

CHAPTER 2

LITERATURE REVIEW

2.1 Characterization of MSWI Fly Ash

MSW incinerator generates solid residues, which represent about 10% by volume and 25-35% by weight of wastes to be incinerated. Solid residues from municipal solid waste incineration (MSWI) are mainly bottom ash and fly ash. Bottom ash is exclusively or partially combusted material that passes through or is discharged from the combustion grate. It is collected and quenched with water in an ash slot before flowing into a storage ash well. After cooled down, the ash is loaded by an overhead crane into a truck to transport away for dumping at an ash sanitary landfill.

Fly ash defined as particulate matters is captured from flue gas by air pollution control (APC) system. These residues involve small components carried over from combustion chamber and volatile elements in flue gas that condense during cooling down process. In the mass flow of a typical mass-burn incinerator fed with all MSW fractions, about one third of solid waste remains as solid residues, while the rest is converted into gaseous compounds and subsequently released into the atmosphere. The weight of fly ash derived from the Phuket's plant averages 3.2% of the feedstock and approximately 11.6% of the total solid residues.

In order to carry out the research and thoroughly understand the behavior of MSWI fly ash, it is essential to concentrate on worthy related information from preceding researches. The basically principal consideration is the properties of MSWI fly ash that are not only physical and mechanical but also chemical and phase compositions.

Mangialardi et al. (1998) ascertained the main characteristics of MSWI fly ash from industrial regions with a view to utilizing the material for making concrete. Their fly ash derived from mass-burn incinerator and collected by electrostatic precipitators (ESPs) was indicated that mass density, determined by pycnometer method, is 2.39 g/cm^3 , approximately 20-30% lower than that of cement. They also studied granulometry of the MSWI fly ash using a stack of ASTM sieves and a laser diffraction analyzer. The results showed that eighty percent of the fly ash passed through a 250- μm screen. Remond et al. (2002) used the same test setup and found that fly ash particles were in form of powder and had a dimension between 50 and 500 microns. Hamernik and Frantz (1991a) reported that mass-burn fly ash met the fineness limit of the percent retained on a standard sieve No. 325 according to ASTM C618; in contrast to their RDF's result, which showed a significant greater percentage of coarse particles. They identified that MSWI fly ash particles retained on a sieve No. 325 were chiefly calcium and carbon particles that result in reactivity.

Bentz et al. (1999) investigated a variety of scanning electron microscope (SEM) and X-ray images of a cementitious material to quantitatively characterize its complex microstructure. MSWI fly ash particles were irregular in shape and tended to be multi-phase in nature. Moreover, a high concentration of calcium chloride could be observed by the strong signals of Ca and Cl in the correspondence with X-ray images. As described by Hamernik and Frantz (1991a) and Remond et al. (2002), MSWI fly ash particles had various shapes: full or hollow spherical particles, long or flat particles, very porous particles, etc. No predominant shape could be distinguished as opposed to coal fly ash, which is usually composed of spherical particles and smooth textures. Round particles appear to be ideal with respect to workability of concrete since they act as a lubricant between the angular and irregular cement particles. The difference in morphological features is probably associated with feeding materials, pre-combustion treatment, and combustion conditions.

Richers and Birnbaum (1997) investigated specific surfaces and pore volumes of MSWI fly ash by application of the Brunauer, Emmett, and Teller (BET) surface method and sorption measurement, respectively. They reported that BET surfaces directly depended on carbon content of the ash. Besides, pore volume grew linearly

with the specific surface of the ash. Therefore, the attention for these physical characteristics of MSWI fly ash is critically needed for prediction the influence of fly ash on hydration chemistry, microstructure development, and properties of cementitious system.

Not only physical properties but chemical and mineralogical compositions influence performance of MSWI fly ash-cement concrete. Chemical compositions of MSWI fly ash can be used to predict the behavior of fly ash in environment and in its application. Major constituents of MSWI fly ash ($\geq 10,000 \mu\text{g/g}$) are: Cl, Si, S, Ca, Na, Al, K, Zn, P, Pb, and Mg. Minor constituents ($1,000 - 10,000 \mu\text{g/g}$) include: Fe, Ti, Sn, Cu, Ba, and Sb. Cr, Cd, Mn, Sr, Rb, Ag, Zr, Ni, Se, Mo, Ti, Th, and U are present in concentrations lower than $1,000 \mu\text{g/g}$. It was observed that Na and K were present predominantly as chlorides created from chlorine in the wastes (Fermo et al., 1999 and 2000). Alba et al. (1997) studied chemical compositions of MSWI residues from facilities with different APC systems, i.e., a semi-dry scrubber and an ESP by X-ray fluorescence (XRF) method. The chemical compositions of both fly ashes did not meet specifications for the use of coal fly ash as a filling material in concrete. Their mass-burn fly ash showed high CaO content, compared with data reported in the same type of facilities. This can possibly be attributed to fed wastes. They also concluded that the high CaO content had been confirmed by the analysis as being a function of particle size.

Rachakornkij (2000) reported the elemental compositions of MSWI fly ashes collected from an ESP without any treatment and downstream of the ESP from dry scrubbers with complex phosphoric acid treatment. The results showed that a product of the treatment of APC residue from mass-burn system by proprietary phosphoric acid washing had low concentration of soluble constituents. This is because these soluble compounds found in surface layer of fly ash particles were leached out during treatment, while leaving kernel of particles intact. He also concluded that chlorides were present as a major condensation product on fly ash particles, such as NaCl and CdCl₂. Large amount of CaCl₂ in fly ash came from reactions in acid gas scrubbers during lime injection. This is the reason why the chloride content of APC residue was much higher than that of fly ash without scrubber residue. High concentrations of Cl

might corrode steel in reinforced concrete while high Na content might promote alkali aggregate reaction that causes cracks in concrete structures.

Heavy metals, such as lead, cadmium, mercury, arsenic, copper, and zinc detected in MSWI fly ash are usually originated from plastics, colored printing inks, batteries, rubber products, and household hazardous wastes (Tchobanoglous et al., 1993). The distribution of metals in incineration residues depends on vapor pressure of metal compounds and temperature of the different residue streams produced. Alba et al. (1997) summarized that Pb, Zn, and Cd were more concentrated in MSWI fly ash than in bottom ash. In contrast, Cu is preferentially found in bottom ash. Goldin et al. (1992) reported that the following metals were present in higher levels in fly ash than in bottom ash: Al, Cd, Hg, Ni, Pb, and Zn. Arsenic was generally present high levels in bottom ash, whilst the concentrations of Ca, Cu, Cr, and Fe were comparable in both fly ash and bottom ash.

The distribution of metals among different types of MSWI residues is also influenced by operating conditions of incinerator. For instance, poor operating temperature of lower than 850°C typically results in reduced vaporization of relatively volatile metals and potentially increases carryover of particulate, including noncombustible carbonaceous materials. These operating conditions are attributable to increased volumes of captured fly ash that contains decreased metal concentrations. Goldin et al. (1992) concluded that metal concentrations in the ash reflected the process of oxidation and removal of organic components in refuse that occurred during incineration and the differences in volatility and solubility of individual elements.

In addition, Plüss and Ferrell (1991) studied the characterization of lead and other heavy metals in MSWI fly ash by microchemical analysis techniques, X-ray element mapping and image analysis methods. They revealed that the bulk of lead and most heavy metals were associated with silicate glasses of varying compositions. These metals presented as pure small particles, as pure small areas within glassy particles, and as varying amounts within or on the surface of glassy particles and other aggregates. They also investigated the formation of heavy metals in MSWI fly ash

using a semi-quantitative elemental analysis. The results indicated that Pb, Zn, Cu, Cr, Sn, Sb, and Ti presented as oxide or hydroxide forms, rather than chloride, sulfide, or carbonate forms.

Mineralogical compositions of MSWI fly ash are deemed to predict its reactions and leaching behavior. For this reason, thorough understanding of mineralogy of the ash is necessary to determine its potential utilization. Many researches have studied mineralogical characteristics of MSWI fly ash by X-ray diffraction (XRD) technique (Kirby and Rimstidt, 1993; Alba et al., 1997; Remond et al., 2002; Fermo et al., 1999; Racharkornkij, 2000). This method is used to identify compounds within a sample and to study crystalline structures by means of diffraction patterns produced when the sample is irradiated.

Halite (NaCl) and sylvite (KCl) are the predominant mineral phases in MSWI fly ash. Minor constituents are portlandite ($\text{Ca}(\text{OH})_2$), lime (CaO), hematite (Fe_2O_3), silicate, and calcium aluminate. Iron (Fe), ingersonite (Ca_2SO_4), gehlennite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), and gismondine ($\text{CaAl}_2\text{SiO}_8 \cdot 4\text{H}_2\text{O}$) are also slightly detected in MSWI fly ash. Mangialardi et al. (1998) found Ca_3SiO_3 and $\text{NaAlSi}_3\text{O}_8$ (albite) in their ESP fly ash. Relative soluble calcium sources in the MSWI fly ash are anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and calcium chloride hydroxide (CaClOH). It is important to note that sulphate can react with certain cement components to form ettringite ($\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). Its ability to absorb water and cause expansion of concrete results in the decrease in durability.

Analysis of MSWI fly ash phases using this method allows the identification of only few crystalline phases because of great complexity of patterns and numerous possible peak overlapping. For this reason, Fermo et al. (2000) investigated the MSWI fly ash leached with water and HCl solutions using XRD spectrometer in order to identify more crystalline phases, in particular, of silicates which are the main components of fly ash matrix. They reported the diffraction patterns of the unleached sample in the same fashion with other researches. The XRD patterns of fly ash leached with water were gehlennite, gypsum, anhydrite, calcite, and syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$), compared with the diffractogram after treatment with HCl and H_2O_2 that

were gehlenite, gismondine, and ettringite. Besides these compounds, other crystalline phases in the MSWI fly ash as muscovite ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$), leucite (KAlSi_2O_6), nephelite ($\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), quartz, adularia (KAlSi_3O_8), kaliophilite (KAlSiO_4), alite (Ca_3SiO_5), belite (Ca_2SiO_4), and mayorite ($\text{MgFe}_2(\text{SiO}_4)_3$) were identified with less confidence; they were, however, confirmed by micro FT-IR spectra.

Rachakornkij (2000) also investigated mineralogy of MSWI fly ash leached with water. He found calcium hydrated salts present in forms of calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium aluminum oxide ($\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$), calcium aluminum hydroxide ($\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$), calcium chloride hydroxide (CaClOH) and calcium chloride hydroxide hydrate ($\text{CaCl}_2\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$). In addition, hydrocalumite, $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ or $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$, was exclusively present in washed fly ash. Fractionated MSWI fly ashes separated using an air classification revealed different phases in fine and coarse fly ash fractions. Along with XRD analyses, KCl, CaClOH, and $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ were found in small quantities in fine fly ash when relative peak height was used to compare the amount of each phase. On the contrary, NaCl was found in larger quantity in fine fly ash than in coarse fly ash.

2.2 Properties of MSWI Fly Ash as a Cement Replacement

Due to its hazardous nature and lack of cementitious property, MSWI fly ash requires any treatment that would make it more feasible for disposal or use in construction applications with minimum environmental impact. The use of additives, such as Portland cement, lime, pozzolans, gypsum, silicate, and other types of similar binders, to solidify and stabilize the ash can immobilize metals and inhibit leaching. In general terms, stabilization is a process in which additives are mixed with waste to minimize the rate of contaminant migration from the waste and to reduce the toxicity of the waste. Likewise, solidification employs additives by which the physical nature of the waste (as measured by the engineering properties of compressive strength and/or permeability) is altered during the process. Thus, objectives of stabilization and solidification would encompass not only the reduction in waste toxicity and

mobility but also the improvement in the engineering properties of the stabilized materials (Rebeiz and Mielich, 1995; LaGrega et al., 2001).

Many Portland cement concrete-making companies successfully use coal fly ash as a replacement of cement in their mix design. In practice, most fly ashes can be introduced into concrete in one of two ways: a) a blended cement containing fly ash may be used in place of Portland cement; and b) fly ash may be introduced as an additional component at the concrete-mixing plant (Berry and Malhotra, 1987). The first method is simpler because it is free from the complications of batching additional materials but more uniform control. The second is flexible and allows for more complete exploitation of qualities of fly ash as a component of concrete. However, the properties of fly ash must be considered in determining the mix proportions. Partial cement replacement, one of the basic mix-proportioning methods, requires a direct replacement of a portion of the Portland cement by fly ash.

Unlike coal fly ash, few studies have been done on MSWI fly ash and its utilization as a cement replacement material in Portland cement concrete. Properties of concrete containing MSWI fly ash were studied by Harmernik and Frantz in 1991. Their fly ashes obtained from mass-burn and RDF incinerators were very similar to Class-C pozzolans but did not satisfy one or more of the ASTM C618 limits. Unit weight of their concrete decreased while increasing the percent fly ash replacement. This is because the specific gravity of their fly ashes were lower than that of cement and their fly ashes required more water which also had a low specific gravity. However, the addition of MSWI fly ash increased setting time and decreased compressive strength of concrete. The mass-burn fly ash concrete seemed to produce compressive strength significantly lower than RDF concrete. RDF fly ash also required less water for certain workability than mass-burn fly ash.

In 1992, Rashid and Frantz investigated the properties of concrete and concrete masonry using MSWI ashes collected from mass-burn and RDF facilities as fine aggregates. Their concrete containing RDF bottom ash had very low compressive strength because of expansion due to gas generation. However, both ashes produced better results in concrete masonry than in concrete since the requirement in compressive strength for masonry was lower than for concrete. The

porous texture of the masonry also reduced expansion and cracking produced by gas generation. Triano and Frantz (1992) studied durability and performance of concrete incorporating MSWI fly ashes from both mass-burn and RDF plants. They concluded that the performance of concrete varied significantly depending on type of MSWI fly ash. Concrete containing RDF fly ash had higher compressive strength than control concrete. Even though concrete with mass-burn fly ash had lower strength, it had outstanding resistance to surface scaling when exposed to deicing salts in a freeze-thaw environment.

Ali and Chang (1994) studied properties of bricks made of cement-MSWI combined ash obtained from RDF incinerator. They observed that the compressive strength increased with increasing cement content and with increasing ash content of up to 40 percent. They investigated flexural strength and found that it increased with increasing cement but was lower at higher ash contents. They summarized that flexural strength was not proportional to compressive strength of incinerator ash-based bricks. Moreover, their bricks showed excellent abrasion resistance and lower water absorption.

Another research examined mechanical properties of the use of mass-burn incinerator fly ash in mortar was revealed by Mangialardi et al. in 1998. Both compressive and flexural strengths of fly ash mortars increased with curing time. Nevertheless, preliminary compressive and flexural strength measurements indicated that the mechanical behavior of mortars was adversely affected by an increase in the ash content. To improve these properties, they suggested that the ash should be washed in water and milled prior to application.

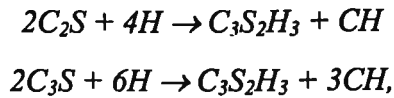
Rachakornkij (2000) studied the utilization of MSWI fly ash in mortars. His mass-burn fly ash was fractionated using an air classifier into two fractions; namely, fine and coarse so that the influence of particle size of MSWI fly ash on strength development of mortars could be investigated. At 28 days of 15% fly ash replacement, all MSWI fly ash-cement mortars exhibited superior strength development than the control. The compressive strength of raw fly ash mortar was comparable to that of coarse fly ash mortar. Fine fly ash mortars had the lowest compressive strength of all, although its strength was still much higher than the

control. These results showed that the effect of fine particles was not significant on compressive strength of fly ash mortars. He reported that the observed superior strength performance of MSWI fly ash-cement mortars was unexpected since the fly ash did not demonstrate self-cementitious characteristic. Furthermore, MSWI fly ash mortars had less reactive cement components than control and the fly ash by itself did not produce any hydration product in the paste that is similar to cement. Therefore, the additional strength might come from other mechanisms. Attempts were made to specify the sources of the additional strength by microstructural examination and XRD analyses of the hydration products of fly ash-cement pastes. He found a new chemical phase that identified exclusively in the paste was hydrocalumite ($C_3ACaCl_2 \cdot 10H_2O$). Moreover, high water absorption capacity of the fly ash was responsible for the superior strength property of the fly ash-cement mortars.

2.3 Hydration and Pozzolanic Reactions of MSWI Fly Ash-Cement Pastes

Portland cement is composed of a number of compounds, which react with water leading to the setting and hardening of the cement. All compounds present in Portland cement clinker are anhydrous. When brought into contact with water, these compounds are attacked or decomposed and form hydrated compounds. The main hydrates can be broadly classified as calcium silicate hydrates and tricalcium aluminate hydrates. The progress of hydration of cement can be determined by different means, such as the measurement of: (a) the amount of $Ca(OH)_2$ in the paste; (b) the heat evolved from hydration; (c) the specific gravity of the paste; (d) the amount of chemically combined water; (e) the amount of unhydrated cement present (using X-ray quantitative analysis); and (f) indirectly from the strength of the hydrated paste (Neville, 1995).

Dicalcium silicate ($2CaO \cdot SiO_2$ or C_2S) and tricalcium silicate ($3CaO \cdot SiO_2$ or C_3S) generally react with water to produce calcium hydroxide ($Ca(OH)_2$ or CH) and amorphous product of low basicity of calcium silicate hydrate ($C_3S_2H_3$ or C-S-H gel). The approximation of C-S-H gel, the final product of hydration of both calcium silicates, can be written as follow.



where C: CaO, S: SiO₂, H: H₂O, CH: Ca(OH)₂.

These are not stoichiometric equations and do not stop when the solution is saturated with calcium hydroxide. When hydration continues, the further lime liberated by the reaction is deposited as crystals of calcium hydroxide. The hydrated silicates formed remain stable in contact with the saturated lime solution, but if it is placed in water, it undergoes hydrolysis, liberating some lime into solution until the concentration is raised to the value required to stabilize it (Lea, 1971).

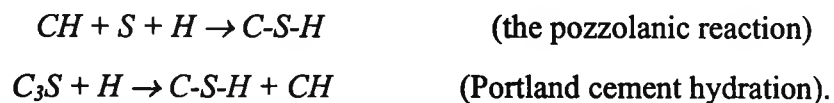
The reaction of C₂S is considerably slower and substantially produces less calcium hydroxide than that of C₃S. Calcium hydroxide from C₂S is not detected until after many weeks; however, the C-S-H gels produced are the same types as those from C₃S. The composition of C-S-H gel changes during the period of the reaction and varies with water-to-solid ratio of the mix and temperature. The C-S-H gels obtained in the hydration of both calcium silicates are very poorly-crystallized or near-amorphous formed in cement pastes at ordinary temperature (Lea, 1971).

The amount of tricalcium aluminate (3CaO·Al₂O₃ or C₃A) present in Portland cement is comparatively small but its behavior and structural relationship with other phases in cement make it of interest. The reaction between C₃A and water is very violent and leads to immediate stiffening of the paste, known as flash set. To prevent this action, gypsum (CaSO₄·2H₂O) is added to cement clinker. Gypsum and C₃A react to form insoluble calcium sulfoaluminate (C₃A·3CaSO₄·32H), but eventually tricalcium aluminate hydrate is formed. However, the stable form of calcium aluminate hydrate ultimately existing in the hydrated cement paste is probably the cubic crystal C₃AH₆ (Neville, 1995).

ASTM C618, chemical requirements for natural pozzolan, prescribes that for use with Portland cement concrete, the sum of SiO₂, Al₂O₃, and Fe₂O₃ must be at least 70%. Coal fly ash is commonly considered pozzolan. Pozzolans are materials, which, though not cementitious in themselves, contain certain constituents that will

combine with lime in the presence of water at ordinary temperatures to form stable insoluble compounds with cementitious properties. It is generally accepted that, in the pozzolanic reaction of coal fly ash, Ca(OH)_2 produced during cement hydration reacts with silicate and aluminate phases of the fly ash to produce calcium silicate and aluminate hydrates. However, cement hydration and pozzolanic reactions do not proceed independently. Pozzolanic reactions depend on the amount of calcium, alkalis, sulphates, silicate, and aluminate ions released into the liquid phase from both cement and fly ash (Berry and Malhotra, 1987; Wesche, 1991).

Natural pozzolans generally contain 60 to 85% SiO_2 , so the main pozzolanic reaction involves the formation of C-S-H gel. This C-S-H gel is similar to that produced by the hydration of the principal calcium silicate compound (i.e., C_3S) of Portland cement:



The pozzolanic reaction is slow, thus the rate of strength development and the heat of hydration associated with its reaction are relatively minimal. On the other hand, the hydration of C_3S in Portland cement is faster, therefore its reaction rate is higher. It should be noted that the former is a lime-consuming reaction, whereas the latter is lime-producing reaction (Berry and Malhotra, 1987).

For coal fly ash, the pozzolanic reaction starts when the glass of the fly ash particles dissolves. Decomposition of the glass network appears to be strongly dependent on the alkalinity of pore water. The glass structure of fly ash is only decomposed substantially beyond a pH of about 13.2 or 13.3. High pH can be achieved by adding NaOH in the fly ash; however, that may reduce the solubility of Ca(OH)_2 due to common ion effect. Many experiments demonstrated sensitivity of the reaction of fly ash to the composition of the surrounding solution that the alkalinity of pore water is of paramount importance.

As a consequence of the decomposition of glass structure, silica and alumina segments are forced into pore water. This process is hindered by the precipitation layers of lime and C-S-H gel that are developed by the hydration of cement. Initially, the dissolution of the fly ash is a slow process. Due to high calcium content in pore water in the early state of hydration, the C-S-H structures will precipitate in the vicinity of the fly ash particles. It causes any further decomposition of glass network to slow down. Later, when the pH increases and the calcium ion concentration decreases, the rate of the fly ash dissolution will increase (CUR, 1992).

Although, the hydration products of Portland cement do not have very clear diffraction peaks, due mainly to their semi-amorphous nature and over-lapping peaks of the hydrated and anhydrous compounds. X-ray diffraction has long been used for the recording of hydration progress and the identification of the hydrated products.

Remond et al. (2002) determined the products of hydration due to the presence of MSWI fly ash. The tests were carried out on different cement pastes by X-ray diffraction method. Furthermore, they studied pore structure of C-S-H formed in the presence of MSWI fly ash by differential scanning calorimeter (DSC) test. The DSC method measures the heat released by a sample as it undergoes chemical and physical changes while being heated or cooled at a constant rate. During the test, the heat flux peaks were assumed to correspond to solidification of the water in cement paste pores. The positions and shapes of the peaks were essentially influenced by two parameters: the composition of pore solution in cement pastes and the size of pores. They concluded that new hydration products formed in the cement pastes containing MSWI fly ash were calcium chloroaluminate hydrate ($C_3A \cdot CaCl_2 \cdot H_{10}$) or Friedel's salt, calcium sulfoaluminate hydrate ($C_3A \cdot 3CaSO_4 \cdot H_{32}$) or ettringite and thenardite (Na_2SO_4). The DSC results were reasonable to deduce that freezing of pore solution were attributed to a higher concentration of salts in the pore solution of the MSWI fly ash-cement paste. In addition, incorporating the MSWI fly ash did not change the pore structure of the C-S-H gel in cement paste.

Rachakornkij (2000) used XRD method to investigate the hydration process of MSWI fly ash-cement pastes by evaluating the amount of reduction in the starting materials and the increase in the hydration products. The former was estimated by measuring the characteristic peak intensities of C_3S at $51.83^\circ 2\theta$ instead of $34.44^\circ 2\theta$. Although the relative intensity of C_3S at that 2-theta angle was only 55% of relative intensity at $34.44^\circ 2\theta$, the peak has relatively no interference. The latter was determined from the peak intensity of $Ca(OH)_2$ at $34.11^\circ 2\theta$ that was the strongest and free of overlapping peaks from other crystalline phases. The rate of reduction in C_3S was very high during the first three days of curing that consistent with the rate of strength gain. This agrees well with the characteristic of the rapid reaction of C_3S to form C-S-H gel and $Ca(OH)_2$. After 14 days of the maximum intensity of $Ca(OH)_2$, the intensities started to decrease gradually. One possible explanation was the pozzolanic reaction taken place in the pastes. The results from XRD analysis and scanning electron microscope equipped with energy dispersive X-ray (EDX) detector showed the formation of hydrocalumite ($C_3A \cdot CaCl_2 \cdot 10H_2O$) after the age of 7 days. However, the MSWI fly ash was not self-cementitious since its paste did not solidify. The fly ash also seemed to retard hydration of cement because fewer $Ca(OH)_2$, the hydration product, were observed at the same age as the cement paste.

Ampadu and Torii (2001) studied the microstructures and hydration characteristics of the pastes containing ecocement. The new ecocement, a type of hydraulic cement, was designed to use MSWI ashes in amounts of up to 50% of raw material in manufacturing process. The X-ray diffraction pattern of ecocement showed its resemblance to ordinary Portland cement (OPC). Hydration products in both fly ash-cement and OPC pastes using XRD technique revealed the presence of calcium hydroxide, ettringite, and monosulfoaluminate hydrate. The DSC analysis verified the presence of Friedel's salt in fly ash-cement pastes as a weak peak around $300^\circ C$. Both XRD and DSC results indicated that the amount of calcium hydroxide formed in the cement pastes were more than that in corresponding cement paste with MSWI fly ash.

2.4 Leaching and Extraction Procedures

According to the Notification of Ministry of Industry No. 6, B.E. 2540 (1997), issued under Factory Act, B.E. 2539 (1996), stabilized and solidified materials must be tested the leachate characteristics by leachate extraction procedure and determined the concentrations of contaminants in extraction fluid. This test is similar to the toxicity characteristic leaching procedure (TCLP) adopted in 1986 by the U.S. EPA under the Hazardous and Solid Waste Amendments of 1984 (HSWA). This TCLP regulatory test (U.S. EPA SW-846 Method 1311) was adopted as a replacement for the extraction procedure (EP) toxicity test to determine whether a waste exhibits hazardous characteristics based on the U.S. EPA Toxicity Characteristic (TC) criteria (40 CFR 261.24). The TCLP is widely used to evaluate the effectiveness of stabilization and later replaced the EP toxicity test in 1990.

Like the TCLP test method, leachate extraction procedure described in the Notification No. 6 (1997) requires that the stabilized material is crushed to a particle size smaller than 9.5 mm. Except for the extraction fluid made with 80% of sulfuric acid and 20% of nitric acid in deionized (DI) water to a pH of 5.0 is selected to mimic conditions in a municipal landfill. This extraction fluid somewhat likes the leachant prepared from the synthetic precipitation leaching procedure (SPLP) regulatory test (U.S. EPA SW-846 Method 1312). The SPLP extraction fluid is a 60/40 mixture of sulfuric acid and nitric acid combined with water to a pH of 4.2 ± 0.05 for the east site of the Mississippi river or 5.0 ± 0.05 for its west side. It is believed that SPLP is better suited than TCLP to evaluate the effectiveness of in-situ stabilization since the extraction fluid is more realistic than acetic acid fluid that is used in the TCLP test (LaGrega et al., 2001).

The crushed sample is then mixed with a weak acid extraction liquid, in a liquid-to-solid weight ratio of 20:1. It is further agitated in a rotary extractor for a period of 18 hours at 30 rpm. After 18 hours of agitation, the sample is filtered through a 0.6 to 0.8- μm glass fiber filter, and the filtrate is defined as the extract. This extract is analyzed for a wide variety of hazardous waste constituents including volatile and semi-volatile organics, metals, and pesticides so that the results are compared to the regulatory levels. Waste that leaches one or more contaminants in

excess of specified levels is classified as a characteristic hazardous waste. At present, there are only eight metals addressed in the TCLP limits; namely, silver (Ag), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and selenium (Se).

The TCLP is subject to criticism with its use for the evaluation of stabilization effectiveness for several reasons. First, solidified sample is broken down to pass the 9.5-mm sieve, thus reducing beneficial effects of macro- and micro-encapsulation. It has been shown that as the particle size reduces, the leachability increases. Further, the low-pH environment during extraction may not be representative of the real-world field conditions of a secure landfill although it may be representative in a sanitary landfill containing domestic garbage (LaGrega et al., 2001).

However, a stabilized material with high alkalinity, such as cement-based stabilization, may rapidly increase the pH conditions. Cement-based waste forms typically have a pore-water pH of 10 to 12 because of the excess amount of calcium hydroxide present in the pores during cement hydration. Due to high alkalinity of concrete, leachability of most trace elements from MSWI fly ash in fly ash-cement concrete appears to be very low. These trace elements in MSWI fly ash originate from municipal solid waste and condense in fly ash during the combustion process. Most elements precipitate on the fly ash particles during cooling process of the flue gas and therefore deposited on the surface of fly ash particles. Most trace elements, particularly metals, can be chemically stabilized as metal hydroxide forms in the high pH pore water in fly ash-cement concrete (Cheng and Bishop, 1992).

Wadge and Hutton (1987) investigated leachability of some elements in fly ashes from both coal combustion and refuse incineration. Their experimental procedure was developed from Young and Wilson (1982) to evaluate initial leaching from a solid waste material. The laboratory setup was a repetitive shaking test using distilled water as a model leachate to simulate rainwater at high solid-to-liquid ratio. The measurement of total concentrations of trace elements revealed several differences between their fly ashes because of contrasting compositions of the starting materials and possibly different combustion conditions. They also concluded that Se was the great critical trace element with regard to ground water quality, despite being

present at relatively low concentrations in both residues. Results from the sequential extraction test indicated that Cd and Pb in the MSWI fly ash exhibited great environmental mobility. These summaries were not entirely consistent with the leaching test data, but notably marked uptake of Cd and Pb by crops grown on incineration fly ash amended soils.

Buchholz and Landsberger (1995) studied leachate characteristics of MSWI residues by several leaching procedures: viz., TCLP, water batch extraction, and sequential extraction. Their analysis conducted on combined ashes, bottom ash, bulk fly ash, and size-fractionated fly ash to investigate the distribution trends of metals among the different-sized particles. The TCLP leachate of MSWI fly ash showed that the levels of Hg and Pb in the fly ash leachate exceeded regulatory limits. Neither the combined ash nor the bottom ash leachates exceeded the TCLP limits for any metals. They concluded that the single greatest factor in determining the availability and concentration of metals in leachate of MSWI ashes was the pH of resulting solution, not the concentration of metal on the ash particles.

LaGrega et al. (2001) stated that the introduction of an acid source, as in the TCLP, greatly overestimates the leaching potential of a monofill. Any extraction procedure designed for studying MSW landfills, which uses acetic acid for its extraction fluid is not a realistic model of an ash monofill. For assessment of the leachability of monofilled wastes, extraction methods using DI water as the extraction fluid is better representative than procedures using acetic acid according to the TCLP regulatory test. A series of water batch extractions are much more completed to determine leaching dynamics of metals. From water batch extraction test, elements in dynamic leachate can be distinguished into three behaviors (Buchholz and Landsberger, 1995). First, water-leachability constituents in MSWI fly ash were Cd, Cl, Cr, Pb, Se, and S. These elements were preferentially deposited on the surface of fly ash particles and easily washed away with water. Aluminum and silicon were another group, which was the center matrix of fly ash. The third behavior was insoluble elements.

A more thorough characterization of MSWI residues can be achieved by modifying a sequential extraction procedure for the speciation of particulate trace metals. The sequential extraction procedure is a tool to aid in assessing potential short and long term leaching hazards posed by mono- and co- disposal of MSWI ashes. A sequential extraction procedure approximates the total amount of the elements available over the lifetime of monofill. Due to this procedure, the elements of As, Cd, Cu, Hg, Pb, S, and Zn can be identified as potential long-term hazards in MSWI ashes (Buchholz and Landsberger, 1995). Chichester and Landsberger (1996) developed the procedure to determine leaching dynamics of metals from MSWI fly ash using column test that employed doubled DI water. The data acquired from this investigation can provide a preliminary basis to understand the behavior of MSWI fly ash in monofill and allow assessment of the possible hazard posed by the fly ash leachates.

Another research on long-term leaching of metals from concrete using a sequential extraction procedure was exhibited by Webster and Loehr (1996). Their leaching tests used acidic extraction fluid and seawater as leachants. The results showed substantial differences of metal concentrations in the leachates between two leachants. Cadmium and lead concentrations were significantly less for the seawater extractions than for the acidic extractions. Moreover, the amount of Cr leached was two times lower for the seawater extractions than for the acidic extractions. This is because the severe environment created during the acidic sequential extractions. Also, the acidic leaching test is likely to be encountered in real-world concrete applications.