all aggregates were placed in an oven at 110 ºC for 24 hours to remove moisture. The bottom ash was then ground, sieve analyzed, and blended to obtain a similar particle size for the fine aggregate replacement and to meet the ASTM gradation specification. Figure 5-2 and Figure 5-1 shows the particle size distributions of the bottom ash, fine aggregate, and coarse aggregate with the corresponding ASTM grading requirements. It can be seen from the gradation curves that all aggregates satisfied the gradation requirements of ASTM C33 (ASTM, 2011).

Figure 6-1. MSWI bottom ash

Several tests were conducted to determine the basic physical properties of aggregates and the results along with the corresponding test methods are listed in Table 6-1. The fineness modulus of MSWI bottom ash was slightly higher than that of the fine aggregate, indicating that the bottom ash was a little coarser than the natural sand. In addition, relatively lower specific gravity and considerably higher absorption capacity for the bottom ash were observed compared to those of the natural aggregates. These findings may indicate that the ash is lighter and highly porous aggregate; therefore, a reduction in workability is expected when the fine aggregate is replaced with the bottom ash in concrete.

Table 6-1. Basic physical properties of aggregates

Properties	Fineness modulus	Specific gravity (OD)	Absorption capacity, %
Cement	-	3.15	-
Fine aggregate	2.36	2.66	2.0
MSWI bottom ash	2.52	2.20	12.8
Coarse aggregate	3.81	2.60	3.9
Test methods	ASTM C33 (ASTM, 2011)	ASTM C127 (ASTM, 2012b) and C128 (ASTM, 2012c)	

6.2.2 *Chemical treatment*

The main purpose of the treatment is to avoid undesirable expansion of concrete due to the metallic aluminum induced hydrogen gas evolution (Equation 6.1) and the creation of aluminates (Equations 6.2 and 6.3) that can significantly reduce the overall performance of concrete (Müller and Rübner, 2006, Keppert et al., 2012, Rubner et al., 2008). MSWI bottom ash was subjected to a chemical treatment using the NaOH solution and a conversion of metallic aluminum into a stable

form was performed. The NaOH solution was adopted because of its high pH and market availability. The Molecular Biology Grade NaOH beads were used with its purity greater than 98%. The aqueous NaOH solution of concentration 1 mol/liter was used with ash-to-solution mass ratio of 1:1. For practical and convenience purposes, as well as a large volume requirement, regular tap water was used to make the NaOH solution. The ash was submerged in the solution and the reservoir was placed on a shaking table. The reservoir was vibrated for an hour, soon after the submersion and at the end of each day. The reaction occurred violently and a large amount of hydrogen gas began to be released from the ash soon after the initiation of the treatment. The treatment was carried out for three days as a constant weight of the ash was obtained. After a completion of the treatment, the ash was filtered and washed in tap water to remove the solution. The treated ash was then dried in an oven at 110 ºC for 24 hours.

In order to evaluate effects of the chemical treatment and to assess the remaining metallic aluminum content in the ash, volume of hydrogen gas emission was measured in separate experimental setup for both of the untreated and treated MSWI bottom ash. In order to increase the surface area to react, both types of the ashes were ground and sieved under dry condition to their particle size smaller than 90 μm before submerging in the NaOH solution. As shown in Figure 6-2, the reaction vessel was connected to the gas collection burette through the Tygon tube. A magnetic stirrer was installed under the reaction vessel to maximize the reactivity of the ash and volume of hydrogen gas trapped in the collection burette was measured. The duration of the test was 24 hours and the weight of the reaction vessel was measured hourly to check the reaction progress and to confirm a completion of the reaction within a given test period. For a comparison

purpose, the test was also conducted using pure metallic aluminum and aluminum oxide (Al_2O_3) powder with their particle size 90 μm under the identical conditions. The entire test setup was stored in an indoor environment with an ambient temperature of 23 ºC at atmospheric pressure.
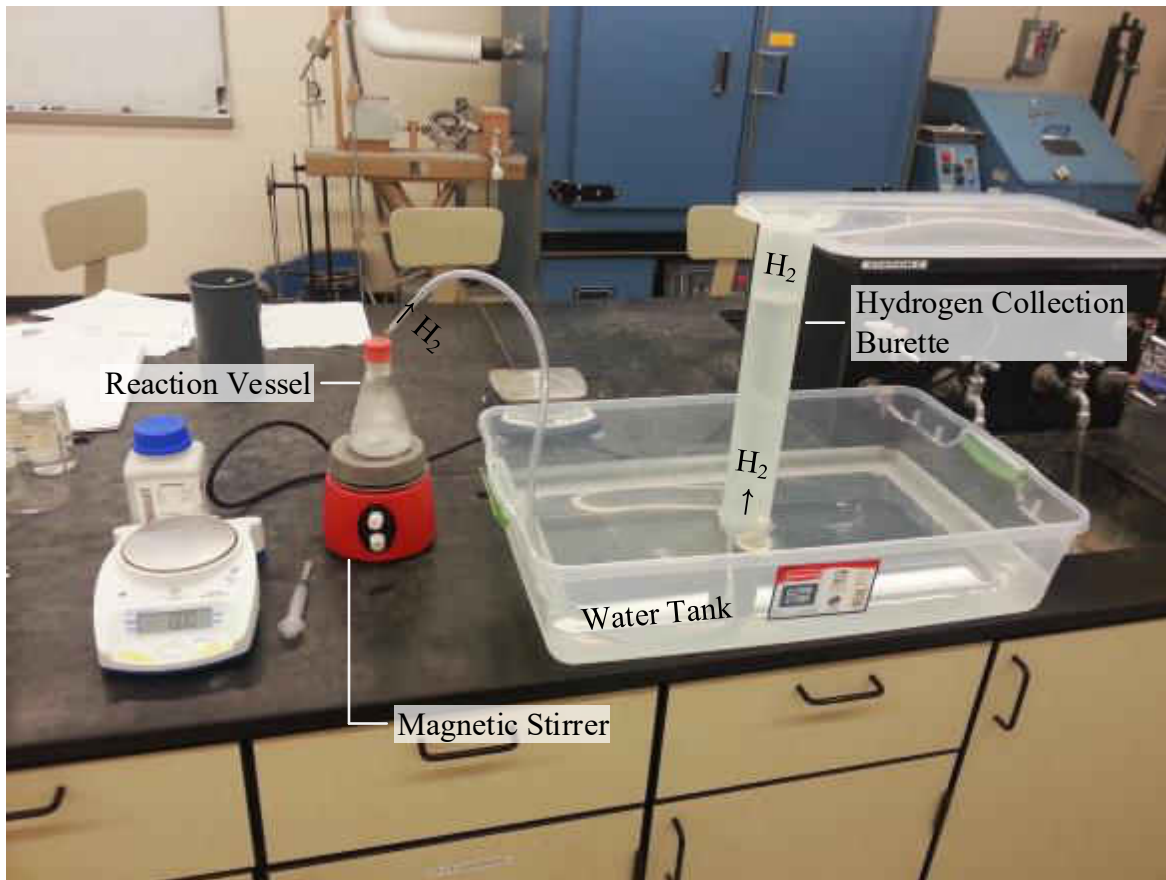

Figure 6-2. Test setup for the volume of hydrogen gas emission

6.2.3 *Experiments*

Chemical elemental compositions of the untreated and treated MSWI bottom ash were evaluated by energy dispersive x-ray spectroscopy (EDX) analysis. Information regarding the phase compositions of both types of the ashes was determined by X-ray diffraction (XRD) analysis.

Nine different types of concrete specimens were prepared to test mechanical performance of the ash-combined concrete. The mixture proportions of the concrete specimens are listed in Table 6-2. With the exception of the control mixture (C), other mixtures contained either untreated (U) or treated (T) MSWI bottom ash as the replacement for fine aggregate. The amount of fine aggregate replaced by the bottom ash was varied from 10% to 50% by weight. A constant water-to-cement ratio of 0.5 was used for all mixtures. Three 100×200-mm^2 cylinder specimens were prepared for each of the nine mixture IDs and the 28-day compressive strength was tested in accordance with ASTM C39 (ASTM, 2012a). All specimens were vibration-compacted using a shaking table. All concrete specimens were stored in an indoor environment with an ambient temperature of 21 ± 1 ºC and relative humidity of $70 \pm 3\%$, and removed from the cylinder molds three days after the casting.

Table 6-2. Mixture proportions of concrete specimens per cubic meter (kg/m^3)

Mixture ID	w/c	Water	Cement	FA	Untreated ash	Treated ash	CA
C	0.5	180	360	761	-	-	949
U10	0.5	180	360	685	76	-	949
U20	0.5	180	360	609	152	-	949
U30	0.5	180	360	533	228	-	949
U50	0.5	180	360	381	381	-	949
T10	0.5	180	360	685	-	76	949
T20	0.5	180	360	609	-	152	949
T30	0.5	180	360	533	-	228	949
T50	0.5	180	360	381	-	381	949

6.3 Results and discussion

6.3.1 *Metallic aluminum contents*

Measured volume of hydrogen gas and calculated metallic aluminum content for all tested materials are listed in Table 6-3. The metallic aluminum content was calculated from the measured volume of hydrogen gas based on Equation 6.1 with the perfect gas assumption, considering the environmental conditions. Hydrogen gas released from the aluminum powder was 1,345 ml/g, which is nearly identical to the maximum theoretical value of hydrogen gas evolution for a pure metallic aluminum (1,350 ml/g), indicating the aluminum powder used in this test exhibited 99.6% of purity. For the aluminum oxide power, as expected, hydrogen gas evolution was not detected even when the concentration of the solution was greatly increased. For the untreated MSWI bottom ash, hydrogen gas began to be released as soon as the ash was mixed with the solution and a considerable amount of gas evolution was observed during the test. The calculated metallic

aluminum content in the untreated ash was 0.03% by weight. According to the measured volume

of hydrogen gas, the maximum possible gas evolution per each concrete cylinder specimen (100

$\times$ 200 mm^2) is 48 ml when 10% of fine aggregate is replaced with the untreated bottom ash that

accounts for about 3% of the concrete volume. For the concrete specimen with 50% fine aggregate

replacement, these values can be increased up to 240 ml of the gas evolution, occupying 15% of

the entire volume. For the treated bottom ash, on the other hand, only 5-10 ml of hydrogen gas

evolution was detected during the entire test period of 24 hours. The calculated metallic aluminum

content from the treated bottom ash was approximately 0.004-0.005% by weight. The test results

demonstrated that the chemical treatment was successful in converting the metallic aluminum in

the bottom ash into a stable form and therefore the hydrogen gas evolution may be neglected when

the treated bottom ash is utilized as a fine aggregate replacement in concrete.

Table 6-3. Measured volume of hydrogen gas evolution and metallic aluminum content

Material	Mass (g)	NaOH solution		H$_2$ vol. (ml)	H$_2$ vol./mass (ml/g)	Al content (g)
		Conc. (M)	Vol. (ml)			
Al powder	0.29	1	10	390	1,345	0.289
Al$_2$O$_3$ powder	1	1	10	-	-	-
	150	3	400	-	-	-
Untreated ash	100	2	400	40	0.40	0.030
	150	3	400	60	0.40	0.044
Treated ash	100	2	400	5	0.05	0.004
	150	3	400	10	0.07	0.007

6.3.2 *Chemical characteristics*

The compositions of the elements present in the MSWI bottom ash before and after the treatment are tabulated in Table 3-2. Changes in the weight percentages were also provided in the table to assess the effect of the treatment. The major elements present within the bottom ash are oxide, calcium, and silicon, accounting for approximately 80% and 85% of the untreated ash and treated ash, respectively. Notable variations in the composition contents found after the treatment were the reduced percentage of magnesium, silicon, sulfur, and chlorine, and the increased percentage of sodium and calcium. Sulfur, which may exist as sulfates and magnesium are highly soluble, and the solubility of chlorine is increased when the water contains dissolved alkali hydroxide (Earnshaw and Greenwood, 1997); therefore, theses compositions seem to be dissolved out during the treatment and washing process. The increased sodium content observed from the treated bottom ash is most likely the result of the chemical treatment using the NaOH solution. In regard of the aluminum, only a small reduction in the aluminum content was observed from the treated bottom ash compared to the untreated ash.

XRD results for the untreated and treated MSWI bottom ash are shown in Figure 6-3 and Figure 6-4, respectively. Several types of calcium silicate hydrates were detected in the ash, including xonolite and jaffeite, as the result of an incineration process. When materials containing calcium oxide and silica are heated above 100 ºC in the moist sealed condition, hydrothermal reactions take place and calcium silicate hydrates form with varying phases depending on the calcium/silicate ratio, temperature, and pressure (Barnes and Bensted, 2002, Hewlett, 2004, Fingerloos, 2007).

Many other minerals were also detected with low amounts in addition to the listed minerals, indicating MSWI bottom ash is a highly heterogeneous material. The XRD analyses on both types of the bottom ashes show a good correlation with the observations from the EDX results.
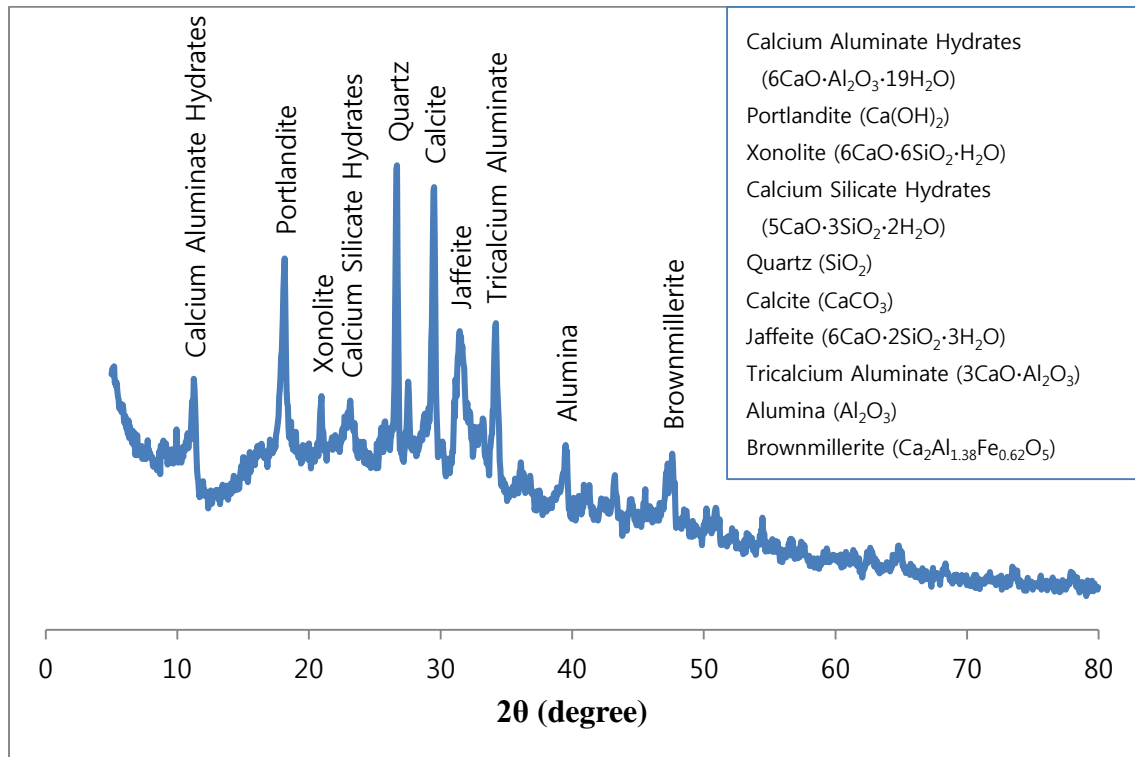

Figure 6-3. XRD analyses of the untreated bottom ash
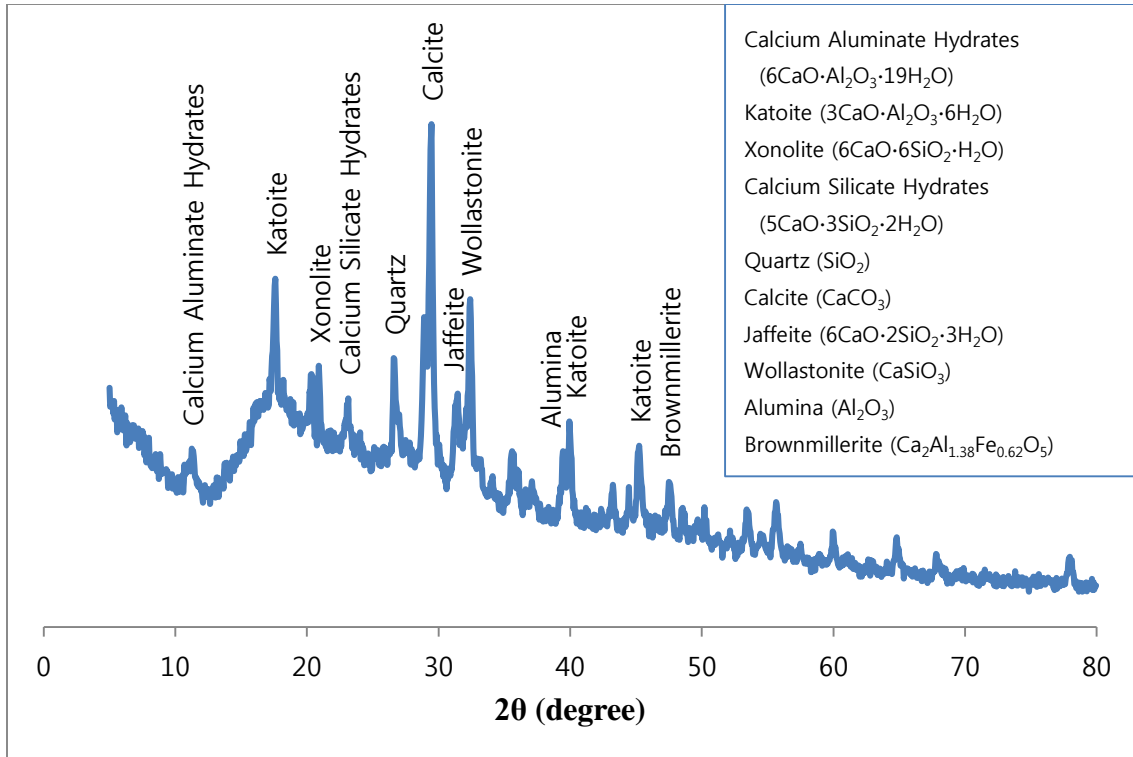
Figure 6-4. XRD analyses of the treated bottom ash

The main mineral components of the ash before and after the treatment were distinct; portlandite, quartz, and calcite for the untreated ash and katoite, calcite, and wollastonite for the treated ash. Bottom ash appears to undergo following chemical reactions during chemical treatment and washing process:

$$Ca(OH)_2) + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \tag{6.4}$$

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2 \tag{6.5}$$

$$3CaO \cdot Al_2O_3 + 6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O \tag{6.6}$$

90
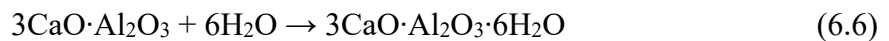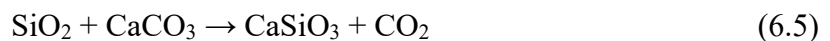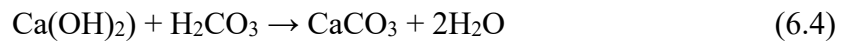
Calcium silicate hydrates including xonolite and jaffeite were still observed after the treatment and their contents seem to be remained constant. The XRD peak for alumina from the treated bottom ash exhibited nearly identical intensity compared to that of the untreated ash, confirming its high stability (Hewlett, 2004, Patnaik, 2003) and chemical resistance (Khamirul Amin et al., 2012) that agrees with the test results shown in Table 6-3. For other minerals containing aluminum, on the other hand, the contents appear to be reduced after the treatment. A large amount of tricalcium aluminate transformed into more stable katoite due to its high thermodynamic equilibrium constant (Onori et al., 2011), and the same conversions seemed to occur for calcium aluminate hydrates (Tan et al., 2011) and metallic aluminum during the treatment. These phase conversions of aluminum-containing minerals to form a compound that is more stable during the treatment well explain the negligible amount of hydrogen gas evolution observed from the treated bottom ash.

6.3.3 *Compressive strength of concrete*

The compressive strength of concrete are compared in Figure 6-5 with the strength ratio. As expected, the compressive strength decreased rapidly with increasing replacement ratio when fine aggregate was replaced with the untreated bottom ash. This was expected because of the expansion of concrete by the hydrogen gas evolution from the metallic aluminum in MSWI bottom ash. While the control specimen exhibited smooth and clean surface without voids or cracks, visible defects and network of bubbles were easily observed from the specimens with the untreated bottom ash. The size of cracks and density of voids tend to increase with increasing ash replacement ratio, and expansion of concrete was evident. For the concrete specimens with the treated bottom ash, on the

other hand, no signs of concrete expansion or defects were found from the external and internal inspection. As the replacement ratio increased, the compressive strength of the specimens with the untreated bottom ash decreased more gradually than the untreated ash specimens. For the specimens with 50% replacement of both untreated and treated ashes, a large drop in the compressive strength was observed. This is most likely due to a reduced workability that caused the trapping of air inside the concrete during the casting. As mentioned earlier, the bottom ash is highly porous, exhibiting considerably higher absorption capacity than the natural aggregates (Table 6-1), thus more mixing water will be required for the proper consistency especially when a large amount of bottom ash is incorporated in concrete.
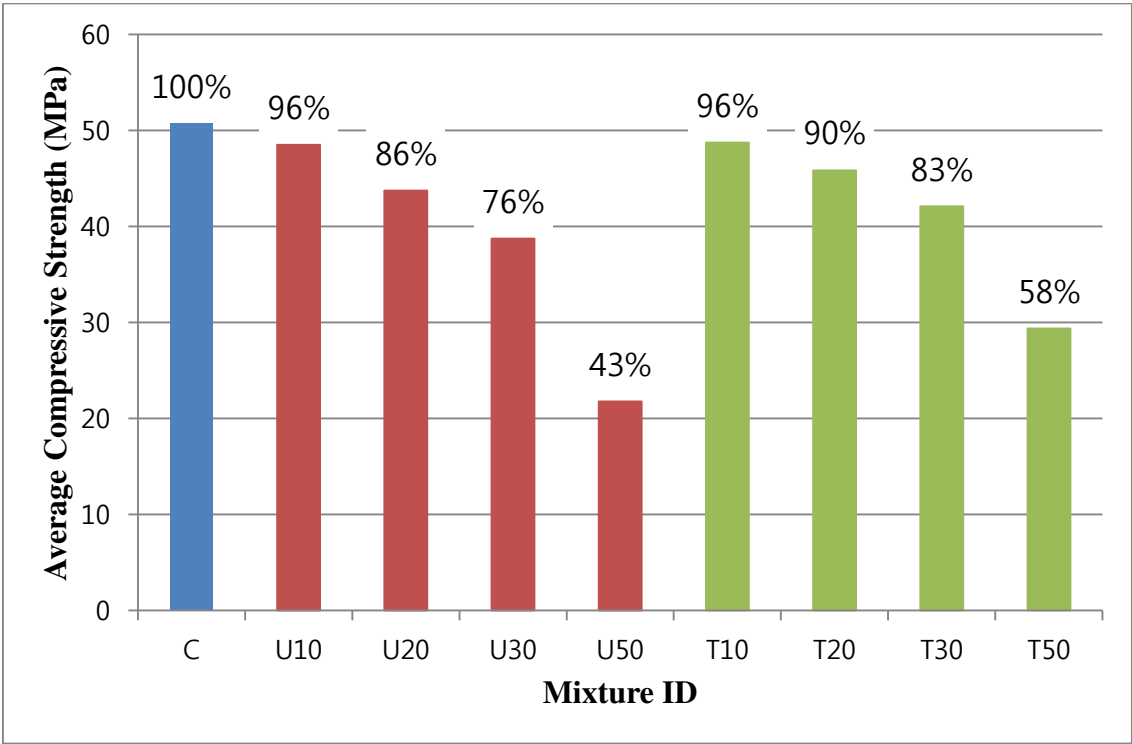

Figure 6-5. Average compressive strength measured at 28 days for all concrete specimens and their strength ratio compared to the control specimen

6.4   Conclusions

In this paper, municipal solid waste incineration (MSWI) bottom ash was subjected to a chemical treatment to avoid hydrogen gas evolution when used in concrete that can eventually lead to a significant reduction of the concrete performance. Mechanical performance of the concrete with bottom ash was then tested by replacing fine aggregate with the ash in concrete specimens with varying ratios. Based on the experimental investigation, the following conclusions can be drawn:

The chemical treatment of MSWI bottom ash successfully transformed metallic aluminum into a stable form and therefore negligible amount of hydrogen gas evolution was detected from the treated bottom ash. Analyses on the chemical elemental compositions and the phase compositions of the untreated and treated bottom ash confirmed that the transformations of the aluminum compound towards the more stable phase were successful. The treatment used in this study was relatively simple and cost effective; therefore, it might be a feasible and practical treatment method to be adopted by industry for a large amount of bottom ash utilization as a construction material.

Expansion of concrete was evident from all specimens with the untreated bottom ash. Visible defects and network of bubbles were easily observed from the concrete specimens with the untreated ash and the size of cracks and density of voids tend to increase with increasing replacement ratio. For the concrete specimens with the treated bottom ash, on the other hand, no signs of concrete expansion or defects were found from the external and internal inspection.

Compressive strength of the concrete specimens with the treated bottom ash was superior to that

of the untreated ash specimens. The concrete specimens with 10%, 20%, and 30% fine aggregate replacements with the treated bottom ash were 96%, 90%, and 83% of the compressive strength of the control specimen, respectively. However, a considerable reduction in the compressive strength was observed from the concrete specimens with 50% replacement due to a reduced consistency of concrete. MSWI bottom ash is a highly porous material, therefore, it is recommended to use a plasticizer when mixing the ash in concrete for a proper workability.

In addition to a chemical treatment to eliminate hydrogen gas evolution, ashes are need to be further treated to deplete other potential contaminants, such as highly soluble salt content and heavy metal concentration, which can be a risk to human health. Therefore, regulations and standard leaching test procedures must also be developed to determine the potential environmental impacts when MSWI ashes are utilized in concrete. Moreover, a methods of recycling the fluid used for the chemical treatment has to be developed.

CHAPTER 7: LEACHING INVESTIGATION OF WTE BOTTOM ASH - COMBINED PCC[7]

7.1 Introduction

In 2014, the U.S. produced municipal solid waste (MSW) of 256 million tons per year with 53.8% of landfilling, 34.5% of recycling and composting, and 11.7% incineration (US EPA 2014). Beneficial reuse of waste-to-energy (WTE) ash residues (or called as MSW incineration ashes) has received a large attention because WTE can be a renewable energy source as well as a component of MSW management. (Chandler et al. 1997, US EPA 2014). Typical recycling of WTE BA is to reuse in the area of road construction sector; for example, WTE BA can be used the partial replacement of fresh fine aggregate mixed with Portland cement concrete (PCC) (Chandler et al. 1997; Quina et al. 2011). To use of WTE BA mixed with PCC, it is necessary to identify the environmental consequences associated with the leachate from the BA and PCC.

When PCC is recycled with WTE BA as aggregates for base or sub-base in pavement system, cement hydration will occur due to reaction of silicate phases of cement and the reactive chemical compounds in BA with water from precipitation (Li et al, 2012; Shi et al. 2009; Forteza et al. 2004). Cement hydration might affect the leaching of contaminant from the PCC including WTE BA because the constituents of the PCC and the BA produces calcium silicate hydrates (C-S-Hs) and new solid phases during the process. However, the leaching characteristics from recycled PCC

---

[7] A part of this dissertation will appear as peer-reviewed journal papers, co-authored by the author of dissertation.

including WTE BA has been limitedly investigated in associated with cement hydration because the process is complicated depending upon many variables such as pH, temperature, curing time, and the amount of the materials. There is a lack of comprehensive study to investigate leaching behavior from crushed PCC including WTE BA based on chemical reaction and interaction among alkaline and heavy metals in the PCC and WTE BA.

This chapter presents the leaching characteristics of major alkaline elements (e.g., Ca, Al, Si, Na, and K) and minor heavy metals (e.g., Cu, Fe, Mg, Ti, and Zn) from crushed PCC including WTE BA through the Synthetic Precipitation Leaching Procedure (SPLP) (EPA method 1312) tests. Based on the material characterization of WTE BA 'as received' by Energy Dispersive X-ray (EDS) and X-ray diffraction (XRD), the leaching behavior of alkaline substances and heavy metals in associated with the cement hydration was investigated as considering chemical properties such as oxidation reaction potential (ORP) and pH measured in the test. The leaching characteristic of the contaminants in accordance with chemical reaction (i.e., cement hydration) in the leaching from PCC including WTE BA was quantified and comprehensively discussed.

7.2   Materials

7.2.1   *Sample Preparation for PCC Containing BA*

BA was screened to particle size range passing 4.75 mm up to 75 μm to meet the requirement for the fine aggregate replacement in PCC. Sand particle size passing 4.75 mm was used as fine aggregate. Limestone with nominal maximum size of 19 mm was used as coarse aggregate. According to ASTM C192, five different sets of concrete specimens (cylindrical specimen in 100

96

× 200 mm^2) with water-to-cement (w/c) ratio of 0.5 were casted with 10, 20, 30, or 50% of the fine aggregate replaced by BA. All specimens were air-cured in order to make no pre-leachate from the wet curing. These crushed concrete (particle sizes ranging from 20 to 40 mm) were used to investigate the leaching potential of major and minor constituents using the SPLP test.

7.3   Experimental Methods

7.3.1   *SPLP Batch Test*

SPLP batch tests (EPA method 1312) were conducted to assess the realistic leaching from PCC containing BA when used at sites exposed to stormwater infiltration. Extraction fluid was prepared by mixing sulfuric and nitric acids to obtain a solution with a pH of 4.2 to simulate stormwater from the east of the Mississippi river. The High Density Polyethylene (HDPE) bottles containing leaching solution and samples at solid-to-liquid ratio of 1:20 were agitated in a rotary tumbler at 30 rpm for 24 hours. All SPLP extracts were then filtered out by using a 0.25-μm filter paper under 350 kPa pressure, preserved with nitric acid at pH < 2, and stored at 4 °C. Leaching tests were conducted in triplicate.

The batch tests were continued for 72 hours (3 days) to investigate time effect on leaching substance exposed to stormwater synthetic solution. Major alkaline elements and trace heavy metal concentrations in the eluate were determined with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). A total of ten elements, Al, Ca, Na, Si, and K (major alkaline elements) and Cu, Fe, Mg, Ti, and Zn (minor heavy metals) were chosen to be evaluated in this study. Pb, Cr, Hg, Cd, and As were measured but those elements were under detection limits through ICP-OES.

Major elements including Al, Ca, Na, Si and K were present at concentrations too high to be detected with minor elements. The sampling solutions were diluted at a ratio of 1:50 and the concentrations of the major elements were reanalyzed. Leaching behavior of alkaline elements and heavy metals was investigated for the PCC specimen containing 10, 20, 30, and 50% WTE BA as fine aggregate replacement. Triplicate tests including a BA alone specimen acting as the control were conducted to evaluate the leaching potential from the reuse of BA in PCC.

After 1 day of the batch leaching test using synthetic stormwater solutions (pH = 4.2), the concentration and pH of leachate were measured. Typically, the pH of the leaching solution from PCC is higher than stormwater because of the high alkalinity imparted from carbonates and hydroxides of PCC (De Windt et al. 2011; Izquierdo et al. 2008). Average ORP values as well as pH were also measured after the test (Table 7-1)

Table 7-1. Chemical Properties of Leachate

BA content (%)	0	10	20	30	50	100
pH	12.05	11.18	11.5	12.17	11.98	11.62
ORP (mV)	80	100	98	75	85	105

7.4 Results and discussion

7.4.1 *Chemical Analysis of WTE BA*

Chemical elemental analysis and mineralogy analysis of WTE BA were carried out using the EDS and XRD, respectively. Average chemical compositions (elemental and oxide form) are listed in Table 7-2. The EDS results show that the major alkaline elements of the BA are Ca, Si, Al, Na,

and K, the minor elements are Mg, Fe, and S, with heavy metal contents of Ti, Cu, and Zn. XRD pattern exhibits major mineral phases in the BA, such as portlandite ($Ca(OH)_2$), quartz (SiO_2), and calcite ($CaCO_3$) and minor compounds are calcium aluminate hydrate ($Ca_2Al(OH)_7 \cdot 5H_2O$), jaffeite ($Ca_6(Si_2O_7)(OH)_6$), and tricalcium aluminate ($Ca_3Al_2O_6$) as shown in Figure 7-1. XRD results are found to be in agreement with EDS analysis. Although BA appears to contain less soluble compounds, exposure to acidic stormwater may lead to potential leaching of elements while incorporating into PCC.

Table 7-2. Average Chemical Composition of BA (% by weight)

Element	BA	Oxide Form	BA
O	45.19	-	-
Na	3.90	Na_2O	5.74
Mg	1.70	MgO	3.12
Al	4.60	Al_2O_3	9.50
Si	8.00	SiO_2	18.81
P	0.90	P_2O_5	2.28
S	3.70	SO_3	10.16
Cl	2.00	Cl	2.25
K	0.87	K_2O	1.15
Ca	25.30	CaO	38.92
Ti	1.38	TiO_2	2.52
Fe	1.10	Fe_2O_3	3.68
Cu	0.80	CuO	1.10
Zn	0.56	ZnO	0.77
Total	100	Total	100

7.4.2 *Chemical Composition from Cement-WTE BA Hydration*

Chemical compositions of hydrated WTE BA were also determined by XRD analysis (see Figure 7-1b). In comparison of mineral structures of cement to those of BA, possible chemical reactions might be explained during hydration. From XRD of the BA, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) were found. The presence of these hydration products may be explained by the balance between aluminate and sulfate in the BA. During BA-water interactions, supersaturated mixture with respected to relatively high calcium, sulfate ions and a low concentration of aluminate ions may lead to the quick formation of large crystals of ettringite which might be considered fail set. Hydraulic cement binder starts to occur from generating new solid phases and precipitates the binding of ionized alkaline and heavy metals from supersaturated aqueous substances in the cement-water mixture (Figure 7-1c). There are several possible toxic element stabilization of ettringite in the BA-combined cement hydration.

Magnesium Aluminum Hydrate, $Mg_6Al_2(OH)_{18}4.5H_2O$ (Figure 7-1c) is one of good examples to explain toxic waste stabilization in BA-combined cement paste in XRD results. Cationic substitutions may take place in the ettringite that Mg^{2+}, Zn^{2+} and Fe^{2+} can replace Ca^{2+} in the crystal lattice.
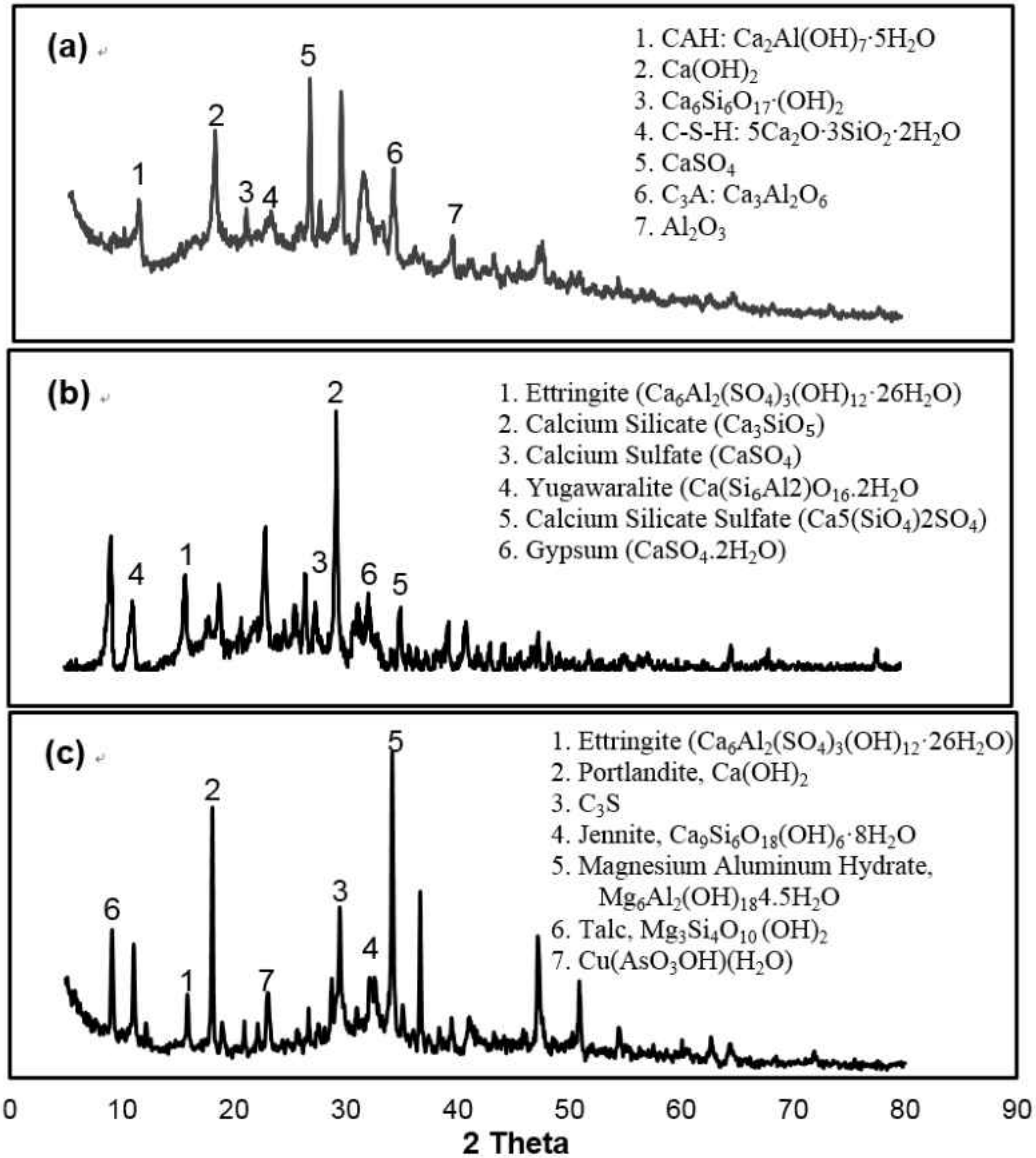
Figure 7-1. XRD pattern of: (a) MSWI BA, (b) Hydrated BA, and (c) Cement Paste with MSWI BA

### 7.4.3 *Leaching of Alkaline from PCC Containing BA*

Figure 7-2 shows the relative concentrations of all major alkaline elements (Ca, Al, Si, Na, and K), which is the ratio of the leaching concentration of PCC including 10, 20, 30, and 50%　BA contents divided by the leaching concentration of 100% BA. Depending on the leaching characteristics, the relative concentrations were divided into two types: one is the concentrations presenting lower increasing rate at low BA contents (10%-30%) (see Figure 7-2a), and the other is the concentrations presenting higher increasing rate at low BA contents (10%-30%) (see Figure 7-2b). Leaching concentrations of the alkaline elements for PCC specimens containing lower BA contents (10%-20%) were relatively less than those for higher BA contents (50%). The released concentrations typically increased with increasing BA content included in the cement of the PCC. Moreover, the relative concentrations of selected alkaline (i.e., Al and Si) were significantly low, which are less than 10%, for the PCC specimens with lower BA (10%-30%).

Figure 7-3 shows the leaching concentration of selected major alkaline elements (i.e., Al and Si) measured from the tests with different BA contents. For these alkaline elements, the leaching concentrations remained low, which is less than 20%, in the lower BA contents ranged from 10% to 30%. The concentration of the alkaline rapidly increases when the BA contents is higher than approximately 30%. Hence, the release of Al and Si shows a fitted plot as an exponential function of BA contents. Leachate concentrations of Al and Si for the control peaked at 34223.2 and 886.7 μg/L. For the 40% BA−PCC specimen, the concentrations peaked at 6065.4 and 181.3 μg/L, respectively, which are only less than 20% compared to the concentration from 100% of BA. As

ionized elements increases, pH can be increased in the solution. The Al ion might be consumed through cement hydration as follow:

$$2Al^+ + 4OH^- + 2H_2O \rightarrow 2Al(OH)_3 + H_2 \tag{7.1}$$

Further, the Al included in the cement and BA reacts with ionized oxygen as well as hydroxyl group in the solution. According to Pourbaix diagram of Al, the Al is changed to AlO_2^- as a radical form and might transform as a stable form (i.e., aluminum oxide, Al_2O_3) in the range of pH higher than 8.5. Therefore, even though the leaching of Al increases, the Al can be reduced remarkably in the solution. In the lower BA contents from 10% to 30%, the concentration of Al in the solution due to oxidation and hydration of Al. Beyond 30% of BA, the Al increases significantly because the amount of Al for oxidation and hydration of Al is reduced. Similarly, silicon ion (Si^{4+}) can be consumed by cement hydration and the concentration decreased significantly. The Si^{4+} is dissolved out from the cement and BA and reacts with solute and stormwater in the solution. The Si is controlled as follow:

$$2C_3S + H_2O \rightarrow C\text{-}S\text{-}H + 3Ca(OH)_2 \tag{7.2}$$
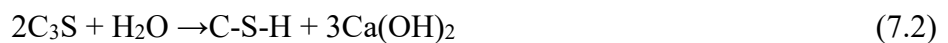
Also, in high pH ($\approx$11.5-12.2) with Eh (V) ranged between -0.1 to -0.9, the silicon mostly exists the radical of Si_2H_6 in the solution. Therefore, the ionized silicon can be reduced significantly in the solution.
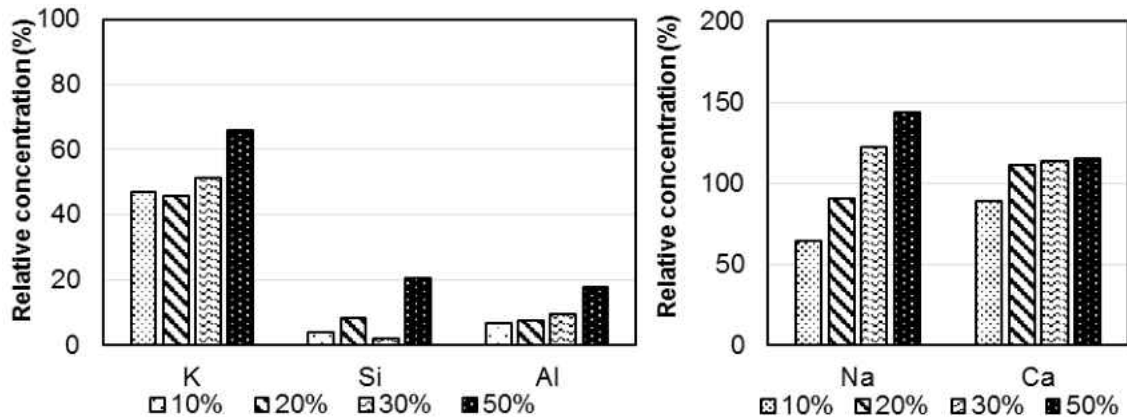
Figure 7-2. Relative concentration of alkaline substances (K, Si, Al, Na, and Ca): (a) lower increasing rate at low BA contents (10%-30%); and (b) higher increasing rate at low BA contents (10%-30%).
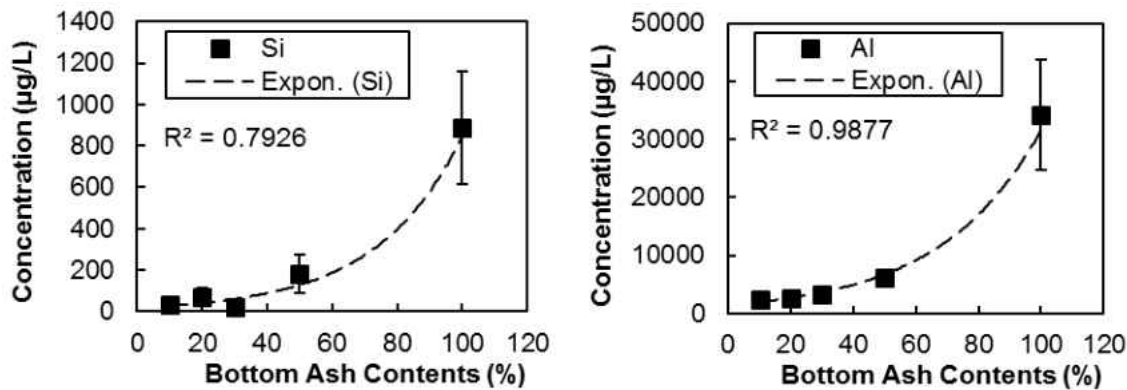

Figure 7-3. Release concentration of Si, Al, and K from PCC containing MSWI BA.

### 7.4.4 *Leaching of Heavy Metals from PCC Containing BA*

Effect of BA contents for releasing minor heavy metals including Cu, Fe, Mg, Ti and Zn from PCC with BA in 1 day was characterized. Since these elements are possibly released from both BA and PCC, the leaching behavior for the minor elements can be more complicated than that of the major

elements (Tang et al. 2015; Xue et al. 2009). Typically, the cement matrix physically and chemically captures heavy metals, which may be transformed into more stable and insoluble compounds, thus decreasing the likelihood of heavy metal contamination (Tang et al. 2015; Xue et al. 2009). Leaching of minor elements and heavy metals appears to follow two types of patterns with increasing BA content after the first day (Figure 7-4).

A significant reduction in Cu, Mg, and Zn were observed when the BA is incorporated into PCC (compared to the BA alone). However, Fe and Ti were insensitive to BA content. Release of Cu and Mg were significantly reduced at 20-30% BA. Fig. 4 shows the relative concentration of heavy metals, which is the ratio of the leaching concentration with different percent of BA contents divided by the concentration of 100% BA. Similar to selected alkaline (Al, Si, and K), the optimum addition of BA to capture metal elements exists between 20-30% of BA. Cu bearing minerals are believed to provide sites to encapsulate metals into the PCC (Chen et al. 2008), thus reduced leaching was observed for Cu and concentrations ranged from 45.5 to 15.1 µg/L. As Cu existing as a stable form (i.e., Cu_2O) in the cement and BA dissolves into the stormwater, ionized Cu and pH can be increased in the solution. However, the Cu in the cement and BA acts with the solute in the solution. According to Pourbaix diagram of the Cu, the leaching of the Cu is actively generated in the range of pH higher than 8.5. Most of copper element or compounds will be encapsulated in the cement matrix physically. Small amount of copper ion from copper oxide may react with cement component. $Cu(AsO_3OH)(H_2O)$ was found from XRD data (Figure 7-1c).

Mg ranged from 475.9 µg/L for the PCC without BA to 181.3 µg/L for the PCC with BA (Figure 7-5). According to Pourbaix diagram of the Mg, the Mg exist as MgO in the range of pH

higher than 8.5. After incineration process which is combustion, most of either Mg element or compounds may be oxidized. Magnesium or magnesium oxide can form magnesium oxide in the cement matrix. The Mg reacts with water and generate magnesium hydroxide from the cement as follows:

$$Mg + 2H_2O \rightarrow \quad Mg(OH)_2 + H \uparrow \tag{3}$$

$$MgO + 2H_2O \rightarrow \quad Mg(OH)_2 \tag{4}$$
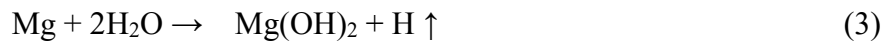
Therefore, even though the leaching of Mg increases, the ionized Mg can be reduced significantly in the solution. Further, magnesium ion may react with other oxyhydroxides (-O, -OH) and silicates ($SiO4^{4-}$). From XRD data, $Mg_3Si_4O_{10}(OH)_2$ and $Mg_3(PO_2)(H_2O)_{22}$ were found.
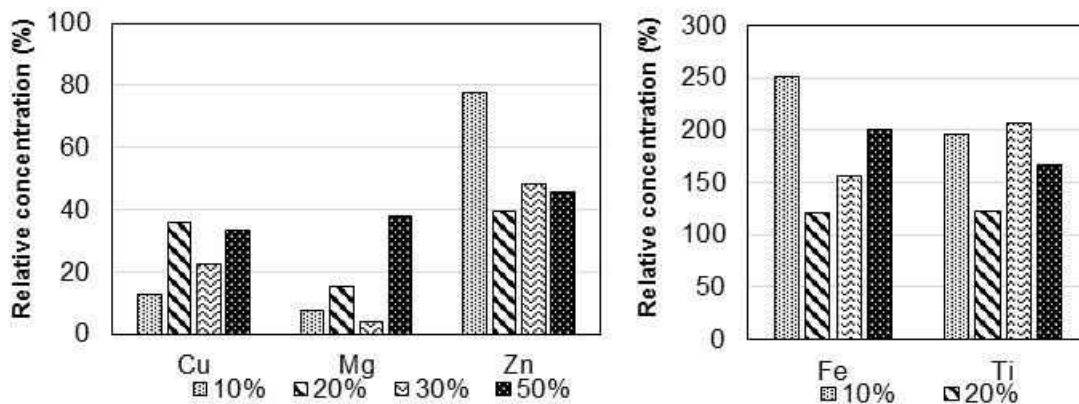

Figure 7-4. Relative concentration of heavy metals (Cu, Mg, Zn): (a) lower increasing rate at low BA contents (10%-30%); and (b) higher increasing rate at low BA contents (10%-30%).
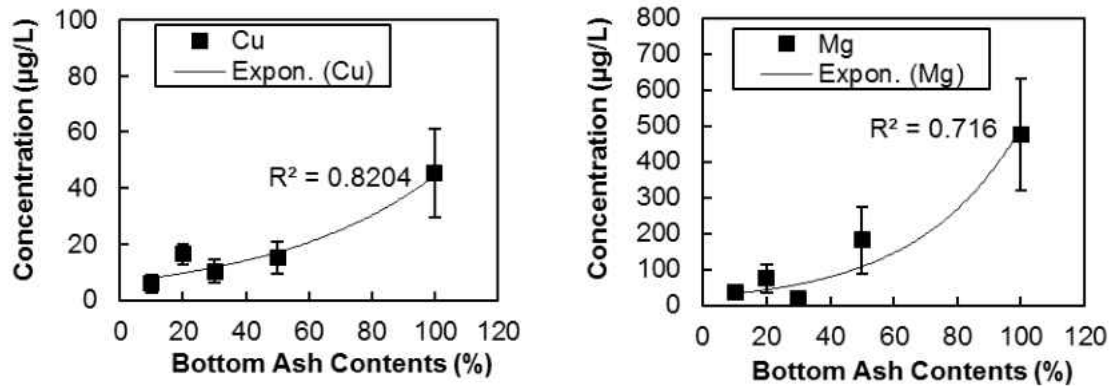
Figure 7-5. Release concentration of Cu and Mg from PCC containing MSWI BA.

7.5   Conclusions

In this chapter, the chemical characteristics and leaching behavior of WTE BA when used in PCC were investigated. Chemical analysis of WTE BA was conducted by using petrographic analysis tools such as EDS and XRD. A series of SPLP batch tests were conducted to investigate the release of major alkaline elements (e.g., Ca, Al, Si, Na, and K) and minor heavy metals (e.g., Cu, Fe, Mg, Ti, and Zn) from crushed PCC containing varied proportions of WTE BA. The released concentrations typically increased with increasing BA content included in the cement of the PCC. Crushed PCC mixed with the WTE BA demonstrated significant reduction of Al and Si because those alkaline might be consumed through cement hydration. Leaching of all major alkaline elements mostly showed the lowest concentrations for the crushed PCC containing 10-20% BA contents. The crushed PCC mixed with BA appeared to be less promising to encapsulate the heavy metals. A significant reduction in Cu, Mg, and Zn were observed when the BA is incorporated into PCC (compared to the BA alone). However, Fe and Ti were insensitive to BA content.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATION

8.1   Conclusions

Finally, an overview of the major conclusions drawn from this study is summarized as below:

- Many countries, especially European and Asian have already successfully implemented systematic approach towards the beneficial utilization of WTE ashes. Although research and demonstration projects ensure the beneficial utilization of WTE ashes as a feasible option, currently there is no recycling of ash in the U.S. This is due to the nationwide inconsistency in ash management, regulations, and standard leaching test procedures. In addition, debates regarding highly soluble salt content and heavy metal concentration in WTE ashes further discourage their utilization.

- Incorporation of MSWI ashes in concrete significantly reduces the release of toxic elements, thus it is recognized by many researchers that this treatment is an encouraging option for ash utilization.

- For the specimens incorporating ground bottom ash, mechanical and durability characteristics were inferior compared to those of the ordinary cement paste. This is mainly attributed to the swelling of cement paste due to the development of hydrogen gas. For the fly ash specimens, on the contrary, the compressive strength was similar or higher than the control specimen. For the specimens with 20% and 30% fly ash addition, much lower void content was observed compared to that of the control specimen. This is due to

the fact that the fine particle of fly ash caused an increase in the packing density of cement paste and consequently increased compressive strength and reduced void content.

- A reduction in overall performance of concrete with ash replacement of fine aggregate is most likely attributed to (1) hydrogen gas evolution as a result of a chemical reaction of metallic aluminum in high alkaline environment of concrete and (2) segregation of paste and aggregate due to considerably low consistency of concrete with the increased amount of bottom ash content.

- The chemical treatment of MSWI bottom ash successfully transformed metallic aluminum into a stable form and therefore negligible amount of hydrogen gas evolution was detected from the treated bottom ash. Analyses on the chemical elemental compositions and the phase compositions of the untreated and treated bottom ash confirmed that the transformations of the aluminum compound towards the more stable phase were successful. The treatment used in this study was relatively simple and cost effective; therefore, it might be a feasible and practical treatment method to be adopted by industry for a large amount of bottom ash utilization as a construction material.

- Crushed PCC mixed with the WTE BA demonstrated significant reduction of Al and Si because those alkaline might be consumed through cement hydration. Leaching of all major alkaline elements mostly showed the lowest concentrations for the crushed PCC containing 10-20% BA contents. The crushed PCC mixed with BA appeared to be less promising to encapsulate the heavy metals. A significant reduction in Cu, Mg, and Zn were observed when the BA is incorporated into PCC (compared to the BA alone).

However, Fe and Ti were insensitive to BA content.

8.2   Recommendation

Generally, the chemical elements and their concentration in the ashes are highly variable with waste source, location of incineration facility, and quality of incineration process. Therefore, it is highly recommended to chemically characterize the ashes prior to utilize them in concrete and to make a statistical study of its temporal variation to make asseveration. For example, high metallic aluminum content in the ashes is the most critical factor reducing the overall performance of concrete due to the hydrogen gas evolution. Even very small amount of metallic aluminum can cause a considerable volume expansion of concrete. Thus, the maximum allowable ash replacement ratio may need an adjustment depending on the total content of metallic aluminum.

In addition to a chemical treatment to eliminate hydrogen gas evolution, ashes are need to be further treated to deplete other potential contaminants, such as highly soluble salt content and heavy metal concentration, which can be a risk to human health. Moreover, a methods of recycling the fluid used for the chemical treatment has to be developed.

The long-term potential environmental impacts due to leaching of heavy metals from WTE ashes should be monitored when MSWI ashes are utilized in concrete. Since there was no appropriate utilization criterion for the WTE BA, further leaching investigation is recommended to better simulate the field scenario.

APPENDIX: APPROVAL LETTERS

McDonald, Christine <Christine.McDonald@dot.state.fl.us>   ↪ Reply all | ∨

To: ■ Jinwoo An; Cc: ☐ jinwooan@texas.edu; ⊻   Tue 10/27/2015 8:07 AM

Mr. An - Thank you for contacting us and we approve of the reproduction of portions of the Introduction, Literature Review and Chapter 3 in Research Report BDK78-977-20, *Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials*. Generally, we only ask that a statement that identifies the Florida Department of Transportation as the source be included in your dissertation. Please let me know if I can be of any further assistance.

_____

Christine McDonald, B.S.J.
Public Information Specialist
Florida Department of Transportation
5007 NE 39th Avenue, Gainesville, FL 32609
(352) 955-6624 Office
(850) 412-8332 E-Fax
christine.mcdonald@dot.state.fl.us

Centennial
FDOT
1915 ★ 2015

: Permission from Florida Department of Transportation (FDOT) for using the paper entitled, 'Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials'.

[University of Central Florida] Inquiring a copyright permission ⌃

BK Beesley, Karin <Karin.Beesley@tandf.co.uk>
To: Jinwoo An; ⌄

👍 ↩ Reply all | ⌄
Wed 11/11/2015 3:54 AM

Our Ref: KB/TRMP/P5596

11th November 2015

Dear Jinwoo An

Thank you for your correspondence requesting permission to reproduce the following article published in our journal in your printed thesis and to be posted in your university's repository.

Investigation on the side effects of municipal solid waste incineration ashes when used as mineral addition in cement-based material, published on iFirst 10th September 2015.

We will be pleased to grant permission on the sole condition that you acknowledge the original source of publication and insert a reference to the article on the Journals website:

This is the authors accepted manuscript of an article published as the version of record in Road Materials and Pavement Design, 2015

http://www.tandfonline.com/doi/full/10.1080/14680629.2015.1083463

Please note that this license does not allow you to post our content on any third party websites or repositories.

Thank you for your interest in our Journal.

Yours sincerely

Karin Beesley
Permissions Administrator
Taylor & Francis Group
Taylor & Francis Group is a trading name of Informa UK Limited, registered in England under no. 1072954

: Permission from Taylor & Francis Group for using the papers entitled, "Investigation on the Side Effects of Municipal Solid Waste Incineration Ashes when Used as Mineral Additions in Cement-Based Materials," Road Materials and Pavement Design (2015).

: Permission from ASCE Journal of Computing in Civil Engineering for using the papers entitled, "Sustainable Utilization of MSWI Bottom Ash as Road Construction Materials, Part I: Physical and Mechanical Evaluation".

Jinwoo An
To: copyright@icepublishing.com; Cc: jinwooan@utexas.edu;

↻ | ∨

Fri 10/23/2015 12:18 PM

To whom it may concern,

Hello. My name is Jinwoo An who is a Ph.D. candidate in civil engineering department at University of Central Florida (UCF).

I have one published journal paper "J. Y. Kim, B. H. Nam*, B. A. Al Muhit, K. M. Tasneem, **J.W. An**, Effect of chemical treatment of MSWI bottom ash for its use in concrete, Magazine of Concrete Research, 2015, 67(4), 179-186" at ICE Publishing. As an author, I am seeking a permission to reproduce material from my own journal paper published with ICE Publishing for my Ph.D dissertation.

I would be greatly appreciate if you can provide me the copyright permission at your earliest convenience.

Best Regards,
Jinwoo An
Jinwoo An, Ph.D. candidate
Graduate Teaching Assistant (GTA)
Graduate Research Assistant (GRA)
University of Central Florida
Department of Civil, Environmental
and Construction Engineering (CECE)
jinwooan@knights.ucf.edu

: Permission from Magazine of Concrete Research for using the papers entitled, "Effect of chemical treatment of MSWI bottom ash for its use in concrete,".

REFERENCES

Alba, N., VaÂzquez, E., GassoÂ, S., & Baldasano, J. M. (2001). Stabilization/solidification of MSW incineration residues from facilities with different air pollution control systems: Durability of matrices versus carbonation. *Waste Management, 21*, 313-323.

Ampadu, K. O., & Torii, K. (2001). Characterization of ecocement pastes and mortars produced from incinerated ashes. *Cement and Concrete Research, 31*(3), 431-436.

An, J., Golestani, B., Nam, B. H., Lee, J (2015). Sustainable Utilization of MSWI Bottom Ash as Road Construction Materials, Part I: Physical and Mechanical Evaluation. Airfield and Highway Pavements 2015: Innovative and Cost-Effective Pavements for a Sustainable Future, pp. 225-235, Miami, FL, June 7-10, 2015.

An, J., Kim, J., Golestani, B., Tasneem, K., Muhit, B., Nam, B., & Behzadan, A. (2014). Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials. Report No. BDK78-977-20, Tallahassee, FL: Florida Department of Transportation.

ASTM. (2008). Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle *C191 - 08*. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. (2009). Standard Test Method for Density of Hydraulic Cement *C188 - 09*. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. (2012a). Standard Guide for Petrographic Examination of Aggregates for Concrete *C295 / C295M - 12*. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. (2012b). Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens *C39 / C39M - 12a*. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. (2012c). Standard Test Method for Density and Void Content of Hardened Pervious Concrete *C1754 / C1754M - 12*. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. (2013a). Standard Test Method for Density and Void Content of Freshly Mixed Pervious Concrete *C1688 / C1688M - 13*. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. (2013b). Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes *C1585 - 13*. West Conshohocken, PA: American Society for Testing and Materials.

Aubert, J. E., Husson, B., & Sarramone, N. (2006). Utilization of municipal solid waste incineration (MSWI) fly ash in blended cement: Part 1: Processing and characterization of MSWI fly ash. *Journal of Hazardous Materials, 136*(3), 624-631.

Aubert, J. E., Husson, B., & Vaquier, A. (2004). Metallic aluminum in MSWI fly ash: quantification and influence on the properties of cement-based products. *Waste Management, 24*(6), 589-596.

Bertolini, L., Carsana, M., Cassago, D., Quadrio Curzio, A., & Collepardi, M. (2004). MSWI ashes as mineral additions in concrete. *Cement and Concrete Research, 34*(10), 1899-1906.

Bortoluzzi, E. A., Broon, N. J., Bramante, C. M., Felippe, W. T., Tanomaru Filho, M., & Esberard, R. M. (2009). The Influence of Calcium Chloride on the Setting Time, Solubility, Disintegration, and pH of Mineral Trioxide Aggregate and White Portland Cement with a Radiopacifier. *Journal of Endodontics, 35*(4), 550-554.

Chandler, A. J. (1997). *Municipal solid waste incinerator residues*. New York, NY: Elsevier.

Collivignarelli, C., & Sorlini, S. (2002). Reuse of municipal solid wastes incineration fly ashes in concrete mixtures. *Waste Management, 22*(8), 909-912.

Cordeiro, G. C., Toledo Filho, R. D., Tavares, L. M., & Fairbairn, E. M. R. (2008). Pozzolanic activity and filler effect of sugar cane bagasse ash in Portland cement and lime mortars. *Cement and Concrete Composites, 30*(5), 410-418.

EPA. (2010). Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2010, from http://www.epa.gov/waste/nonhaz/municipal/pubs/msw07-fs.pdf

Filipponi, P., Polettini, A., Pomi, R., & Sirini, P. (2003). Physical and mechanical properties of cement-based products containing incineration bottom ash. *Waste Management, 23*(2), 145-156.

Giampaolo, C., Mastro, S. L., Polettini, A., Pomi, R., & Sirini, P. (2002). Acid neutralisation capacity and hydration behaviour of incineration bottom ash–Portland cement mixtures. *Cement and Concrete Research, 32*(5), 769-775.

Gutteridge, W. A., & Dalziel, J. A. (1990). Filler cement: The effect of the secondary component on the hydration of Portland cement: Part I. A fine non-hydraulic filler. *Cement and Concrete Research, 20*(5), 778-782.

Jurič, B., Hanžič, L., Ilić, R., & Samec, N. (2006). Utilization of municipal solid waste bottom ash and recycled aggregate in concrete. *Waste Management, 26*(12), 1436-1442.

Kim, J, Nam, B. H., Al Muhit, B. A., Tasneem, K. M., An, J. (2014). Effect of chemical treatment of MSWI bottom ash for its use in concrete. *Magazine of Concrete Research*, *67*(4), 179-186.

Kim, J., Tasneem, K. M., Nam, B. H. (2014). Material Characterization of Municipal Solid Waste Incinerator (MSWI) Ash As Road Construction Material. Geo-Hubei 2014, GSP 254: Pavement Performance Monitoring, Modeling, and Management, pp. 100-108, Yichang, Hubei, China, July 20-22, 2014.

Müller, U., & Rübner, K. (2006). The microstructure of concrete made with municipal waste incinerator bottom ash as an aggregate component. *Cement and Concrete Research, 36*(8), 1434-1443.

Mehta, P. K., & Monteiro, P. J. M. (2006). *Concrete: microstructure, properties, and materials*. New York, NY: McGraw-Hill.

Michaels, T. (2010). The 2010 ERC Directory of Waste-to-Energy Plants. Washington, DC: Energy Recovery Council

Mindess, S., Young, J. F., & Darwin, D. (2003). *Concrete*. Upper Saddle River, NJ: Prentice Hall.

Moosberg-Bustnes, H., Lagerblad, B., & Forssberg, E. (2004). The function of fillers in concrete. *Materials and Structures, 37*(2), 74-81.

Naik, T. (2008). Sustainability of Concrete Construction. *Practice Periodical on Structural Design and Construction, 13*(2), 98-103.

Nassar, R.-U.-D., & Soroushian, P. (2011). Field investigation of concrete incorporating milled waste glass. *Journal of Solid Waste Technology & Management, 37*(4), 307-319.

Ørnebjerg, H., Franck, J., Lamers, F., Angotti, F., Morin, R., & Brunner, M. (2006). Management of Bottom Ash from WTE Plants: An overview of management options and teratment methods. Copenhagen, Denmark: International Solid Waste Association, Working Group on Thermal Treatment of Waste.

Patnaik, P. (2003). *Handbook of inorganic chemicals*. New York, NY: McGraw-Hill.

Pera, J., Coutaz, L., Ambroise, J., & Chababbet, M. (1997). Use of incinerator bottom ash in concrete. *Cement and Concrete Research, 27*(1), 1-5.

Polettini, A., Pomi, R., & Carcani, G. (2005). The effect of Na and Ca salts on MSWI bottom ash activation for reuse as a pozzolanic admixture. *Resources, Conservation and Recycling, 43*(4), 403-418.

Polettini, A., Pomi, R., Sirini, P., & Testa, F. (2001). Properties of Portland cement — stabilised MSWI fly ashes. *Journal of Hazardous Materials, 88*(1), 123-138.

Rapp, P. (1935). *Effect of calcium chloride on portland cements and concretes.* Paper presented at the Proceedings of the 14th Annual Meeting of the Highway Research Board, Washington, DC.

Rashid, R., & Frantz, G. (1992). MSW Incinerator Ash as Aggregate in Concrete and Masonry. *Journal of Materials in Civil Engineering, 4*(4), 353-368.

Rosskopf, P. A., Linton, F. J., & Peppler, R. B. (1975). Effect of various accelerating chemical admixtures on setting and strength development of concrete. *American Society for Testing and Materials, 3*(4), 322-330.

Rubner, K., Haamkens, F., & Linde, O. (2008). Use of municipal solid waste incinerator bottom ash as aggregate in concrete. *Quarterly Journal of Engineering Geology and Hydrogeology Quarterly Journal of Engineering Geology and Hydrogeology, 41*(4), 459-464.

Saikia, N., Kato, S., & Kojima, T. (2007). Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash. *Waste Management, 27*(9), 1178-1189.

Scrivener, K. L., & Kirkpatrick, R. J. (2008). Innovation in use and research on cementitious material. *Cement and Concrete Research, 38*(2), 128-136.

Sikalidis, C. A., Zabaniotou, A. A., & Famellos, S. P. (2002). Utilisation of municipal solid wastes for mortar production. *Resources, Conservation and Recycling, 36*(2), 155-167.

Sorlini, S., Abbà, A., & Collivignarelli, C. (2011). Recovery of MSWI and soil washing residues as concrete aggregates. *Waste Management, 31*(2), 289-297.

Soroka, I., & Setter, N. (1977). The effect of fillers on strength of cement mortars. *Cement and Concrete Research, 7*(4), 449-456.

Tasneem, K. M., Nam, B. H., Eun, J. (2015). Sustainable Utilization of MSWI Bottom Ash as Road Construction Materials, Part II: Chemical and Environmental Characterization. *Airfield and Highway Pavements 2015: Innovative and Cost-Effective Pavements for a Sustainable Future* , pp. 593-604, Miami, FL, June 7-10, 2015.

Torii, K., Tomotake, H., Osafo, A. K., & Echigo, T. (2003). Compatibility between ecocement produced from incinerator ash and reactive aggregates in ASR expansion of mortars. *Cement and Concrete Research, 33*(4), 571-577.

Van Oss, H. G., & Padovani, A. C. (2003). Cement Manufacture and the Environment Part II: Environmental Challenges and Opportunities. *Journal of Industrial Ecology, 7*(1), 93-126.

Vehlow, J. (2012). Waste-to-Energy Ash Management in Europe. New York, NY: Springer.

Wiles, C. C. (1996). Municipal solid waste combustion ash: State-of-the-knowledge. *Journal of Hazardous Materials, 47*(1–3), 325-344.

Worrell, E., Price, L., Martin, N., Hendriks, C., & Meida, L. O. (2001). Carbon dioxide emissions from the global cement industry. *Annual Review of Energy and the Environment, 26*(1), 303-329.

Psomopoulos, C. S., Bourka, A., and Themelis, N. J. (2009). "Waste-to-energy: A review of the status and benefits in USA." Waste Management, 29(5), 1718-1724.

Wiles, C. C. (1996). "Municipal solid waste combustion ash: State-of-the-knowledge." Journal of Hazardous Materials, 47(1–3), 325-344.

Chandler, A. J. (1997). Municipal solid waste incinerator residues, Elsevier, New York, NY.

Bertolini, L., Carsana, M., Cassago, D., Quadrio Curzio, A., and Collepardi, M. (2004). "MSWI ashes as mineral additions in concrete." Cement and Concrete Research, 34(10), 1899-1906.

Berg, E., and Neal, J. (1998). "Municipal Solid Waste Bottom Ash as Portland Cement Concrete Ingredient." Journal of Materials in Civil Engineering, 10(3), 168-173.

Hasselriis, F., Waste-to-Energy Ash Management in the United States, in Encyclopedia of Sustainability Science and Technology. 2012, Springer: NY. p. 11737-11758.

Becquart, F., Bernard, F., Abriak, N. E., and Zentar, R. (2009). "Monotonic aspects of the mechanical behaviour of bottom ash from municipal solid waste incineration and its potential use for road construction." Waste Management, 29(4), 1320-1329.

Aubert, J. E., Husson, B., and Vaquier, A. (2004). "Metallic aluminum in MSWI fly ash: quantification and influence on the properties of cement-based products." Waste Management, 24(6), 589-596.

RCRA Solid Waste Programs. EPA530-K-02-019I. Waste and Emergency Response., 2011, U.S. Environmental Protection Agency (U.S. EPA), Washington, DC.

P. Filipponia, A. Polettinia, R. Pomia, P. Sirinib. Physical and mechanical properties of cement-based products containing incineration bottom ash, Waste Management No.23, 2003,pp. 145–156.

Chai Jaturapitakkul, Raungrut Cheerarot. Development of Bottom Ash as Pozzolanic Material , Jourcal of materials in civil engineering, 2003, pp. 48-53

Jill R. Pan, Chihpin Huang, Jung-Jen Kuo, Sheng-Huan Lin. Recycling MSWI bottom and fly ash

as raw materials for Portland cement, Waste Management No.28, 2008, pp. 1113–1118.

Rubner, K., Haamkens, F., and Linde, O. (2008). "Use of municipal solid waste incinerator bottom ash as aggregate in concrete." Quarterly Journal of Engineering Geology and Hydrogeology Quarterly Journal of Engineering Geology and Hydrogeology, 41(4), 459-464.

Luca Bertolinia, Maddalena Carsanaa, Davide Cassagoa, Alessandro Quadrio Curziob, Mario Collepardi, MSWI ashes as mineral additions in concrete, Cement and Concrete Research, Vol.34, 2004, pp.1899–1906

Müller, U., and Rübner, K. (2006). "The microstructure of concrete made with municipal waste incinerator bottom ash as an aggregate component." Cement and Concrete Research, 36(8), 1434-1443.

Rosmadi Abdul Rashid1 and Gregory C. Frantz. MSW INCINERATOR ASH AS AGGREGATE IN CONCRETE AND MASONRY, Journal of Materials in Civil Engineering, Vol. 4, No. 4, November, 1992.

Bruder-Hubscher, V., Fagarde, F., Leroy, M. J. F., Coughanowr, C., and Enguehard, F. (2001), "Utilization of bottom ash in road construction: evaluation of the environmental impact," Waste Management & Research 2011, Vol. 19, No. 6, pp. 545.

Forteza, R, Far, M., Seguí, C., Cerdá, V. (2004) "Characterization of bottom ash in municipal solid waste incinerators for its use in road base", Waste Management. 24. 899-909.

ASTM (2011). "Standard Specification for Concrete Aggregates." C33 / C33M - 11a, American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2012). "Standard Test Method for Density, Relative Density (Specific Gravity), and

Absorption of Coarse Aggregate." C127 - 12, American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2012). "Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate." C128 - 12, American Society for Testing and Materials, West Conshohocken, PA.

ASTM C1064, "Standard Test Method for Temperature of Freshly Mixed Hydraulic-Cement Concrete," American Society for Testing and Materials, West Conshohocken, PA (2009)

ASTM C191-13, "Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle," American Society for Testing and Materials, West Conshohocken, PA (2009)

ASTM C39 / C39M - 12a, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens", American Society for Testing and Materials, West Conshohocken, PA (2012)

Walker, H. N., Lane, D. S., Stutzman, P. E., (2006). Petrographic Methods of Examining Hardened Concrete: A Petrographic Manual. Report No. FHWA-HRT-04-150, Virginia Department of Transportation, Richmond, VA, July 2006.

AHMADI, B., SOBHANI, J., SHEKARCHI, M. & NAJIMI, M. 2014. Transport properties of ternary concrete mixtures containing natural zeolite with silica fume or fly ash. *Magazine of Concrete Research,* 66**,** 150-158.

ASTM 2011. Standard Specification for Concrete Aggregates. *C33 / C33M - 11a.* West Conshohocken, PA: American Society for Testing and Materials.

ASTM 2012a. Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens. *C39 / C39M - 12a.* West Conshohocken, PA: American Society for Testing and Materials.

ASTM 2012b. Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate. *C127 - 12.* West Conshohocken, PA: American Society for Testing and Materials.

ASTM 2012c. Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate. *C128 - 12.* West Conshohocken, PA: American Society for Testing and Materials.

AUBERT, J. E., HUSSON, B. & VAQUIER, A. 2004. Metallic aluminum in MSWI fly ash: quantification and influence on the properties of cement-based products. *Waste Management,* 24**,** 589-596.

BARNES, P. & BENSTED, J. 2002. *Structure and performance of cements,* London, UK, Taylor & Francis.

BERTOLINI, L., CARSANA, M., CASSAGO, D., QUADRIO CURZIO, A. & COLLEPARDI, M. 2004. MSWI ashes as mineral additions in concrete. *Cement and Concrete Research,* 34**,** 1899-1906.

BRUDER-HUBSCHER, V., LAGARDE, F., LEROY, M., COUGHANOWR, C. & ENGUEHARD, F. 2001. Utilisation of bottom ash in road construction: evaluation of the environmental impact. *Waste Management & Research,* 19**,** 545-556.

CHANDLER, A. J. 1997. *Municipal solid waste incinerator residues,* New York, NY, Elsevier.

EARNSHAW, A. & GREENWOOD, N. 1997. *Chemistry of the Elements,* Burlington, MA, Elsevier Butterworth-Heinemann.

EPA. 2010. *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2010* [Online]. Washington, D.C.: U.S. Environmental Protection Agency, Solid Waste and Emergency Response. Available: http://www.epa.gov/waste/nonhaz/municipal/pubs/msw07-fs.pdf.

FERREIRA, L. F. B., COSTA, H. S. S., BARATA, I. I. A., JÚLIO, E. N. B. S., TIAGO, P. M. N. & COELHO, J. F. J. 2014. Precast alkali-activated concrete towards sustainable construction. *Magazine of Concrete Research,* 66**,** 618-626.

FINGERLOOS, F. 2007. Fire design of concrete structures – materials, structures and modelling. *fib Bulletin No. 38.* Lausanne, Switzerland: Fédération Internationale du Béton.

FORTEZA, R., FAR, M., SEGUí, C. & CERDÁ, V. 2004. Characterization of bottom ash in municipal solid waste incinerators for its use in road base. *Waste Management,* 24**,** 899-909.

GAO, Y., ZHANG, H., TANG, S. & LIU, H. 2013. Study on early autogenous shrinkage and crack resistance of fly ash high-strength lightweight aggregate concrete. *Magazine of Concrete Research,* 65**,** 906-913.

GÖKÇE, H. S. & ŞIMŞEK, O. 2013. The effects of waste concrete properties on recycled aggregate concrete properties. *Magazine of Concrete Research,* 65**,** 844-854.

HEWLETT, P. C. 2004. *Lea's chemistry of cement and concrete,* Oxford, UK, Elsevier Butterworth-Heinmann.

IZQUIERDO, M., VAZQUEZ, E., QUEROL, X., BARRA, M., LOPEZ, A. & PLANA, F. Use of bottom ash from municipal solid waste incineration as a road material.   International Ash

Utilization Symposium, 2001 Lexington, KY. 594-603.

JURIČ, B., HANŽIČ, L., ILIĆ, R. & SAMEC, N. 2006. Utilization of municipal solid waste
    bottom ash and recycled aggregate in concrete. *Waste Management,* 26**,** 1436-1442.

KEPPERT, M., PAVLÍK, Z., CERNY, R. & REITERMAN, P. Properties of concrete with
    municipal solid waste incinerator bottom ash.   International Association of Computer
    Science and Information Technology, 2012 Singapore. IACSIT Press, 127-131.

KHAMIRUL AMIN, M., LOY CHEE, W., MANSOR, H., ISMAYADI, I. & MOHD HAFIZ
    MOHD, Z. 2012. Phase Transformations of α-Alumina Made from Waste Aluminum via a
    Precipitation Technique. *International Journal of Molecular Sciences,* 13.

KWAN, A. K. H., CHEN, J.-J., NG, P.-L. & FUNG, W. W. S. 2013. Adding limestone fines, fly
    ash and silica fume to reduce heat generation of concrete. *Magazine of Concrete Research,*
    65**,** 865-877.

LUCIDO, S. P. & WILSON, W. Bituminous Pavement Constructed with Municipal Solid Waste
    Combustor Ash: Construction, Performance, and Economic Issues 10th Annual North
    American Waste-to-Energy Conference, 2002 Philadelphia, PA. ASME, 225-239.

MÜLLER, U. & RÜBNER, K. 2006. The microstructure of concrete made with municipal waste
    incinerator bottom ash as an aggregate component. *Cement and Concrete Research,* 36**,**
    1434-1443.

ONORI, R., POLETTINI, A. & POMI, R. 2011. Mechanical properties and leaching modeling of
    activated incinerator bottom ash in Portland cement blends. *Waste Management,* 31**,** 298-
    310.

PATNAIK, P. 2003. *Handbook of inorganic chemicals,* New York, NY, McGraw-Hill.

RUBNER, K., HAAMKENS, F. & LINDE, O. 2008. Use of municipal solid waste incinerator bottom ash as aggregate in concrete. *Quarterly Journal of Engineering Geology and Hydrogeology Quarterly Journal of Engineering Geology and Hydrogeology,* 41**,** 459-464.

SARAVANAKUMAR, P. & DHINAKARAN, G. 2014. Durability aspects of HVFA-based recycled aggregate concrete. *Magazine of Concrete Research,* 66**,** 186-195.

SORLINI, S., ABBÀ, A. & COLLIVIGNARELLI, C. 2011. Recovery of MSWI and soil washing residues as concrete aggregates. *Waste Management,* 31**,** 289-97.

TAN, Y. N., LIU, Y., ZHANG, Z. B., HUANG, B. Y. & GROVER, L. M. 2011. Hydroxyapatite formation on surface of calcium aluminate cements. *Advances in Applied Ceramics,* 110**,** 464-468.

WANG, X.-Y. 2013. Simulation of temperature rises in hardening Portland cement concrete and fly ash blended concrete. *Magazine of Concrete Research,* 65**,** 930-941.

Chandler, A.J., Eighmy, T.T., Helmar, J. Hartlén, O., Kosson, D.S., Sawell, S.E., van der Sloot, H.A., and Vehlow, J., Municipal Solid Waste Incinerator Residues. Studies in Environmental Science 67. 1997, Amsterdam, the Netherlands: Elsevier.

Management of Bottom Ash from WTE Plant. 2006, Working Group on Thermal Treatment of Waste, The International Solid Waste Association (ISWA).

Quina, M.J., Bordado, J.C.M., and Quinta-Ferreira, R.M., Percolation and Batch Leaching Tests to Assess Release of Inorganic Pollutants from Municipal Solid Waste Incinerator Residues. Waste Management, 2011. 31(2): p. 236-245.

De Windt, L., Dabo, D., Lidelöw, S., Badreddine, R., and Lagerkvist, A., Mswi Bottom Ash Used as Basement at Two Pilot-scale Roads: Comparison of Leachate Chemistry and Reactive Transport Modeling. Waste Management, 2011. 31(2): p. 267-280.

Izquierdo, M., Querol, X., A. Vazquez, Josa, E., and López-Soler, A., Comparison Between Laboratory and Field Leachability of MSWI Bottom Ash as a Road Material. Science of The Total Environment, 2008. 389(1): p. 10-19.

Tang, P., Florea, M.V.A., Spiesz, P., and Brouwers, H.J.H., Characteristic and application potential of municipal solid waste incineration (MSWI) bottom ashes from two waste-to-eneregy plants. Construction and Building Materials, 2015. 83: p. 77-94.

Xue, Y., Hou, H., Zhu, S., and Zha, J., Utilization of municipal solid waste incineration ash in stone mastic asphalt mixture: Pavement performance and environmental impact. Construction and Building Materials, 2009. 23(2): p. 989-996.

Chen, J.S., Chu, P.Y., Chang, J.E., Lu, H.C., Wu, Z.H., and Lin, K.Y., Engineering and Environmental Characterization of Municipal Solid Waste Bottom Ash as an Aggregate Substitute Utilized for Asphalt Concrete. Journal of Materials In Civil Engineering, 2008. 20: p. 432-439.