Final Report

Evaluating the Use of Waste-to-Energy Bottom Ash as Road Construction Materials

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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

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16. Abstract

Current management practice, existing regulations, and environmental consequences of municipal solid waste incineration (MSWI) ash utilization were comprehensively reviewed worldwide and nationwide in the U.S. Efforts were made to physically and chemically characterize different types of MSWI ash and also to evaluate their influence on engineering properties of cement paste and concrete when part of Portland cement (PC) and fine aggregate are replaced with ground and sieved MSWI ash. Fundamental properties of MSWI bottom ash and fly ash were studied by conducting physical, microstructural, and chemical tests. Cement paste and concrete cylinders were cast with various amounts of ash additions and their strength and durability were investigated as the replacement ratio of ash increases.

The MSWI bottom ash was also used to replace fine aggregate in hot-mix asphalt (HMA). Varying proportions of bottom ash and fine aggregate were tried in an effort to determine the optimum ratio of bottom ash to fine aggregate, as determined by performance tests such as the Marshall stability test and the moisture susceptibility test. For the optimum replacement ratio of bottom ash, the optimum binder content required was evaluated.

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EXECUTIVE SUMMARY

Municipal solid waste incineration (MSWI) ash has 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 MSWI ashes instead of landfill disposal. On the other hand, the U.S. has shown a lack of consistent and effective management plans as well as environmental regulations for the use of MSWI ashes. Many studies demonstrated the beneficial use of MSWI 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., however, the recycling of MSWI ash has been hindered, and they are mostly disposed of in landfills. In this report, current management practice, existing regulations, and environmental consequences of MSWI ash utilization are comprehensively reviewed worldwide and nationwide in the U.S.

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 characterize the influence of different types of ash on engineering properties of cement paste and concrete specimens when part of Portland cement and fine aggregate were replaced with ground and sieved MSWI ash. Cement paste and concrete cylinders were cast with various amounts of mineral and fine aggregate additions, respectively, and their strength and durability were investigated. For the specimens incorporating bottom ash, mechanical, and durability characteristics were inferior compared to those of the control specimens. A reduction in overall performance of cementitious materials with ash replacement is attributed to (1) hydrogen gas evolution as a result of a chemical reaction of metallic aluminum in high alkaline environment and (2) segregation of paste and aggregate due to considerably low consistency with the increased amount of bottom ash content.

The MSWI bottom ash was also used in hot-mix asphalt (HMA) by replacing portions of fine aggregate (passing sieve no. 4) in the total aggregate. The bottom ash was used to replace the fine aggregate, which is smaller than 4.75 mm, at the ratio of 0%, 10%, 20%, 30%, and 40% so that the optimum amount of the bottom ash in HMA was evaluated. For each proportioning, three specimens were prepared following the Marshall mix design, and tested with the Marshall Stability and Flow test and moisture susceptibility. Testing results showed that 20% replacement of bottom ash exhibited highest stability and moisture resistance. At the selected 20% of bottom ash replacement, optimum binder content was also evaluated. The results showed that the optimum binder content for the specimens containing 0% (control mixture) and 20% bottom ash were 5.7% and 6.8%, respectively. The MSWI bottom ashes are lightweight aggregates that contain higher porosity; thus they require higher amount of asphalt binder.

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1. INTRODUCTION

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 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 (hot mix asphalt (HMA) and Portland cement concrete (PCC))?

- Would using the WTE bottom ash as an ingredient in HMA and PCC 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., HMA and PCC).

1.2. Research Objectives

In Florida, since Cosentino et al. [1], any further study on the WTE bottom ash (BA) as road construction materials has not been conducted. In particular, Cosentino et al. [1] characterized only the physical properties of the WTE BA not the mechanical properties of ash mixed HMA and 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 HMA and PCC;

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

- To evaluate the mechanical performance of the WTE BA-mixed HMA and PCC with emphasis on pavement applications considering Florida's climatic condition.

2. LITERATURE REVIEW

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 [2-8]. For example, many European countries beneficially utilize MSWI bottom ash as a sustainable transportation material with environmental criteria set by their strategic regulations [3-5, 9]. In the U.S., MSW are being produced more than any other country in the world; however, the recycling rate is considerably low [10]. 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 [11]. The total of 86 MSW Waste to Energy (WTE) plants are being operated in 24 states of the U.S. as of 2010 [12], where major users of MSWI plants are Connecticut, New York, New Jersey, Pennsylvania, and Virginia [7]. Typical residue produced from these incineration plants are MSWI bottom ash (BA) and fly ash (FA), and those are mostly combined to be disposed of in sanitary landfill in the U.S. [8].

2.1. Incineration of 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 [3]. 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) [3]. 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 [4, 13] 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 [13]. Later, the emission was reduced

drastically by implementing APC devices to treat toxic flue gases with sorbents using dry/semi dry and wet scrubber systems [3, 6, 13]. 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% [14].

2.2. Properties of MSWI Ashes

Based on historical data [2, 3], different elemental compositions of MSWI products, BA, FA, and APC residues, were investigated and they are summarized in Table 2.1.

2.2.1. MSWI 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 [3, 4]. Major forms of compounds are oxides, hydroxides, and carbonates. According to research studies using different spectroscopic analyses [15-18], 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% [19]. 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) [15]. 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 [3]. The BA has a pH ranging from 10.5 to 12.2, partly due to the presence of hydroxide formation of CaO [3].

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 [3] 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 [3]. 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 [3, 9, 20-24]. 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 [3].

Despite of the fact that the BA has considerable amount of heavy metals, due to the relatively low level of leaching potential, the BA is often considered as a benign material. The aging and weathering processes of BA can further reduce the reactivity and potential of heavy metal release by the reaction between CO_2 and water, which form stable complex compounds in BA [25-29]. Aging is also known to transform metallic Al to stable Al_2O_3, thereby reduce the potential of

hydrogen gas formation [3, 30]. 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) [2, 3]

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

2.2.2. MSWI 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 [3]. The FA is characterized with fine particulate matters, dusty appearance with gray to dark gray color [3, 31]. The FA mostly contains oxide form of calcium, different metal salts, chloride compounds, and heavy metals [3, 19]. 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% [19]. When FA is subjected to a treatment with lime (CaO) scrubber, $Ca(OH)_2$ is obtained as end product [3].

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 [19, 32, 33]. Due to the presence of highly soluble salts, Cl, and heavy metals, the FA is not considered for direct utilization as transportation materials [3, 4, 6, 19]. 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 $CaCl_2$ [3]. Moreover, similar to the BA, large content of metallic Al in FA makes the utilization of FA uncertain [34-36].

The presence of readily soluble salt, such as Cl and Na in FA can significantly contaminate drinking water system [19, 32]. 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, 19]. 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 [6], (2) chemical stabilization using carbon dioxide/phosphoric acid (CO_2/H_3PO_4), ferrous sulfate ($FeSO_4$) [6], sodium sulfide (Na_2S) [6], and orthophosphate (PO_4^{3-}) [3], (3) solidification using lime, cement, asphalt, and gypsum, and (4) thermal treatment, such as vitrification and pyrolysis [3, 6].

2.3. Leaching of MSWI 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, [29, 37]. 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 [2-6].

Evaluation of leaching from MSWI ashes, leachate, and run off from landfill and application

sites have been performed mostly in European countries [3-5, 9], but also at small extent in the U.S. [4, 8]. 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 [38, 39]. 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 [40]. Substantial Pb leaching has also been confirmed by the researchers in Korea and Japan [41]. Danish researchers [42] 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 [28, 43-46] and FA [47] 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 [48]. 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 [49, 50]. 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 [51, 52]. Similarly, Zn leaching also follows the same characteristics of Cu when BA is in acidic condition [53].

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 [54-64], PCC product [20, 35, 37, 65, 66], and embankment fill [67-69]. The U.S. studies reported that heavy metal concentration in leachate mostly meets the leaching requirements [70] and often meets the U.S. drinking water standard [71]. 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 [13]. 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 [8, 42].

Researchers confirmed significant reduction of leaching potential of BA, FA, and combined ash when incorporated with cement and concrete [37, 55, 57, 66]. Spanish researchers formulated granulated material with combined ash and cement to use as secondary building material [57]. 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 [72] and three categories of landfill criteria [73] 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 [37, 54, 55, 66].

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Table 2.2: Leaching results for MSWI BA, APC residue, and formulated concrete mixture (mg/kg) [57]

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 [73]
[b] Spanish landfill criteria [72]
[c] LOD = limit of detection

2.4. Utilizations of MSWI 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 [20, 59, 65, 66, 74-76]. Although sometimes FA is considered to have similar properties with cement [19, 77, 78], 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 [20, 21, 35, 65]. 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 [20]. 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 [76]. Unlike the addition of BA, the FA addition in concrete reduces the workability [20]. 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 [20, 65, 74, 75, 78].

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2.5. Management Practices of MSWI 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 [3-5, 9]. 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 [79]. Leaching potential from ash residue can be reduced significantly by being physically encapsulated in asphalt [80].

Confederation of European Waste-to-Energy Plants (CEWEP) [81] reported that around 371 WTE plants treated approximately 85% of the total MSW in Europe during 2001 to 2011. As a result, incineration and recycling were increased by 7% and 12%, respectively, and landfilling was reduced by 19% [81]. Figure 2.1 shows MSW production and recycling in European countries in 2003 [5] and in the U.S. [11]. Compared with other European countries, the U.S. is the highest waste-generation country [10] 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 [4-6]. In the U.S., on the contrary, most MSWI plants combine BA and FA in one stream and disposed of in landfills [4, 13].

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

2.5.1. The Netherlands

Approximately 80% of the BA produced is recycled in civil engineering purpose after certain treatment scheme, such as ferrous and non-ferrous metal recovery and size reduction [5]. It is encouraged to use BA, considering it as a special category for the application as embankment fill, road base, and disposal into landfill [5]. Only the Netherlands among European countries utilizes FA in a small extent [4, 6]. About 30% of FA and APC residue are used as filler material in asphalt as the alternative of limestone [6]. Significant part of these residues has been exported to German and used as backfilled material in coal and salt mines [6].

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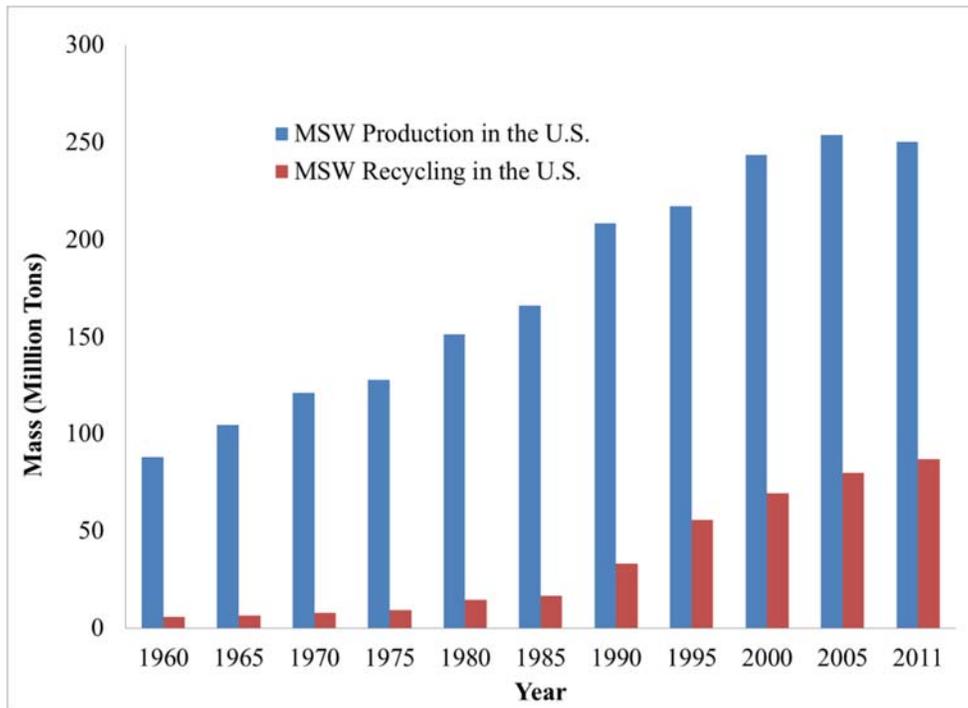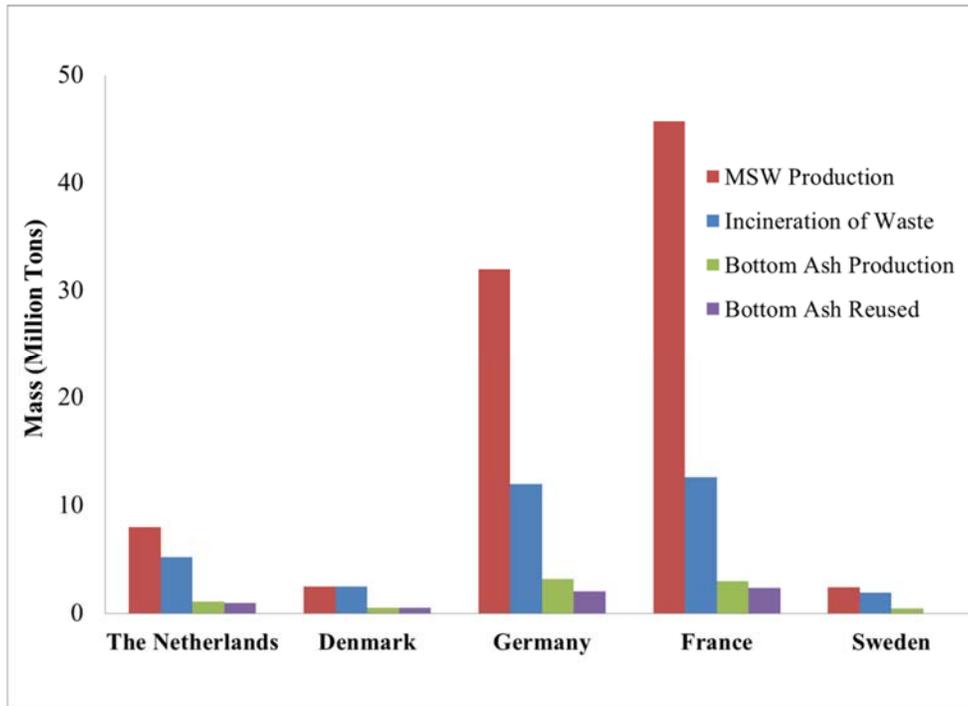
Figure 2.1: MSW management in European countries in 2003 [5] (top) and in the U.S. [11] (bottom)

2.5.2. Denmark

BA is considered as a suitable gravel substitute as subbase material when used with asphalt or concrete cover to avoid a direct contact with soil and water [5]. Denmark aimed at recycling 98% of BA into building and road construction and embankment fill after screening, crushing, and ferrous metal recovery [5]. APC residues, including FA and acid cleaning end product, are considered as special hazardous waste, required to landfill after treatments [6]. 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 [6].

2.5.3. 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 [3, 5]. A reduction in leaching potential makes BA suitable for the utilization as road construction and secondary building materials [4, 9]. Salt content of ash and dry scrubber residues are subjected to backfill in the old mines to prevent subsidence [4, 6]. A small quantity of APC residue is disposed of in a landfill after stabilization [6].

2.5.4. France

France recycles 79% of BA produced in the civil constructions [5]. BA treatments involve ferrous and non-ferrous metal removal, size reduction, and sometimes cement stabilization [5]. 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 [6]. Thermal treatment is also considered as a new option for ash treatment, which is not very common, yet [6].

2.5.5. 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 [5]. 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 [6].

2.5.6. 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 [6]. 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 [4].

2.5.7. 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 [4]. 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 [2, 4, 8].

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. [4]: (1) geotechnical applications, including base and subbase, embankment [69, 85], (2) hot-mix asphalt [80, 86], and (3) Portland cement concrete [4, 86]. 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 [4, 69].

Table 2.3: Research projects on MSWI ash as road construction materials in the U.S. [4, 69]

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. [4, 69], 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

2.6. Management Practices of MSWI Ashes

European countries have implemented more strategic and scientific regulations for MSWI ash management compared to those of U.S. Environmental regulations in European countries are based on leaching criteria set by standard test procedures [5] for beneficial utilization of BA and disposal of FA after treatments. In the U.S., on the contrary, BA and FA are combined to be disposed as combined ash. Environmental regulations of MSWI ashes in European countries and U.S. are summarized below.

2.6.1. The Netherlands

It is encouraged to use BA as embankment fill and road base with ensuring minimum rain water infiltration [5]. The regulatory framework, Federal Waste Management Plan (Landelijk Afvalbeheer Plan, LAP) does not permit mixing of BA and FA [4, 5] and Dutch Waste Incineration Directive requires the LOI to be less than 5% [5]. Based on the standard column leaching test (NEN 7343, liquid/solid ratio (L/S) = 1-10) [87], two utilization categories (1 and 2) are distinguished for the BA application of maximum 15-m layer [5]:

- There is no restriction for category 1 with allowed filtration of 300 mm/year.

- Utilization is restricted for category 2 with allowed filtration of 6 mm/year through the liners.

Since high leaching of Cu and Mo from BA hardly meets the leaching criteria for the category 2 utilization, Dutch Ministry of Environment consider MSWI BA as special category with less stringent leaching criteria for Cu, Mo, and Sb, in order for the continuous utilization of BA [5].

2.6.2. Denmark

European Committee for Standardization (CEN) sets three categories, 1 to 3, based on the leaching criteria using the compliance standard batch leaching test (CEN prEN 12457, L/S = 2,) [88]. Categories 1 and 2 have the strict leaching criteria, while category 3 has lenient criteria. MSW ash is categorized as soil and inorganic residue; BA mostly falls under category 3 and never falls under category 1 due to the high inorganic constituent. Some of the details of the regulations are as follow [4, 5]:

- Category 2 BA can be utilized in roads, paths, cable graves, floors and foundations, parking lots, noise banks, and ramps.

- Category 3 BA is not allowed to utilize in parking lots, noise banks, and ramps.

- Ash residue can be applied to dikes, dams, and embankments with the approval from Danish Environmental Protection Act [5].

- All MSWI ash application should be covered with liner.

- Utilization site has to be remote from drinking water well over 30 m.

- BA should be placed above the ground water table.

- The average thickness of the BA layer should be 1 m, while thickness requirements for

the specific applications are: 0.3 m for path, 4 m for ramps, and 5 m for noise bank.

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

- Maximum particle size should be 50 mm.

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

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

However, according to Danish Soil Pollution Act [5], it is recognized that BA utilization area was determined as contaminated land that pose obstacle for BA beneficial use.

2.6.3. Germany

Despite having state wide variation in regulations, Germany encourages the research and development in an effort to improve treatment techniques, separation schemes, and beneficial utilization of MSWI ash [4, 5]. Based on the German regulation set by Board of German States of Ministers (LAGA) [5], BA is required some treatment schemes before utilization as road construction:

- Reduction of salt content by water quenching.

- Ferrous and non-ferrous metal recovery.

- 3-month maturation.

- Meeting the standard leaching criteria based on batch leaching test (DEV S4, L/S = 10) [89]

- Total organic carbon content should be less than 1.0 wt. %.

In addition, ash beneficial use as secondary building material is required to meet additional standard for mechanical properties [5, 9], including density, mechanical strength, grain size distribution, and freeze-thaw-stability.

2.6.4. France

Standard batch leaching test (NF X31-210, L/S = 20) [90] has been designed to classify BA in three categories, V, M, and L, for the utilization in civil application.

- Category V: BA with low leaching potential for immediate use as road base.

- Category M: after 12-month maturation, BA should be tested to confirm if the material is eligible for reuse.

- Category L: must be landfilled.

It has been reported that after 9 months of maturation, BA mostly meet category V, exhibiting least leaching potential [5]. In order to utilize those BA with 9-month maturation, however, additional requirements must be met [5]:

- Physical and chemical data of aged BA must be documented.

- Embankment thickness should be less than 3 m.

- Application should be limited in area with less potential of inundation.

- Distant from drinking water well should be no less than 30 m.

2.6.5. Sweden

There is no national regulation on the use of BA, thus the rules on its use significantly vary regionally regulated by local environmental authority. However, Denmark enforces higher landfill tax in order to encourage the alternative beneficial use option for BA [5, 6].

2.6.6. United States

Despite of having many studies regarding successful demonstration projects of MSWI ash utilization in transportation applications [4, 69, 85], acceptance of ash is still under debate. Absence of proper Federal regulation and guidance and their variable applicability in different states hinder the implementation of the beneficial use of MSWI ash.

2.6.6.1. **Federal Regulation**

In the U.S., BA and FA are mixed together and disposed of in landfill as combined ash [13]. According to Resource Conversation and Recovery Act (RCRA), MSWI ashes are required to pass the Toxicity Characteristic Leaching Procedure (TCLP) (SW-846 EPA Method 1311) [70, 91] to be considered as non-hazardous waste. FA often fails TCLP; however, BA with lower in hazardous constituents generally passes. Hence, in the U.S. the two are combined and disposed in order to avoid the high cost and negative stigma that requires special disposal technique for hazardous waste.

Without considering the field leaching scenario, Environmental Protection Agency (EPA) devised the TCLP leaching test using acetic acid to classify simply whether ash is hazardous or non-hazardous. Hence, TCLP leaching test results often overestimate leaching potential as compared to field condition [4]. For this reason, alternative leaching tests method has been developed to better simulate the field performance. The Synthetic Precipitation Leaching Procedure (EPA Method 1312) [4] has been practiced using sulfuric/nitric acid of 40/60 by weight and EPA has been working with Leaching Environmental Assessment Framework (LEAF) to characterize leachates and run off from the field [92]. LEAF tests are designed to understand the dependence of pH and mass transfer rate on batch or column leaching test with varied liquid to solid ratio [92]. In addition to the environmental criteria set by EPA, Federal Highway Administration (FHWA) provided guideline for MSWI ashes use in pavement construction [93], such as granular base and asphalt concrete application.

2.6.6.2. **State Regulation**

Several states have been considering MSWI ash for beneficial use by implementing some state rules and regulations. One extensive survey [94] revealed that 28 states require TCLP tests, while 9 states have their substitute testing procedures. 20 states permit ash utilization, but 9 states do not permit [4, 94]. Disposal as ash monofill with daily cover is a typical practice for ash management with limited application in asphalt paving and concrete [4, 8].

Few states, including New Hampshire and Massachusetts permit demonstration research projects [4]. Some states have their own administrative codes that include groundwater, surface water, soil, or air quality [4]. For example, Washington DC and California enforce leaching test, Waste Extraction Test (WET) [4, 95, 96] with more stringent threshold limit for inorganic substance than those of TCLP test. Similarly, New York has comprehensive waste management regulations requires TCLP test and SW-924 extraction test [4] using distilled water as a leachant. Some states, including Pennsylvania and Illinois only recognize ash as special waste [4, 96, 97].

Having the highest number of MSWI plants and aiming at 75% recycling by 2020 [98], Florida Administrative Code (FAC) includes chapter intended to the extensive ash management strategy for landfill and recycling to meet TCLP and drinking water standard, respectively [92, 99]. Reuse

Target Levels (RTLs) are also recommended by Florida Department of Environmental Protection (FDEP) as describes in the document of Guidance for Preparing Municipal Waste-to-Energy Ash Beneficial Use Demonstration [100]. This document provides the guidance for the Department and the WTE ash generator to prepare the acceptable Beneficial Use Demonstrations (BUDs).

2.6.7. Comparison of Leaching Regulation among Different Countries

Different countries implemented their own leaching test procedure depending on the regulatory and environmental perspective that results in wide variation in threshold values for particular chemical constituent for the MSWI ash utilization. In order to compare the variation among different country standards, an effort was made to compile the legislative limit values and they are summarized in Table 2.4.

Table 2.4: Summary of leaching criteria for different constituents from MSWI BA residue for utilization in various countries (mg/L) [5, 71, 101]

Element	The Netherlands Column (L/S = 1-10) 2005	Denmark Batch (L/S = 2) 2000	Germany Batch (L/S = 5) 1994	France Batch (L/S = 5) 1994	US EPA Toxicity Criteria[a] 1987	US Drinking Water Standard 2009
Cl	440	300	125			
F	14.4					4
SO$_4$	3,250	400	300	500		
Na		150				160
As	0.35	0.005		0.1	5	0.01
Ba	7.75	0.4			100	2
Pb	0.41	0.01	0.025	0.5	5	0.015
Cd	0.00305	0.004	0.0025	0.05	1	0.005
Cr	0.06	0.05	0.1	0.05	5	0.1
Cu	0.165/1.15[b]	0.2	0.15			1[c]
Hg	0.00375	0.0001	0.00005	0.01	0.2	0.002
Mn		0.1				
Ni	0.175	0.007	0.02			0.1
Zn	0.7	0.15	0.15			5[c]
Co	0.115					
Mo	0.13/1.15[a]					
Sb	0.06/0.1[a]					0.006
Se	0.0135				1	0.05
Sn	0.115					
V	4.8					
Ag					5	0.1[c]
Tl						0.001

[a] Code of Federal Regulation (CFR) 40-261.24 [101]
[b] The Netherlands consider BA to fall under special category with less strict leaching criteria for Cu, Mo, and Sb [5]
[c] Secondary drinking water standards [102]

3. MATERIAL CHARACTERIZATION OF MSWI ASHES

3.1. Introduction

According to a recent research work [7], 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 [2] 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 [55, 59, 103] as well as aggregate for reinforced concrete structures [21, 104, 105]. 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.

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 [20]. 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 [20, 34] 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.
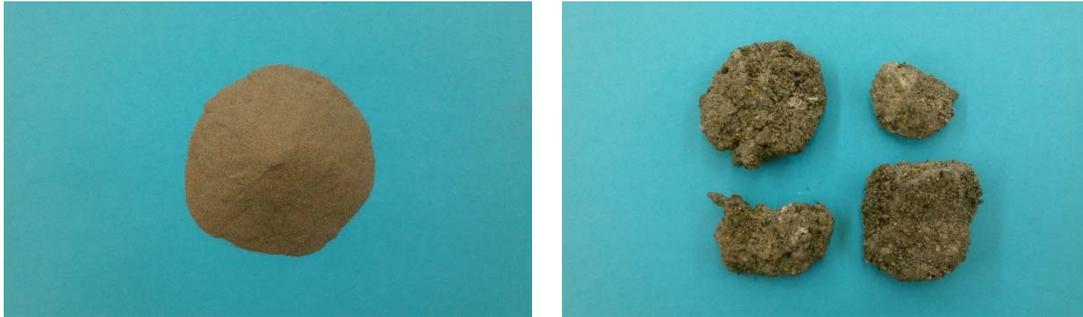
Figure 3.1: Photographs of MSWI fly ash (left) and bottom ash (right)

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 [106]). In addition, high absorption capacity was obtained from the bottom ash compared to that of typical natural aggregate, 0.5 to 4% [106]. 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 [107], 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 [108]
Absorption capacity, %	N/A	12.8	ASTM C127 [108]
Unit weight (oven dry), kg/m^3	2,104	2,195	ASTM C29 [109]
L.A. abrasion mass loss, %	N/A	43	ASTM C535 [110]

3.4. Microstructural and Chemical Properties

The microstructural morphology of each ash obtained from SEM is shown in Figures 3.2 and 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 higher 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 [21, 34, 105]:

$$2Al + 4OH^- + 2H_2O \rightarrow 2Al(OH)_3 + H_2\uparrow \tag{3.1}$$
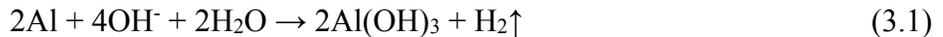
As a result, a network of bubbles are entrapped inside a concrete and the strength and durability of the entire structure can be greatly reduced [20, 21, 34, 104]. It is important to note that high Ca contents were observed from the both ashes. Therefore, it may be possible to use the ashes for supplementary cementitious materials (SCMs) if the negative effects, high concentration of Cl and development of hydrogen gas can be eliminated by proper treatments.
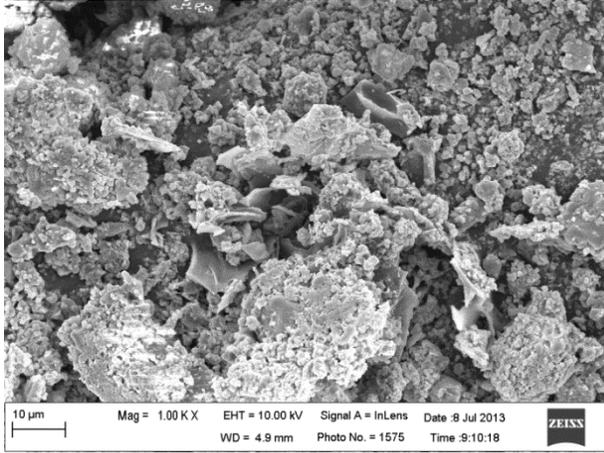
(a) 1,000X
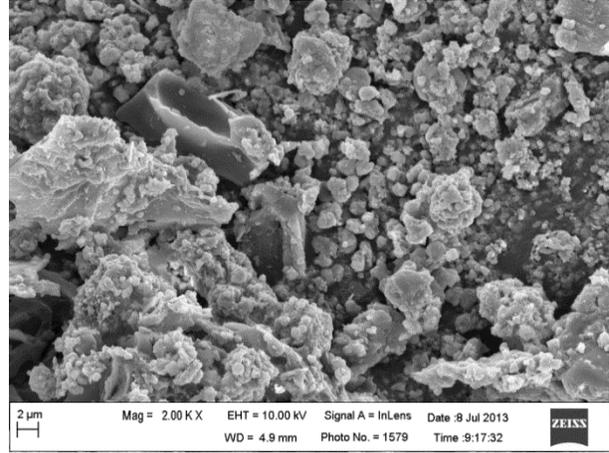
(b) 2,000X
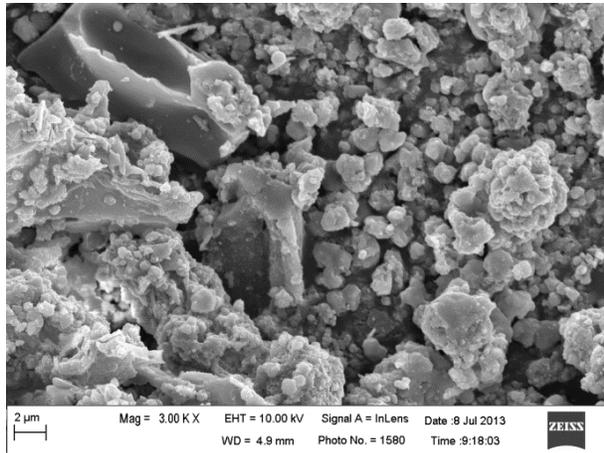
(c) 3,000X
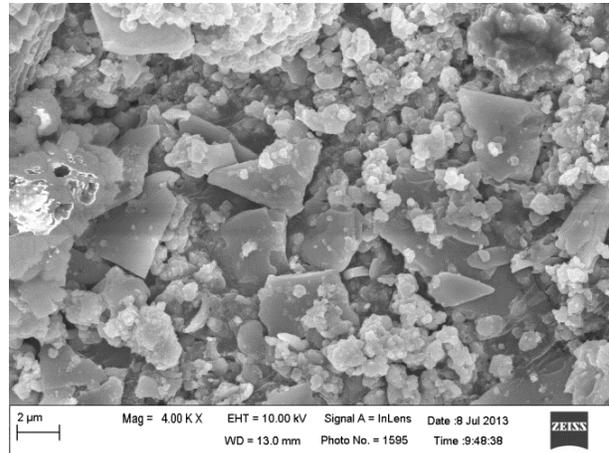
(d) 4,000X
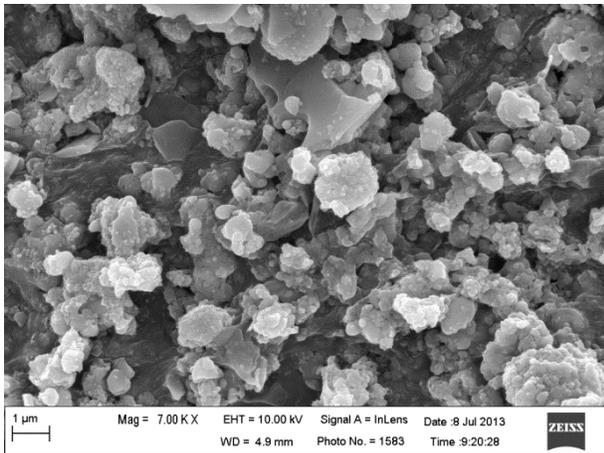
(e) 7,000X
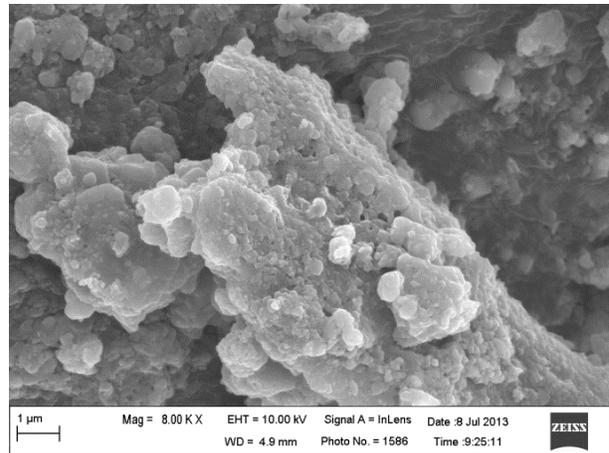
(f) 8,000X

Figure 3.2: SEM images of MSWI FA with varied magnifications
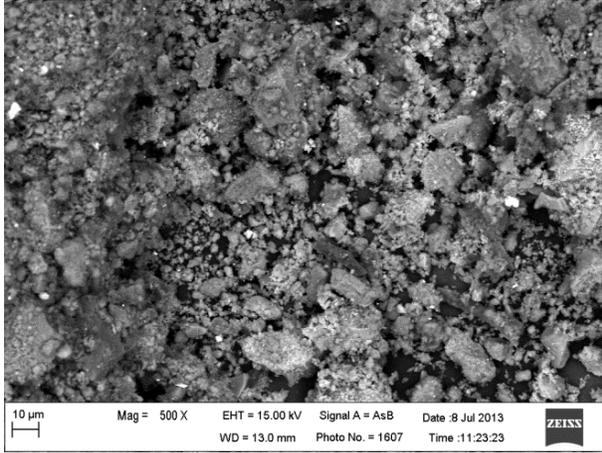
(a) 500X
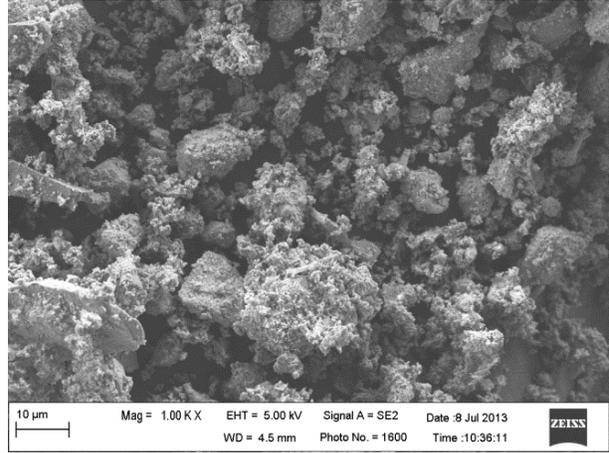
(b) 1,000X
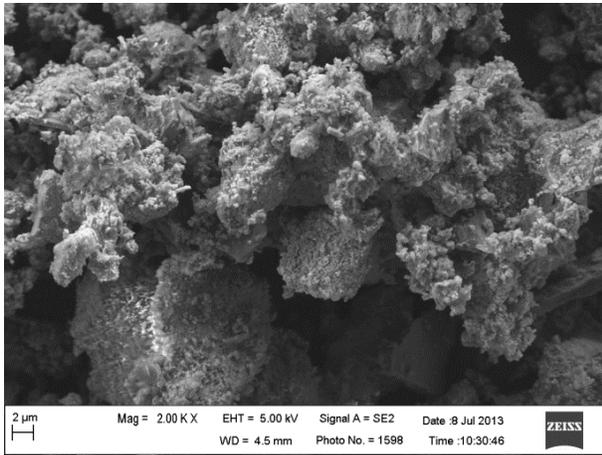
(c) 2,000X
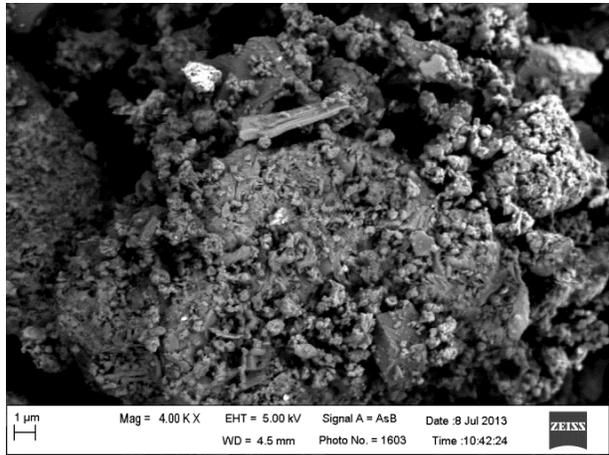
(d) 4,000X
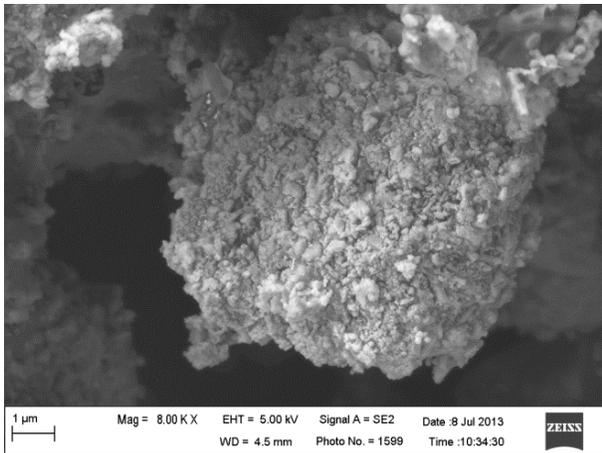
(e) 8,000X

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
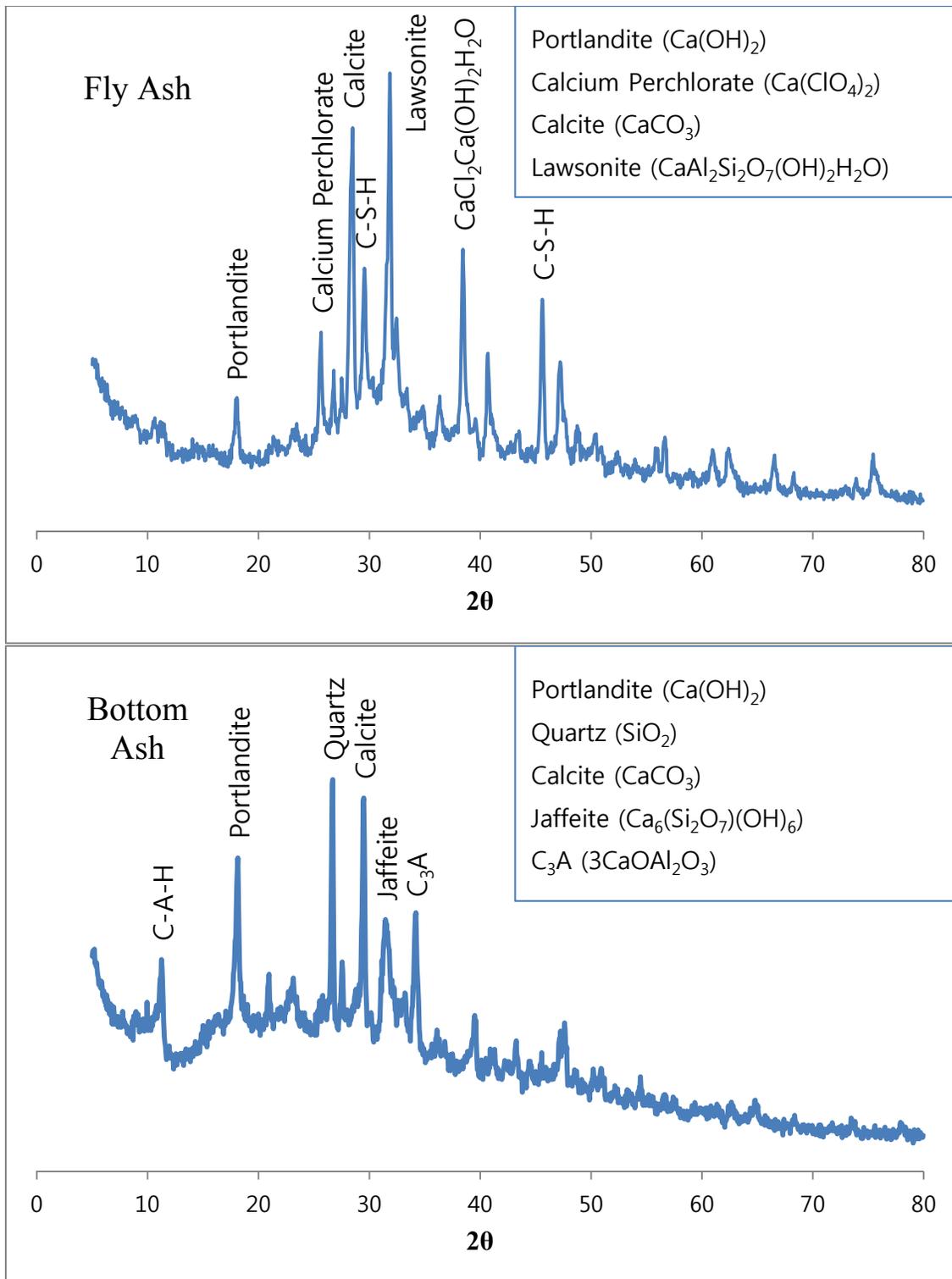
Figure 3.4: XRD of MSWI fly ash (top) and bottom ash (bottom)

3.5. Hydrogen Gas Evolution

In order to evaluate the emission of hydrogen gas by the oxidation reaction of metallic aluminum given by equation (3.1), 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 [34]. 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 (3.1), 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.

In order to assure similar particle sizes for all the materials, 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 (0.0035 in.)). Aluminum and aluminum oxide powders used in this test were obtained from Alcoa, Inc., Rockdale, TX and N.T. Ruddock Company, Cleveland, OH, respectively. According to the material data sheet provided each merchandise, both powders have particle sizes of 90 μm (0.0035 in.) and over 99% of purity.

Fly ash, ground bottom ash, aluminum powder, and aluminum oxide powder were submerged in sodium hydroxide (NaOH) solution. Molecular biology grade sodium hydroxide beads were ordered from Fisher Scientific, Hanover Park, IL. All reaction materials used in this test were prepared their particle size smaller than or equal to 90 μm (0.0035 in.). A schematic illustration of the experimental setup to measure the volume of hydrogen gas is shown in Figure 3.5. The reaction vessel is attached to hydrogen collection burette through Tygon 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 ℃ (73 ℉) at atmospheric pressure.
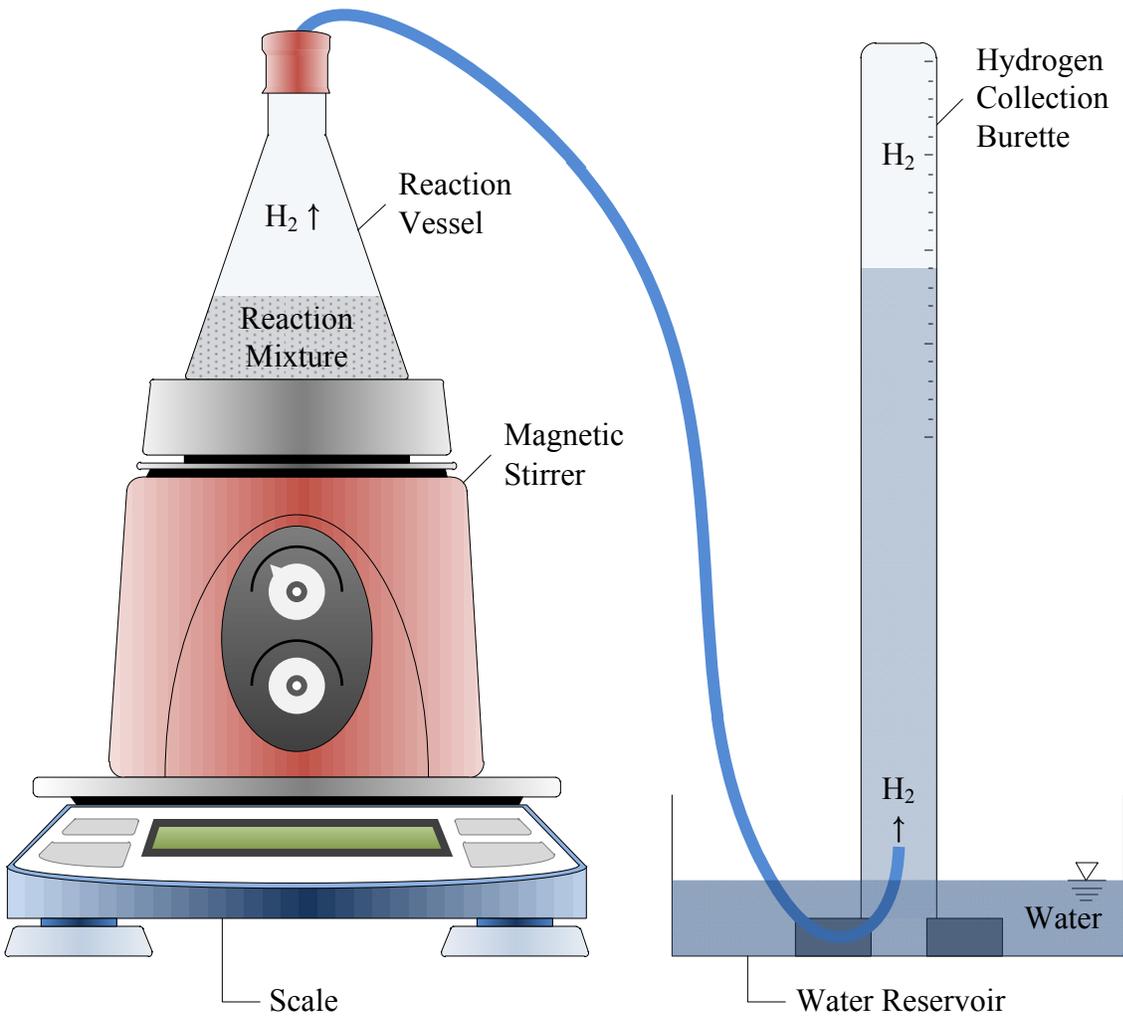
Figure 3.5: Test setup for volume of hydrogen gas measurement

The measured volume of hydrogen gas and calculated metallic aluminum content are presented in Table 3.3. 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 (21.6 ft^3/lb) at temperature of 23 ºC (73 ºF) and atmospheric pressure. The obtained hydrogen gas volume was 1,344.8 ml/g (21.5 ft^3/lb); 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 3.3: Measured volume of hydrogen gas and calculated metallic aluminum content of each material

Material	Mass [g]	NaOH solution		H_2 gas volume [ml] ([in.^{3}])	Gas vol. / unit mass [ml/g] ([in.^{3}/lb])	Calculated Al content	
		Concent-ration [M]	Volume [ml] ([in.^{3}])			Mass [g] ([oz])	Weight ratio [%]
Al	0.29	1	10 (0.6)	390 (23.8)	1,345 (37,224)	0.29 (0.010)	99.62
Al_2O_3	1	1	10 (0.6)	0	0	0	0
	150	3	400 (24.4)	0	0	0	0
Fly ash	20	1	150 (9.2)	0	0	0	0
	100	2	400 (24.4)	50 (3.1)	0.5 (13.8)	0.04 (0.001)	0.04
	150	3	400 (24.4)	60 (3.7)	0.4 (11.1)	0.04 (0.001)	0.03
Ground bottom ash	10	1	30 (1.8)	0	0	0	0
	100	2	400 (24.4)	40 (2.4)	0.4 (11.1)	0.03 (0.001)	0.03
	150	3	400 (24.4)	60 (3.7)	0.4 (11.1)	0.04 (0.001)	0.03

3.6. 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.

4. CHARACTERIZATION OF MSWI ASHES WHEN USED AS CEMENT REPLACEMENT

4.1. Introduction

According to a recent US government report [111], approximately 250 million tons (551 billion pounds) of waste were generated in the US during 2010, but only 34% (85 million tons (187 billion pounds)) of which was either recycled or composed. The rest was combusted and/or disposed at landfills. Incineration is a means to convert waste to energy and also an efficient way to reduce not only the solid waste volume but also landfill space required; thus, the incineration of solid waste has played an important role in the municipal solid waste management. Because these ashes are produced worldwide in ever increasing quantities, recycling of MSWI ashes have been a major challenge; thus, public agencies are investing significant portions of their budgets to reduce the amount of disposed MSWI ashes.

Due to the large quantity consumptions of the materials and relatively low quality requirements, the use of MSWI ashes in civil construction has been considered to be one of the most attractive options for increasing the recycling rate of municipal solid waste. Recently, many research studies were performed to find feasibility for incorporating MSWI ashes into civil materials. The European countries have led the successful practice of using the benefits of MSWI ashes and they are now widely used in road construction as a gravel material in compacted base layers [55, 59, 103]. It was demonstrated that MSWI bottom ash is classifiable as adequate soil for embankment and land fill, and a proper material for granular layers (bases and sub-bases) [55]. However, not many successful use of ash addition in concrete has been reported. This is mainly attributed to the side effect due to the presence of aluminum [20, 21, 34, 104].

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 [112] 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 [2].

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 [105, 113]. The main side effect due to the presence of high concentration of metallic aluminum is the evolution of hydrogen gas [21, 34, 105]. As tested in the previous chapter, 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 [21]:

Hydrogen gas produced by 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 [20, 21, 34, 104]. The focus of this chapter is characterization of the influence of MSWI ashes on cement paste properties when part of Portland cement is replaced with ground and sieved MSWI ashes. Cement paste cylinders were cast with various types and amounts of mineral additions and their strength and durability were investigated.

4.2. Experimental Procedure

MSWI ash samples were collected from a refuse-derived fuel (RDF) waste-to-energy (WTE) facility in Florida in April, 2013. Both ashes involved a wide range of particle sizes: fly ash up to 0.1 mm (0.004 in.) and bottom ash up to 50 mm (2 in.). The ashes contain moisture that has been a result of a quenching process in the incineration facility and therefore, the ashes were oven-dried. The oven dried density (ASTM C188 [114]) 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 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 (0.0035 in.)). The ashes were further sieved with two more sieves, No. 200 and No. 400 (opening sizes of 75 and 37 μm (0.0029 and 0.0015 in.), respectively) in order to assess their particle size distribution, and the results are shown in Figure 4.1.

The mixture proportions of the cement paste specimens are listed in Table 4.1. Each mixture was prepared in 30-liter (1.06-ft^3) batches, and three types of cylinders having different height were cast for each batch: four 100 × 200-mm^2 (4 × 8-in.^{2}); one 100 × 100-mm^2 (4 × 4-in.^{2}); and two 100 × 50-mm^2 (4 × 2-in.^{2}) cylinders. 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. All test specimens were stored in an indoor environment at all times with an ambient temperature of 21 ± 1 ℃ (70 ± 2 ℉) and relative humidity of 70 ± 3%, and removed from the cylinder molds three days after casting.

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 [115]. A Humboldt H-3050 Vicat Consistency was used, and all mixtures remained in the hard-rubber conical mold (60-mm (2.5-in.) diameter at the top, 70-mm (3-in.) diameter at the bottom, and 40-mm (1.5-in.) height) throughout the test period.
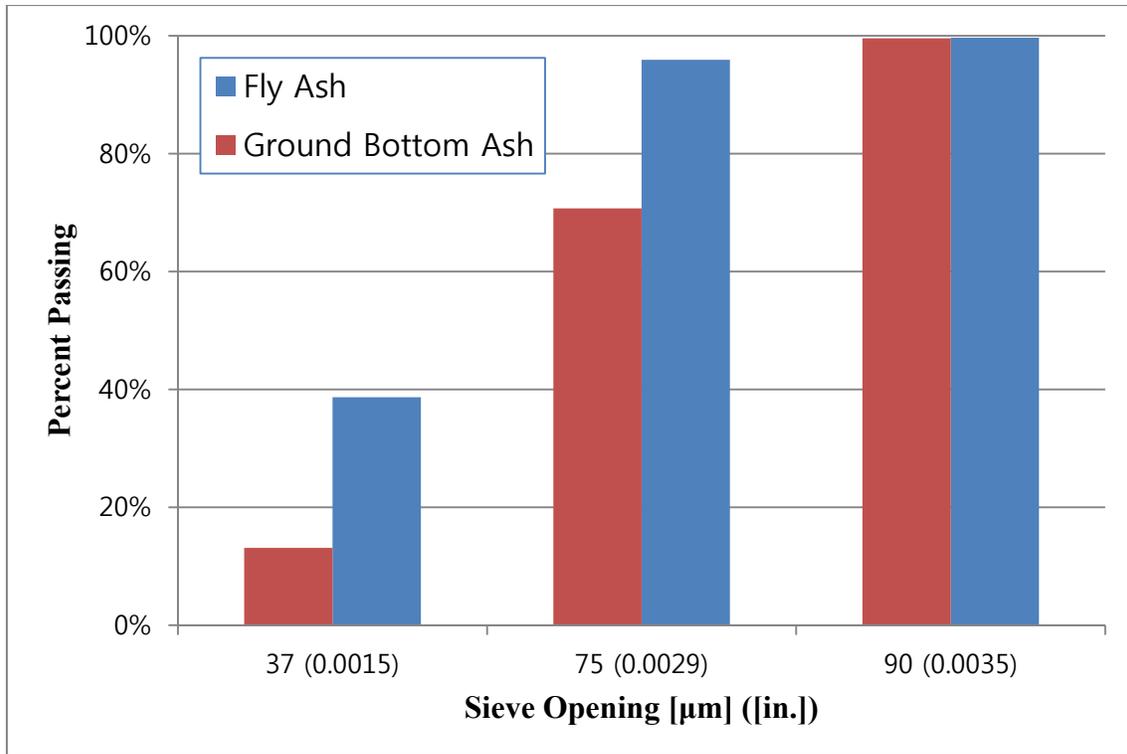
Figure 4.1: Particle size distribution of MSWI ashes

Table 4.1: Mixture proportions of cement paste specimens per cubic meter [kg/m^3] ([lb/ft^3])

Paste ID	W/C	Water	Cement	Fly ash	Ground bottom ash
C	0.5	180 (11.2)	360 (22.5)		
F10		180 (11.2)	324 (20.2)	36 (2.2)	
F20		180 (11.2)	288 (14.2)	72 (4.5)	
F30		180 (11.2)	252 (15.7)	108 (6.7)	
B10		180 (11.2)	324 (20.2)		36 (2.2)
B20		180 (11.2)	288 (14.2)		72 (4.5)
B30		180 (11.2)	252 (15.7)		108 (6.7)

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 (4-in.) diameter and 200-mm (8-in.) height for each mixture were prepared and their density was measured in accordance with ASTM C1688 [116] when freshly mixed and ASTM C1754 [117] when hardened.

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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 [118] and ASTM C1754 [117], respectively. For the permeability test, two disc specimens with 100-mm (4-in.) diameter and 50-mm (2-in.) height were prepared for each Past ID listed in Table 4.1 and the rate of one-dimensional water absorption into the specimens from a water reservoir was measured with other surfaces sealed with UGL Latex Base DryLok. As illustrated in Figure 4.2, a water reservoir was installed beneath each cement paste cylinder and the height of water level was controlled to be approximately 2 mm (0.1 in.) 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 (4-in.) diameter and height were prepared, and dry and submerged mass of each specimen were measured until the submerged mass becomes constant.
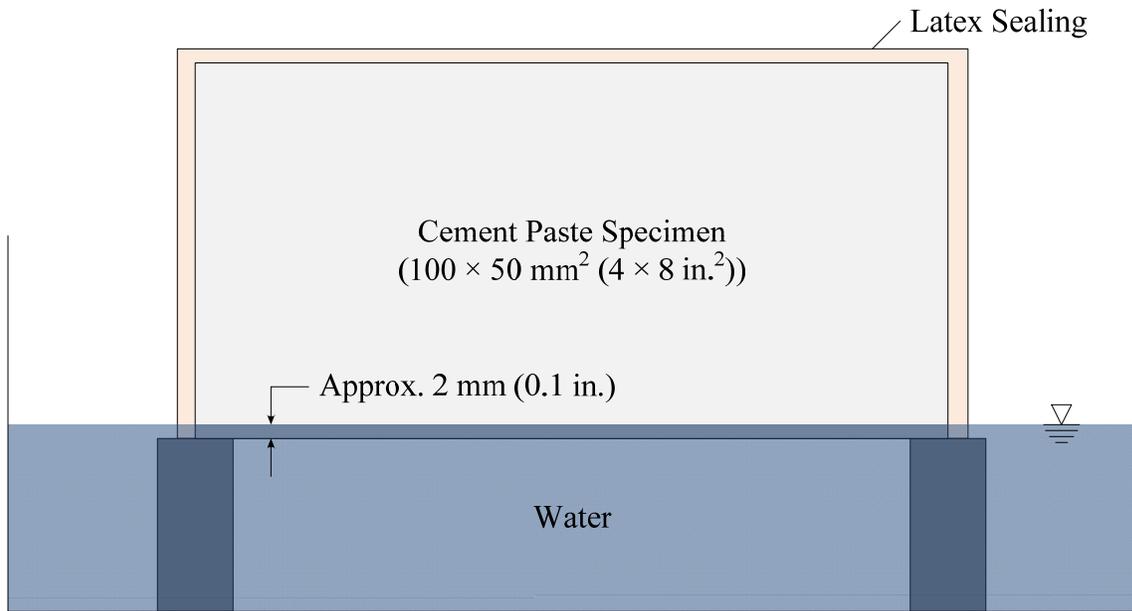
Figure 4.2: Configuration of one-dimensional water absorption test setup

In order to evaluate the influence of replacing materials on mechanical property of cementitious materials, three replicate cement paste cylinders (100×200-mm^2 (4×8-in.^{2})) were prepared for each mixture and their compressive strength were determined at 28 days of curing according to ASTM C39 [119].

4.3. Visual Inspection

A visual inspection was conducted to detect surface defects of cement paste cylinder specimens after removing from cylinder molds. Figure 4.3 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.

4.4. Setting Time

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 4.2. 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 conducted in the previous chapter (Table 3.2 and Figure 3.4, respectively), MSWI ashes contain several beneficial chemical elements and minerals. However, these components are present in much smaller quantities compared to the 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 3.2). 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 [120-122] . 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.

(a) C
No cracks or voids

(b) F10
Minor longitudinal cracks

(c) F20
Small air voids

(d) F30
Large air voids

(e) B10
Minor longitudinal cracks

(f) B20
Minor longitudinal and
transverse cracks

(g) B30
Moderate longitudinal and
transverse cracks

Figure 4.3: Photographs of cement paste cylinder specimens and their surface conditions

Table 4.2: Averaged properties of the fresh and hardened cement paste specimens

Paste ID	Setting time [hour]		Density [kg/m^3] ([lb/ft^3])		Void content of hardened cement paste [%]	28-day compressive strength [MPa] ([Psi])
	Initial	Finial	Fresh	28-day		
C	5.4	9.2	1,878 (117)	1,825 (114)	22.8	28.3 (4105)
F10			1,839 (115)	1,748 (109)	26.0	26.5 (3844)
F20			1,815 (113)	1,705 (106)	17.9	43.2 (6266)
F30	2.1	5.2	1,803 (113)	1,681 (105)	12.3	27.1 (3931)
B10			1,790 (112)	1,699 (106)	23.6	15.4 (2234)
B20			1,739 (109)	1,634 (102)	25.2	26.8 (3887)
B30	6.9	12.0	1,718 (107)	1,607 (100)	25.3	15.1 (2190)

4.5. Fresh and Hardened Density

Measured average densities of the fresh and hardened cement paste are provided in Table 4.2 and the ratios of average hardened density-to-fresh density for all mixtures are compared in Figure 4.4. As seen in Table 4.2, 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 ash and bottom ash and the density ratio decreased with increasing ash addition for both ashes.

Based on the hydrogen gas evolution test results conducted in the previous chapter, the maximum volume of hydrogen gas release per one cylinder specimen (100-mm (4-in.) diameter by 200-mm (8-in.) height) for each mixture was calculated and the results are presented in Table 4.3. 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 (1570 ml (96 in.^{3})). Hardened-to-fresh density ratio of each mixture is in good agreement with calculated hydrogen gas-to-cylinder volume ratio.
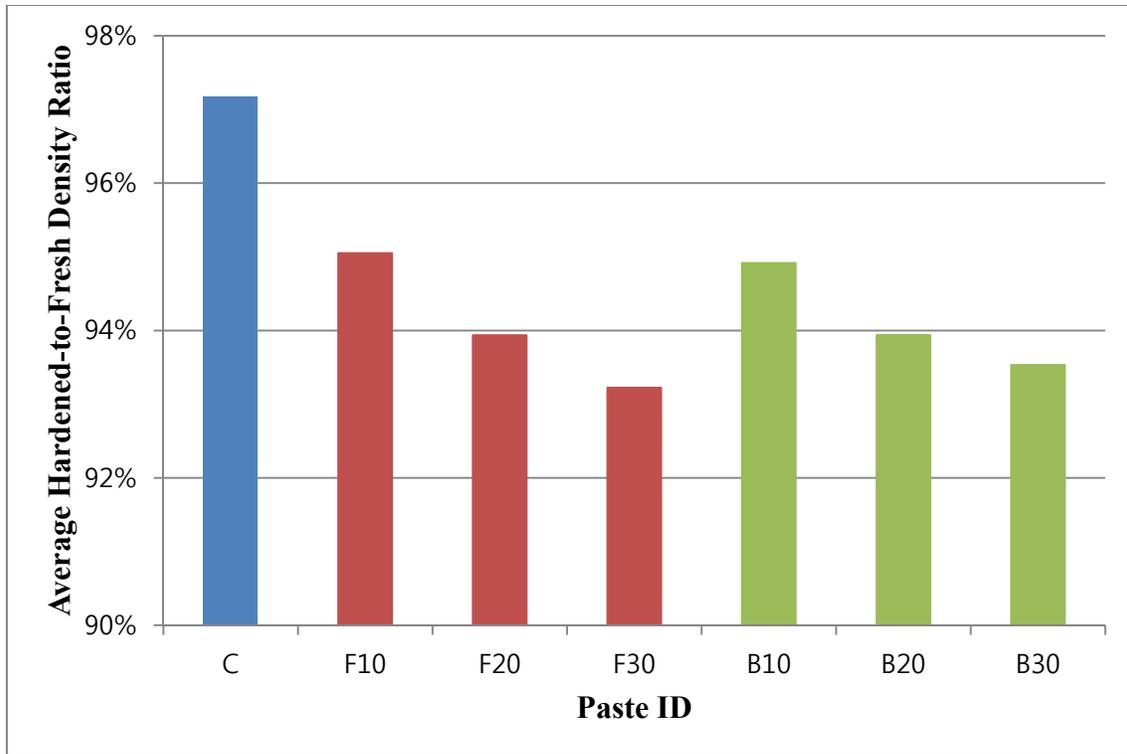
Figure 4.4: Average density ratios (hardened density / fresh density) for all mixtures

Table 4.3: Calculated metallic aluminum contents and maximum volume of hydrogen gas evolution per one cylinder specimen (100-mm (4-in.) diameter by 200-mm (8-in.) height)

Paste ID	Ash content [g/cyl] ([oz/cyl])	Calculated metallic Al content [g/cyl] ([oz/cyl])	Calculated hydrogen gas release	
			Volume [ml/cyl] ([in.^{3}/cyl])	Gas / cylinder volume ratio [%]
F10	56.52 (2)	0.02 (0.0007)	25.4 (1.6)	1.6
F20	113.04 (4)	0.04 (0.0014)	50.9 (3.1)	3.2
F30	169.56 (6)	0.06 (0.0021)	76.3 (4.7)	4.9
B10	56.52 (2)	0.02 (0.0007)	22.6 (1.4)	1.4
B20	113.04 (4)	0.03 (0.0011)	45.2 (2.8)	2.9
B30	169.56 (6)	0.05 (0.0018)	67.8 (4.1)	4.3

4.6. Water Absorption and Void Content

Figure 4.5 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.
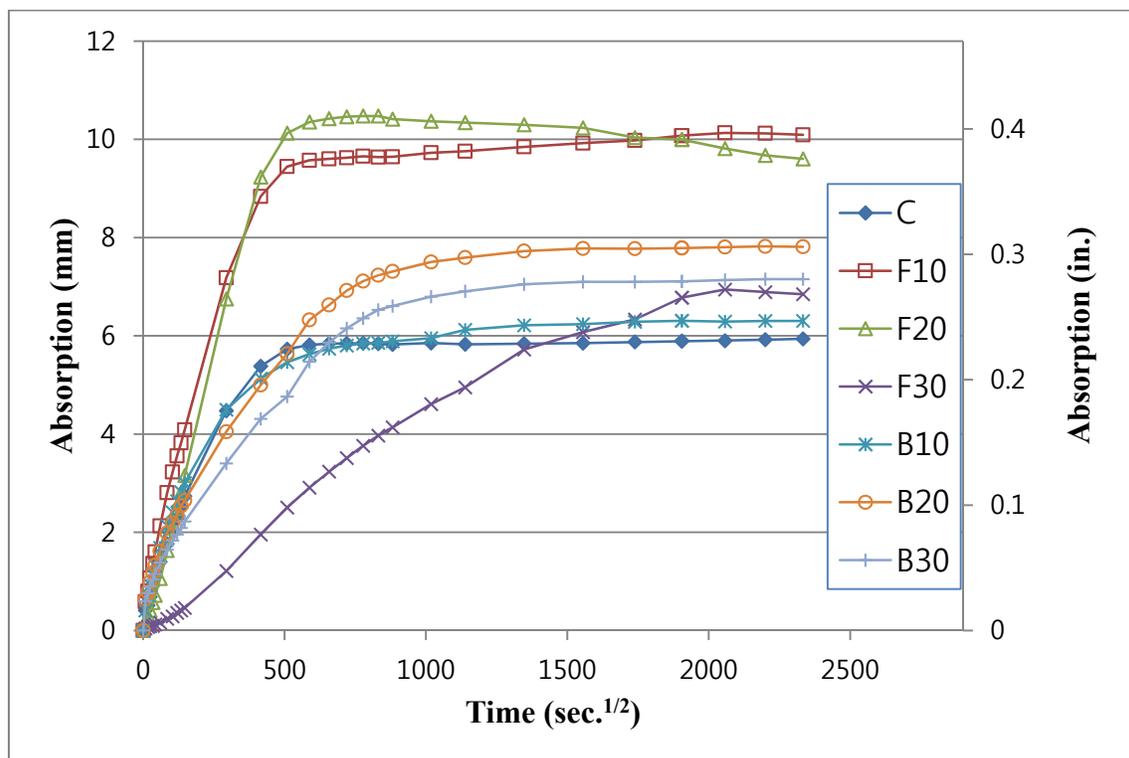
Figure 4.5: Water absorption for all cement paste cylinders

Measured void content of hardened cement paste are provided in Table 4.2. 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.

4.7. Effects of Cement Replacement with MSWI Ashes on Cement Paste Properties

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 4.3) and the reduced density (Figure 4.4). 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 [123-126]. When fine particles with a maximum size of 125 μm (0.005 in.) are incorporated in cement, these particles fill the intergranular voids between cement particles [124] and consequently increases the compressive strength as well as the durability [127, 128]. 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 3.3), both ashes released similar amount of gas, approximately 0.4 ml/g (11.1 in.^{3}/lb); 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 4.1) and their particle surface is smoother as seen in the SEM images (Figures 3.2 and 3.3). 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 4.2. In spite of the apparent surface air voids observed for F20 and F30 specimens in Figure 4.3, 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 4.3 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.
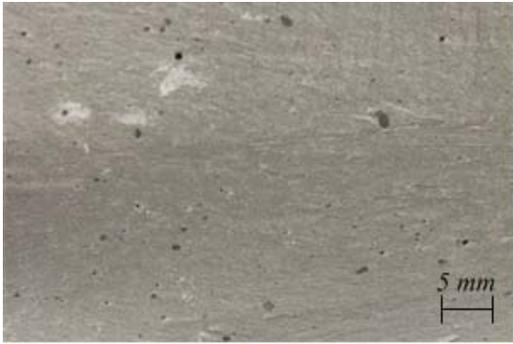
(a) C
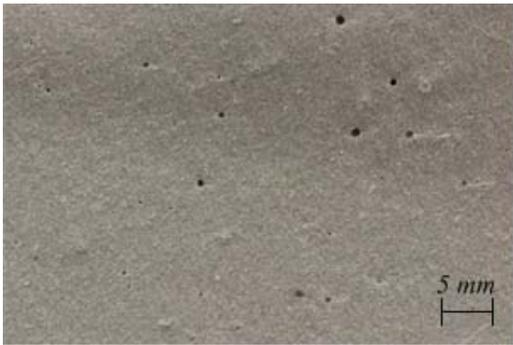
(b) F10

(c) B10
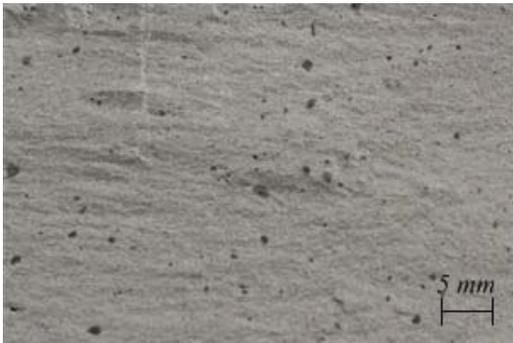
(d) F20

(e) B20

(f) F30

(g) B30

Figure 4.6: Photographs of cement paste section. Note: 5 mm = 0.2 in.

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 the fractured surface of each cement paste was examined. Figure 4.6 shows the condition of the cement paste section of each specimen. For the bottom ash specimens, higher amounts of entrapped air were observed with increasing replacement ratio. For the fly ash specimens, on the other hand, the pore concentration appears to decrease with increasing the replacement ratio. Considering the fact that both ashes release a 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.

4.8. Compressive Strength

The average compressive strength of cement pastes measured at 28 days is plotted in Figure 4.7, and the values are given in Table 4.2. As expected, overall compressive strength of fly ash specimens was 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 replacement. The compressive strength of the F20 specimen was 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 the B20 specimen was approximately 75% higher than that of B10 and B30 specimens.

In the same way as other properties, both development of hydrogen gas and filler effect were coupled to influence the compressive strength of the cement paste cylinders. An increase of strength was attributed to the fine particles of ash acting as fillers, while the production of hydrogen gas due to the reaction of metallic aluminum caused a decrease in strength. Another source of strength decrease was the reduced amount of hydration product with increasing ash replacement. Although it was obvious that influence of these three combined effects increased with increasing percentage of ash replacement, these effects were difficult to generalize due to a trade-off between the effects. Similar compressive strength measured from the specimens with 10% and 30% replacements was mostly likely due to the trade-off of the factors that simultaneously influenced the compressive strength. The notable increases in the compressive strength for 20% replacements for both ashes, on the other hand, were likely attributable 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 4.6.
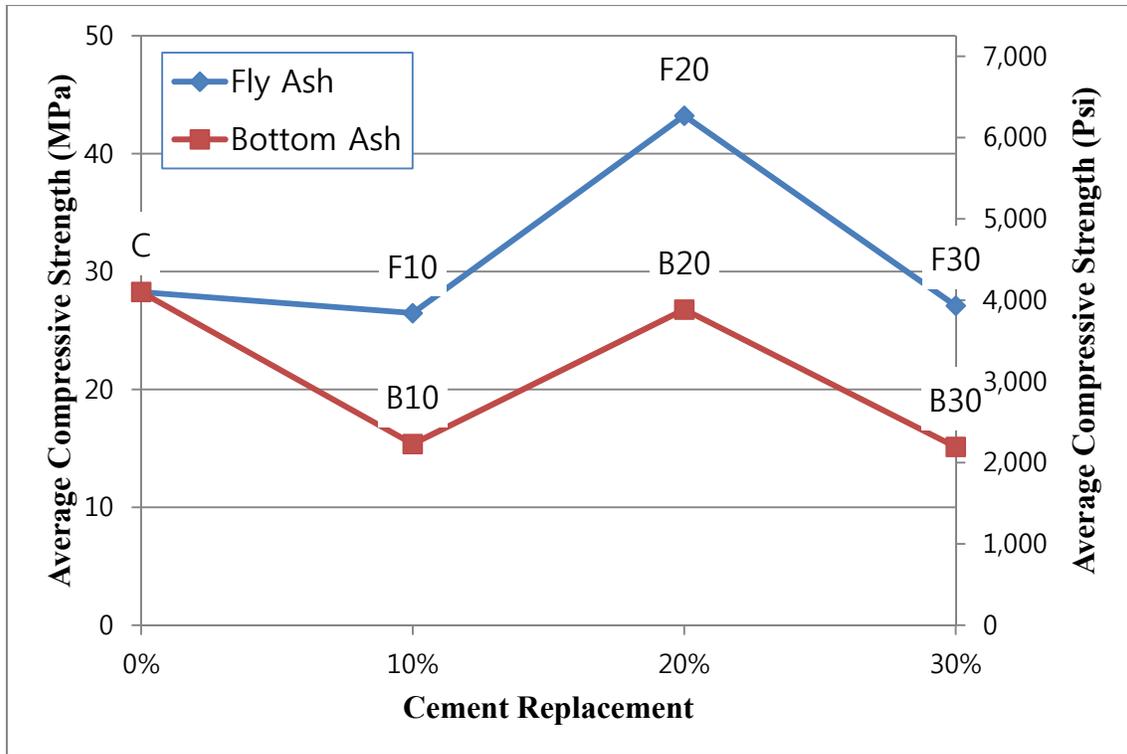
Figure 4.7: Average compressive strength measured at 28 days for all cement paste cylinders

4.9. Summary

In this chapter, MSWI fly ash and ground bottom ash were used as partial replacement of cement in cement paste specimens. 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.

5.   CHARACTERIZATION OF MSWI BOTTOM ASH WHEN USED AS FINE AGGREGATE REPLACEMENT IN PCC

5.1.   Introduction

The prospects for MSWI bottom ash (BA) lie within the realm of substitution aggregate in the place of natural aggregates. Due to the environmental perspective as well as its cost effectiveness, BA is considered as a potential ingredient for use as a recycled construction material in concrete. Numerous research studies has been conducted globally in order to increase the recyclability of MSW and a number of studies were focused on the use of BA in concrete: as sub-bases for pavement structures [129], embankment [130], Portland cement replacement material [59], aggregate replacement material [131]. However, there are no established ASTM standards for the utilization of MSWI BA as a potential construction material. This is mainly because unfamiliarity with the concrete properties when BA is used as a partial replacement of fine aggregate.

In this chapter, sand was replaced with BA in accordance with existing ASTM standards and the feasibility of the use of BA in concrete was evaluated. BA replaced concrete was subjected to mechanical property and durability tests according to ASTM standards.

5.2.   Experimental Procedure

5.2.1. Materials

Ordinary Portland cement (OPC) Type-I conforming to ASTM C 150 was used in the concrete as the primary binding material. Florida Department of Transportation (FDOT) certified sand passing 4.75 mm was obtained from CEMEX and used as a fine aggregate. The gradation curve of the sand met the ASTM requirement (ASTM C33) as shown in Figure 5.1. Fineness modulus of fine aggregate was 2.36, which also complies with the ACI requirement (2.3 to 3.1).

Limestone obtained from CEMEX with nominal maximum size of 19 mm was used as coarse aggregate. The sieve analysis for the coarse aggregate (Figure 5.2) demonstrated that the particle sizes for the coarse aggregate fell inside the ASTM certified zone (ASTM C 136).

MSWI BA was sourced from a refuse derived fuel (RDF) incineration plant in Florida. BA was oven dried at 105 °C for 24 hours and then sieved (according to ASTM C 33) to obtain the particle size range similar to that of fine aggregate. The particle size distribution curve of BA (Figure 5.3) show similar pattern as sand and most importantly, follow the ASTM C 33 standard. Fineness modulus of BA was found to be 2.51 which indicate that BA contains coarser particles in comparison with natural sand.
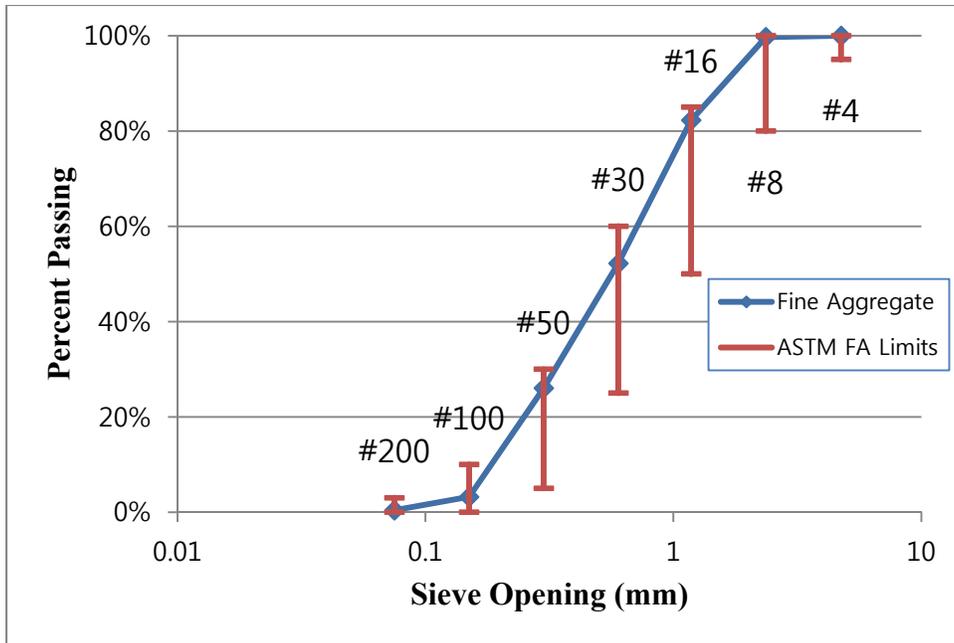
Figure 5.1: Gradation curve for fine aggregate (ASTM C33)
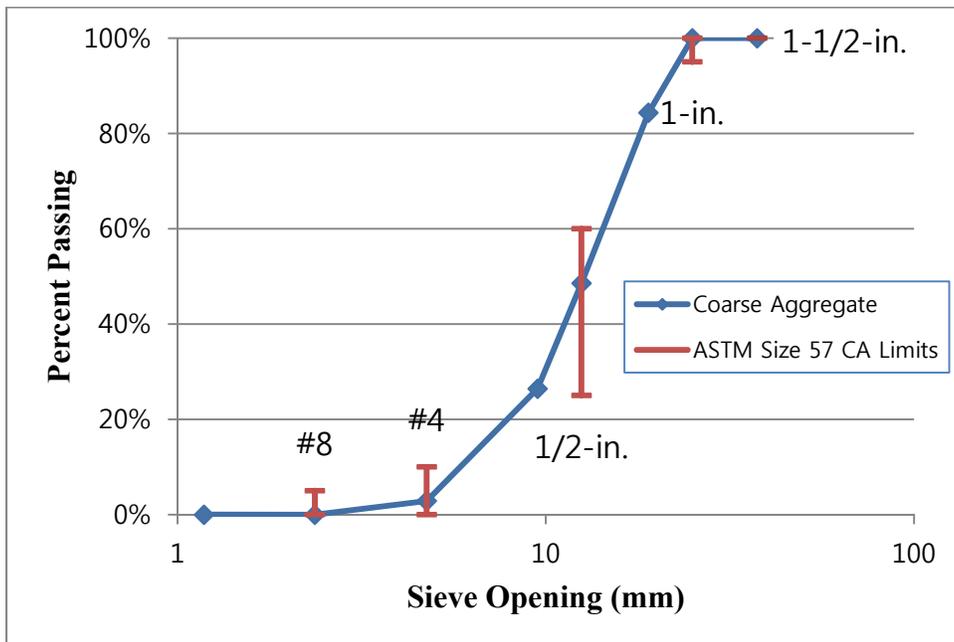
Figure 5.2: Gradation curve for coarse aggregate (ASTM C 136)
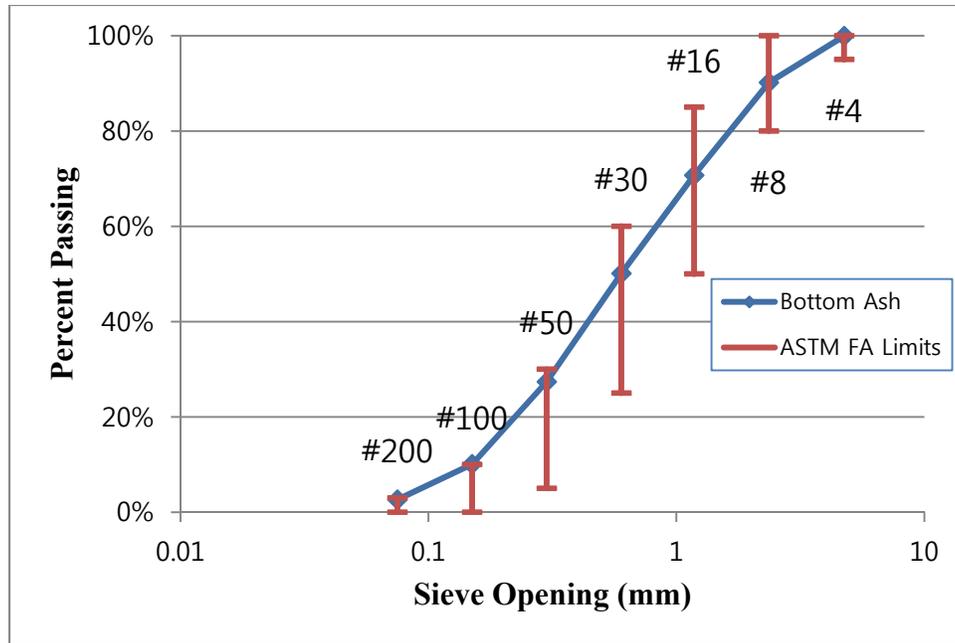
Figure 5.3: Particle size distribution of BA (ASTM C 33)

Bulk specific gravity of materials was obtained according to ASTM C127 and C128 and their results are summaries in Table 5.1. According to the results, specific gravity of BA is approximately 20% lower than that of fine aggregate; therefore, density of concrete specimen is expected to decrease with increasing amount of ash addition.

Table 5.1: Physical properties of materials

Property	Value		
	Fine aggregate	Coarse aggregate	MSWI BA
Bulk specific gravity	2.7	2.6	2.2
Fineness modulus	2.36	6.86	2.51
Bulk density (kg/m^3)	1703	1451	---
Absorption (%)	2	3.85	---
Void content (%)	---	39	---

5.2.2. Specimen Preparation

Five different batches of concrete specimens were casted with 0%, 10%, 20%, 30%, and 50% replacement of sand with BA. The mix proportions for all five batches are tabulated in Table 5.2. Water-to-cement ratio (w/c) was kept constant at 0.5 by weight of cement. The actual mixing was carried out according to ASTM C 192 in a rotary drum mixer. Cement and BA was poured into

45

the mixer following the mixing with half of the water. After a while the rest of the water was poured and kept mixing for three minutes. The mixer was kept at rest for three minutes followed by another two minutes of mixing. Slump test was carried out according to ASTM C 143 to obtain the workability of control concrete and concrete mix with BA replacement. The mixing procedure described above was followed for each of the five batches.

Table 5.2: Mix proportions of concrete specimens

Mixture	Cement (kg)	Water (kg)	Fine aggregate (kg)	Coarse aggregate (kg)	Bottom ash (kg)
Control	3.60	1.80	7.50	9.34	-
R-10	3.60	1.80	6.75	9.34	0.75
R-20	3.60	1.80	6.00	9.34	1.50
R-30	3.60	1.80	5.25	9.34	2.25
R-50	3.60	1.80	3.75	9.34	3.75

Three specimens (100×200 mm^2) for compressive strength tests and three specimens (100×50 mm^2) for absorption (ASTM C 1585) and porosity (ASTM C 1754) tests were prepared for each of the five batches of concrete mix. The fresh concrete density of each specimen from all different batches were measured in accordance with ASTM C 1688 and sealed before keeping for curing. The specimens were demolded three days after the casting and cured in air for 28 days. Concrete specimens were tested for compressive strength at day 28 using Instron universal testing machine (UTM). The absorption test specimens were coated with epoxy paint on three surfaces exposing the bottom surface as the source where the water can percolate vertically.

5.3. Slump

Measured properties of concrete are summarized in Table 5.3. Based on the slump tests, control concrete showed the highest slump of 25 mm, while R-10 showed a slump of 12.5 mm and R-50 showed virtually no slump. This range was defined as very low workability range by Neville [132]. The gradual decrease in slump can be attributed to the irregular/angular particle shape of BA [131]. With the increase in BA content, amount of angular particle also increase, and thus, slump value decreased.

Table 5.3: Measured properties of fresh and hardened concrete

Specimen	Slump (mm)	Density (kg/m³)		Compressive strength		
		Fresh	Demolded	Average (MPa)	Standard deviation (MPa)	Variance (MPa²)
Control	25.0	2430	2262	51	0.43	0.18
R-10	12.5	2397	2215	49	0.68	0.47
R-20	6.2	2388	2212	44	1.52	2.32
R-30	3.1	2378	2183	39	2.48	6.16
R-50	0	2179	2020	22	3.62	13.10

5.4. Fresh and Hardened Density

It is evident that the fresh concrete density was decreasing with the increment of BA content As the specific gravity of BA is lower than that of sand (Table 5.1), the same volume of BA will result in lower weight, and eventually, lower density. Similar trend as fresh concrete density was observed for hardened density. Moreover, the densities have slightly decreased after 28 days for each of the batches in comparison with fresh density. The reason can be attributed to the loss of moisture content from the surface of the specimens as those were air cured which leads to a slight reduction in weight. Moreover, the volume of the specimens have increased in the range of 5-8% due to the hydrogen gas evolution from the reaction between metallic aluminum (Al) present in the BA and alkaline environment of concrete [130].

5.5. Visual Observation

The hardened specimens of different replacement ratios of BA are shown in Figure 5.4. Control specimen does not possess visual evidence of large pores on the surface. It is observed that the number of surface pores increased with the increase in BA content. R-50 specimen showed almost perforated concrete cylinder. Although the increasing number of surface pores can be caused by hydrogen gas evolution, the tremendously deteriorated structure of R-50 can be caused by slump loss also. As R-50 showed no slump, there was little workability and consistency of the mixture. Even though this specimen was subjected to same vibration duration and intensity, due to the lack of consistency, the whole mixture was segregated.

<table>
<tr><td>(a) Control</td><td>(b) R-10</td><td>(c) R-20</td></tr>
</table>

<table>
<tr><td>(d) R-30</td><td>(e) R-50</td></tr>
</table>
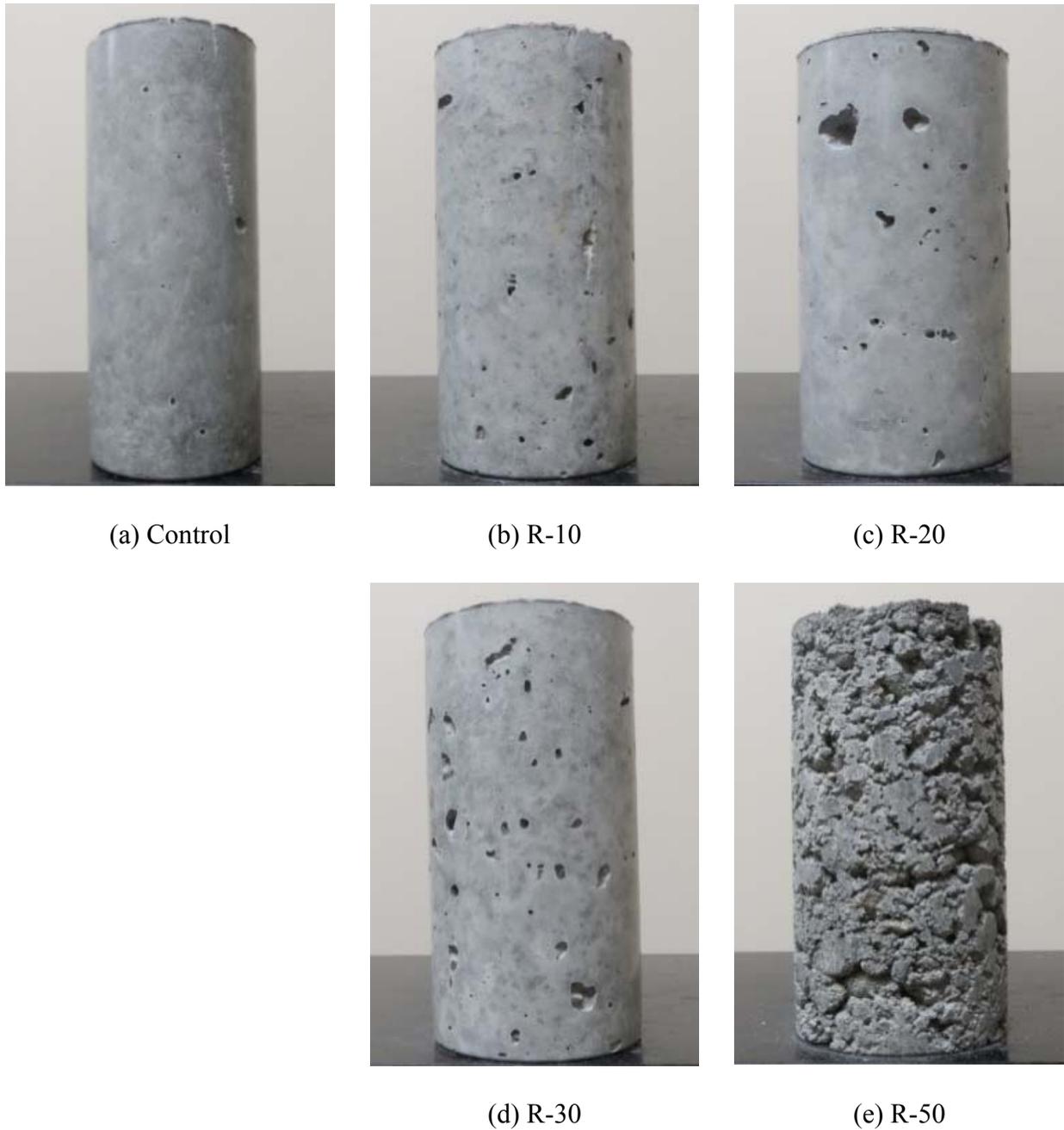
Figure 5.4: Photos of MSWI bottom ash replaced concrete with various replacement ratios

5.6. Compressive Strength

The compressive strengths shown in Figure 5.5 also validate the conclusion drawn from the visual evidence. The compressive strength of the control specimen was 51 MPa which topped the R-10 specimen with 49 MPa. R-50 specimen failed at 22 MPa which is 57% lower than that of control specimen. The compressive strength data for the concrete specimens have a decreasing

trend with the increase in BA content as seen from Figure 5.5 and Table 5.3. It is established that the compressive strength depends on the strength of the cement matrix, the aggregates, and the matrix-aggregate interfacial bond. The decrease in compressive strength in this study can be attributed to the use of weaker aggregate. This conclusion can be validated by the visual inspection of crack propagation through the aggregate. The R-50 specimen showed some cement-aggregate bond failure. Another explanation can be related to the air content of the hardened concrete. Cheng [131] reported that the air content of hardened concrete increases with increase in BA content in concrete, which leads to the decrease in density and, eventually, compressive strength. The standard deviation of the strengths also increases with increasing BA content. This statistical evidence points out the spreading of the compressive strength with the increment of BA percentage in concrete. As seen from Table 5.3, the variance of R-30 and R-50 increased drastically compared to those of other specimens, which also correlates to the 24% and 57% decrease in strength, respectively, relative to that of control specimen. With the increase in BA content, air content of the hardened concrete increased, and workability of fresh specimen decreased. Due to the lack of workability, segregation of aggregate and paste may occur during the vibration and compaction, making uniform strength in all specimens uncertain. However, the control specimen and R-10 showed 8.34% and 4.75% higher compressive strength than the compressive strengths reported by [130] with same amount of BA replacement and with similar w/c ratio (0.52).
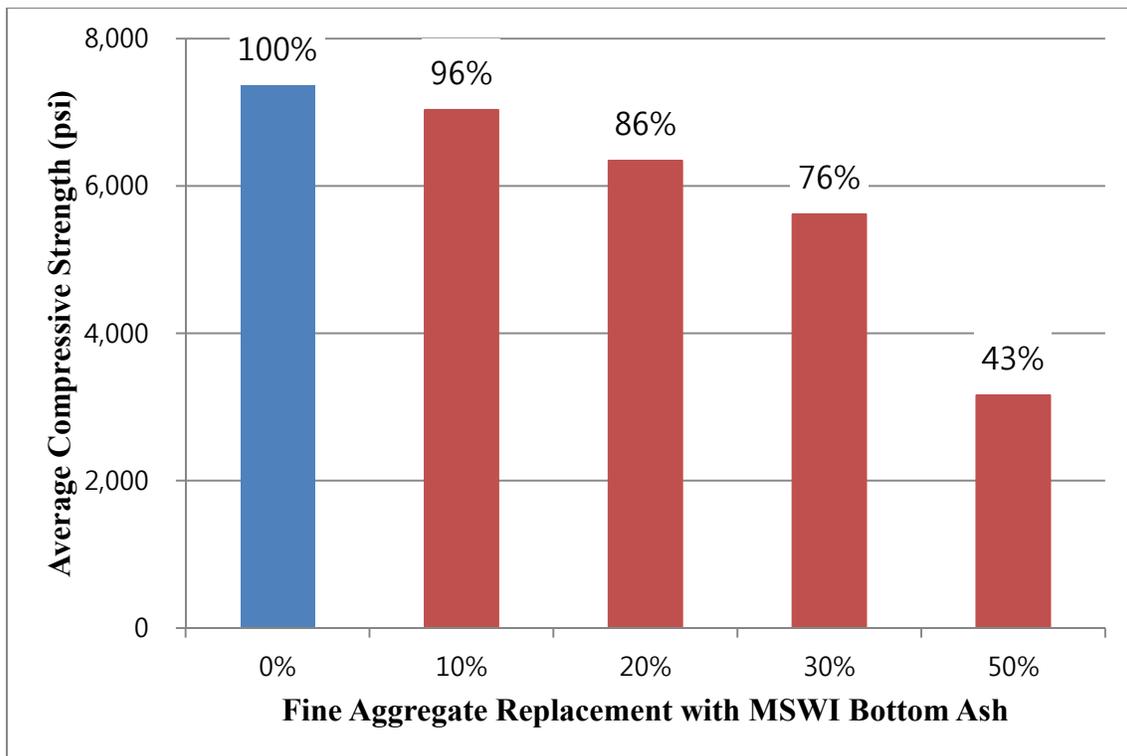
Figure 5.5: Compressive strengths of concrete specimens with different replacement ratios of BA with sand

Figure 5.6 shows the representative failure mode of each concrete specimen during the compressive strength test. Control concrete and R-10 showed explosive mode of failure with crack propagation through the coarse aggregate itself rather than through the cement paste. R-20 specimens showed several columnar cracks all around the specimens. R-30 and R-50 specimens got crushed and buckled under the loading. It can be concluded that control specimen and R-10 do not have large difference in failure modes and failures occur due to the weaker aggregates rather than aggregate-paste bond. R-20 shows pure compression columnar crack failure which includes both aggregate and aggregate-cement bond failure. From this analysis, it is evident that as BA content is increasing, the cement paste-aggregate bond is getting weaker and eventually fails before the failure of aggregate.

(a) Control

(b) R-10

(c) R-20

(d) R-30

(e) R-50

Figure 5.6: Failure modes of concrete samples with 0%, 10%, 30% and 50% BA replacement

5.7. Absorption Capacity

Figure 5.7 shows the weight increase ratio of concrete specimens by absorbing water for over 30 days. The absorption rates were decreased for all the specimens approximately after 3 days. The control concrete showed the lowest amount of absorption which indicates that the control specimen is least permeable. Absorption of R-10 after 5 days of testing was 30.6% higher than that of control concrete specimen. R-30, being 44.9% higher than control concrete, shows the highest absorption capacity among the specimens. R-50 and R-20 shows almost identical absorption. Although R-50 possess the lowest density among the specimens (Table 5.3), which indicate larger number of pores as seen in Figure 5.4 and can be resulted in higher permeability, the absorption data does not support that assumption. This is most like due to the lack of consistency of the concrete mix. R-50 contains large number and large sizes of pores and this may eventually lead to the decrease in contact area for the water to percolate through the specimen. Hence, the absorbed mass of water after three days of testing is lower than the amount it would have absorbed if the contact area was uniform.
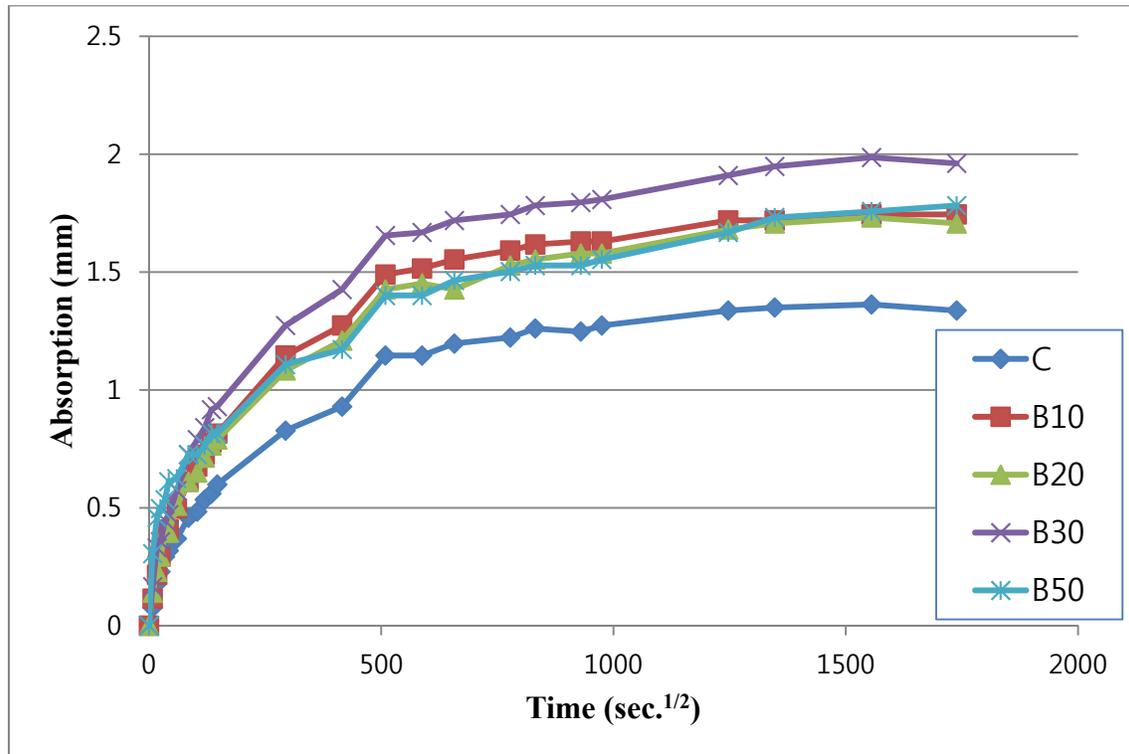
Figure 5.7: Absorption capacity for concrete specimens with time

5.8. Summary

MSWI BA was used as partial replacement for fine aggregate in concrete with various proportions. A series of tests was carried out in order to evaluate properties of concrete incorporated BA and the conclusions obtained through the experiments can be summarized as follows:

- The density of BA concrete decreased with increase in BA/sand ratio due to the lower specific gravity of BA and larger amount of air content produced.

- The 28-day compressive strength of concrete with 10% replacement was comparable to the control concrete. With further increasing amount of BA content, however, the strength was decreased and the variability and spreading of compressive strength also increased. While concrete with 20% ash replacement exhibited compression mode of failure, concrete with 30% and 50% replacement crushed by detachment and spalling of cement paste-aggregate bond.

- The absorption capacity of the control concrete specimen was lowest. Specimens with 30% of ash addition showed the highest absorption with 45% higher absorption than that of the control concrete. The low absorption of specimen with 50% replacement could be attributed to the small contact area due to the presence of considerably large pores on the surface.

- 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 BA content.

6.   CHARACTERIZATION OF MSWI BOTTOM ASH WHEN USED AS FINE AGGREGATE REPLACEMENT IN HMA

6.1.   Introduction

This chapter presents the study on evaluation of mechanical performance of hot-mix asphalt (HMA) containing different amounts of municipal solid waste incineration (MSWI) bottom ash (BA) and also optimum binder content for the asphalt mixture containing the optimum BA. The BA was used as replacement of fine aggregate which is smaller than sieve No. 4 (4.75 mm). The Marshall mix design was used for the specimen preparation and the HMA specimens were prepared by replacing the virgin aggregate with 10, 20, 30 and 40 % of BA by the total weight of the virgin fine aggregate. As performance tests of the mixture, the Marshall Stability and flow test and indirect tensile (IDT) test were used. Details of testing procedure as well as testing results are presented herein.

6.2.   Materials

The binder grade used in this research was PG 67-22, which is the most commonly used asphalt binder in the state of Florida. The asphalt binder was supplied by Mariani Asphalt Company (Bradenton, FL). The physical properties of the asphalt binder are summarized in Table 6.1.

Table 6.1: Physical properties of the asphalt binder

Test	Test method	Specification	Test results
Rotational viscosity @ 135 ºC, 20 rpm spindle # 21	T 316	3.0 Max	0.465 Pa.s
Rotational viscosity @ 165 ºC, 20 rpm spindle # 21	T 316	3.0 Max	0.128 Pa.s
Dynamic shear (G*/sin δ, 10 rad/s)	T 315	1.0 min @ 67 ºC	1.09 kPa
Ring and ball soft point	T 53	-	54 ºC
Penetration @ 25 ºC	T 49	-	59 dmm
Flash point	T 48	230 ºC	344 ºC

(note: Pa.s = pascal-second; 1 dmm = 0.1 mm)

The virgin aggregate used in this study was limestone obtained in Orlando. Limestone aggregate was supplied by CEMEX Co. (Orlando, FL) with a maximum size of 25 mm. The sand was also limestone by fracturing the bigger particles.

The BA appears a grayish light-weight, porous and absorptive material. A visual inspection of the ash indicated that it contained small amounts of unburned organic material such as chunks of broken glasses, metal and papers which was separated manually before sieving. The photograph

of BA sample 'as is' is shown in Figure 6.1. The BA that passes sieve No. 4 (4.75 mm) was used as replacement of virgin fine aggregate in the mixture. Physical properties of MSWI BA are summarized in Table 6.2.

Figure 6.1: Visual inspection of BA aggregate

Table 6.2: Physical properties of MSWI bottom ashes

Properties	Bottom ash	Test methods
Specific gravity (oven dry)	2.20	ASTM C127 [108]
Absorption capacity, %	12.8	ASTM C127 [108]
Unit weight (oven dry), kg/m^3	2,195	ASTM C29 [109]
L.A. abrasion mass loss, %	43	ASTM C535 [110]

6.3.   Sample Preparation

6.3.1. Mix Proportioning and Mix Design

The BA was used to replace the fine aggregate in the mixture; thus the BA was sieved out and smaller than sieve No. 4 (4.75 mm) was used in this study. The aggregate was tested according to ASTM C136 and the gradation of the aggregate used in the mixture is shown in Figure 6.2. The asphalt mixture contains the BA with percentages of 0 % (control mix), 10 %, 20 %, 30 % and 40 % by the total of fine aggregate in weight. The virgin and ash aggregates were fractioned into individual sieve sizes to provide the requirement of fine aggregate, and then recombined again to meet the requirement of gradation. Table 6.3 presents the detailed information how each fraction of fine aggregate was replaced with the BA. Since the gradation of BA has the same gradation as the virgin aggregate to be replaced, the gradations of total aggregate for all HMA specimens are same.
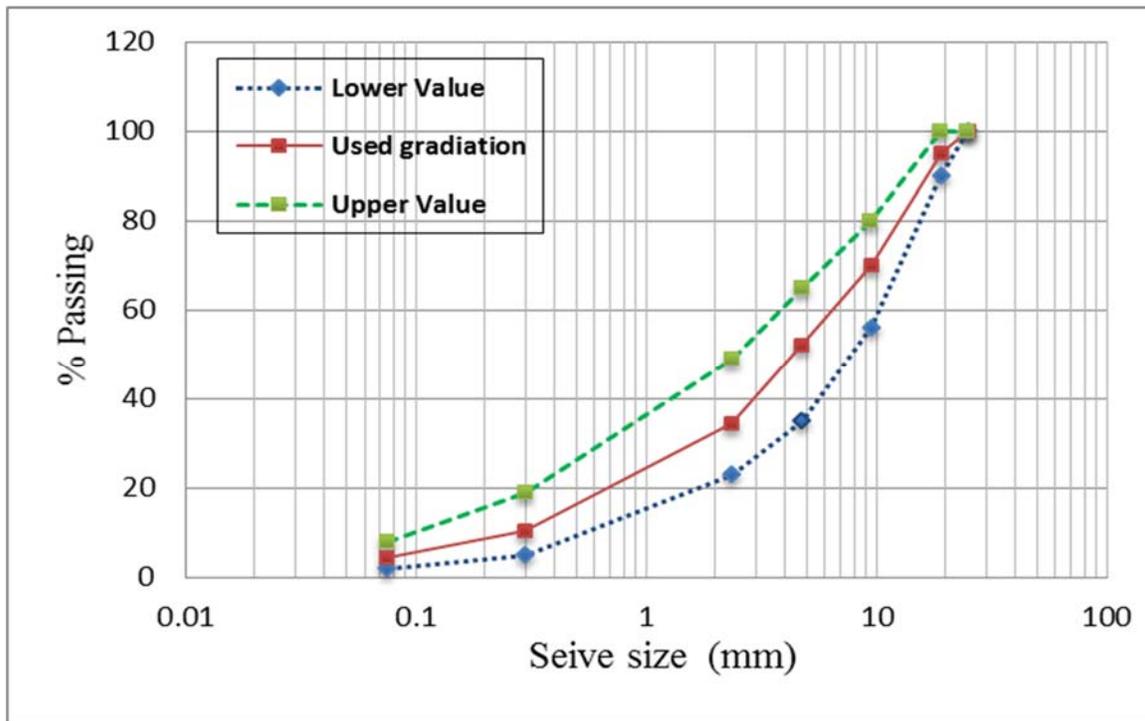
Figure 6.2: Gradation curve of used aggregate and limits

Table 6.3: Aggregate replacement with the BA of 0, 10, 20, 30, and 40%

Sieve No. (size)	Replacement ratio of BA				
	0%	10%	20%	30%	40%
	Virgin agg (g)	BA (g)	BA (g)	BA (g)	BA (g)
19 mm	58	0	0	0	0
12.5 mm	173	0	0	0	0
9.5 mm	115	0	0	0	0
# 4	207	0	0	0	0
# 8	201	20	40	60	80
# 16	109	11	22	33	44
# 30	92	9	18	28	37
# 50	75	7	15	22	30
# 100	40	4	8	12	16
# 200	31	3	6	9	12
Pan	49	5	10	15	20

(Note: Each cell represents the weight of each fraction used in the total mixture)

Due to the limited amount of BA, the researchers decided to make smaller specimens (4-in. diameter HMA); thus the Marshall Mix design was used for the sample preparation. For each proportioning, three specimens were prepared for performance tests, and the average value of three specimens is reported in later sections. Batches of specimens were prepared, each containing 1,200 g of aggregate. At first, asphalt mixture specimens were prepared with 0% BA (control mix) to determine the optimum binder content for the virgin aggregate, found to 5.7%. Then, the mixtures with 10, 20, 30, and 40% of replacement by the BA were prepared with this percentage of binder content.

6.3.2. Optimum Binder Content of Samples with Virgin Aggregate

The aggregate was heated and then mixed with different amounts of asphalt binder so that some were above and some were below the expected optimum asphalt content. In general, the optimum asphalt content ranged from 4% to 7%. The trial binder contents were 4%, 4.5%, 5%, 5.5%, 6% and 6.5% by total weight of the mixture. The samples were compacted with 75 blows on each side with the standard Marshall hammer as specified in ASTM D6927. Three samples were prepared at each binder content. A total of 18 samples were prepared (3 at each asphalt content for 6 different asphalt content).

After compaction, the samples were removed from the molds and allowed to cool. The samples were weighted dry in air (W_D), allowed to soak 3 minutes in water, and weighted while submerged in water (W_{sub}), removed from the water, blotted dry, and again weighted in air (W_{SSD}).

The bulk specific gravity of the sample G_{mb} is then determined by:

$$G_{mb} = \frac{W_D}{W_{SSD} - W_{sub}} \tag{6.1}$$

The volume of sample in ml is equal to W_{SD} - W_{sub} when weighted in grams.

The Voids in Total Mix (VTM) are determined for each sample by comparing the average bulk density for each asphalt content to the theoretical max density (TDM) for that asphalt content. Max theoretical specific gravity of the mixtures were conducted following ASTM D2041.

$$VTM = \left(1 - \frac{G_{mb}}{G_{mm}}\right) 100 \tag{6.2}$$

Where G_{mb} is the specimen bulk density and G_{mm} is the max theoretical specific of the mixtures.

The voids filled with asphalt (VFA) are determined by the following equation:

$$VFA = \left[\frac{VMA - VTM}{VMA}\right] 100 \tag{6.3}$$

After the samples were weighted in air and water, the samples were then tested for stability and flow according to ASTM D6927. After all data was collected, plots were developed to show the relationship between the various properties and asphalt content as shown in Figure 6.3. Each data point on the figures represents the average of three specimens. For the selection of the optimum asphalt content, the specifications presented in Table 6.4 were considered.

With respect to the above graphs, the binder content at 4% void is 5.7 % of the total mix which meets the other specification criteria. This content has been used to make samples with 0, 10, 20, 30 and 40 percent ash replacement.

Table 6.4: Optimum asphalt binder specification limits

Test Property	Specification	Results
Marshall Stability (lbf)	1500 minimum	3005
Flow 0.01 inch	8-16	14.8
Void in Total Mix (percent)	3-5	4
Void filled with Asphalt Cement	70-80	78
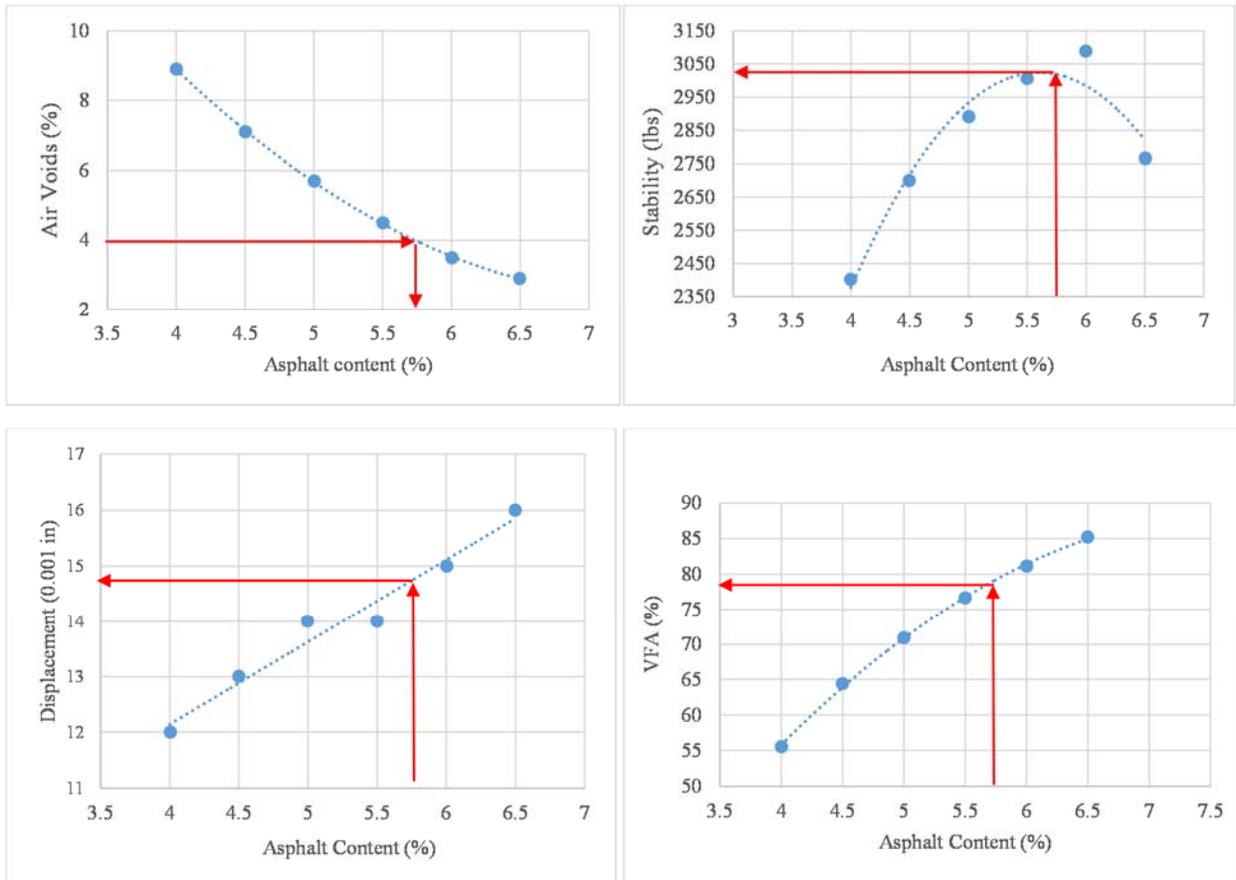
Figure 6.3: Graphical Illustration of determining optimum asphalt binder of virgin aggregate by Marshall Method

6.4. Results of Performance Tests

6.4.1. Marshall Stability and Flow Test

The Marshall Stability and Flow test has been conducted according to ASTM D 6927 with 4-in. diameter samples. The testing setup is shown in Figure 6.4. The "Stability" and "Flow" values obtained from the Marshall test indicate the strength and deformation characteristics of HMA samples, respectively. For each set, three specimens were prepared, and testing results were averaged. Specimens were placed in a water bath at 60℃ for 30-40 min and then loaded at a ratio of 50.8 mm/min (2 in./min.) and the stability and flow values were recorded. Laboratory compaction was prepared by using 75 blows of the Marshall hammer per side. The results of the stability and flow are shown in Figures 6.5 and 6.6, respectively.
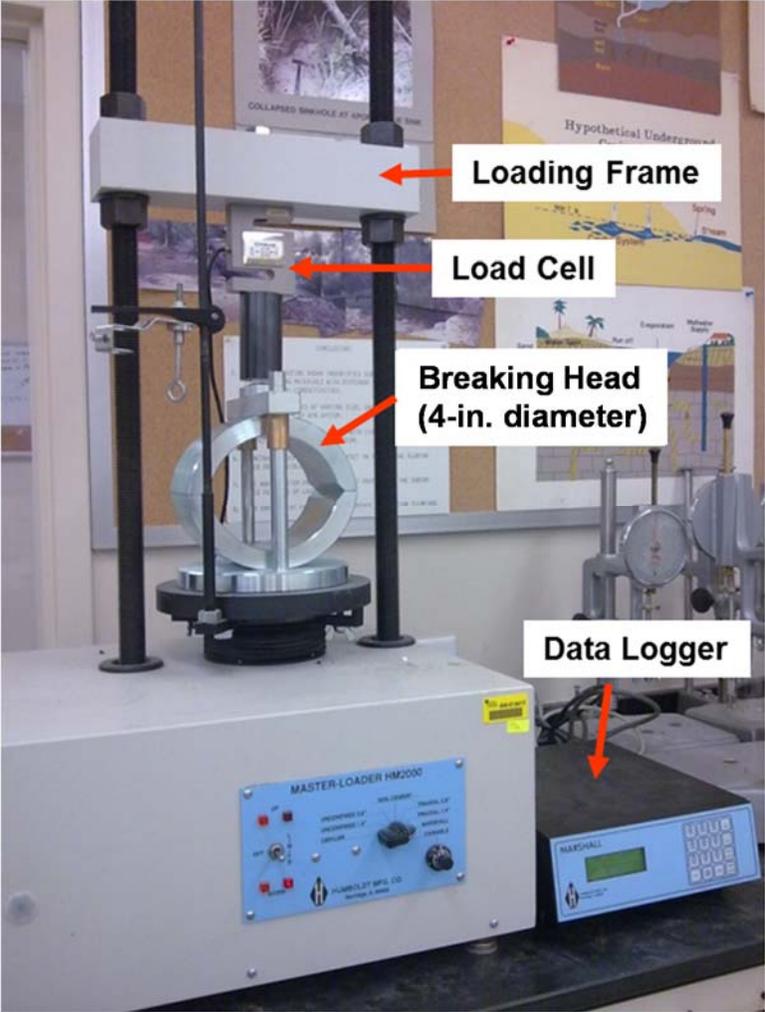
Figure 6.4: Marshall test apparatus and 4-in. breaking head at the UCF geotechnical laboratory
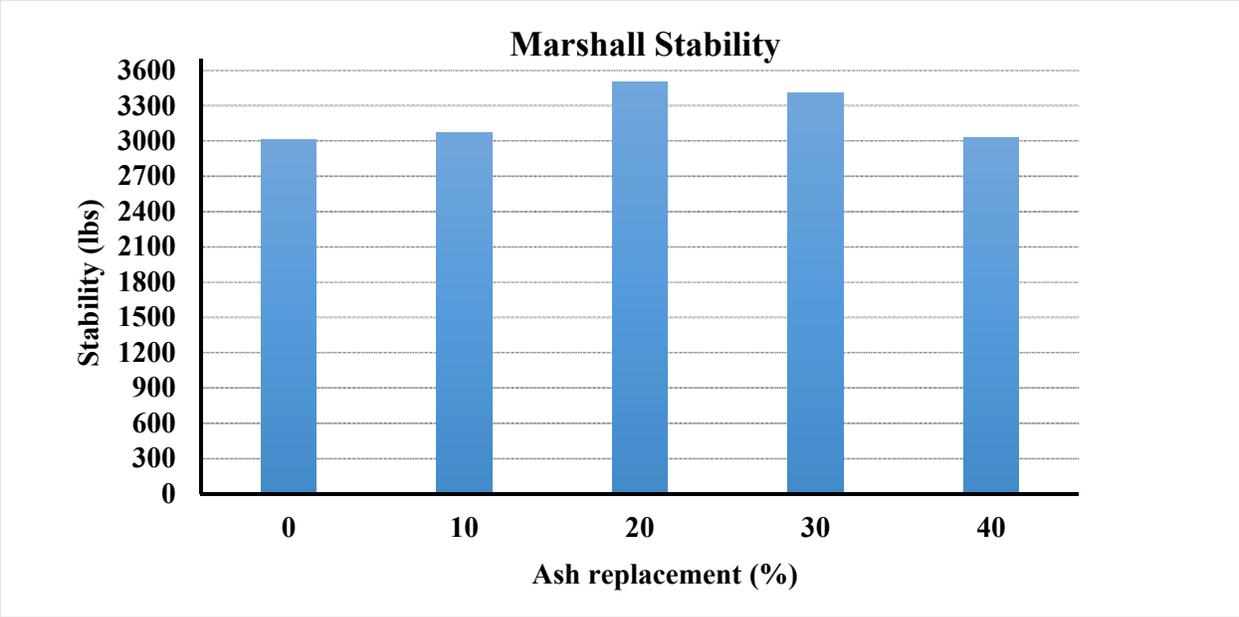
Figure 6.5: Marshall stability result
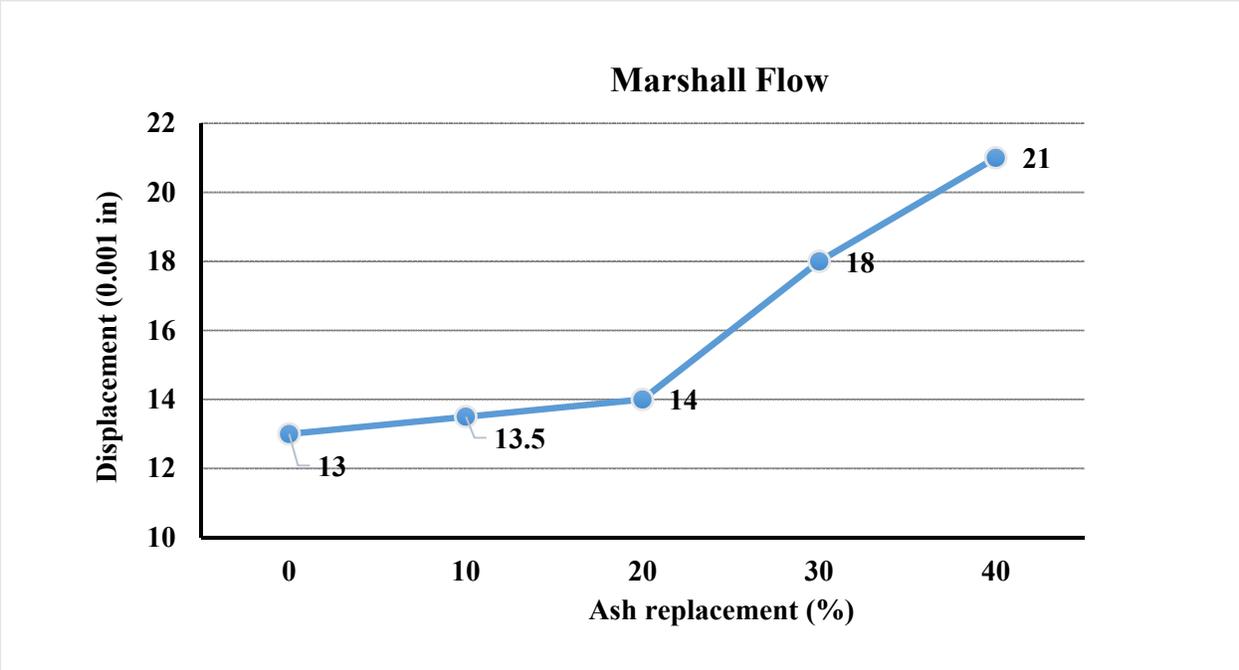
Figure 6.6: Flow test result

As the content of bottom ash in the mixture increases from 0 to 10, 20, 30 and 40 percent the Stability increased 2, 16.5, 13.3 and 0.5 percent and the Flow increased 4, 8, 38 and 61 respectively. Due to the particle surface roughness of the bottom ash aggregate, the stability increased from 0% to 20% replacement, but the lack of binder content caused decreasing in stability after 20 % replacement.

6.4.2. Moisture Susceptibility Test

The moisture susceptibility test, also known as Lottman test (ASTM D4867), was conducted to measure the effect of water on the tensile strength of HMA paving. Following the test procedure, each set of samples is divided into two subsets with approximately same air voids (7±1 %.). One subset is maintained dry while the other wet-conditioned. Test temperature is at 25 ^{0}C. The procedure of moisture susceptibility test is shown in Figures 6.7 through 6.9. Dry samples were sealed and kept in water bath at 25^{0}C for adjusting the temperature. Wet samples, after partially saturation (see Figure 6.7) had to be soaked in distilled water at 60^{0}C for 24 hours (see Figure 6.8), and soaking in a water bath at 25^{0}C for an hour (see Figure 6.9) for adjusting the temperature. Strain rate was at 2 (in./min). Indirect tensile strength of each sample is determined using the Indirect Tensile Test (IDT) device. Calculation formula is as follow:

$$S_t = 2P/\pi tD \ (psi) \tag{6.4}$$

where, S_t is tensile strength (psi), P is maximum load (lbf), t is specimen thickness (in.), D is specimen diameter (in.)

$$TSR = (\frac{S_{tm}}{S_{td}})100 \tag{6.5}$$

where TSR is tensile strength ratio (%), and S_{tm} and S_{td} are average tensile strength of the moisture conditioned subset and the dry subset, respectively (psi).

Several state Departments of Transportations (DOTs) require using anti-strip agents as an additive in HMA pavements. Florida specifications allow adding anti-strip agent with 0.25% to 0.50% by weight of asphalt binder. To clearly observe the impact of ash in HMA on its moisture damages, no anti-strip agent was used to the mixtures. The results are shown in Figures 6.10 and 6.11. Each data on the figures represents the average of three specimens.

Figure 6.7: Partially saturating wet-subsets using vacuum

Figure 6.8: Wet subsets, soaking in distilled water at 60 ºC for 24 hours

Figure 6.9: Wet subsets, adjusting the temperature by soaking in a water bath at 25 ºC
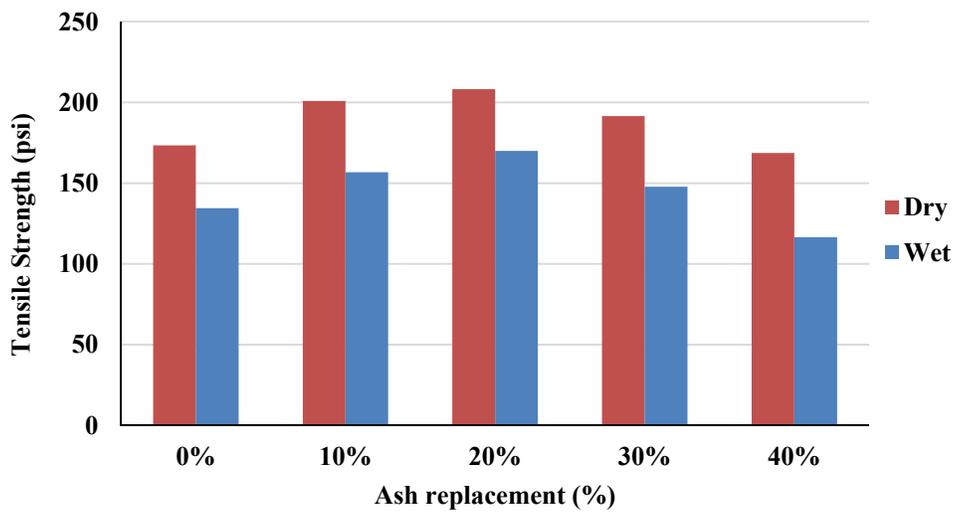
Figure 6.10: Tensile strength of dry and wet samples
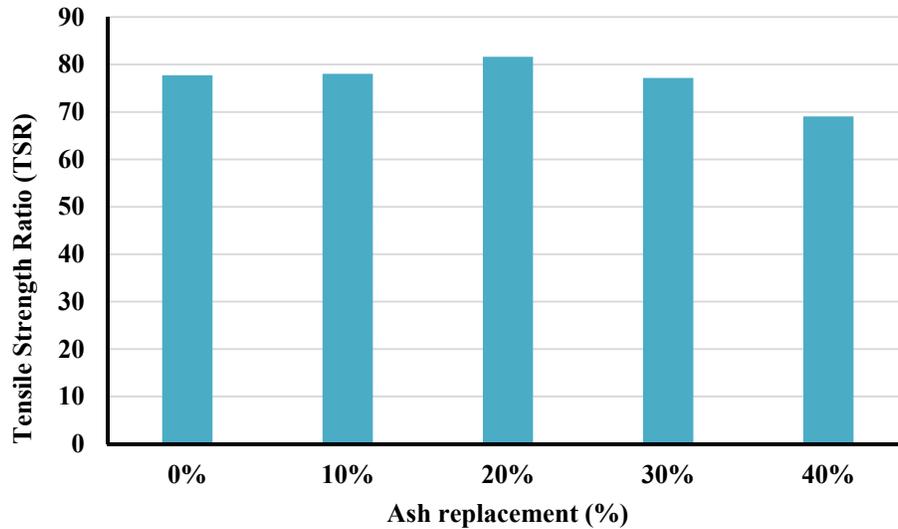
Figure 6.11: Tensile strength ratio

6.4.3. Evaluation of IDT 'Stiffness'

The results of IDT testing show that the strength increased up to 20% BA and decreases after that ratio. The results obtained from IDT testing show the same trend as the results of the Marshall stability test. The stiffness of the mixtures was also evaluated as the percentage of BA increased in the mixture. The researchers propose a new stiffness index, which is the slope of load and displacement from IDT testing. The slope determined from the load-displacement curve can be referred as IDT 'stiffness' hereafter and denoted as 'k' value.

Figure 6.12 indicates the load-displacement curves obtained from IDT testing (tested under dry condition) with all the HMA specimens that contain 0, 10, 20, 30, 40 percent of BA. Steeper slopes indicate stiffer materials which lead to higher strength. As seen in Figure 6.12, the 'k' value increases with increasing the BA content until 20%, and it decreases after 20%. Each load-displacement curve was recorded and the IDT 'stiffness' was obtained. The detailed procedures to construct load-displacement curves and to determine the k values are presented in Appendix A. The determined k values for the 0, 10, 20, 30, and 40% BA are presented in Figure 6.13.
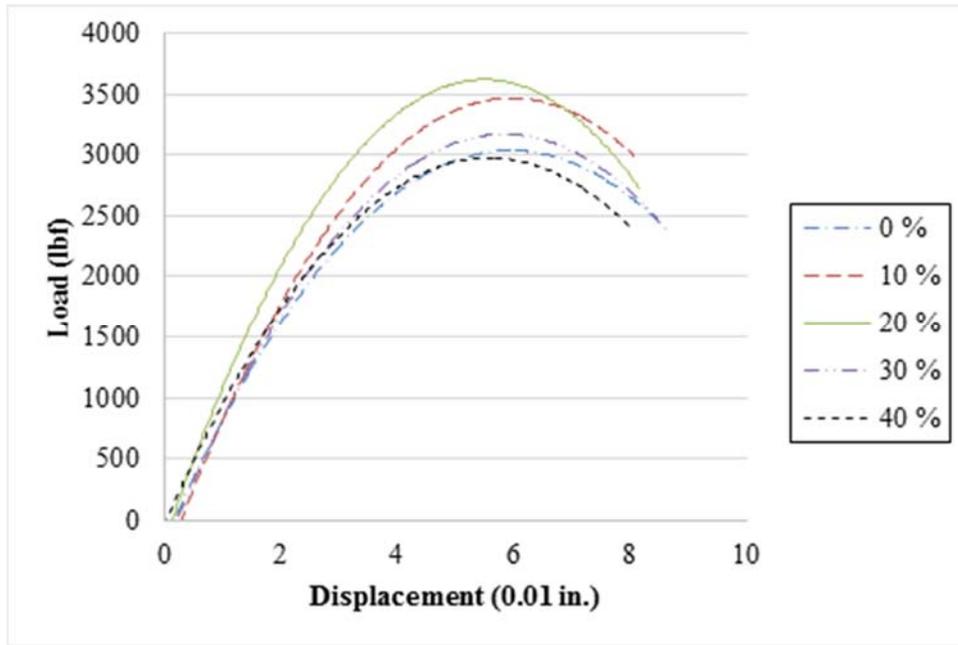
Figure 6.12: Load-displacement curve for dry samples
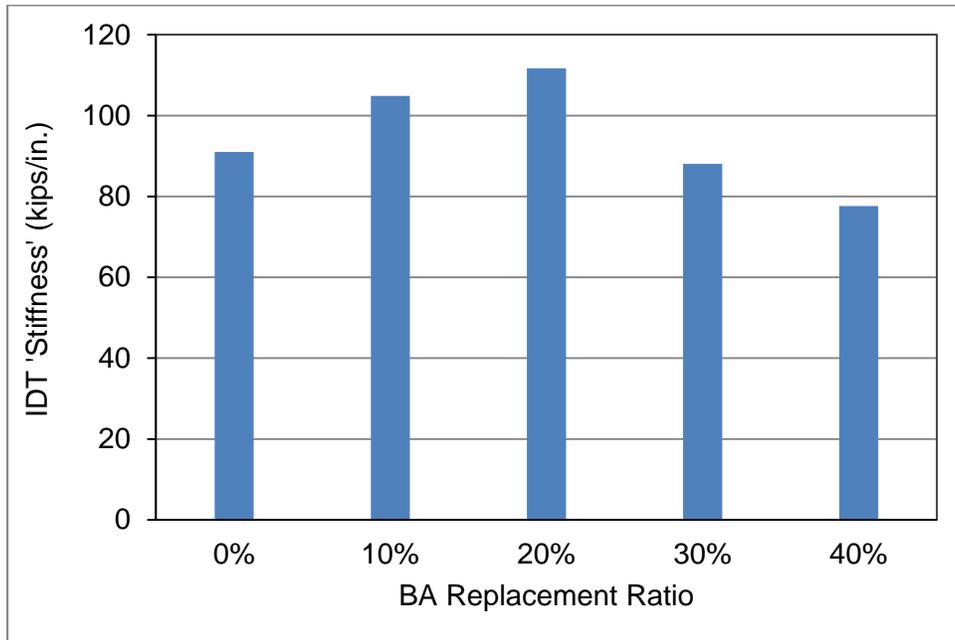
Figure 6.13: IDT 'stiffness' for the HMA specimens

6.5. Optimum Asphalt Binder for the 20% BA

According to the Marshall and moisture susceptibility tests, the optimum content of BA was determined as 20% replacement of fine aggregate in the mixture. Since the BA is lightweight aggregate that absorbs higher asphalt due to higher porosity, it may require higher amount of virgin asphalt to maintain optimum film thickness. Therefore, it is necessary to find out the optimum binder content for the 20% replacement of BA. The Marshall mix design was used and the procedure to find out the optimum binder content is shown in Figure 6.13. The procedure involves stability, air voids, flow and VFA as criteria for determining the optimum binder. As seen in the figure, the optimum binder content has been determined at 6.8 % by the total weight of the mix. As compared in Figures 6.3 and 6.13, the optimum binder contents for the specimens of 0% BA and 20% BA are 5.7% and 6.8%, respectively. In other words, increasing the BA up to 20% in the total aggregate requires greater amount of binder content. Although the optimum binder content is 6.8% for the 20% BA, 5.7% binder content still meet the criteria of stability, air voids, flow and VFA.
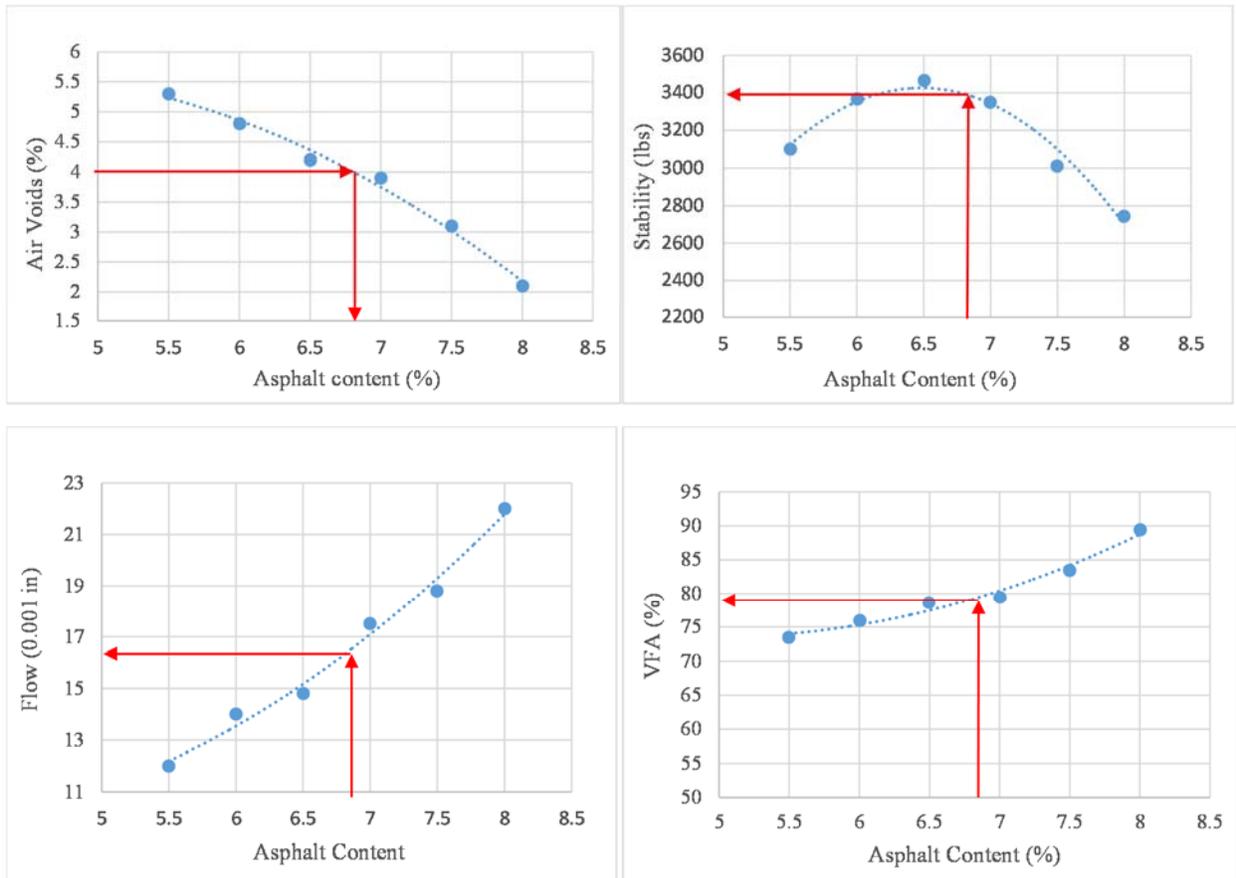
Figure 6.14: Graphical illustration of determining optimum asphalt binder at 20% BA replacement by Marshall Method

Table 6.5: Optimum asphalt binder at 20% BA replacement

Test property	Specification	Results
Marshall Stability (lbf)	1500 minimum	3080
Flow 0.01 inch	8-16	16.2
Void in Total Mix (percent)	3-5	4
Void filled with Asphalt Cement	70-80	78

6.6. Summary

This study analyzed the mechanical performance of asphalt mixtures containing different amounts of MSWI BA as an aggregate replacement. 10, 20, 30 and 40% by the total weight of the virgin fine aggregate was replaced by the BA which has same gradation of the virgin aggregate. Marshall Stability and flow test and moisture susceptibility were conducted on the MSW-BA asphalt mixtures to evaluate the engineering properties of the different mixes. It was found that by increasing the replacement ratio from 0 % to 20%, stability increased but 30% and 40% BA replacement lead to decreasing the stability. Same trend was observed in tensile strength at moisture susceptibility test. Both test results indicated that as a fine aggregate replacement in mixture, 20 % can be good candidate for the optimum replacement ratio. Flow test results show that displacement keep increasing by increasing the BA replacement. The optimum asphalt binder with virgin aggregate found at 5.7 % of the total mix while for the 20% BA replacement it was observed at 6.8 %.

7. SUMMARY AND CONCLUSION

7.1. Summary

Florida regulations have established a 75 percent statewide recycling goal to be achieved by 2020. Recovery and recycling of waste-to-energy (WTE) fly ash and bottom ash offer significant potential contribution to meet this goal. The objectives of this study were to evaluate the benefits of using WTE ashes as road construction materials in hot mix asphalt (HMA) and Portland cement concrete (PCC) with emphasis on their applications in Florida.

Chapter 2 provides the background and literature review regarding current management practice, existing regulations, and environmental consequences of MSWI ashes utilization, worldwide and nationwide in the U.S.

In Chapter 3, 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 ashes and to determine their contents. To evaluate the main side effect of ashes 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.

In Chapter 4, efforts were made to characterize the influence the ashes on engineering properties of cement paste specimens when part of Portland cement was replaced with ground and sieved MSWI ashes. Cement paste cylinders were cast with various amounts of mineral additions and their strength and durability were investigated.

In Chapter 5, fine aggregate was replaced with MSWI bottom ash in accordance with existing American Society for Testing and Materials (ASTM) standards and the feasibility of the use of the ash in concrete was evaluated. Bottom ash replaced concrete was subjected to mechanical property and durability tests according to ASTM standards.

In Chapter 6, the effects of MSWI bottom ash in HMA were studied. The fine aggregate (smaller than sieve no. 4) was replaced with the bottom ash at different replacement ratio of 0%, 10%, 20%, 30%, and 40%. Performance tests used were the Marshall stability and flow test and moisture susceptibility test. For the selected ratio of bottom ash, the optimum binder content was also investigated.

7.2. Conclusions

Based on the results of this study, the following conclusions and recommendations are made and summarized below.

7.2.1. Concrete Application

- Many countries, especially European and Asian have already successfully implemented systematic approach towards the beneficial utilization of MSWI ashes. Although research and demonstration projects ensure the beneficial utilization of MSWI 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 MSWI 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.

- Both MSWI fly ash and bottom ash 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.

- 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.

- The density of bottom ash concrete decreased with increase in bottom ash/sand ratio due to the lower specific gravity of the ash and larger amount of air content produced.

- The 28-day compressive strength of concrete with 10% replacement was comparable to the control concrete. With further increasing amount of BA content, however, the strength was decreased and the variability and spreading of compressive strength also increased. While concrete with 20% ash replacement exhibited compression mode of failure, concrete with 30% and 50% replacement crushed by detachment and spalling of cement paste-aggregate bond.

- 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.

7.2.2. Asphalt Application

- A comprehensive literature study regarding the use of MSWI BA in HMA has concluded that using the BA may require higher amount of binder content because the BA involves lower density and specific gravity as well as higher absorption compared to other types of aggregates such as granite, dolomite, and limestone.

- The BA was used to replace the fine aggregate (passing sieve no. 4) in HMA. The results of the Marshall Stability and flow test show that the highest stability exhibited at 20% replacement of BA while the flow increases with increasing the BA content.

- Indirect tensile (IDT) testing was conducted for evaluating the moisture susceptibility. Testing results show that both moisture- and dry-conditioned specimens have the optimum amount of BA at 20%; the tensile strength increases until 20% BA and decreases after that. The highest tensile strength ratio (TSR) was also found at 20% replacement of BA.

- For the 20% BA replacement, the optimum binder content was found at 6.8%. Considering the optimum binder content at 5.7% for the control mixture, replacing 20% of BA requires higher amount of asphalt binder.

7.3. Recommendations

7.3.1. Concrete Application

For the cement replacement, the specimens with 10% and 30% replacement exhibited about half of the compressive strength of the control specimen. The cement paste with 20% cement replacement, on the other hand, exhibited approximately equal compressive strength, compared to that of the control specimen.

For the fine aggregate replacement, it is also recommended to replace up to 20% depending on the application. According to the experimental investigations, concrete with 20% ash replacement exhibited compression mode of failure. For the concrete specimens with 30% and 50% replacement, on the other hand, specimens were crushed by detachment and spalling of cement paste-aggregate bond.

Following detailed specifications are proposed when replacing cement or aggregate in concrete.

- Replacing coarse aggregate with bottom ash may not be recommended. Some of the reasons are: (1) the strength of bottom ash is significantly less than that of typical coarse aggregate used in concrete, (2) when bottom ashes are ground or sieved through small particles, their porosity could be reduced; however, when used as coarse aggregate, workability will be considerable reduced due to their high porosity, and (3) it is difficult to comply the ASTM coarse aggregate gradation with bottom ash, especially in the large size region.

- The particle size of the ash should be compatible with the material to be replaced. For example, bottom ash is recommended to be ground and sieved through particles size less than 75 μm for the cement replacement application, not only to have similar particle size compared to the cement, but also to ensure the micro-filling effect. For the fine aggregate replacement, the ashes would be ground (if necessary) and sieved to comply with the ASTM specification of fine aggregate gradation.

- 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 recommended to chemically characterize the ashes prior to utilize them in concrete. For example, metallic aluminum content in the ashes can be a 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.

- Less water content (i.e., lower water-to-cementitious materials ratio) is likely to reduce the hydrogen gas evolution effect, due to the less reactivity. However, it is expected to be

neither practical nor effective.

- The use of plasticizer is recommended. Low consistency of concrete and the large pores created on the surface may be avoided by the use of plasticizer when mixing concrete.

- In order to utilize the MSWI ashes as supplementary cementitious materials in concrete, development of material processing technology for MSWI ashes would be necessary prior to using them in concrete. For example, proper treatments of MSWI ashes (e.g. chemical treatment) will be able to eliminate the aluminum content; thus, detrimental effects in concrete can be reduced.

7.3.2. Asphalt Application

The MSWI BA has been used to replace fine aggregate in HMA and performance tests were conducted. The recommendations for the HMA application of MSWI BA are summarized as below.

- The MSWI BA is much more brittle than normal limestone aggregates. The L.A. abrasion value of the BA is 43 while typical Florida's limestone aggregates show their abrasion values in the low to mid 30's; granite aggregates can be less than 20 [133]. In addition, large portions of the MSWI BA are smaller than sieve no. 4 (4.75 mm). Thus, using the BA as replacement of fine aggregate in HMA is recommended.

- When 20% of fine aggregate in HMA was replaced with the MSWI BA, the strength, stiffness, and moisture resistance were maximized. Thus, the optimum proportioning to maximize the strength performance of HMA would be at the 20% replacement.

- Increasing the replacement ratio of BA increases the optimum binder content; 0% and 20% replacement ratio of BA resulted in the optimum binder content of 5.7% to 6.8%, respectively. Additional binder of 1.1% is required to maintain the optimum performance of the mixture. Thus, for the selected 20% replacement of BA, it is recommended to use the binder content of 6.8%.

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APPENDIX A: IDT 'STIFFNESS' MEASUREMENTS
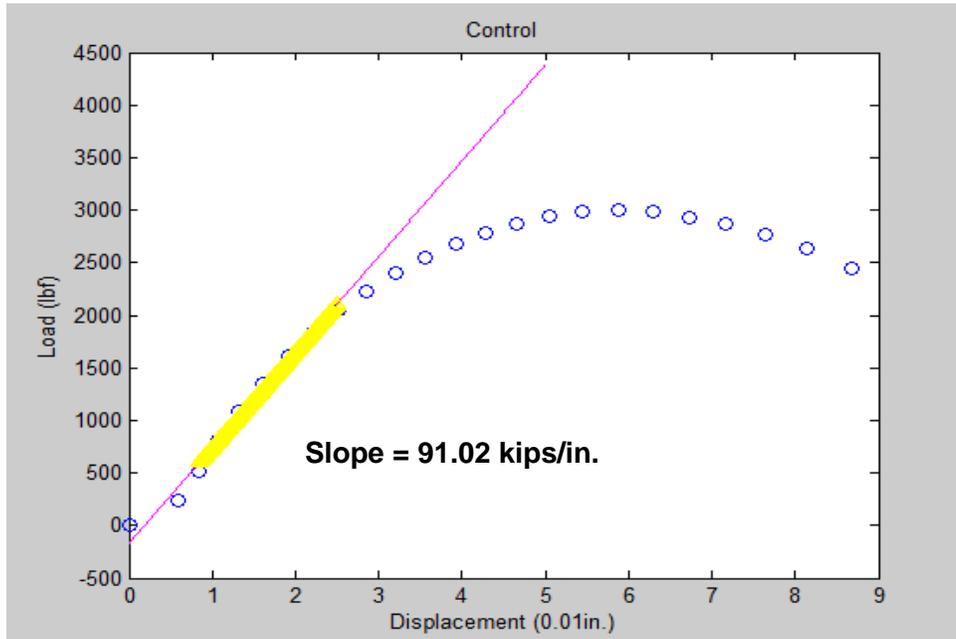
Figure A.1: IDT 'stiffness' for the control mixture (0% BA)
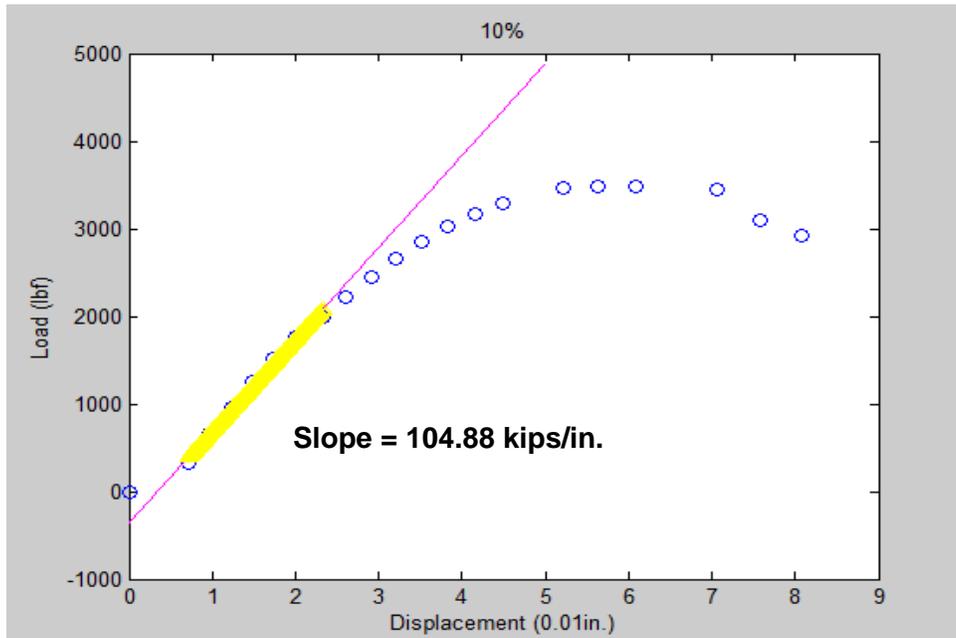
Figure A.2: IDT 'stiffness' for the mixture with 10% BA
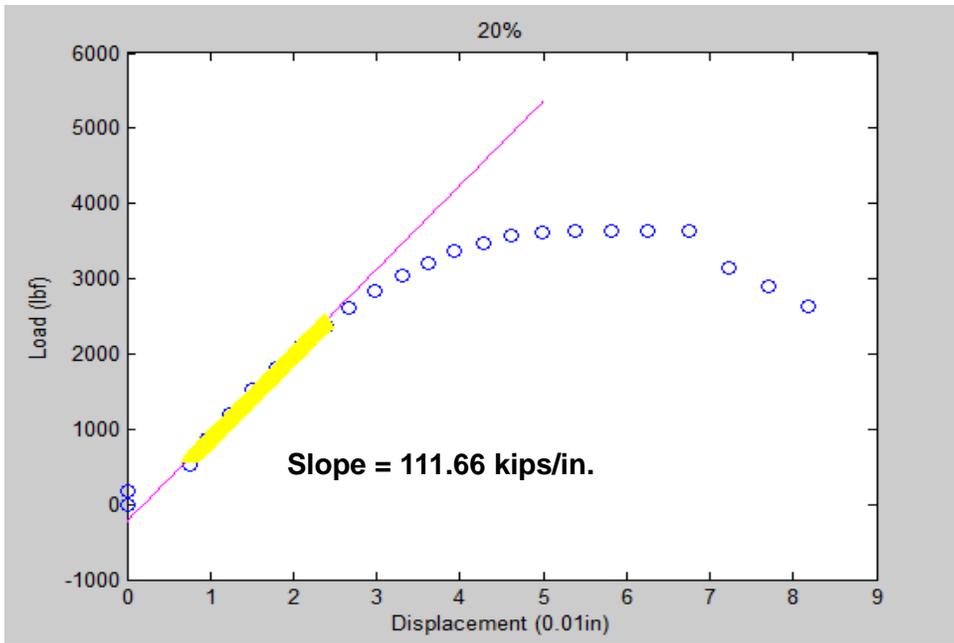
Figure A.3: IDT 'stiffness' for the mixture with 20% BA
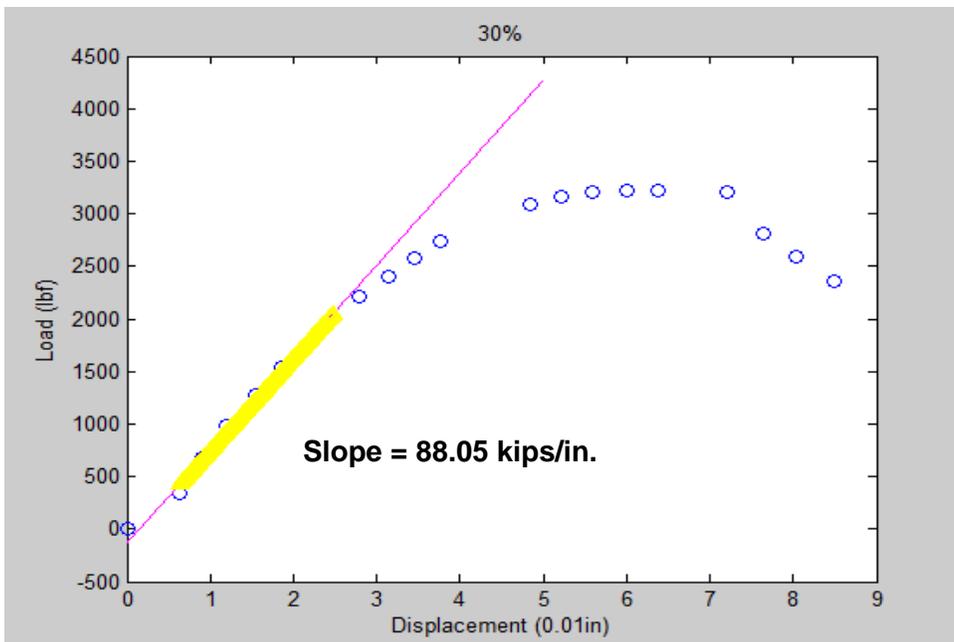
Figure A.4: IDT 'stiffness' for the mixture with 30% BA
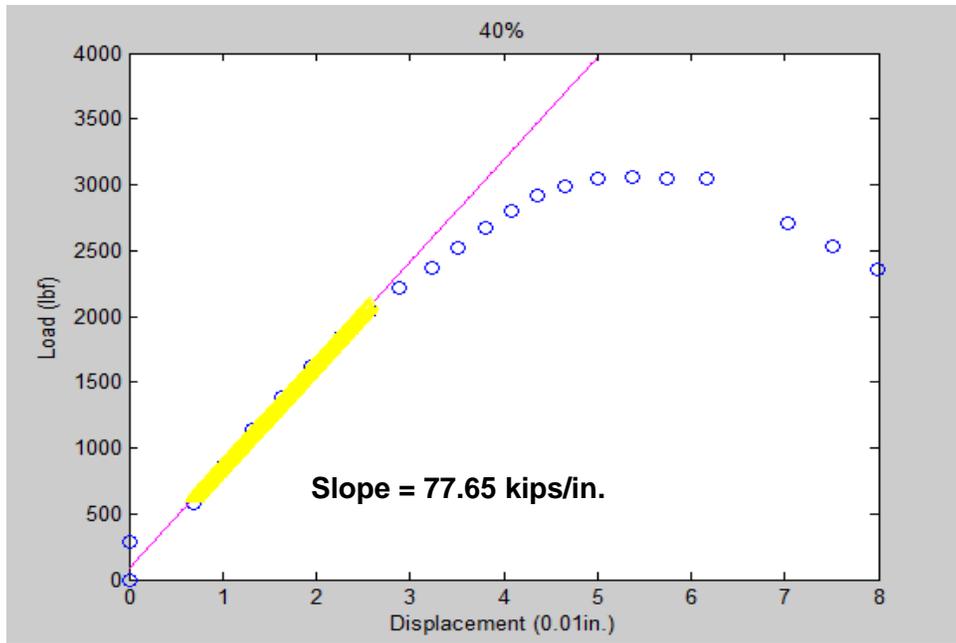
Figure A.5: IDT 'stiffness' for the mixture with 40% BA