



CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Characterization of MSWI Fly Ash

4.1.1 Sieve Analysis

One of the parameters to determine features of MSWI fly ash as a cement replacement material in concrete is particle size distribution. The particle size relates to water demand, pore structure, and strength development of fly ash concrete. Grain size distribution of as-received MSWI fly ash was determined according to ASTM C136-95, Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates. Figure 4.1 presents a good grading curve of the raw Phuket MSWI fly ash particles that are present mainly in large fractions with its mean particle size ($d_{50\%}$) of around 1000 microns (1 millimeter).

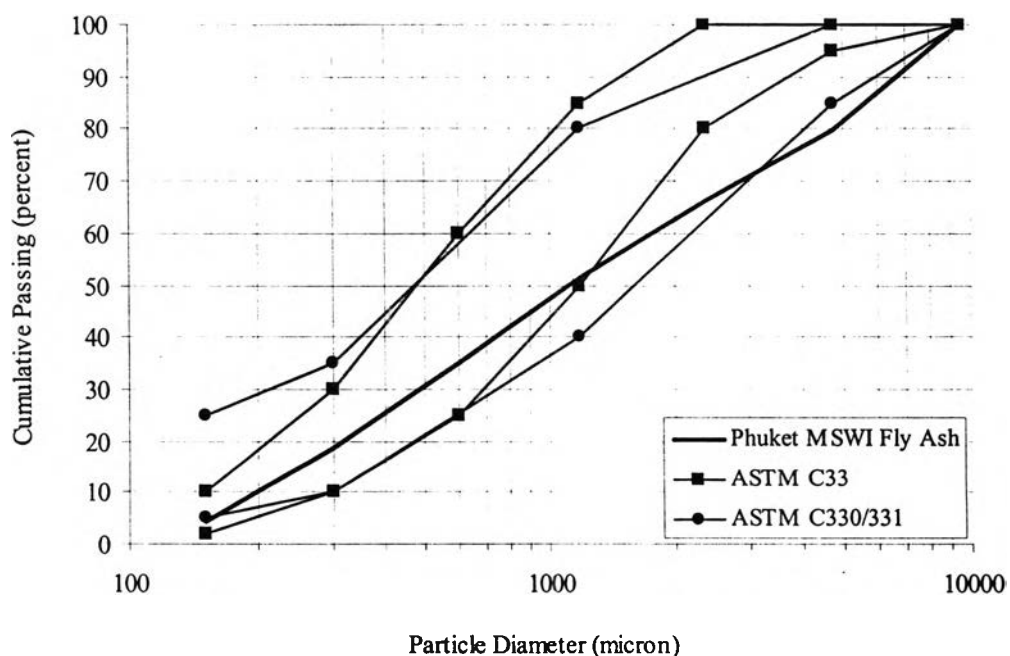


Figure 4.1 Grain Size Distribution Curve of Phuket MSWI Fly Ash

The figure also compares gradation curve of Phuket MSWI fly ash to the requirements in ASTM C33-93, Standard Specification for Concrete Aggregates. Raw Phuket incinerator fly ash fails this limits because it has too few coarse particles. However, it is almost satisfied the ASTM C330-89 and C331-94 (ASTM C330/331), standard specifications of lightweight aggregates for structure concrete and concrete masonry units. Due to its most large particle sizes, Phuket MSWI fly ash seems to be used as a fine aggregate replacement material in fly ash concrete for future researches.

Grain size distribution of as-received Phuket MSWI fly ash is similar to the analysis result from NJIT1 MSWI fly ash as shown in Figure 4.2. This NJIT1 fly ash was sampled from the proprietary fly ash treatment unit of a mass-burn MSW incineration facility. The ash was treated with complex phosphoric acid and carried out to directly replace sand in MSWI fly ash mortars. Although its particle size distribution was close to fine aggregate limits (ASTM C330/331), NJIT1 fly ash was not suitable for use as a total fine aggregate replacement owing to its exclusively high water absorption capacity (Rachakornkij, 2000).

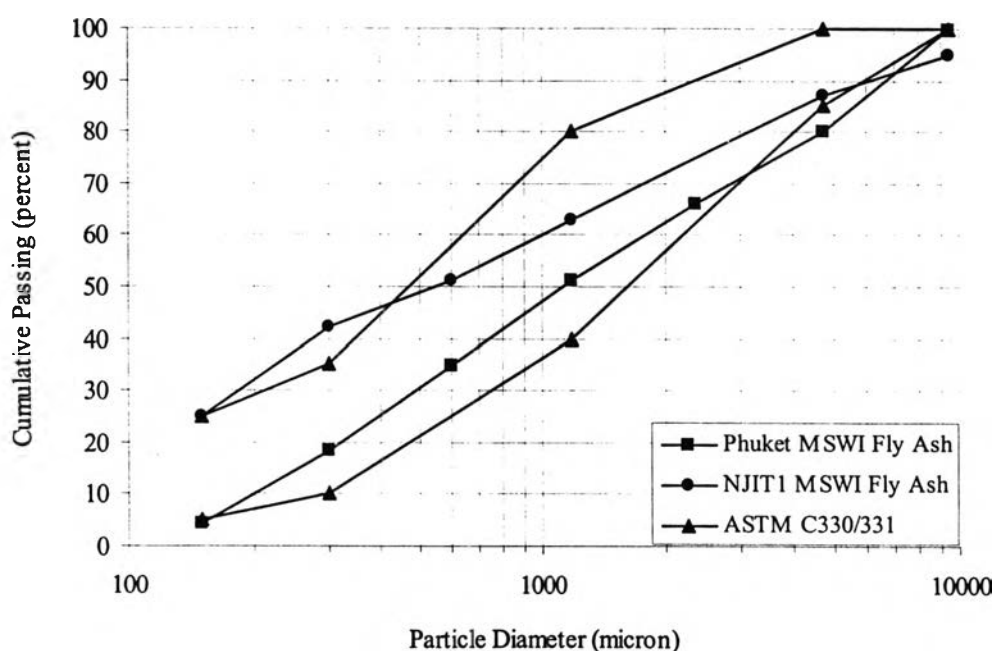


Figure 4.2 Grain Size Distribution Curves of Phuket and NJIT1 MSWI Fly Ashes

4.1.2 Particle Size and Specific Surface Area

After passed through a standard sieve No. 200 (75-micron openings), sifted MSWI fly ash used to make fly ash-cement mortars in following experiments was determined particle size distribution using a particle size analyzer. Figures 4.3 and 4.4 show particle size distribution curves of sifted MSWI fly ash with its cumulative curve and particle size distribution of the ash in comparison to those of Portland cement and coal fly ash. Coal fly ash present in this test was obtained from Mae Moh power plant, Thailand.

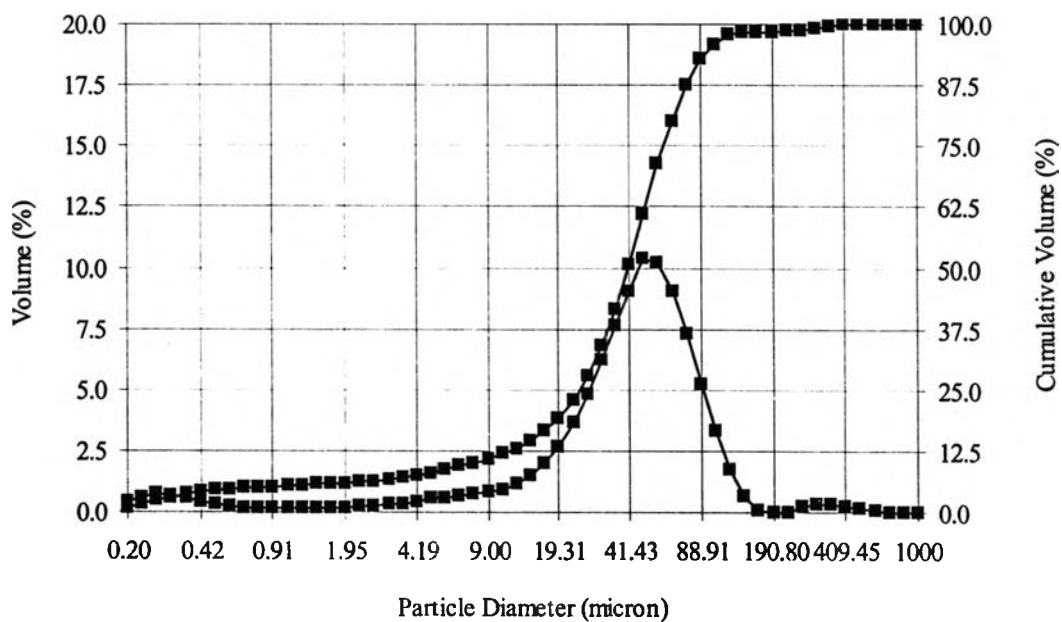


Figure 4.3 Particle Size Distribution and Cumulative Curves of Sifted MSWI Fly Ash

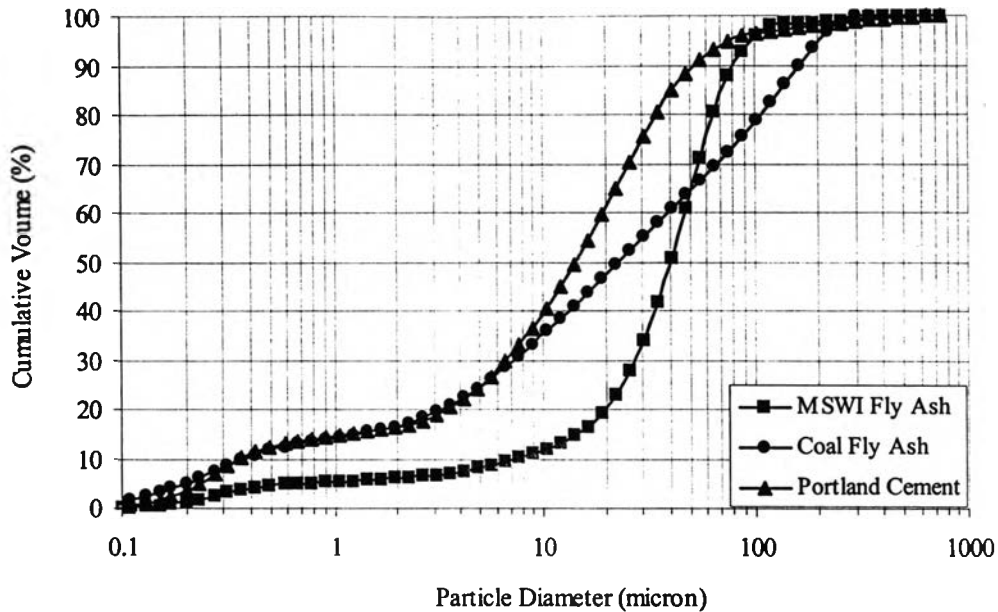


Figure 4.4 Comparison of Cumulative Particle Size Distribution Curves of Sifted MSWI Fly Ash, Coal Fly ash, and Portland Cement

The figures indicate that sifted Phuket MSWI fly ash is in the form of powder, which is coarser than Portland cement and coal fly ash particles. Fine textures of MSWI fly ash are agglomerated at almost same size with the main particle dimensions between 30 and 80 microns. Due to the fact that Phuket MSWI fly ash was first graded and opted only fine particles for testing, coal fly ash and Portland cement are then much better grading particles. The result also shows that Phuket MSWI fly ash had many fine particles. These fine particles will be consistent with water demand and workability in concrete. When workability is kept constant, water demand decreases with the increase in fineness. However, as will be pointed out in next section, fly ash particles are not merely fine but also round-shaped that can advantageously influence concrete performance.

Table 4.1 shows specific surface area and particle sizes with different percentiles of cumulative particle size distribution curves. The NJIT2 MSWI fly ash stated as a comparison in this section was not acquired as same as that mentioned in section 4.1.1. This batch was much finer that was taken from downstream of lime-injected acid gas scrubber units of the NJIT incinerator plant.

Table 4.1 Specific Surface Area and Particle Sizes of Phuket MSWI Fly Ash

Sample	Specific Surface Area (cm ² /g)	d _{10%} (microns)	d _{50%} (microns)	d _{90%} (microns)
Phuket MSWI Fly Ash	3969	7.86	46.59	92.06
NJIT2 MSWI Fly Ash	-	-	25.36	133.62
Coal Fly Ash	2370	0.43	27.32	191.64
Portland Cement	3380	0.42	16.56	63.33

Note: Analysis results for NJIT2 MSWI fly ash (Rachakornkij, 2000), coal fly ash, and Portland cement were reported as references.

Specific surface area, one of the standard tests for fineness determination, is defined as a number of units of surface area contained in a unit of mass. Table 4.1 presents that specific surface areas of MSWI fly ash, coal fly ash, and Portland cement determined by Blain air-permeability method are 3969, 2370, and 3380 cm²/g, respectively. The specific surface area of the MSWI fly ash was not easy to determine because the irregularly shaped particles of MSWI fly ash pack more loosely than the spherical particles of coal fly ash. The resistance of MSWI fly ash to air flow is lower, thus resulting in a misleadingly high air flow. On the other hand, the porous structure that may be caused by carbon on MSWI fly ash particles also allows air to flow rapidly through them, thereby leading to high specific surface area of the ash.

On the ground that Blain air-permeability method measures time taken place when a known volume of air passes through the MSWI fly ash compacted in a fixed bed. Particle shapes of MSWI fly ash influence pores and characteristics of compacted grains. This air can rapidly flow through irregular and porous MSWI fly ash particles. Therefore, specific surface of MSWI fly ash is considerably high even though the particle size is large. Accordingly, specific surface may not be in directly consistent relationship with fineness of fine particles, particularly for irregular materials such as MSWI fly ash. Although, specific surface is not so much informative as a full-size distribution curve, it is rapidly and conveniently obtained and has proved to be a satisfactory method to roughly describe physical quality of fly ash and other fine texture materials when they use in cement such as water demand and workability.

Because of the porous and irregular surface features, another method to determine specific surface of MSWI fly ash is Brunauer, Emmett and Teller (BET) technique, in which nitrogen adsorption isotherms are measured. The BET method measures the totality of voids existing in the surface of grains, thus data obtained by this method will be about 3 to 4 times greater than the Blain values (Wesche, 1991). The BET result seems more suitable to use for determine the specific surface of MSWI fly ash since given more precise solution.

4.1.3 Bulk Specific Gravity

ASTM Standard C188-95 deals with specific gravity determination in cement. Portland cement and Phuket MSWI fly ash were determined in the usual manner by displacement of liquid in a density bottle using kerosene. Table 4.2 shows bulk specific gravity and other physical properties of Phuket MSWI fly ash compared to the others.

Table 4.2 Physical Properties of MSWI Fly Ash

Sample	Sg @ 25°C	Moisture Content (%)	LOI (%)	pH	Conductivity (mmho/cm)
Phuket MSWI Fly Ash	2.51	1.29	9.70	12.8	57.9
NJIT2 MSWI Fly Ash	2.26	2.83	12.94	11.8	25.7
Coal Fly Ash	2.50	0.23	2.05	11.3	0.021
Portland Cement	3.14	0.67	1.12	11.7	4.53
DI water	1.00	-	-	7.02	0.001

Note: Analysis results for NJIT2 MSWI fly ash (Rachakornkij, 2000), coal fly ash (Jaturapitakkul, 1993), Portland cement, and DI water were reported as references.

As shown in Table 4.2, bulk specific gravity of Phuket MSWI fly ash is 2.51 that is comparable to those of NJIT2 MSWI and coal fly ashes. It is also consistent to many researches that mass density of mass-burn incinerator fly ash was about 20-30% lower than that of cement (Hamernik and Frantz, 1991a; Mangialardi et al., 1998; Rachakornkij, 2000). Bulk specific gravity of MSWI fly ash directly influences unit weight of fly ash concrete. That is, when MSWI fly ash is introduced in concrete, unit weight of the MSWI fly ash concrete decreases due to the low specific gravity of the MSWI fly ash. The specific gravity of MSWI fly ash depends on the specific

gravity of the minerals of which the fly ash is composed and also on the presence of porous particle (whose specific gravity may be less than 1). Fineness of material is another factor affecting bulk specific gravity. Jaturapitakkul (1993) and Rachakornkij (2000) fractionated their fly ashes using an air classifier and summarized that the finer the fly ash became, the higher its specific gravity would be.

4.1.4 Moisture Content and Loss on Ignition (LOI)

Moisture of MSWI fly ash normally depends on the way in which this material is stored after leaving the APC devices. Moisture content of fly ash collected directly from the ash pits is generally low. On the other hand, fly ash taken from the landfill commonly has high moisture content. Phuket MSWI fly ash is usually stored in a fly ash pit and then dumped into an ash landfill close to the plant. Although Phuket MSWI fly ash was gathered from the ash monofill, moisture content of the ash (1.29%) was somewhat lower than that of NJIT2 fly ash (2.83%) since the ash was just disposed of into the landfill after incineration process. Compared to those of coal fly ash (0.23%) and Portland cement (0.67%), moisture content of MSWI fly ash is much higher. However, it is still within the limits of 3% required by ASTM C618-95.

Loss on ignition is a measure of the amount of organic matter, carbonates, and chlorides present. Nonetheless, it has been known that carbon is the most significant component of ignition loss. This carbon is decisive in determining of water requirement for concrete. The amount of water necessary to obtain a paste at normal consistency is higher when carbon in the ash increases. Variation in carbon content in MSWI fly ash may also lead to uncertain behavior with respect to air entrainment, some air-entrainment agents and other agents becoming adsorbed by the porous carbon particles. Table 4.2 also shows high LOI value of Phuket MSWI fly ashes. This high content may not be only caused by unburned carbon from the combustion process but the large amount of lime and chloride from flue gas treatment system. Compare to the ASTM C618 specifications, LOI of Phuket MSWI fly ashes (9.74% for raw MSWI fly ash and 9.70% for sifted MSWI fly ash) is rather higher than the 6% limits for both Class-C and Class-F pozzolans.

4.1.5 pH and Conductivity

Because of the air pollution control (APC) system of Phuket incinerator plant, lime (CaO) is designed to treat acid gas in order to produce harmless CaCl_2 and CaSO_4 powders. These alkaline products and other alkaline materials, such as oxides and carbonates of calcium, sodium, and potassium in fly ash contribute to high pH value. Table 4.2 indicates that pH of Phuket MSWI fly ash (12.8) is exclusively the highest among other fly ashes and cement which range from 11.3 to 11.8.

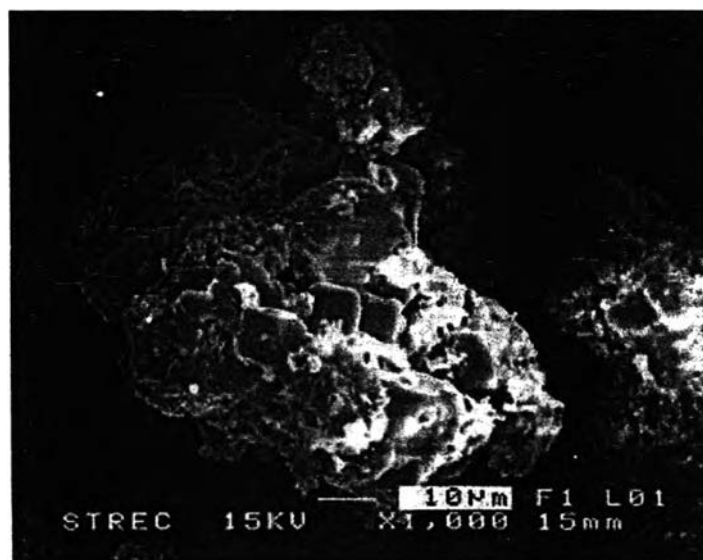
pH of MSWI fly ash can be used as an indicator to evaluate the effectiveness of stabilized materials particularly in cement-based stabilization. Most trace elements such as heavy metals can be chemically stabilized as insoluble metal hydroxides in high-pH pore water in MSWI fly ash concrete. Therefore, MSWI fly ash is usually injected with excess lime to obtain high pH and high soluble alkali compounds in order to pass the regulatory limits of the Notification of Ministry of Industry No. 6 (1997) or TCLP test.

Conductivity of Phuket MSWI fly ash (57.9 mmho/cm) is also the highest. This conductivity of fly ash solutions is indicative of the ability of solution to conduct a current via movement of ions. When ion concentration increases, more current can be conveyed, thus resulting in high conductivity. That is, MSWI fly ash has more soluble compounds when it is in contact with water and gives more ions. Therefore, conductivity of the MSWI fly ash is high. Moreover, high conductivity may indicate that washing of MSWI fly ash with water can enhance the MSWI fly ash qualities prior to applied utilization since alkalinity in the ash derived from sodium and calcium salts and other chloride compounds will be reduced.

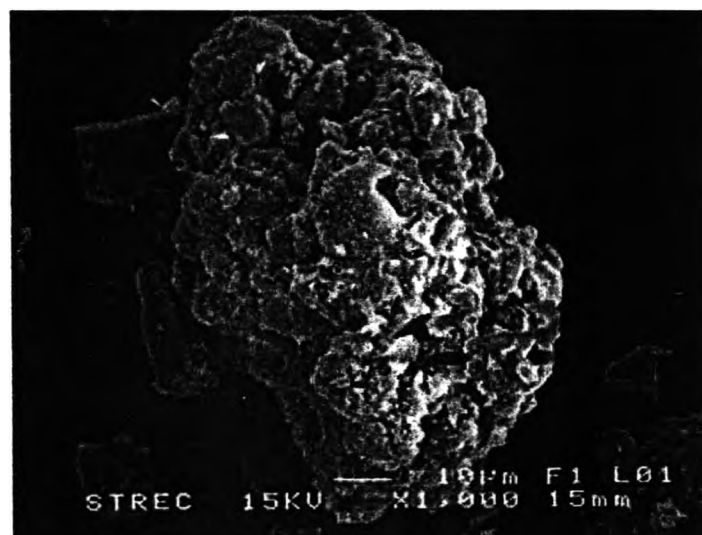
4.1.6 Morphology

Microstructures of MSWI fly ash particles were studied by scanning electron microscope (SEM). Scanning electron micrographs of Phuket MSWI fly ash at 1000x magnification are shown in Figures 4.5 (a) and (b). For Portland cement and coal fly ash, their photographs are presented in Figures 4.6 (a) and (b) with higher magnifications of 3700x and 1700x, respectively.

Figure 4.5 shows that Phuket MSWI fly ash particles are irregular and angular shapes with plenty of pores in their surface. MSWI fly ash is assembled with tiny angular particles. On the contrary, coal fly ash is usually composed of small round particles that were almost spherical. The visible size of Phuket MSWI fly ash particle from the picture is about 50 to 80 microns while that of coal fly ash is around 15 to 40 microns. The rough surface particles of MSWI fly ash may be identified as unburned carbon. This carbon in MSWI fly ash particle is responsible high specific surface value as stated in section 4.1.2.



(a) Phuket MSWI Fly Ash 1000x



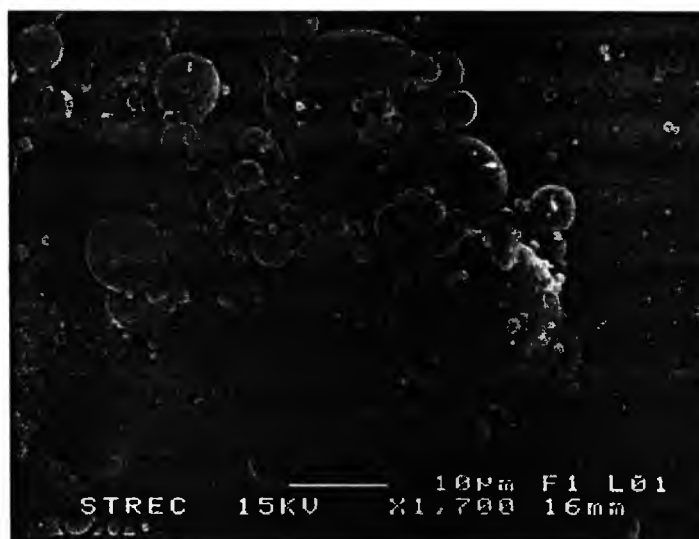
(b) Phuket MSWI Fly Ash 1000x

Figure 4.5 SEM Photographs of Phuket MSWI Fly Ash

Moreover, large carbon content in MSWI fly ash was associated with a high water requirement in concrete incorporating the ash. This is also true for MSWI fly ash from other sources. The NJIT MSWI fly ash particles showed high degree of surface roughness and had high absorption capacity value (170%) whereas the absorption capacity of coal fly ash and cement were 12% and 72%, respectively (Jaturapitakkul, 1993; Rachakornkij, 2000).



(a) Portland Cement 3700x



(b) Coal Fly Ash 1700x

Figure 4.6 SEM Photographs of Portland Cement and Coal Fly Ash

Particles of MSWI fly ash are usually irregular and angular which may be resulted from the nature of solid wastes and the combustion conditions of the plant. For coal fly ash, the final shape will be irregular if combustion temperature is so low that the mineral ash fails to melt. When combustion temperature of the power plant reaches 1500°C, the majority of particles are round-shaped and hollow with smooth surfaces (Wesche, 1991). Round particles appear to be ideal with respect to workability of concrete since they act as a lubricant between the angular and irregular particles of cement and aggregates. Therefore, the more round particles present in fly ash, the better the fly ash concrete performance will be. Furthermore, color of fly ash particles can roughly suggest their chemical compositions and potential applications in term of esthetical reasons. Particles rich in iron oxide constitution have a dark to blackish color.

4.1.7 Bulk Chemical Compositions

Table 4.3 shows chemical compositions of raw and sifted Phuket incinerator fly ashes determined by X-ray fluorescence (XRF) spectroscopy. The analytical results of chemical compositions of Mae Moh coal fly ash and Portland cement were given for comparison. All elemental compositions of these fly ashes were reported in oxide forms, the general format used in cement and concrete technology field. The table shows that chemical compositions of raw and sifted MSWI fly ashes are insignificantly different. Thus, fractionation does not too much influence elemental compositions of the fly ashes. This is in agreement with previous investigations by Jaturapitakkul (1993) and Rachakornkij (2000) who studied chemical compositions of fractionated coal and MSWI fly ashes, respectively. They reported that most fractionated fly ashes had some slight variation in the oxide compositions when particle sizes changed.

Table 4.3 Chemical Compositions of Phuket MSWI Fly Ashes, Coal Fly Ash, and Portland Cement

Compositions	Raw Phuket MSWI Fly Ash	Sifted Phuket MSWI Fly Ash	Mae Moh Coal Fly Ash	Portland Cement
Al ₂ O ₃	2.32	2.42	28.27	5.42
CaO	34.83	34.40	11.92	63.82
CuO	0.05	0.05	0.05	-
Fe ₂ O ₃	0.82	0.71	14.57	2.92
K ₂ O	6.90	9.12	2.48	0.46
MgO	1.77	1.43	2.13	1.50
MnO	0.05	0.04	0.11	-
Na ₂ O	6.59	7.81	-	0.26
PbO	0.12	0.14	0.04	-
SiO ₂	4.07	3.21	35.43	20.20
SnO ₂	0.08	0.10	-	-
SrO	0.04	0.03	0.09	-
TiO ₂	0.59	0.51	0.38	-
ZnO	0.18	0.54	0.01	-
SO ₃	6.23	5.20	2.35	2.55
P ₂ O ₅	1.63	1.26	-	-
Cl	23.94	23.28	-	-
Br	0.03	0.03	-	-
Rb	0.02	0.02	-	-
LOI	9.74	9.70	-	-
Total	100.00	100.00	97.83	97.13

Note: Analysis results for coal fly ash and Portland cement (Hongpatanporn, 1990) were reported as references. “-” means not reported.

Oxides of Al, Ca, Fe, and Si in fly ash are interesting because they relate to the main compounds referred in Portland cement; namely, C₃S (tricalcium silicate), C₂S (dicalcium silicate), C₃A (tricalcium aluminate), and C₄AF (tetracalcium aluminoferrite). High amount of CaO or lime in raw (34.83%) and sifted Phuket MSWI fly ash (34.40%) were caused by residues from APC system of the plant since excess dry lime injected into flue gas stream reacts with acid gases to produce harmless various salts. For this reason, alkalis (Na₂O and K₂O), chlorides (Cl), and sulphates (SO₃) in MSWI fly ash were present in rather large quantities (5 percent or more). These alkaline compounds (although other alkalis also exist in the MSWI fly ash) have been found to react with some aggregates causing disintegration of concrete

and to strongly affect the rate of strength gain beyond the age of 28 days in concrete. Exclusively high chloride contents of most MSWI fly ashes (23.94% and 23.28% for raw and sifted Phuket MSWI fly ashes) may be derived from the combustion of plastic and newspaper in solid waste stream (Tchobanoglous et al., 1993). These chlorides such as sodium chloride would be additional source of alkalis in MSWI fly ash. The use of such a MSWI fly ash in reinforced concrete should not be allowed because chlorides may lead to corrosion of steel. Moreover, the cause of false setting may be associated with alkalis in concrete ingredients. Since salts, particularly chlorides, in the MSWI fly ash can be leached by water, MSWI fly ash may be introduced as an additional material in concrete by simple process such as washing the ash with water.

Trace elements present in the incinerator fly ash were also originated from the waste stream when they evaporated during combustion. Most elements condensed on the surface of fly ash particles during the cooling process of flue gas. Like trace elements, chloride and sulphate salts, i.e., sodium, potassium, and calcium salts were also present on the surface of fly ash. Examples of these trace elements found in Phuket MSWI fly ash were Cu, Mn, Pb, Sn, Sr, Ti, and Zn that are given in Table 4.3. These elements can dissolve well when fly ash comes in contact with water. However, the leachability of most trace elements in MSWI fly ash concrete appears to be very low due to high alkalinity of the concrete and low concentrations in these constituents.

Table 4.4 indicates ranges of chemical compositions of MSWI fly ashes from various sources with data from bottom incinerator ash and coal fly ash. The table shows that Phuket MSWI fly ash has a predominantly large amount of calcium. This calcium in MSWI fly ash was carried over from reaction products and residual lime in an APC device. High sodium and potassium compositions in Phuket MSWI fly ash were present in chloride forms. Chloride compounds were believed that they came from reactions in acid gas scrubber that utilized lime injection and from volatile metals in incineration process that precipitated on the surface of fly ash particles.

Table 4.4 Percentage of Bulk Chemical Compositions of MSWI Fly Ashes form Various Sources

	Raw Phuket MB	Sifted Phuket MB	NJIT ¹ MB	FA ² MB	FA ³ MB	FA ³ RDF	BA ⁴ RDF	FA ⁵ (coal)
Al ₂ O ₃	2.32	2.42	3.66	10.03	13.74	15.34	4.15	28.27
BaO	-	-	-	0.174	-	-	-	-
Br	0.03	0.03	-	-	-	-	-	-
CaO	34.83	34.40	40.46	17.04	26.62	23.73	7.71	11.92
CdO	-	-	0.016	0.0038	-	-	-	-
Cl	23.94	23.28	17.98	5.50	-	-	0.24	-
Cr ₂ O ₃	-	-	0.02	0.098	-	-	-	-
CuO	0.05	0.05	0.09	0.0288	-	-	-	0.05
Fe ₂ O ₃	0.82	0.71	0.53	1.44	3.24	2.76	4.71	14.57
K ₂ O	6.90	9.12	2.27	3.30	1.97	0.56	0.86	2.48
MgO	1.77	1.43	0.68	1.41	2.44	1.87	1.05	2.31
MnO	0.05	0.04	0.01	0.0871	0.07	0.06	-	0.11
MoO ₂	-	-	-	-	-	-	-	-
Na ₂ O	6.59	7.81	5.50	2.83	2.59	2.14	5.14	-
NiO	-	-	0.007	0.0362	-	-	-	-
P ₂ O ₅	1.63	1.26	0.37	-	1.39	1.06	0.40	-
PbO	0.12	0.14	0.32	0.435	-	-	-	0.04
Rb	0.02	0.02	-	-	-	-	-	-
Sb ₂ O ₃	-	-	0.11	-	-	-	-	-
SiO ₂	4.07	3.21	4.65	10.49	26.71	32.07	26.01	35.43
SnO ₂	0.08	0.10	-	0.0320	-	-	-	-
SO ₃	6.23	5.20	8.01	5.10	10.73	3.00	0.68	2.35
SrO	0.04	0.03	0.04	-	0.03	0.04	-	0.09
TiO ₂	0.59	0.51	0.87	0.73	2.49	2.62	0.62	0.38
ZnO	0.18	0.54	1.05	0.81	-	-	-	0.01
LOI	9.74	9.70	12.94	14.65	4.90	13.40	-	-

Note: from (1) Rachakornkij (2000); (2) Mangialardi et al. (1998); (3) Triano (1992); (4) Berg and Neal (1998); (5) Hongpatanporn (1990);

BA: bottom ash; FA: fly ash; MB: mass-burn; RDF: refuse-derived fuel; “-” means not reported.

Compared review data to those obtained from the study, the obvious difference in chemical compounds among these fly ashes is that RDF fly ash has higher Al_2O_3 and SiO_2 contents but lower amount of SO_3 than in mass-burn fly ash. RDF bottom ash has greater level of Fe_2O_3 but lower concentrations of CaO , Cl , and SO_3 than in both RDF and mass-burn fly ashes. In addition, coal fly ash has exclusively higher Al_2O_3 , Fe_2O_3 , and SiO_2 contents but lower amount of CaO than in incinerator ashes.

Distribution of heavy metals in MSWI ashes depends on vapor pressure of metal compounds and temperature of the different residue streams produced. Most volatile metals, e.g., cadmium, lead, and zinc are found in higher concentrations in fly ash than in bottom ash. On the contrary, copper is preferentially found in bottom ash. This is in agreement by Morf et al. (2000) who investigated the effect of operating conditions and input variations on the partitioning of metals in MSW incinerator. They summarized that about 6% of Cu, 54% of both Zn and Pb, and 90% of Cd in the waste feed were transferred into the combustion flue gas, while the rest was found in the bottom ash. The distribution of metals among different types of ashes was also influenced by operating conditions of the incinerator (Alba et al., 1997). However, heavy metals in Phuket MSWI fly ash sample were analyzed by extraction and performing a total acid digestion as given more detail in section 4.3.

Table 4.5 gives chemical and supplementary optional chemical requirements for Class-C and Class-F pozzolans according to ASTM C618-96. The table shows that chemical compositions of Phuket MSWI fly ashes can not be classified as both Class-C and Class-F pozzolans since some properties of the ash are not satisfied for the ASTM requirements.

Table 4.5 Chemical Compositions of Phuket MSWI Fly Ashes Compared with the ASTM Requirements for Class-C and Class-F Pozzolans

Chemical Composition	ASTM C618 Class-C	ASTM C618 Class-F	Raw Phuket MSWI Fly Ash	Sifted Phuket MSWI Fly Ash
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃ (%min)	50.0	70.0	7.21	6.34
SO ₃ (%max)	5.0	5.0	6.23	5.20
Moisture Content (%max)	3.0	3.0	1.35	1.29
LOI (%max)	6.0	6.0	9.74	9.70
Available alkalines as Na ₂ O (%max)	1.5	1.5	11.13	13.81

Note: Available alkalines as Na₂O (%) = Na₂O (%) + 0.658 K₂O (%)

4.1.8 Mineralogical Compositions

The crystalline phases of Phuket MSWI fly ash observed by X-ray powder diffraction (XRD) spectrometer are shown in Figure 4.7. Most abundant components in crystalline phases of the MSWI fly ash were KCl (sylvite), NaCl (halite), CaCO₃ (calcite), Ca(OH)₂ (portlandite), CaSO₄ (anhydrite), CaCl₂ (calcium chloride), and CaClOH (calcium chloride hydroxide). Moreover, ghehlenite (2CaO·Al₂O₃·SiO₂), revdite (Na₂SiO₅·5H₂O), and hydrocalumite (Ca₈Al(OH)₂₄(CO₃)Cl₂(H₂O)1.6(H₂O)) can be detected in the MSWI fly ash. The results verified that these main minerals consist of major constitutions of Al, Ca, Cl, K, Na, Si, and SO₃ that were detected by XRF. Other phases were very difficult to identify since the pattern was of great complexity and had numerous overlapping peaks. Additionally, the ash sample contained high quantities of poorly crystalline or amorphous materials. Compared mineralogical compositions of Phuket MSWI fly ash to MSWI bottom ashes from other researches, the main crystalline minerals in bottom ashes were quartz (SiO₂), calcite, magnetite (Fe₃O₄), hematite (Fe₂O₃), gypsum, ettringite (C₃A·CaSO₄·32H), and cristobalite (Zevenbergen et al., 1994).

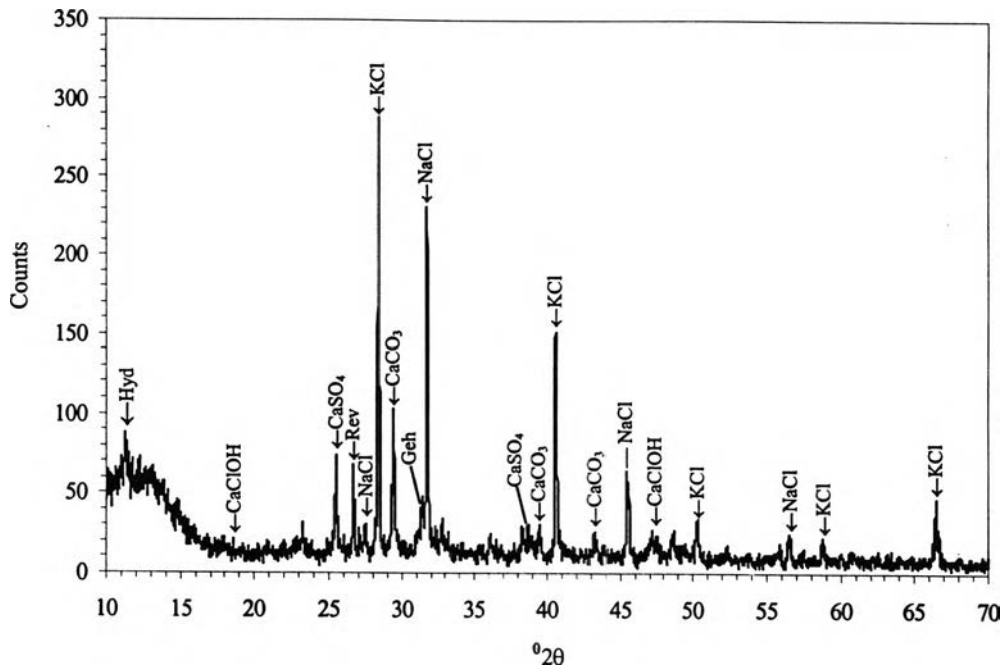


Figure 4.7 XRD Spectrum of Phuket MSWI Fly Ash

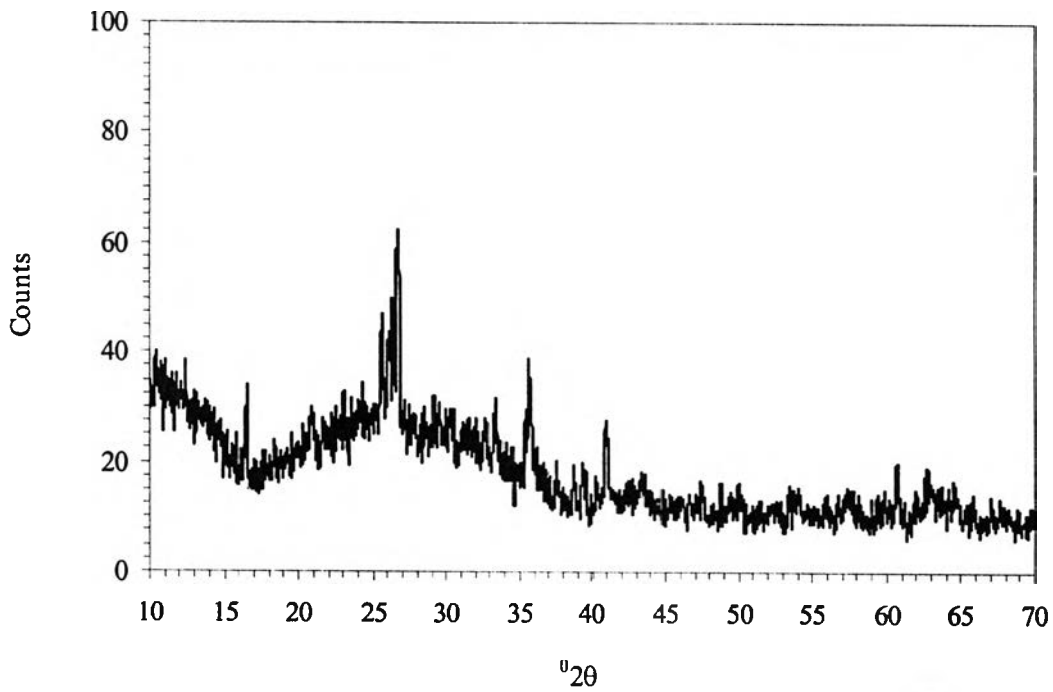


Figure 4.8 XRD Spectrum of Mae Moh Coal Fly Ash

Figure 4.8 illustrates XRD diffraction pattern of Mae Moh coal fly ash. The figure shows that the majority of coal fly ash is amorphous (non-crystalline or glassy phase) that only few crystalline components can be observed. The coal fly ash diffractogram is similar to what has been studied by previous researchers who investigated mineralogical compositions of Mae Moh fly ash (Hongpatanporn, 1990; Chai et al., 2001). They reported that the main crystalline components in lignite fly ash were quartz, anhydrite, calcite, and hematite. Coal fly ash particles are usually composed of glassy phase reactive in concrete and responsible for the pozzolanic properties. That is the reason why coal fly ash has been successfully utilized as a cement replacement material in construction applications.

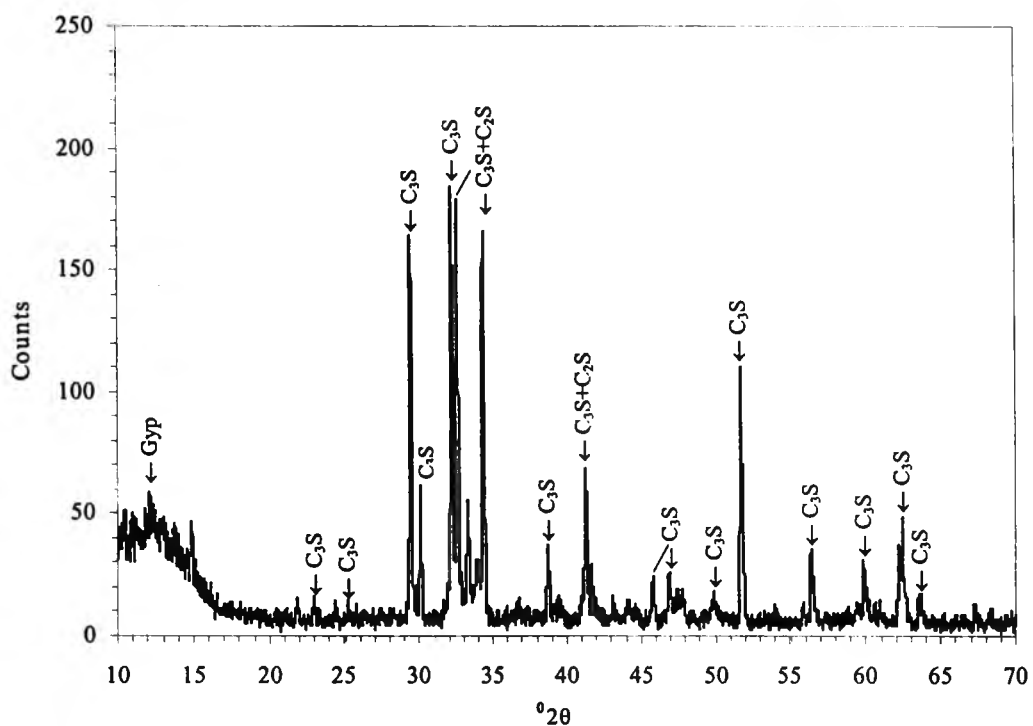


Figure 4.9 XRD Spectrum of Ordinary Portland Cement

Figure 4.9 shows XRD diffractogram of Portland cement used in this study. It can be identified that tricalcium silicate, C_3S , is the main crystalline phase that gives the essential properties of Portland cement. It undergoes an initial and final set within a few hours after mixing. Dicalcium silicate, C_2S , also finds in the Portland cement pattern. It produces little strength at early ages, but gains steadily strength at the later. However, it is not to be expected that the setting and strength properties of these pure

compounds should be identical to those of the minerals occurring in Portland cement since cement contains small amounts of the oxides which influence the reactivity (Lea, 1971). Another phase observed in small intensity in Portland cement clinker was gypsum that can react with C_3A to form ettringite.

4.2 Properties of Portland Cement with MSWI Fly Ash

4.2.1 Normal Consistency and Setting Time

Normal consistency and setting time of MSWI fly ash-cement pastes analyzed using vicat apparatus according to the standard test methods described in the ASTM C187-86 (reapproved 1991) and ASTM C191-92, respectively. Table 4.6 shows that water demand and setting time of MSWI fly ash-cement pastes are higher with the increase in percentage of MSWI fly ash replacement. The influence of MSWI fly ash on the properties of fresh concrete is also linked to the shape of fly ash particles. The increase in water requirement of MSWI fly ash concrete caused by the presence of the MSWI fly ash is usually associated with irregular and rough surface particles that absorb more water than the spherical shape.

Table 4.6 Water Requirement and Initial Setting Time of Phuket MSWI Fly Ash-Cement Pastes

Sample No.	Water Requirement	Initial Setting Time (min)
F00	0.254	65.6
F10	0.260	69.1
F15	0.266	87.2
F25	0.274	98.2

Note: Water requirements were reported in term of water-to-binder ratio ($w/(c+fa)$) at normal consistency.

4.2.2 Compressive Strength Development of MSWI Fly Ash-Cement Mortars

In this experiment, sifted MSWI fly ash was used as a replacement at 0%, 10%, 15%, and 25% by weight of binders (cement + fly ash) to make fly ash mortars. The mix proportions of these mortars were mentioned in Table 3.1 with constant water-to-binder ratio ($w/(c+fa)$) of 0.485.

Figure 4.10 shows the effect of cement replacement using MSWI fly ash on compressive strength of mortar. It can be seen from the figure that all fly ash specimens show lower compressive strength than the control (F00) strength at the same age. The higher the percentage of MSWI fly ash in the mix, the lower the compressive strength will be. Compared to control strength at the age of 60 days, the replacement of MSWI fly ash at 10% and 15% lower the strength about 4% and 5%, respectively. The compressive strength with 25%-MSWI fly ash replacement varies from 71.6% at 1 day to 84.2% at 60 days of control strengths. In each compressive strength curve, the rate of strength gain (slope of the curve) for MSWI fly ash mortar is slower than that for cement mortar at the early age (14 days or before).

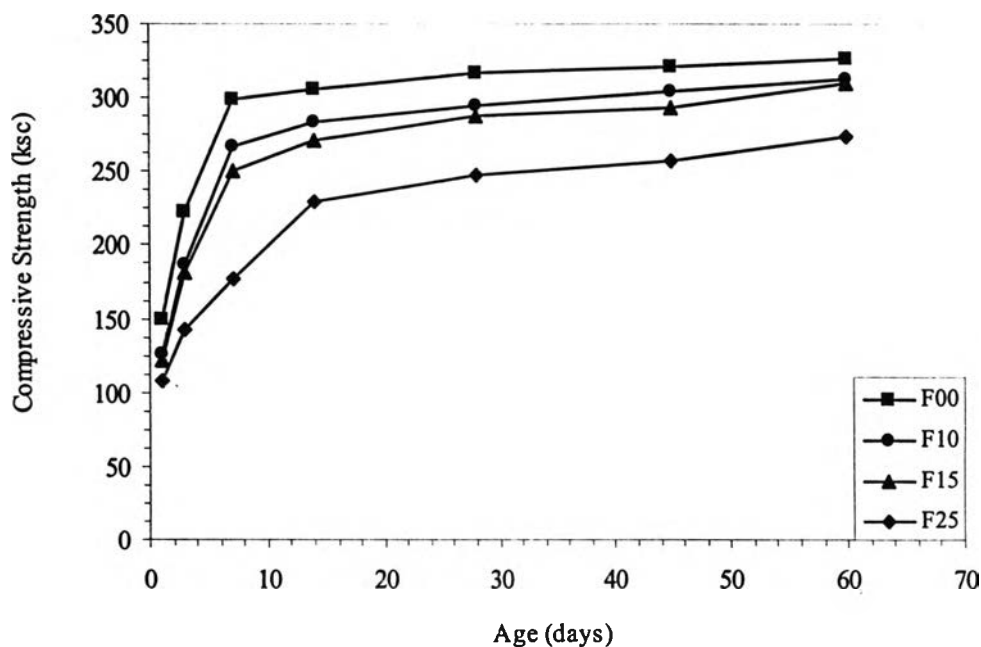


Figure 4.10 Compressive Strength Development of MSWI Fly Ash-Cement Mortars at Different Percent Replacements

Compressive strengths of Mae Moh coal fly ash-cement mortars (MXX) mentioned in this section were studied by Hongpatanporn (1990) whose mortars were mixed with 0%, 10%, 15%, 20%, and 30% coal fly ash replacement. In his experiment, water requirements in coal fly ash mortar mixes were varied in each mix so as to keep a constant flow required by the standard method (ASTM C109).

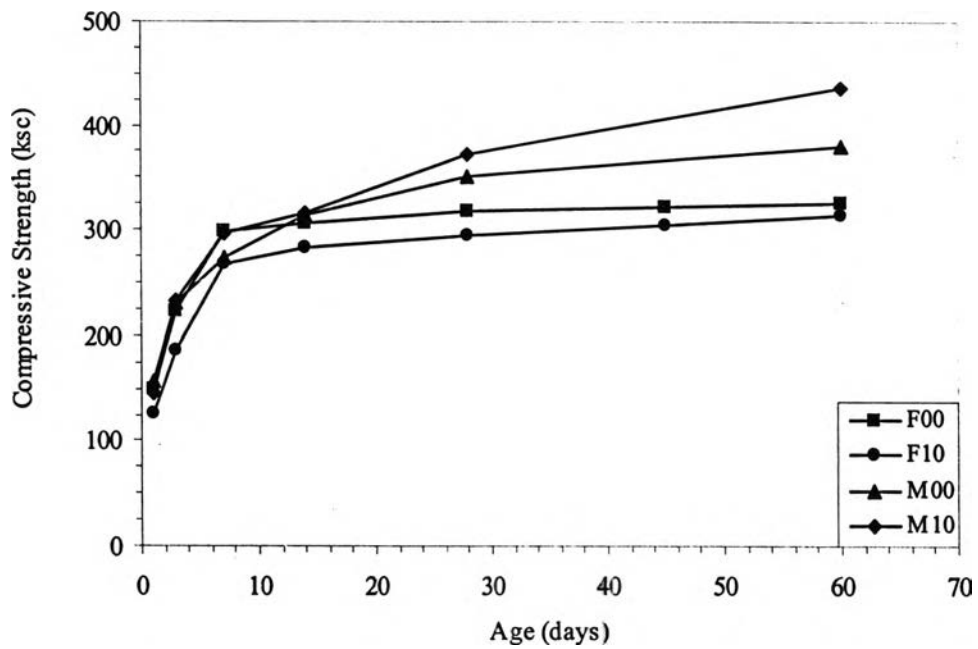


Figure 4.11 Compressive Strength Development of Cement Mortars with 10% for MSWI Fly Ash and Coal Fly Ash Replacements

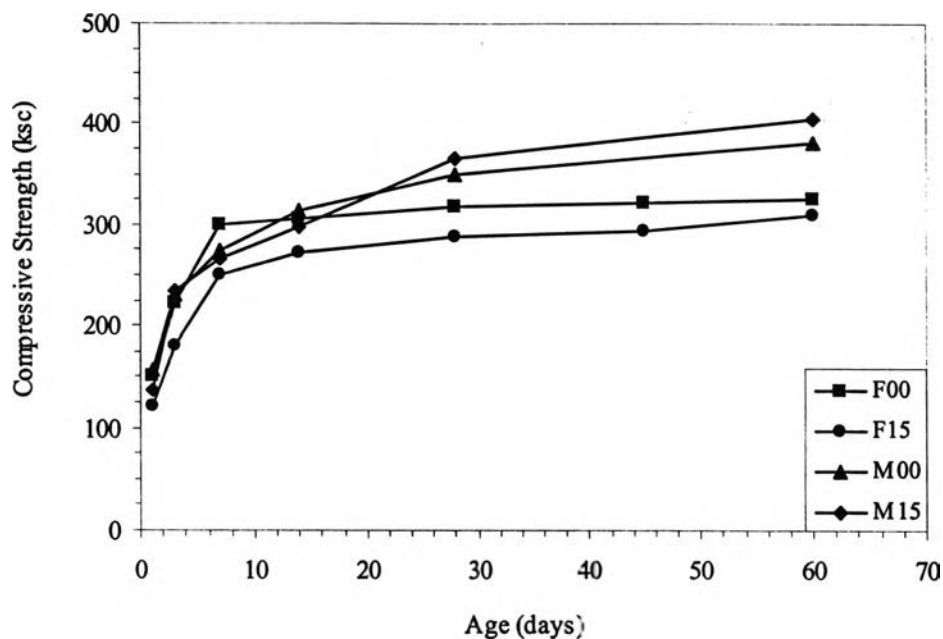


Figure 4.12 Compressive Strength Development of Cement Mortars with 15% for MSWI Fly Ash and Coal Fly Ash Replacements

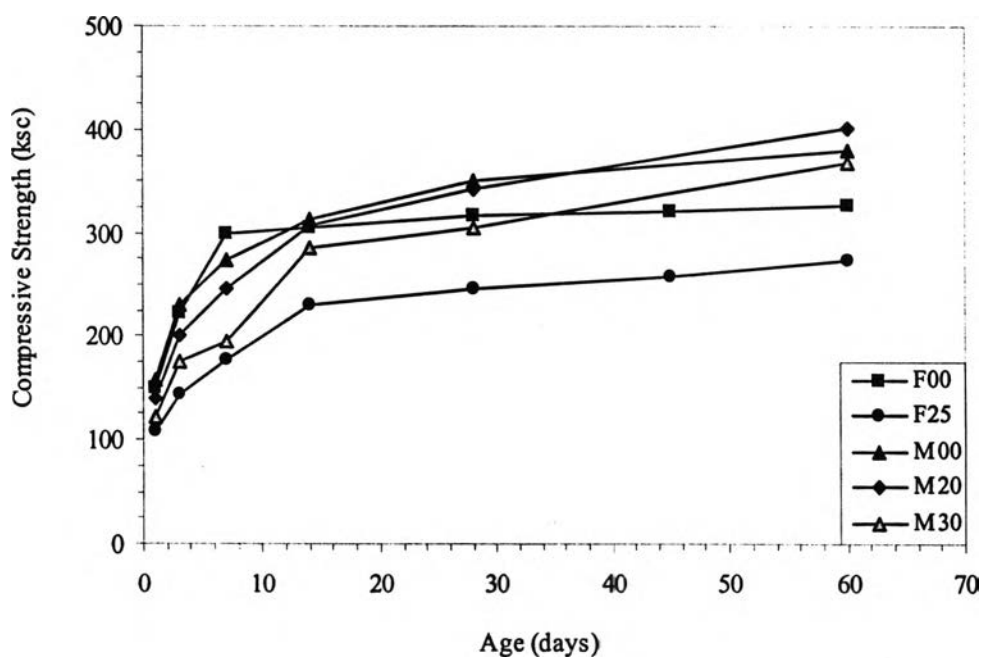


Figure 4.13 Compressive Strength Development of Cement Mortars with 25% for MSWI Fly Ash Replacement and 20% and 30% for Coal Fly Ash Replacements

Figures 4.11 and 4.12 illustrate compressive strength developments of MSWI fly ash and coal fly ash mortars at 10% and 15% replacements, respectively. As seen in both figures, compressive strengths of coal fly ash mortars started to outperform control mortar (M00) at the age of 3 days, while MSWI fly ash mortars had lower compressive strength than control (F00) at all ages as mentioned before. Figure 4.13 shows compressive strength development of MSWI fly ash mortars at 25% replacement and those of coal fly ash mortars at 20% and 30% replacements. After 60 days of curing, 20%-coal fly mortar just had a compressive strength slightly higher than the control. However, its compressive strengths after that age were exclusively high that was about 112% of control at 180 days (Hongpatanporn, 1990). For 30% replacement, coal fly ash mortars showed lower compressive strength at all ages so did Phuket MSWI fly ash mortars.

It can be observed from Figures 4.11 through 4.13 that compressive strengths of MSWI fly ash mortars are very low compared to Hongpatanporn's results. When chemical compositions of both fly ashes were considered, the amounts of SiO_2 plus Al_2O_3 , which contribute to strength development, were very different. In contrast to both oxides' properties, CaO in fly ash retarded the strength gain and causes unsoundness in mortars and concrete as stated by Lea (1971) and Wesche (1991). The amounts of SiO_2 and Al_2O_3 in sifted Phuket MSWI fly ash are 3.21% and 2.42%, respectively. These are exclusively lower than those of Mae Moh coal fly ashes (35.43% for SiO_2 and 28.27% for Al_2O_3). Moreover, the CaO content of MSWI fly ash is extremely high (34.40%) compared to 11.92% of coal fly ash. In addition to these chemical compositions, pozzolanic property may be another factor causing higher compressive strengths since the rates of compressive strength developments in coal fly ash mortar after 28 days of curing increase sharply (observed from the slopes of the compressive strength curves). Whereas coal fly ash mortar continues to gain strength over a long period influential from its pozzolanic reaction, MSWI fly ash does not show this property.

4.2.3 Development of Hydration and Pozzolanic Reactions in MSWI Fly Ash-Cement Pastes

It is generally accepted in pozzolanic reaction of fly ash that Ca(OH)_2 or CH released during cement hydration reacts with silicate and aluminate phases in fly ash to produce calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H). However, cement hydration and pozzolanic reactions do not proceed independently. Water soluble alkalis, sulphates, limes, and organics from fly ash may affect the surface reactions and nucleation and crystallization processes, especially in the early stages of cement hydration. The pozzolanic reactions correspondingly depend on the amount of calcium, alkalis, sulphates, silicate, and aluminate ions released into the liquid phase from cement and fly ash. Due to these complexities, study of the reactions by X-ray diffraction (XRD) analysis between MSWI fly ash and Portland cement is especially useful in developing an understanding of the phenomena, which are resulted from interaction processes.

Figures 4.14 through 4.17 summarized the X-ray diffractograms of hydrated compounds in pure cement pastes and the pastes with 10%, 15%, and 25% Phuket MSWI fly ash replacements. In each figure, paste samples were tested at the age of 1, 3, 7, 14, 28, 45, and 60 days after mixing in the same manner as compressive strength testing. These figures show that major phases indicated in the diffractograms of both pastes are C_2S , C_3S , and Ca(OH)_2 . It was doubtful that peaks of anhydrite (CaSO_4), calcite (CaCO_3), halite (NaCl), and syvite (KCl), major components in MSWI fly ash, did not appear in the XRD patterns of MSWI fly ash pastes. In addition, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can not be detected in the MSWI fly ash-cement pastes though excess dry lime was injected into flue gas for acid gas treatment in APC system.

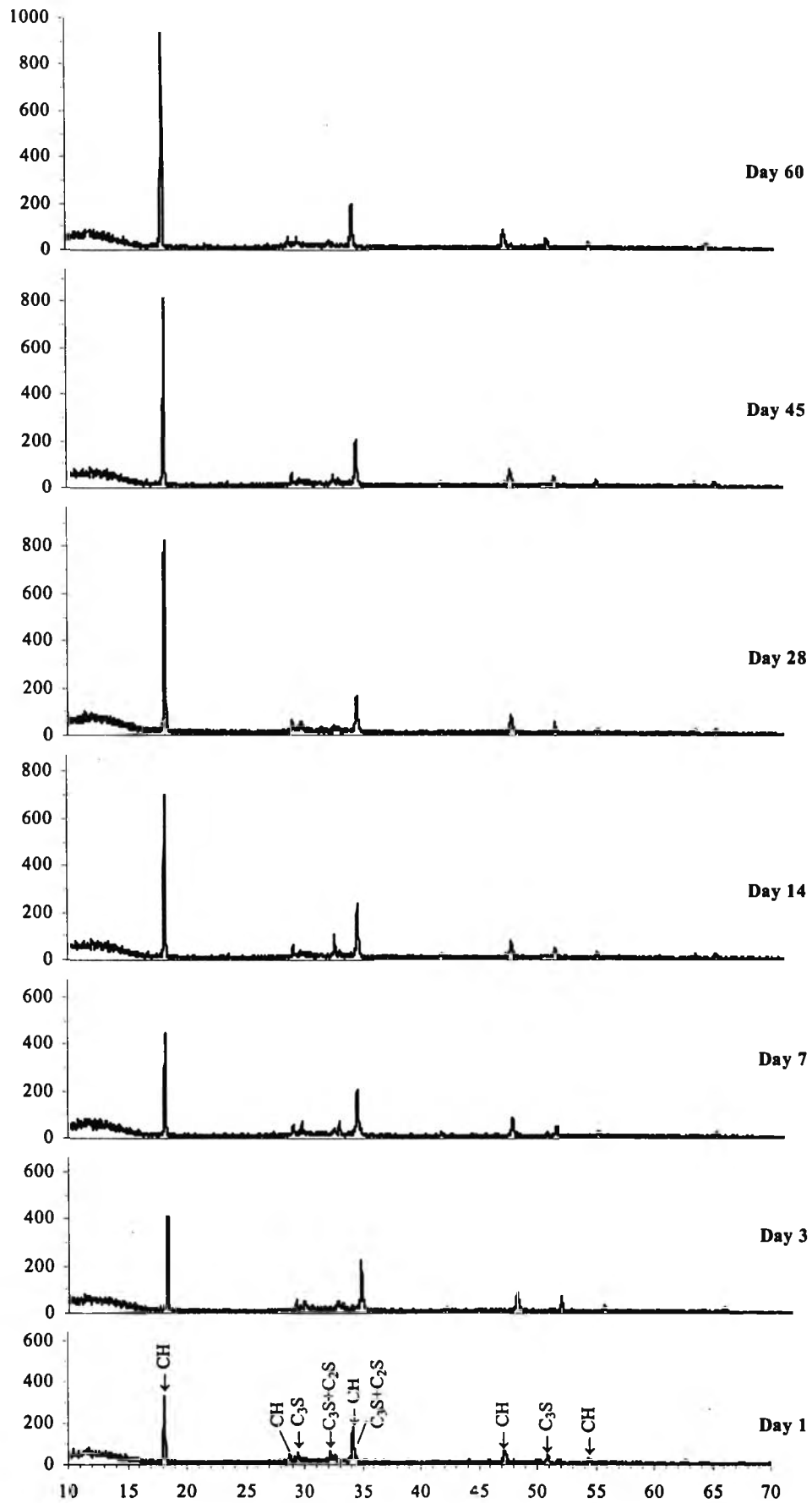


Figure 4.14 XRD Patterns of Cement Pastes at Different Ages

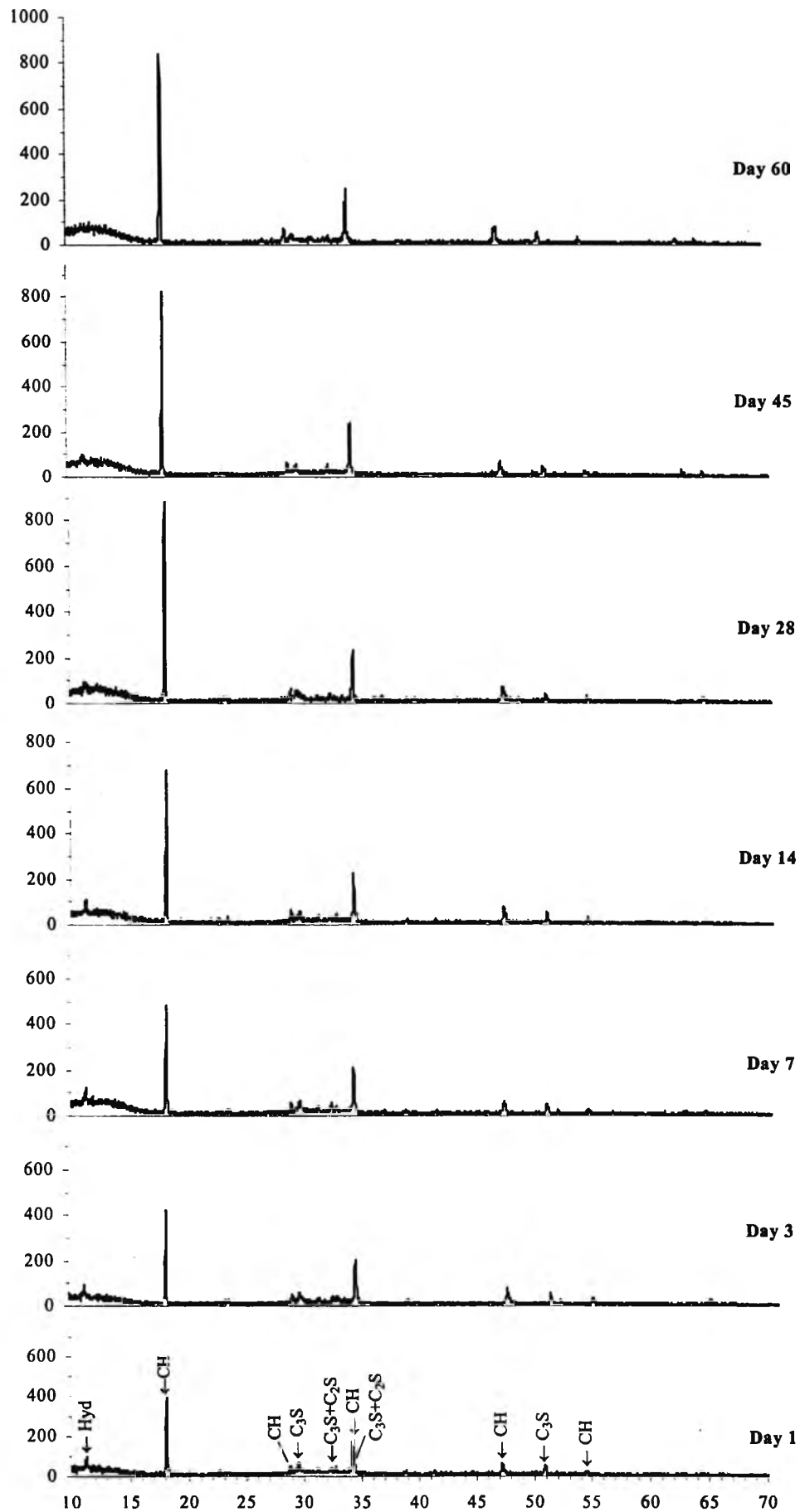


Figure 4.15 XRD Patterns of Cement Pastes with 10% Phuket MSWI Fly Ash at Different Ages

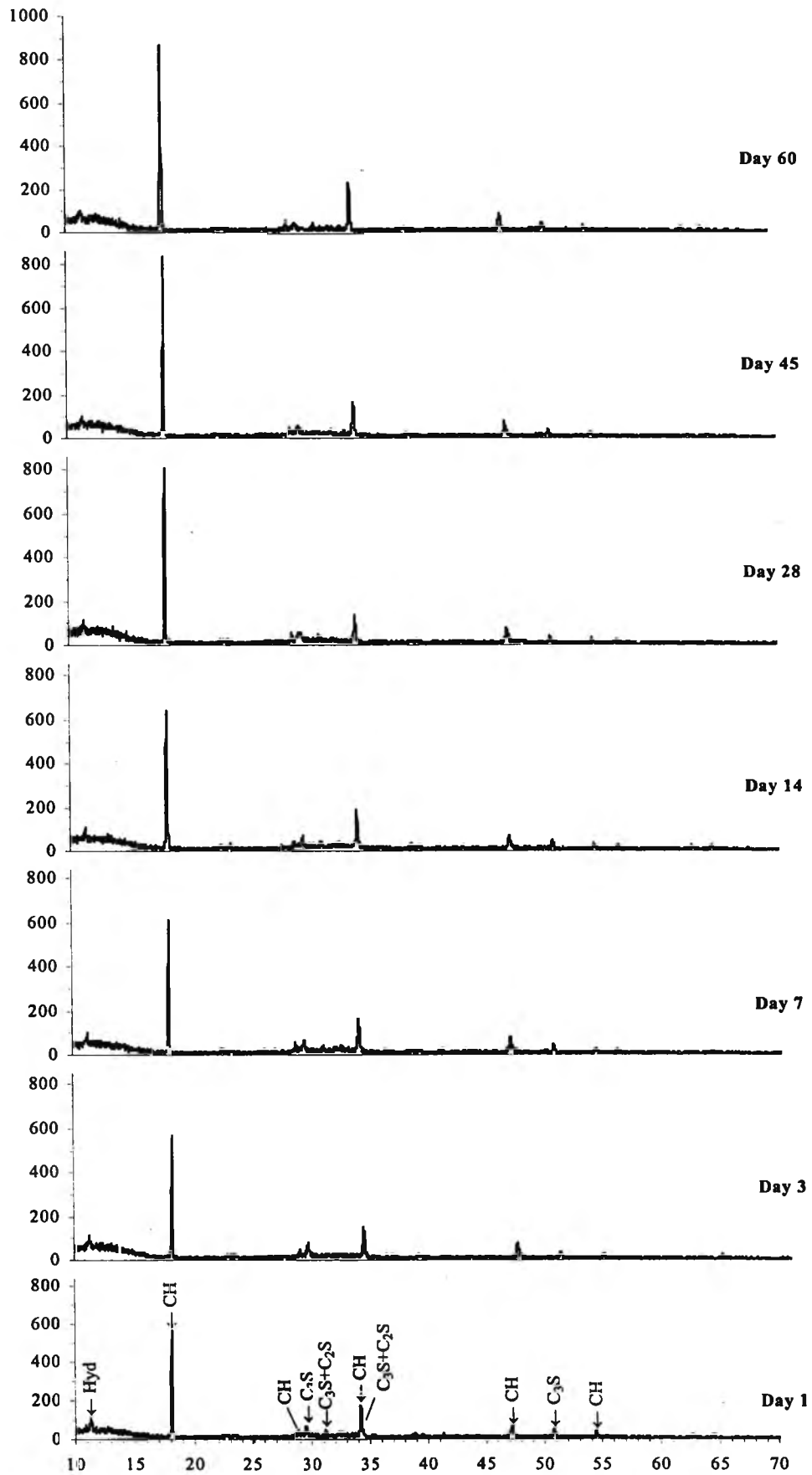


Figure 4.16 XRD Patterns of Cement Pastes with 15% Phuket MSWI Fly Ash at Different Ages

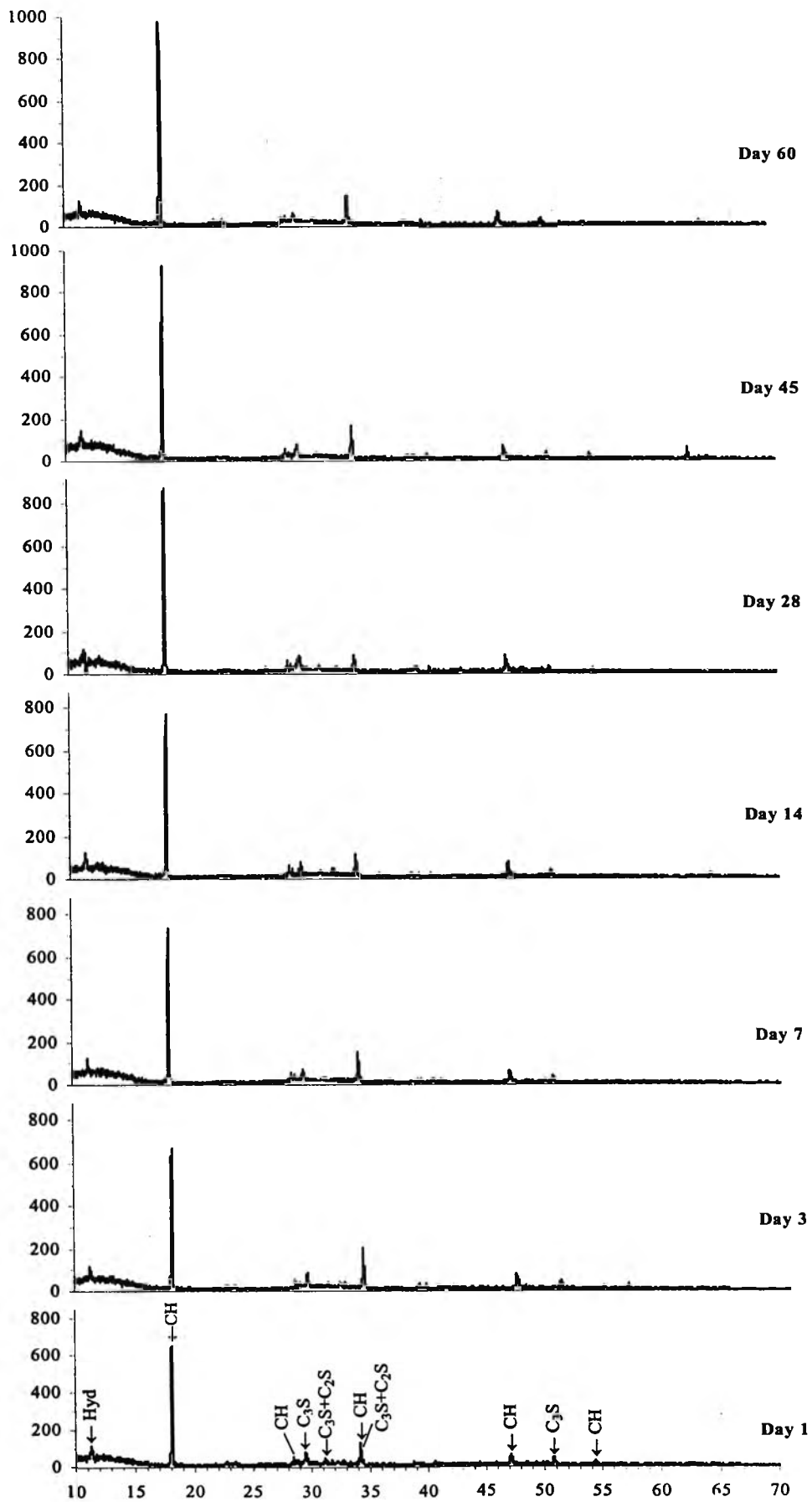


Figure 4.17 XRD Patterns of Cement Pastes with 25% Phuket MSWI Fly Ash at Different Ages

These diffractograms can be identified major phases in both cement paste and the paste with Phuket MSWI fly ash as CH, C₃S, and C₂S. In addition, a small peak of hydrocalcumite ($\text{Ca}_8\text{Al}(\text{OH})_{24}(\text{CO}_3)\text{Cl}_2(\text{H}_2\text{O})1.6(\text{H}_2\text{O})$) was detected in the fly ash-cement paste with insignificant intensity at $11.20^\circ 2\theta$. The obviously strong peaks of CH were $18.11^\circ 2\theta$ and $34.16^\circ 2\theta$, whereas those of C₃S were $29.35^\circ 2\theta$, $34.24^\circ 2\theta$, and $51.71^\circ 2\theta$. Around $32.1^\circ 2\theta$ and $41.2^\circ 2\theta$ diffraction peaks of C₂S and C₃S were overlapping so hard to identify. Other hydration products of cement pastes did not have very clear diffraction peaks, due mainly to their semi-amorphous nature and overlapping peaks of the hydrated and anhydrous compounds.

Investigation on the reduction of starting materials in cement paste and the increase of hydration products can help to evaluate hydration reaction of MSWI fly ash-cement pastes as has been studied by Rachakornkij (2000). According to diffraction patterns, the product of CH from hydration process was determined at its strongest peak intensity at $18.11^\circ 2\theta$ (PDF database from ICDD). The relative intensities of C₃S, the main compound in cement, were considered at $29.35^\circ 2\theta$. Figures 4.18 and 4.19 show the relationship between the intensity value and curing age of both compounds.

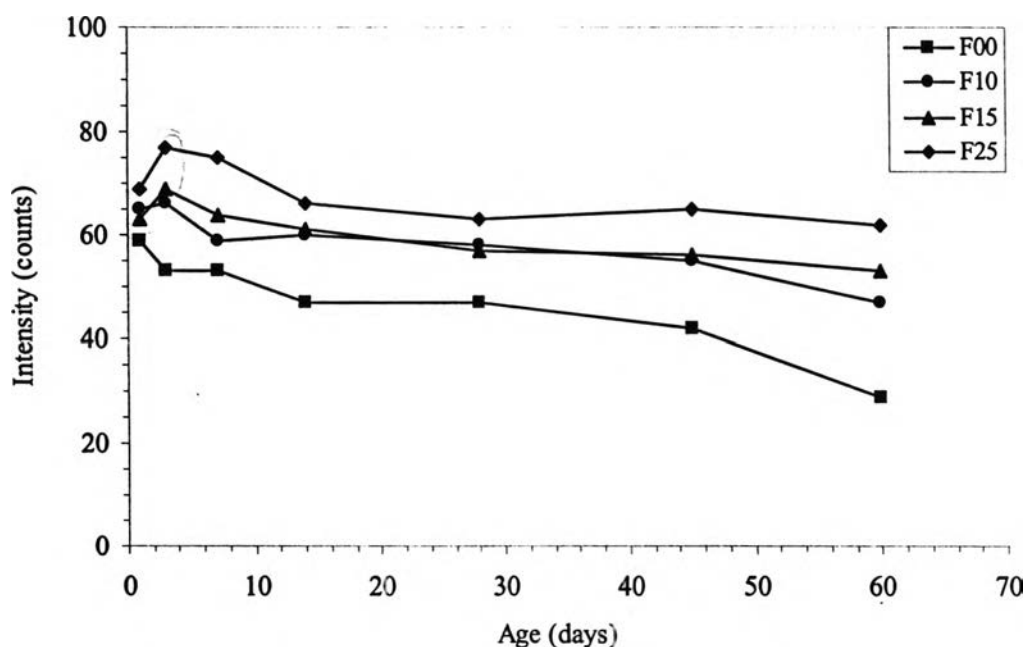


Figure 4.18 Intensity of C₃S at $29.35^\circ 2\theta$ of Cement Pastes with Different Percentage of MSWI Fly Ash Replacements

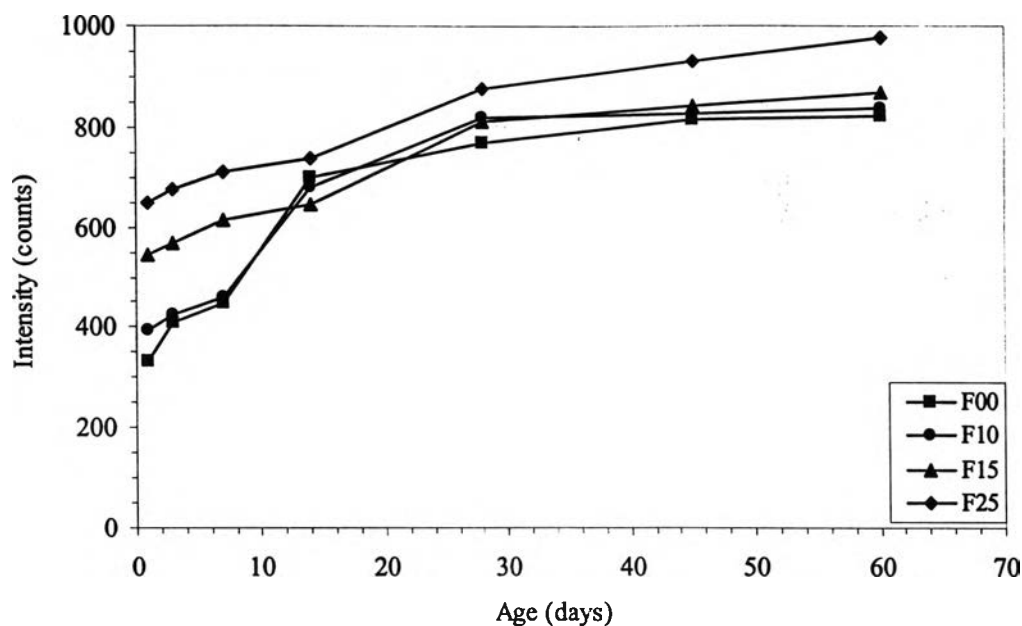


Figure 4.19 Intensity of CH at $18.11^{\circ}2\theta$ of Cement Pastes with Different Percentage of MSWI Fly Ash Replacements

Figure 4.18 shows that the overall intensities of C_3S in control paste are lower than in the MSWI fly ash-cement pastes. The apparent increase in C_3S intensities at the first three days may be caused by the inaccuracy from reading since there is no significant difference in the intensities. However, these can be assumed that C_3S is more largely consumed in the control than in the MSWI fly ash pastes. Then, MSWI fly ash seems to retard the hydration reaction of Portland cement and also the strength development of the pastes.

Calcium hydroxide (CH), the main crystalline product from cement hydration, may notify how the hydration reaction will be when MSWI fly ash is used as an additional binder in cement paste. Furthermore, the intensity of CH in fly ash paste is roughly indicative of the potential of compressive strength of fly ash concrete. Figure 4.19 shows that the intensities of CH in MSWI fly ash-cement pastes were higher than in the control at the same age. The distinguished intensity of CH in the incinerator fly ash-cement pastes may be a result of the nature of the MSWI fly ash that associates with large amount of lime from flue gas treatment process. Then, the observed crystalline intensity of CH in fly ash-cement paste were more influenced by hydrated lime in the MSWI fly ash than resulted from the product from hydration reaction.

4.3 Leachate Characteristics of MSWI Fly Ash-Cement Products

According to the Notification of Ministry of Industry No. 6 (1997), stabilized and solidified matters must be analyzed for the presence of heavy metals in their leachate by leachate extraction procedure. As previously mentioned in section 4.1.7, the overall chemical compositions of Phuket MSWI fly ashes determined by XRF analysis revealed large amount of PbO (0.12% for raw MSWI fly ash and 0.14% for sifted MSWI fly ash). These lead oxides in bulk fly ashes were compared to the U.S. EPA SW-846 Method 1311, the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, so as to determine whether the ash is necessary to analyze individual heavy metal according to the Toxicity Characteristic Leaching Procedure (TCLP). That is if the total analysis of bulk fly ash demonstrates that individual heavy metal concentration is less than or equal to 20 times of the health-based heavy metal limits of waste-derived residues, TCLP may not be necessary for that metal.

Although the XRF results expressed in oxide form, the conversion factor set in the Appendix VII of 40 CFR 266, was used to adjust the concentration limit of lead element into oxide form. The calculated PbO concentration at 20-time health-based limit was 0.011% while XRF analytical results for PbO of raw and sifted MSWI fly ash were 0.12% and 0.14%, respectively. Since the concentration of lead oxide exceeded 20 times of the limits, then Phuket incinerator fly ash required TCLP test to determine lead and other heavy metals in the leachate.

For Thai regulation, the list of regulated heavy metals and their limits are exactly the same as that of the TCLP test. These heavy metal limits are shown in Table 4.7 along with the analytical results from the study. Even though the concentration of lead oxide in Phuket MSWI fly ash failed the 20-time TCLP limits, all heavy metals leached from Phuket fly ash met the regulatory limits. Furthermore, all solidified MSWI fly ash mortar specimens, control sample, and bottom ash passed the limits. Therefore, Phuket MSWI fly ash had a great potential to be utilized as a cement replacement material in concrete since the leachates from the fly ash and the incinerator fly ash products were legally acceptable.

Table 4.7 Leachate Concentrations of Phuket Fly Ash and Fly Ash Mortar Specimens

Element	Limit (mg/L)	Leachate Concentration (mg/L)					
		Phuket MSWI BA	Phuket MSWI FA	F00	F10	F15	F25
Ag	5	<0.02	<0.007	<0.007	<0.007	<0.007	<0.007
As	5	<0.04	<0.007	<0.007	<0.007	<0.007	<0.007
Ba	100	-	1.273	0.393	0.387	0.431	0.433
Cd	1	0.02	<0.004	<0.004	<0.004	<0.004	<0.004
Cr	5	0.03	0.062	0.060	0.076	0.058	0.049
Hg	2	<0.0005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	5	0.16	1.369	<0.050	<0.050	<0.050	<0.050
Se	1	<0.0005	<0.080	<0.080	<0.080	<0.080	<0.080

Note: Analysis results for Phuket MSWI bottom ash (PC Monteney, 2001) were reported as references. BA: Bottom Ash, FA: Fly Ash, “-” means not reported.