CHAPTER 4.

CEMENT CONSTITUENTS

Expansive cement is hydraulic cement, which expands during the early hydration period after hardening. It can be developed and blended with ordinary portland cement, which induces a compressive prestress of sufficient magnitude to compensate for the shrinkage effect when expanding under restraint. **Shrinkage Compensating Cement or Non–Shrink Cement** is expansive cement of which its magnitude of expansion is so small that the prestress developed in concrete is 25 to 100 psi. (0.2-0.7 MPa.)(20). This magnitude is enough to offset tensile stress due to the drying shrinkage of concrete. And **Self–Stressing Cement** is expansive cement with a large magnitude of expansion to produce prestress levels on the order of 1,000 psi. (6.9 MPa.).

Expansive cement was originally developed by Alexander Klein by adding amounts of $C_4A_3\underline{S}$ and $C\underline{S}$ to produce the modified portland cement clinker known as Sulfoaluminate-Type Cement. The expansion in this expansive cement is associated with the formation of a calcium sulfoaluminate hydrate, Ettringite ($3C_6A\underline{S}_3H_{32}$). Ettringite also crystallizes as hexagonal prisms. The exact morphology depends on the supply of ion and the space for crystal growth. In ordinary portland cement, ettringite consists of long slender needles typically 10x0.5 micrometer. The ettringite in expansive cement is rapidly formed as seen by the large quantities of needles. Generally the crystals are not large enough to be seen clearly by optical microscope. But in concrete that has deteriorated from sulfate attack, large crystal of ettringite can be seen.

Henri Lossier classified non-shrink cement by the degree of expansion as shown in table 4.1

Commercial non-shrink cement began in the United States in the late 1960s. ASTM C 845(28) has divided this cement into three types. The expansion characteristic of this expansive cement is based on the formation of ettringite.

Table 4.1 Non-shrink cements classified by Lossier.

Non-Shrink Cement	Level of Expansion (mm/meter)
Non-shrink cements in which expansion just neutralizes the shrinkage	2-5
Slightly expansive cement	5-6
Medium expansive cement	8-10
Highly expansive cement	12-15

The three types of expansive cement are expansive cement type K, expansive cement type M, and expansive cement type S. **Type K expansive cement** is produced by grinding a mixture of portland cement compounds, anhydrous sulfoaluminate ($C_4A_3\underline{S}$), calcium sulfate ($CaSO_4$) and lime (CaO) in a suitable proportion. The other two expansive hydraulic cements, which are expansive cement type M and type S are no longer commercially produced in the United States. They are different from type K cement in the source of aluminate ions for ettringite formation. **Type M expansive cement** is a mixture of portland cement, calcium aluminate cement (CA), and calcium sulfate. **Type S expansive cement** is composed of a very high C_3A portland cement and a large amount of calcium sulfate. The stoichiometry of expansive reactions in the three types of cement can be expressed as:

$$C_4A_3\underline{S} + 8C\underline{S} + 6C + 96H \text{ ----> } 3C_6A\underline{S}_3H_{32} \quad \text{(Type K)} \qquad (4.1)$$

$$CA + 3C\underline{S} + 2CH + H \text{ ----> } C_6A\underline{S}_3H_{32} \quad \text{(Type M)} \qquad (4.2)$$

$$C_3A + 3C\underline{S} + 32H \text{ ----> } C_6A\underline{S}_3H_{32} \quad \text{(Type S)} \qquad (4.3)$$

Their principal constituents and reactive aluminates for ettringite formation of each type of cement are shown in table 4.2.

In China, five types of expansive concrete have been produced and used for either self-stressing or shrinkage compensating purposes. Their application is for high early strength, later strength, low temperature concrete, joint filling and grouting. Table 4.3 shows the types of expansive cement and their constituents.

Table 4.2 Types of non-shrink cement and their constituents.

Expansive Cement	Principal Constituents	Reactive Aluminates Available for Ettringite formation
Type K	1. Portland Cement 2. Calcium Sulfate (Gypsum) 3. Expansive Agent containing $C_4A_3\underline{S}$	$C_4A_3\underline{S}$
Type M	1. Portland Cement 2. Calcium Sulfate 3. Calcium Aluminate Cement (CA & $C_{12}A_7$)	CA & $C_{12}A_7$
Type S	1. Portland Cement high in C_3A 2. Calcium Sulfate	C_3A

Table 4.3 Types of expansive cement in China.

Types	Main constituents
1. Silicate expansive cement	Portland cement Aluminate cement Gypsum
2. Alunite expansive cement	Portland cement Uncalcined alunite Anhydrite, fly ash
3. Sulfoaluminate expansive cement	Portland cement Clinker $C_4A_3\underline{S}$ Gypsum
4. Low heat gypsum-slag expansive cement	Portland cement Slag Anhydrite
5. Aluminate self stressing cement	Aluminate cement Gypsum

4.1 CHEMICAL COMPOSITION OF CONSTITUENTS

Shrinkage compensating cement consists of a mixture of portland cement, an expansive agent in the form of calcium sulphoaluminate and a stabilising agent which is usually fly ash. The amount of expansion will be controlled by the proper proportioning of these three constituents.

4.1.1 ORDINARY PORTLAND CEMENT

Portland cement(28) is hydraulic cement produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, it usually contains one or more of the forms of calcium sulfate as an interground addition. Although portland cement consists of various compounds of calcium, the results of chemical analyses are reported in terms of oxides of the element present.

Fig. 4.1 SEM of unhydrated OPC particles field width of 320 microns (x350).
(David Lange, UIUC)

Major Compound of Cement

The chemical composition of ordinary portland cement is given in table 4.4. The quantities of all components do not add up to 100% due to impurities. The common practice for determining and calculating the compound of cement composition from the oxide analysis by using stoichiometry was originally developed by R.H. Bogue. The simple Bogue calculations given in ASTM C-150 are suitable for most purposes. They are as follows:

$$C_3S = 4.071C - 7.6S - 6.718A - 1.43F - 2.852\underline{S} \qquad (4.4)$$

$$C_2S = 2.867S - 0.7544\,C_3S \qquad (4.5)$$

$$C_3A = 2.65A - 1.692F \qquad (4.6)$$

$$C_4AF = 3.043F \qquad (4.7)$$

These sets of equations are applicable to portland cement with an A/F ratio 0.64 or higher. Other sets of equations should be applied to cement with a A/F ratio less than 0.64. Bogue equations assume the chemical reactions of formation of clinker compounds to have proceeded to completion and the presence of impurities such as MgO and alkalies can be ignored. Typical chemical compound compositions in cement are shown in table 4.4 and table 4.5.

Table 4.4 Typical chemical compound in expansive cement and OPC (%).

Compound	Common Name	Notation	Molecular Weight	Percent by Mass EC.		Percent by Mass OPC.(12)	
				Max. (%)	Min. (%)	Max. (%)	Min. (%)
CaO	Lime	C	56.0794	63.0	42.8	67.0	60.0
SiO_2	Silica	S	60.0848	22.2	9.8	25.0	17.0
Al_2O_3	Alumina	A	101.9612	12.6	5.6	8.0	3.0
SO_3	Sulfur Trioxide	$\underline{S}$	80.0622	10.0	3.2	3.0	1.0
Fe_2O_3	Ferric Oxide	F	159.6922	6.4	1.6	6.0	0.5
MgO	Magnesia	M	40.3114	2.5	0.7	4.0	0.1
Na_2O	Alkalis	N	61.9790	0.2	0.1	1.3	0.2
K_2O	Alkalis	K	94.2034	0.5	0.3		

Table 4.5 Typical composition of major compound in expansive cement and OPC (%).

Compound	Molecular Weight	%by Mass EC.	%by Mass OPC.	
		Max. (%)	Max. (%)	Min. (%)
C_3S	228.323	13.0	55.0	45.0
C_2S	172.2436	51.7	30.0	20.0
C_3A	270.1994	-	12.0	8.0
C_4AF	485.971	-	10.0	6.0
$C_4A_3\underline{S}$	610.2634	17.9		
$C_{12}A_7$	1386.6812	-		
Free lime	56.0794	-		

Hydration Reaction of Portland Cement

The hydration reaction of ordinary portland cement consists of two mechanism reactions, through-solution mechanism and topochemical mechanism. The through-solution hydration involves the dissolution of anhydrous compounds. The formation of hydrates in the solution and all constituents of original compounds react completely. The reaction of topochemical hydration takes place directly at the surface of the anhydrous cement compounds without their going into solution. The through-solution mechanism is dominant in the early stages of cement hydration while at a later stage, hydration of the cement particles may occur by topochemical reaction.

Calcium Silicates Phase

The hydration reactions of two calcium silicates are shown in eqs. 4.8 and 4.9.

$$2C_3S + 6H \text{ ----> } C_3S_2H_3 + 3CH \tag{4.8}$$

$$2C_2S + 4H \text{ ----> } C_3S_2H_3 + CH \tag{4.9}$$

The principal hydration product of cement is a calcium silicate hydrate. The hydrate C_3S is a major compound in cement. Rate of hydration when mixing cement with water can be divided into 5 stages according to the heat of hydration. The stages of reaction are periods of rapid evolution of heat, dormant period, acceleration period, slows down period and steady stage.

The calculations of stoichiometric reactions show that the hydration of C_3S would produce 61 percent of $C_3S_2H_3$ and 39 percent of calcium hydroxide, whereas the hydration of C_2S would produce 82 percent of $C_3S_2H_3$ and 18 percent of calcium hydroxide.

Tricalcium Aluminate Phase

The hydration of tricalcium aluminate involves reactions with sulfate ions, which are supplied by gypsum. The hydration reaction is shown in equation 4.10.

$$C_3A + 3C\underline{S}H_2 + 26H \text{ ----> } C_6A\underline{S}_3H_{32} \tag{4.10}$$

The common name of calcium sulfoaluminate hydrate ($C_6A\underline{S}_3H_{32}$) is ettringite. Ettringite is a stable hydration product only when there is an ample supply of sulfate. If the sulfate is consumed before the C_3A has completely hydrated, ettringite will transform to another calcium sulfoaluminate hydrate containing less sulfate. The transformation reaction is shown in equation 4.11.

$$2C_3A + C_6A\underline{S}_3H_{32} + 4H \text{ ----> } 3C_4A\underline{S}H_{12} \tag{4.11}$$

When monosulfate aluminate comes into contact with the new source of sulfate ions, ettringite can be formed again.

$$C_4A\underline{S}H_{12} + 2C\underline{S}H_2 + 16H \text{ ----> } C_6A\underline{S}_3H_{32} \tag{4.12}$$

Ferrite Phase

Hydration of C_4AF in cement is the same sequence of C_3A but the reaction is slower and with less heat. If the iron content is raised, hydration becomes slower.

Cement with low C_3A and high C_4AF is resistant to sulfate attack. This means that the formation of ettringite from monosulfoaluminate does not occur.

$$C_4AF + 3C\underline{S}H_2 + 21H \text{ ----> } C_6(A,F)\underline{S}_3H_{32} + (A,F)H_3 \qquad (4.13)$$

MICROSTRUCTURE OF HYDRATION PRODUCTS

Hydration products in cement paste consist of various compounds$^{(12)}$. Each compound contributes effects and behavior on the pastes. Summary properties are shown in table 4.6.

A. CSH

Calcium silicate hydrate (CSH) is a major compound of hydrate cement paste. It occupies about 30-50% of the paste volume. It is not a well defined compound. The formula $C_3S_2H_3$ is an approximate description. The C/S ratio varies between 1.5-2.0 and maybe higher. Water content varies and depends on the relative humidities. This is because the water associated with CSH exists in several different states.

CSH is not a well crystallized material and it is very nearly amorphous. It develops as a mass of extremely small irregular particles of indefinite morphology. It forms a spiny appearance like a burr. The spines are seen to radiate outward into the surrounding pore space and have various pointed, blunt, flat, long and thin branches.

It is thought that the varying morphologies reflect the varying compositions of CSH and the conditions of formation within the paste. As hydration proceeds, the underlying CSH grows in thickness and dominants the CSH in mature paste. The spines of CSH begin to intermesh and begin to form a solid bond between two cement grains as hydration reaction proceeded.

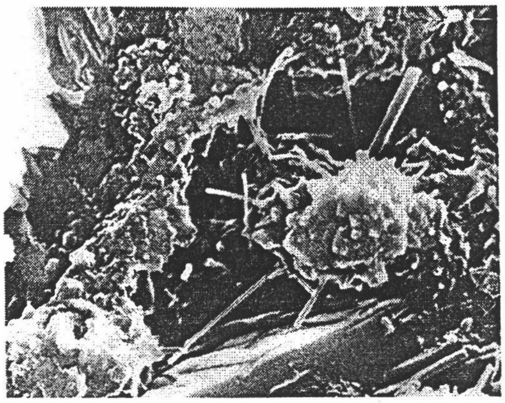


Fig. 4.2 SEM of amorphous CSH, needle of ettringite and flat plate of calcium hydroxide.

B. Calcium Hydroxide

Calcium hydroxide is a well crystallized material with a definite stoichiometry. It occupies 20-25 percent of the hydrated cement paste. It forms a large hexagonal prism morphology. The morphology usually varies from nondescript to stacks of large plate. It depends on available space, temperature and impurities present in the system. Calcium hydroxide may vary in morphology, being either small equal dimension crystals, large flat, plate-like crystals or large thin, elongated crystals. Calcium hydroxide will only grow where free space is available. If it is impeded by another calcium hydroxide crystal, it may stop and grow in another direction.

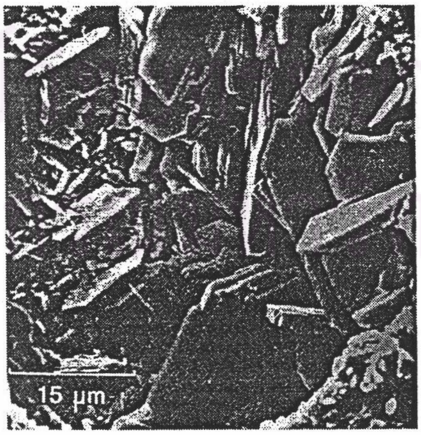


Fig. 4.3 Calcium hydroxide crystals.

C. Ettringite

Calcium sulphoaluminate occupies 10-15 percent of the solid volume in the hydrated cement paste. Ettringite also crystallizes as hexagonal prisms but is typically seen as long slender needles, typically 10x0.5 micron. Ettringite loses considerable amounts of its crystal water on drying.

When first formed, monosulfoaluminate tends to form clusters or “rosettes” of irregular plates. The needles grow into the capillary pores between cement grains. Later, these grow into well developed, but very thin hexagonal plates and convert to monosulfatealuminate.

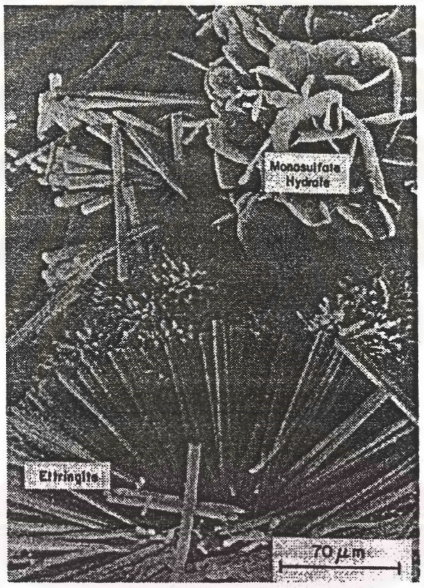


Fig. 4.4 SEM of monosulfate hydrate and ettringite.$^{(6)}$

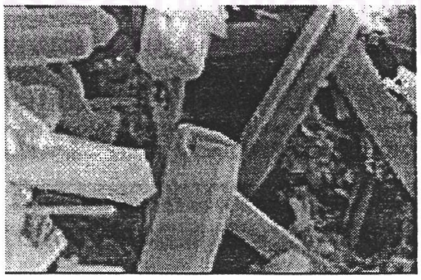


Fig. 4.5 Needle like of ettringite.

D. Other Components

The unhydrated clinker grains may be found in the hydrated cement pastes. There will also be a small amount of magnesium hydroxide. These will not total more than 5 percent of the volume of pastes.

Table 4.6 Properties of the hydration products of portland cement compounds.(12)

Compound	Specific Gravity	Crystallinity	Morphology	Typical Crystal Dimensions
CSH	2.3-2.6	Very poor	Spines; Unresolved morphology	1x0.1 micron
CH	2.24	Very good	Nonporous striated material	0.01-0.1 mm.
Ettringite	~1.75	Good	Long slender prismatic needles	10x0.5 micron
Monosulfoaluminate	1.95	Fair	Thin hexagonal plates; irregular "rosettes"	1x1x0.1 micron

4.1.2 EXPANSIVE AGENT

The expansion of expansive cement is based on the formation of ettringite during the hydration reaction of cement and the expansive agent. Calcium sulphoaluminate, an expansive agent, provides a source of calcium aluminate and sulfate ions to form ettringite.

Major Compound of Expansive Cement

The Bogue equation, calculated for the major compound in ordinary portland cement, can not be applied to the formation of expansive cement. Mehta(6) and Evans(29) introduced a modification of the Bogue equation from a number of different expansive cement tests. The summations of equation are shown in equations 4.14, 4.15, 4.16, 4.17 and 4.18.

Modified Bogue Equation

$$C_2S = 2.86S \tag{4.14}$$

$$C_4AF = 3.0375F \tag{4.15}$$

$$C_4A_3\underline{S} = 7.625\underline{S} - 1.2708F \tag{4.16}$$

$$C_{12}A_7 = 1.9412A - 2.33\underline{S} - 1.2375F \tag{4.17}$$

$$\text{Free lime} = C - 0.65\ C_2S - 0.461\ C_4AF - 0.367\ C_4A_3\underline{S} - 0.485\ C_1 \tag{4.18}$$

Hydration Reaction of Expansive Agent (Related to formation of Ettringite)

At the early stage of hydration, ettringite ($C_6A\underline{S}_3H_{32}$) forms as very small irregular particles around $C_4A_3\underline{S}$. On further hydration, these particles change to needle-like crystals arranged radially around $C_4A_3\underline{S}$ particles.(13) Hydration is assumed to proceed according to the stoichiometry equation shown in equations 4.19 and 4.20.

$$C_4A_3\underline{S} + 8C\underline{S} + 6C + 96H \dashrightarrow 3C_6A\underline{S}_3H_{32} \tag{4.19}$$

$$C_3A + 3C\underline{S} + 32H \dashrightarrow C_6A\underline{S}_3H_{32} \tag{4.20}$$

Ettringite is formed on the surfaces of expansive particles, acting as coating to prevent water and sulfate from reaching the surface of the particles. At that stage, it should not allow a sudden or rapid increase in rate of hydration. The crystals grow in solutions as long as the necessary ingredients are available. But when the crystals become confined, the growth of expansion will stop.

Kalousek and Benton(18) divide the ettringite crystals into two categories; iron ettringite and aluminum ettringite. Iron ettringite is a product of the ferrite phase that does not grow in size. Expansive force does not develop and the paste does not expand. The aluminum ettringite is a product of the aluminate phase. The crystals grow in size by the deposition of the participating irons from the surrounding solution. They are the source of expansion.

Both reactions 4.19 and 4.20 are due to the presence of calcium hydroxide(11). The first reaction occurs earlier. When calcium ions are abundant in mixture, crystallized ettringite is formed in fine grains coating the surface of expansive particles. This coating acts on the adjacent particles to produce expansion. The magnitude of expansion increases with the increasing amount of calcium hydroxide. In the absence of calcium hydroxide no expansion is produced even if ettringite is formed. The ettringite crystals form large crystals in the solution which yield no expansion.

4.1.3 FLY ASH

Fly ash is a fine residue from the combustion of coal. The mineralogical composition can be divided into two categories depending on the calcium content. Low calcium fly ash contains less than 10 percent analytical CaO. High calcium fly ash contains 15-35 percent of analytical CaO according to ASTM C 618 (Fly ash and raw or calcined natural pozzolans). The high calcium fly ash is more reactive because it contains most of the calcium in the form of reactive crystalline compounds. Most fly ash contains approximately 60-85 percent glass, 10-30 percent crystalline compounds and up to about 10 percent unburnt carbon. The chemical composition of fly ash is shown in tables 4.7 and 4.8. The microstructure of fly ash occurs as solid spheres of glass. Sometimes there are a small number of hollow spheres, called cenospheres, and numerous small spheres, called plerospheres. The morphology and surface characteristics of fly ash influence the workability of fresh concrete and concrete strength.

Fly ash is able to react with calcium hydroxide which is called pozzolanic reaction. These reactions are shown in equations 4.21 and 4.22.

$$CaO + H_2O \text{ ----> } Ca(OH)_2 \qquad (4.21)$$

$$2SiO2 + 3Ca(OH)2 \text{ ----> } \underset{(CSH)}{3CaO.2SiO_2.3H_2O} \qquad (4.22)$$

A partial replacement of cement by fly ash is able to increase the strength of concrete in later ages. The strength gained at the later ages is due to the pozzolanic reaction. This reaction causes pore refinement and a replacement of the weaker component that is calcium hydroxide with CSH.

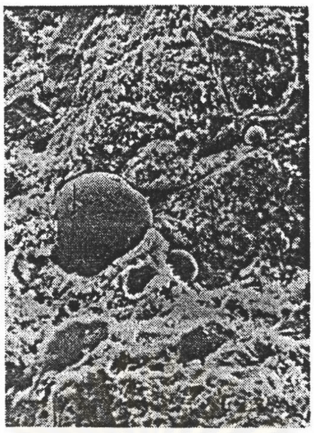


Fig. 4.6 Fly Ash particles bind with other components.

In fresh concrete, the small size and glassy fly ashes can probably reduce the amount of water required for a given consistency. This provides more concrete strength. From table 4.7, SO_3 the content of Mae Moh fly ash is 3.64%. This SO_3 content is lower than the maximum value recommend by ASTM C-618 (Fly Ash and Raw or Calcined natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete), that is 5%. Then, there is no effects of SO_3 in the dimension stability of cement mixture.

Table 4.7 Chemical composition of high, low calcium Fly Ash.

	Low Calcium FA	High Calcium FA	Mae Moh Fly Ash
SiO_2+$Al2O_3$+Fe_2O_3, min %	70.0	50.0	67.12
SO_3, max %	5.0	5.0	3.64
CaO, %	< 10	> 10	22.62
Moisture Content, Max %	3.0	3.0	0.25
Loss of Ignition, Max %	12.0	6.0	0.2

Table 4.8 Typical chemical compound in Fly Ash.

Compound	Range, %	Compound	Range, %
SiO_2	6-45	MgO	3-12
Al_2O_3	6-23	Na_2O	0-11
Fe_2O_3	1-18	K_2O	0-2
CaO	15-44	SO_3	6-30

4.1.4 OTHER CONSTITUENTS

ADMIXTURE, SUPERPLASTICIZER

Admixture is a material other than water, aggregates, hydraulic cements and fiber reinforcement, used as an ingredient of concrete or mortar and added to the batch immediately before or during mixing. ASTM C-494, Standard Specification for Chemical Admixtures for Concrete, divides the water reducing and set controlling chemicals into seven types :

Type A – Water reducing
Type B – Retarding
Type C – Accelerating
Type D – Water reducing and retarding
Type E – Water reducing and accelerating
Type F – High range water reducing
Type G – High range water reducing and retarding

Superplasticizer(6), also called high range water reducing admixtures, is able to reduce 3-4 times the amount of water compared to normal water reducing admixtures. It consists of long-chain, high molecular weight anionic surfactants with a large number of polar groups in the hydrocarbon chain. When adsorbed on cement particles, the surfactant imparts a strong negative charge, which helps to lower the surface tension of the surrounding water. This behavior disperses cement particles in water and seems to accelerate the rate of hydration. Concrete containing superplasticizers shows higher compressive strengths than normal concrete having the same w/c ratio.

4.2 DEVELOPMENT OF MIX PROPORTIONS

4.2.1 TEST PROGRAMS

The upper and lower bound of expansive agent can be calculated from the basic chemical theoretical approach described in chapter 2 and from equation 2.16. Calculation results show that in ordinary portland cement type I with C_3S 45-55% and C_2S 20-30%, the amount of expansive agent in the form of calcium sulphoaluminate will be 8-10% additional into the cement paste mixture to compensate for the drying shrinkage effect. It can also be assumed that this value is based on normal conditions of mixing and w/c = 0.32.

The mix design in this research is based on the research work of Kittikorn(33). The amount of expansive agent is applied into the mixture with 1% to 10% additional according to the weight of cement. This amount of expansive agent is increased up to 15% due to other effects of mixing. Tests of shrinkage compensating cement pastes are carried out in chemical, physical and mechanical properties by time.

1. Chemical Properties
    - XRD of Ettringite content
    - XRD of Calcium Silicate Hydrate content
2. Physical Properties
    - Drying Shrinkage and Expansion
    - Water Adsorption
    - Microstructure by use of a Scanning Electron Microscope
3. Mechanical Properties
    - Compressive Strength
4. Durability
    - XRD of Calcium Hydroxide content

Tests in chemical properties to measure the amount of ettringite and CSH contents at 1, 3, 7 and 28 days by X-ray diffraction method. The test in mechanical property is compressive strength at 1, 3, 7, 14, 28, 56 and 91 days. Tests in physical properties are water adsorption at 28 days and shrinkage at 1, 3, 7, 28, 42 and 56 days. The microstructure of cement pastes at 1, 7 and 28 days is also observed by use of a scanning electron microscope.

4.2.2 MIX PROPORTIONS OF CEMENT PASTE

Mix proportions of shrinkage compensating cement paste in this research use an expansive agent in the form of calcium sulphoaluminate added into the cement mixture in an amount of 1-15% by weight of cement. And fly ash from Mae-Moh, Lampang Province, is mixed to improved cement properties. Properties of materials that are used in this research are as follows ;

- Ordinary portland cement type I (Red Elephant Brand) according to ASTM C-150 is used in the amount of 1,000 g/cement paste 1 liter.
- Admixture type G - High range water reducing and retarding (Daracem 100) according to ASTM C-494 is used to improve workability in the amount of 2.8% by weight of cement.
- Water to cementitious ratio is 0.32 constant.

Variables of tests are as follows ;

1. At cement constant 1,000 g., the amount of expansive agent varies from 0, 1, 3, 5, 10 and 15% additional by weight of cement.

2. At cementitious (Cement and fly ash) constant, the amount of fly ash varies from 15, 20, 25 and 30% replacement by weight of cementitious.

3. At cement and expansive agent addition of 1, 5, 10 and 15%, the amount of fly ash varies from 15, 20, 25 and 30% replacement by weight of cementitious each.

The mix proportions of cement paste are shown in table 4.9. And test programs are shown in table 4.10.

Table 4.9 Mix proportions of cement paste

Mix No.	Net CE. (kg.)	Net. EX. (kg.)	Fly Ash (kg.)	Total Solid (kg.)	CE. (%)	EX. (%)	Fly Ash (%)	W/S	Adm. (lts.)
P00-00	1000	0	0	1000	100.0	0.0	0.0	0.32	2.8
P01-00	1000	10	0	1010	99.0	1.0	0.0	0.32	2.8
P03-00	1000	30	0	1030	97.1	2.9	0.0	0.32	2.8
P05-00	1000	50	0	1050	95.2	4.8	0.0	0.32	2.8
P10-00	1000	100	0	1100	90.9	9.1	0.0	0.32	2.8
P15-00	1000	150	0	1150	87.0	13.0	0.0	0.32	2.8
P00-15	850	0	150	1000	85.0	0.0	15.0	0.32	2.8
P00-20	800	0	200	1000	80.0	0.0	20.0	0.32	2.8
P00-25	750	0	250	1000	75.0	0.0	25.0	0.32	2.8
P00-30	700	0	300	1000	70.0	0.0	30.0	0.32	2.8
P01-15	850	9	152	1010	84.2	0.8	15.0	0.32	2.8
P01-30	700	7	303	1010	69.3	0.7	30.0	0.32	2.8
P05-15	850	43	158	1050	81.0	4.0	15.0	0.32	2.8
P05-30	700	35	315	1050	66.7	3.3	30.0	0.32	2.8
P10-15	850	85	165	1100	77.3	7.7	15.0	0.32	2.8
P10-20	800	80	220	1100	72.7	7.3	20.0	0.32	2.8
P10-25	750	75	275	1100	68.2	6.8	25.0	0.32	2.8
P10-30	700	70	330	1100	63.6	6.4	30.0	0.32	2.8
P15-15	850	128	173	1150	73.9	11.1	15.0	0.32	2.8
P15-30	700	105	345	1150	60.9	9.1	30.0	0.32	2.8

Table 4.10 Test program for shrinkage compensating cement paste

TYPES	EX. (%)	FA. (%)	XRD	SEM	Water Adsorbtion	Shrinkage and Expansion	Compressive Strength
1. Shrinkage Compensating Cement	0	-	X1@1,3,7,28	S1@1,7,28	P00-00	P00-00@1,3,7,14,28,42,56	P00-00@1,3,7,14,28,56,91
	1	-	X2@1,3,7,28	-	P01-00	P01-00@1,3,7,14,28,42,56	P01-00@1,3,7,14,28,56,91
	3	-	-	-	P03-00	P03-00@1,3,7,14,28,42,56	P03-00@1,3,7,14,28,56,91
	5	-	X4@7,28	-	P05-00	P05-00@1,3,7,14,28,42,56	P05-00@1,3,7,14,28,56,91
	10	-	X5@1,3,7,28	S5@1,7,28	P10-00	P10-00@1,3,7,14,28,42,56	P10-00@1,3,7,14,28,56,91
	15	-	-	-	P15-00	P15-00@1,3,7,14,28,42,56	P15-00@1,3,7,14,28,56,91
2. Shrinkage Compensating Cement with Fly Ash	-	15	X7@1,3,7,28	-	P00-15	P00-15@1,3,7,14,28,42,56	P00-15@1,3,7,14,28,56,91
	-	20	X8@7,28	-	P00-20	P00-20@1,3,7,14,28,42,56	P00-20@1,3,7,14,28,56,91
	-	25	X9@7,28	-	P00-25	P00-25@1,3,7,14,28,42,56	P00-25@1,3,7,14,28,56,91
	-	30	X10@1,3,7,28	-	P00-30	P00-30@1,3,7,14,28,42,56	P00-30@1,3,7,14,28,56,91
	1	15	X11@7,28	-	P01-15	P01-15@1,3,7,14,28,42,56	P01-15@1,3,7,14,28,56,91
	1	30	X12@7,28	-	P01-30	P01-30@1,3,7,14,28,42,56	P01-30@1,3,7,14,28,56,91
	5	15	X13@7,28	-	P05-15	P05-15@1,3,7,14,28,42,56	P05-15@1,3,7,14,28,56,91
	5	30	X14@7,28	-	P05-30	P05-30@1,3,7,14,28,42,56	P05-30@1,3,7,14,28,56,91
	10	15	X15@1,3,7,28	S15@1,7,28	P10-15	P10-15@1,3,7,14,28,42,56	P10-15@1,3,7,14,28,56,91
	10	20	X16@7,28	-	P10-20	P10-20@1,3,7,14,28,42,56	P10-20@1,3,7,14,28,56,91
	10	25	X17@7,28	-	P10-25	P10-25@1,3,7,14,28,42,56	P10-25@1,3,7,14,28,56,91
	10	30	X18@1,3,7,28	-	P10-30	P10-30@1,3,7,14,28,42,56	P10-30@1,3,7,14,28,56,91
	15	15	X19@7,28	-	P15-15	P15-15@1,3,7,14,28,42,56	P15-15@1,3,7,14,28,56,91
	15	30	X20@7,28	-	P15-30	P15-30@1,3,7,14,28,42,56	P15-30@1,3,7,14,28,56,91

4.2.3 TEST RESULTS

4.2.3.1 CHEMICAL PROPERTIES (XRD OF ETTRIGITE AND CSH)

The X-ray diffraction method is a method to estimate the compound content of cement. The result pattern obtained from an x-ray photograph or diffractogram of a substance from cement consists of many varying intensity lines. These results show a trace of diffracted energy versus angle turned by the specimen. The diffracted energy for a selected reflection is compared with a standard preparation of the substance to estimate quantity of substance in a specimen. The output from the diffractometry may be processed directly by computer and it needs some further refinement to increase accuracy.

The minimum quantity of a crystalline substance which can be detected by x-rays depends on the intensity of its strongest lines and the intensity of other compounds present. If a mixture consists of two or more materials, then the result lines may coincide due to various compounds present. There are many errors arising from the mechanical performance of the equipment, namely, the selection of monochromatic radiation, the lack of uniformity in specimen preparation, unavoidable background radiation and overlapping of lines in the spectra presents. But many consider the x-ray diffraction method more accurate in determining the quantity of compound in hardened cement paste analysis.

The cement pastes for the study of chemical composition were prepared by using a mixture shown in table 4.9. They were cured in water at room temperature. Specimens were tested at the age of 1, 3, 7, and 28 days. And the hydration of cement paste was stopped by means of acetone. The hydration products were studied by X-Ray Diffraction (XRD).

XRD OF ETTRINGITE

In analyzing the XRD results, the peak at 9.1° was used to estimate the relative concentration of ettringite. Test results are shown in table 4.11 and figs 4.7-4.10. From test results, the intensities of ettringite varied from 55-110 counts at 28 days. Maximum intensities of ettringite come from a mixture of 10% expansive agent addition.

In a mixture with fly ash replacement, ettringite intensities are 24-45 counts at 28 days.

The results show that in the cement paste with an expansive agent, ettringite was mostly formed in the early ages of hydration. This ettringite content increased within the first 7 days, and then only slightly increased up to 28 days. The amount of ettringite increased with a corresponding greater use of the amount of expansive agent.

When the mixture was replaced by an amount of fly ash, ettringite decreased compared with a mixture of ordinary portland cement. As the increase of fly ash replacement was 10%, the amount of ettringite was reduced approximately 10%. This effect is mostly due to the effects of reduction in the expansive agent by fly ash replacement.

XRD OF CALCIUM SILICATE HYDRATE, (CSH)

The test results of Calcium Silicate Hydrate were estimated by XRD peak at 18.1°. Test results are shown in table 4.12 and figs 4.11-4.14. The mixture of ordinary portland cement with an expansive agent shows a slight increase in CSH compared with the mixture of ordinary portland cement. CSH intensities from XRD test are 328-430 counts at 28 days. In the mixture with fly ash replacement, CSH intensities are 227-375 counts at 28 days.

In the mixture with fly ash replacement, the amount of CSH in the paste with 15% fly ash replacement was more than ordinary portland cement paste, approximately 15%. But increasing fly ash replacement results in a decreasing in the CSH content especially in the early ages. This is due to the reduction of cement by fly ash.

In later age, the amount of CSH increases considerably due to the pozzolanic reaction of fly ash as shown in figure 4.12. It can be clearly seen that the CSH content increases slightly up to 7 days. In this period, fly ash acts as an inert material in paste because it does not react with cement. But after 7 days, the glassy sphere of fly ash is broken allowing water and cement to react with it. Then the pozzolanic reaction of fly ash is much reacted as the results in CSH increase.

4.2.3.2 PHYSICAL PROPERTIES

DRYING SHRINKAGE AND EXPANSION

The specimens for drying shrinkage tests were prepared according to ASTM C 157. The specimens were removed from water at the age of 3 days. The drying shrinkage readings were carried out at the ages of 1, 3, 7, 14, 21, 28, 42 and 56 days. The specimens were cured in the air room until the reading time. The average room temperature was 30°C (28°C minimum and 35°C maximum) and the average relative humidity was 80% (70% minimum and 85% maximum). Plastic shrinkage was protected by cover fresh mixture with a plastic sheet.

From the test results, shrinkage of portland cement paste is −1,626 microstrain at 28 days. But when an expansive agent is added in mixtures 1-15%, shrinkage is reduced from −1,595 to −306 microstrain by 28 days. In the mixtures with fly ash replacement, shrinkages are −1,495 to −1,108 microstrain at 28 days. Table 4.13 and figs. 4.15-4.18 show the results of shrinkage and expansion of the mixture.

Drying shrinkage of ordinary cement paste increased until the age of 28 days, then it only slightly increased. When the expansive agent was mixed with portland cement, the shrinkage reduced due to the hydration reaction of calcium sulfoaluminate from the expansive agent. This reaction formed ettringite which was the source of expansion. The magnitude of expansion was increased when the amount of expansive agent was increased. As the expansive agent was increased by 10%, the expansion of cement paste approximately rose by 80%.

In the paste with fly ash replacement, shrinkage was reduced due to the effect of cement replacement with non-expansive materials but fly ash also replaced the expansive agent in the mixture. The magnitude of shrinkage mostly depends on the effects of reduction in cement. Increasing the amount of fly ash in the mixture 10% reduced shrinkage 15-20%.

WATER ADSORPTION

The test of water adsorption was carried out by mixing cement paste according to table 4.9. After 1 day the specimens were demolded and immersed in water for 28 days. The specimens were removed from water. Then the initial weights of the specimens were taken. After that the specimens were dried in an oven at the temperature of 105°C for 7 days and then weighed. The results are based on the initial weight after the removal from water storage at the age of 28 days.

The test results are shown in table 4.14 and figures 4.19-4.20. Water adsorption of ordinary portland cement paste with expansive agent varied from 16.85 to 18.82%. In a mixture with fly ash replacement, water adsorption of cement pastes was reduced 13.53 to 14.95%. Minimum adsorption is obtained from the paste with 30% fly ash replacement.

There was little difference in weight for the various types of specimens. This is probably due to the limitation of specimen size and balance. The weight of water loss on drying rose while increasing the amount of expansive agent, because in the paste containing more expansive agent, more ettringite is formed and this ettringite can adsorb large amounts of water on their surface.

When cement is replaced with fly ash, water loss on drying was less than ordinary portland cement paste, because fly ash makes the paste denser and filled pores due to the pozzolanic reaction. Then water in pores is reduced. The magnitude of water loss decreases by 20% while increasing the fly ash 10%.

MICROSTRUCTURE BY USING AN SCANNING ELECTRON MICROSCOPE

An electron microscope is a technique to display the microstructure of elements. SEM can view specimens that cannot be seen with the naked eye. The results of analysis are difficult to interpret and can not determine the quantities of the compound. The specimen for electron microscope needs to be smooth on the surface.

The specimens were cast with the proportion shown in table 4.9 and cured in water until the testing time which was carried out at the ages of 1, 3, 7 and 28 days.

The specimen surface is made conductible by evaporating on to it a metal film. The target is then made for a focussed beam of electrons. The area or points selected optically can be stimulated by the electronprobe. A general picture of the stimulated area can be displayed on a screen by causing the electron spot to transverse the specimen following a raster that is also locked to the display screen. The methods to prepare the specimen are shown below.

1. Dehydrate the specimen (i.e. all water is removed).
2. Coat with an atom-thin layer of gold.
3. Place in a vacuum so that the electron beam can move without interference.

The electrons are generated from a thin wire in the "gun" of the SEM. Electricity is passed through the wire and then focused by magnets onto the object. When the electrons from the gun strike the surface coated with gold, electrons cannot penetrate the gold coating and bounce off the specimen to a detector. This forms an image of the surface details of the object. Only inanimate items can be viewed under an SEM.

The test results of SEM are shown from fig 4.21 to 4.29. In ordinary portland cement paste on the first day, cement clinker starts to be hydrated. CSH is gradually formed in pore spaces. On the 7th day, CSH becomes more formed. There are more CSH links between the cement particle. On the 28th day, the hydration of the belite phase still proceeds. There is a small amount of calcium hydroxide formed by the hydration process. No ettringite in the pure mixture of cement paste is observed.

In cement paste with an expansive agent, needle-like ettringite forms in the early ages which fills the inner vacant spaces. A large flat plate of calcium hydroxide also forms in the pores due to the hydration reaction of alite and belite. As the hydration reaction process reaches 7 days, calcium sulfoaluminate in the expansive agent has been completely hydrated, while hydration reaction of dicalcium silicate still proceeds. Ettringite changes to prismatic form after 7 days. At 28 days, the hydration reaction of belite still proceeds. Most of the paste is CSH and only a small amount of calcium hydroxide was detected. Hydration products tend to crystallize which gives the appearance of a coating formation around the cement particle and gradually fill the void resulting in very dense paste.

In cement paste with an expansive agent and fly ash at 1 day, the round shape of fly ash still unreacts in the paste. Calcium sulphoaluminate starts to hydrate and ettringite is formed. A small amount of calcium hydroxide is formed in the pores as the hydration reaction proceeds. After 7 days, a large amount of ettringite is formed. The sphere of fly ash starts to break and there is a small amount of CSH coating the surface. At 28 days, a large amount of CSH is formed in the hydrated surface. No round shape of fly ash was observed due to the pozzolanic reaction proceeding. A small amount of calcium hydroxide was found, because calcium hydroxide was transformed into CSH due to the pozzolanic reaction of fly ash.

4.2.3.3 MECHANICAL PROPERTIES

COMPRESSIVE STRENGTH

The specimens of cement paste were prepared by using 5x5x5 cm mold. After 1 day the specimens were demolded and immersed in water. Compressive strength was carried out at the ages of 1, 3, 7, 14, 28, 56 and 91 days. The specimens were cured in the water until the testing time and removed from water 1 day before testing time.

The compressive strength test results are shown in table 4.15 and figures 4.30-4.33. Maximum compressive strength is obtained from a mixture of portland cement paste with 15% expansive agent and fly ash 15% replacement, that is 867 ksc. at 28 days. The compressive strength of ordinary portland cement pastes at 28 days is 785 ksc. The replacement of more than 20% of fly ash reduces compressive strength 627-689 ksc. at 28 days.

The compressive strength of cement paste with an expansive agent slightly increased compared with ordinary portland cement paste, because the empty void was filled with hydrated compound from calcium sulphoaluminate. There were a slight difference between the compressive strength of the paste when the amount of expansive agent was increased.

When cement was replaced with fly ash, the compressive strength gradually increased because the pozzolanic reaction of fly ash started in a later age. The compressive strength of 15% fly ash replacement was more than ordinary portland cement, because CaO in fly ash is highly reactive and produces more CSH in the paste. Increasing the amount of fly ash replacement tends to reduce compressive strength. The magnitude of strength reduction was 15-20% with an increase in the amount of fly ash by 10%.

4.2.3.4 XRD OF CALCIUM HYDROXIDE

Calcium hydroxide in cement pastes can be determined by the XRD technique. The samples were prepared by using a mixture shown in table 4.9. They were cured in water at room temperature. Specimens were tested at the age of 1, 3, 7, and 28 days. And the hydration of cement paste was stopped by means of acetone.

The test results of calcium hydroxide were estimated by XRD peak at 34.1° 2θ. Test results are shown in table 4.16 and figures 4.34-4.37. The increase of calcium hydroxide in ordinary portland cement paste is affected by the increase in the hydration reaction, that is 231 counts at 1day and 294 counts at 28 days. A minimum amount of calcium hydroxide is obtained in a mixture with 30% fly ash replacement, that is 212 counts at 28 days.

4.2.4 EFFECTS OF ETTRINGITE IN EXPANSION

Ettringite in ordinary portland cement paste is produced from the hydration reaction of tricalcium silicate. In a mixture that contains an expansive agent in the form of calcium sulfoaluminate, Ettringite is also formed in large amounts by a hydration reaction. So, the amount of ettringite in a mixture with calcium sulfoaluminate will occur much more than in ordinary portland cement paste. The amount of ettringite in ordinary portland cement paste is reduced with time, because ettringite is converted into calcium monosulfoaluminate. The amount of ettringite is reduced for 7 days then it becomes constant. But in the mixture with an expansive agent, ettringite increases until 7 days then it become constant.

In the mixture with fly ash replacement, the amount of ettringite is reduced with increase amount of fly ash. This effect is mostly due to the effects of reduction in the expansive agent by fly ash replacement.

Formation and the amount of ettringite are related to the dimension of pastes. Figure 4.38 shows the relation between the amount of ettringite and expansion of cement paste. As the amount of ettringite increased, the expansion increased. This expansion is directly proportion to the amount of ettringite.

4.2.5 DEVELOPMENT OF STRENGTH WITH CSH

The amount of calcium silicate hydrate depends on the hydration reaction of cement. In ordinary portland cement type I, CSH is produced only from the hydration reaction of portland cement. But in the mixture with fly ash, its pozzolanic reaction produced more CSH compared to the mixture of ordinary portland cement.

CSH in a mixture with fly ash increased in later ages, after 14 days. So, the compressive strength of the mixture with cement and fly ash increased in later ages. In the early ages, the amount of CSH is much lower than in later ages because fly ash replaces cement in the mixture, which leads to the hydration reaction reduced. But in later ages, pozzolanic reaction of fly ash occurs which produces more CSH. Then the compressive strength of mixture is increased. The relation between CSH and compressive strength is direct. An increase in CSH will result in increased compressive strength as shown in figure 4.39.

In the mixture with an expansive agent, the compressive strength and CSH is the same as the mixture of ordinary portland cement. This is because the chemical composition of cement remains the same as the mixture of ordinary portland cement.

4.2.6 EFFECTS OF $Ca(OH)_2$ IN DURABILITY

Calcium hydroxide in cement paste can limit its durability because it is more soluble than CSH. Leaching of calcium hydroxide can provide an entry of aggressive agents. The pastes that have a high content of calcium hydroxide are likely to be prone to leaching and have greater potential to deteriorate.

From the test results, it is noted that calcium hydroxide increases as the hydration reaction occurs. The magnitude of the increase of calcium hydroxide is up to 7 days after which the increase rate slows down. In the mixture of portland cement paste with an expansive agent, there is an increase in calcium hydroxide in the early ages. But after 7 days, calcium hydroxide was reduced due to the hydration reaction to form ettringite consuming calcium hydroxide.

In the paste with fly ash replacement, there was a reduction in calcium hydroxide in later age. This reduction was caused by the pozzolanic reaction of fly ash which consumes calcium hydroxide and forms CSH. This reaction increases both the paste density and compressive strength.

Calcium hydroxide can limit the durability of cement paste because it is more soluble than CSH. Leaching of calcium hydroxide can provide deterioration of paste by forming carbonic acid. The presence of calcium hydroxide in the paste tends to reduce the durability of the paste. In ordinary portland cement paste, there is more calcium hydroxide compared with the paste with expansive agent and fly ash, then this paste tends to be less durable than the paste with expansive agent and fly ash.

Table 4.11 XRD test results of ettringite (Peak 9.1)

Mix No.	Peak Intensities (Counts)			
	1 Day	3 Days	7 Days	28 Days
P00-00	67.0	64.0	54.0	55.0
P01-00	67.0	81.0	97.0	98.0
P05-00	70.0	87.0	109.0	107.0
P10-00	69.0	95.0	102.0	110.0
P00-15	40.0	50.0	46.0	45.0
P00-20	NA	NA	40.0	39.0
P00-30	30.0	35.0	32.0	24.0
P01-15	44.0	52.0	56.0	57.0
P01-30	NA	NA	66.7	65.0
P05-15	NA	NA	NA	90.0
P05-20	NA	NA	NA	75.0
P05-30	NA	NA	NA	70.0
P10-15	NA	NA	NA	97.0
P10-20	NA	NA	NA	87.0
P10-30	NA	NA	NA	80.0

Note : NA = Not Analysis

Table 4.12 XRD Test results of Calcium Silicate Hydrate, CSH (Peak 18.1)

Mix No.	Peak Intensities (Counts)			
	1 Day	3 Days	7 Days	28 Days
P00-00	228.0	292.8	318.5	328.0
P01-00	236.2	267.1	298.8	316.1
P05-00	248.0	276.0	316.0	332.0
P10-00	286.2	288.0	332.2	344.0
P00-15	257.0	285.0	293.0	375.0
P00-20	NA	NA	229.5	275.0
P00-30	200.0	210.0	213.0	227.0
P01-15	288.0	323.0	293.0	340.0
P01-30	NA	NA	285.6	240.0
P05-15	NA	NA	NA	350.0
P05-20	NA	NA	NA	300.0
P05-30	NA	NA	NA	260.0
P10-15	NA	NA	NA	360.0
P10-20	NA	NA	NA	310.0
P10-30	NA	NA	NA	265.0

Note : NA = Not Analysis

Table 4.13 Shrinkage and expansion of shrinkage compensating cement paste

Mix No.	Shrinkage (Microstrain)							
	1	3	7	14	21	28	42	56
P00-00	5	-62	-740	-1272	-1563	-1626	-1729	-1745
P01-00	33	46	-600	-1279	-1482	-1595	-1701	-1686
P03-00	40	72	-218	-725	-965	-1184	-1286	-1307
P05-00	45	87	71	-439	-729	-883	-890	-936
P10-00	45	84	74	-110	-150	-200	-250	-270
P15-00	49	100	150	150	80	85	-35	-40
P00-15	57	62	-709	-1105	-1300	-1360	-1446	-1467
P00-20	50	54	-534	-995	-1200	-1296	-1366	-1416
P00-25	48	40	-496	-911	-1143	-1231	-1307	-1309
P00-30	44	55	-397	-858	-1059	-1108	-1167	-1186
P01-15	30	45	-500	-1100	-1250	-1340	-1400	-1400
P01-30	24	30	-410	-900	-1040	-1120	-1170	-1180
P05-15	32	70	60	-370	-610	-720	-795	-800
P05-30	32	60	50	-300	-500	-600	-650	-660
P10-15	30	60	50	-90	-145	-177	-220	-240
P10-20	30	55	47	-90	-130	-160	-189	-210
P10-25	35	50	45	-79	-120	-150	-183	-195
P10-30	35	53	58	-80	-120	-144	-170	-183
P15-15	40	70	90	100	70	60	-30	-30
P15-30	50	65	66	70	60	24	-20	-30

Table 4.14 Water adsorbtion in shrinkage compensating cement paste

Mix No.	CE. (kg.)	Ex. (%)	Ex. (kg.)	Fly Ash (%)	Fly Ash (kg.)	Total Solid (kg.)	W/S	Adm. (lts.)	Water Content (%)
P00-00	1000	0	0	0	0	1000	0.32	8.0	16.85
P01-00	1000	1	10	0	0	1010	0.32	8.0	16.88
P03-00	1000	3	30	0	0	1030	0.32	8.0	17.06
P05-00	1000	5	50	0	0	1050	0.32	8.0	17.94
P10-00	1000	10	100	0	0	1100	0.32	8.0	18.53
P15-00	1000	15	150	0	0	1150	0.32	8.0	18.82
P00-15	850	0	0	15	150	1000	0.32	8.0	14.95
P00-20	800	0	0	20	200	1000	0.32	8.0	14.52
P00-25	750	0	0	25	250	1000	0.32	8.0	13.98
P00-30	700	0	0	30	300	1000	0.32	8.0	13.53
P01-15	850	1	9	15	152	1010	0.32	8.0	15.32
P01-30	700	1	7	30	303	1010	0.32	8.0	14.00
P05-15	850	5	43	15	158	1050	0.32	8.0	16.69
P05-30	700	5	35	30	315	1050	0.32	8.0	16.07
P10-15	850	10	85	15	165	1100	0.32	8.0	17.97
P10-20	800	10	80	20	220	1100	0.32	8.0	17.54
P10-25	750	10	75	25	275	1100	0.32	8.0	17.33
P10-30	700	10	70	30	330	1100	0.32	8.0	17.21
P15-15	850	15	128	15	173	1150	0.32	8.0	18.03
P15-30	700	15	105	30	345	1150	0.32	8.0	17.54

Table 4.15A Compressive strength of shrinkage compensating cement paste

Mix No.	Compressive Strength (ksc.)						
	1	3	7	14	28	56	91
P00-00A	532	584	628	664	716	800	824
P00-00B	536	572	600	648	708	780	792
P00-00C	524	568	596	636	704	776	788
Avg.	**531**	**575**	**608**	**649**	**709**	**785**	**801**
P01-00A	512	560	628	688	736	824	840
P01-00B	516	544	600	668	728	804	824
P01-00C	508	544	600	660	716	800	804
Avg.	**512**	**549**	**609**	**672**	**727**	**809**	**823**
P05-00A	516	564	636	676	748	832	848
P05-00B	516	552	632	664	740	828	828
P05-00C	504	548	612	656	736	816	828
Avg.	**512**	**555**	**627**	**665**	**741**	**825**	**835**
P10-00A	532	580	648	700	768	852	872
P10-00B	512	560	636	680	756	828	840
P10-00C	512	552	628	680	744	824	856
Avg.	**519**	**564**	**637**	**687**	**756**	**835**	**856**
P15-00A	544	596	660	716	788	864	876
P15-00B	520	572	636	696	764	828	868
P15-00C	512	552	628	684	764	848	844
Avg.	**525**	**573**	**641**	**699**	**772**	**847**	**863**
P00-15A	304	380	504	676	828	908	912
P00-15B	304	368	492	664	816	892	904
P00-15C	292	360	492	668	816	888	900
Avg.	**300**	**369**	**496**	**669**	**820**	**896**	**905**

Table 4.15B Compressive strength of shrinkage compensating cement paste

Mix No.	Compressive Strength (ksc.)						
	1	3	7	14	28	56	91
P00-20A	296	360	476	632	788	860	880
P00-20B	284	336	464	600	760	832	864
P00-20C	280	352	460	612	768	840	864
Avg.	**287**	**349**	**467**	**615**	**772**	**844**	**869**
P00-25A	284	344	444	560	700	776	816
P00-25B	280	320	420	532	684	760	800
P00-25C	272	324	432	544	684	760	780
Avg.	**279**	**329**	**432**	**545**	**689**	**765**	**799**
P00-30A	296	320	416	500	640	700	740
P00-30B	264	324	432	480	628	692	720
P00-30C	272	312	392	472	612	688	716
Avg.	**277**	**319**	**413**	**484**	**627**	**693**	**725**
P01-15A	288	376	480	692	840	880	916
P01-15B	280	360	472	668	828	880	884
P01-15C	280	364	468	660	832	868	896
Avg.	**283**	**367**	**473**	**673**	**833**	**876**	**899**
P01-30A	276	328	440	540	628	720	748
P01-30B	268	300	416	512	628	720	736
P01-30C	268	320	420	512	600	704	720
Avg.	**271**	**316**	**425**	**521**	**619**	**715**	**735**
P05-15A	300	380	496	700	848	900	916
P05-15B	284	372	480	688	844	900	896
P05-15C	284	364	472	676	836	880	884
Avg.	**289**	**372**	**483**	**688**	**843**	**893**	**899**

Table 4.15C Compressive strength of shrinkage compensating cement paste

Mix No.	Compressive Strength (ksc.)						
	1	3	7	14	28	56	91
P05-30A	292	320	452	548	648	732	732
P05-30B	268	312	432	528	644	720	760
P05-30C	272	300	428	516	628	716	744
Avg.	**277**	**311**	**437**	**531**	**640**	**723**	**745**
P10-15A	284	388	500	728	868	920	940
P10-15B	284	380	484	704	856	908	916
P10-15C	280	364	484	688	840	908	908
Avg.	**283**	**377**	**489**	**707**	**855**	**912**	**921**
P10-30A	288	304	440	548	644	736	768
P10-30B	276	308	432	536	640	736	756
P10-30C	272	292	420	524	632	736	736
Avg.	**279**	**301**	**431**	**536**	**639**	**736**	**753**
P15-15A	300	380	520	736	880	924	944
P15-15B	292	360	504	720	868	912	936
P15-15C	284	372	496	704	852	908	924
Avg.	**292**	**371**	**507**	**720**	**867**	**915**	**935**
P15-30A	292	336	452	572	664	756	760
P15-30B	260	312	440	540	648	748	760
P15-30C	276	304	424	544	640	744	752
Avg.	**276**	**317**	**439**	**552**	**651**	**749**	**757**

Table 4.16 XRD Test Results of Calcium Hydroxide (Peak 34.1)

Mix No.	Peak Intensities (Counts)			
	1 Day	3 Days	7 Days	28 Days
P00-00	231.4	234.0	267.8	294.8
P01-00	147.0	250.0	281.0	275.8
P05-00	175.0	240.0	275.0	286.0
P10-00	196.9	255.0	285.0	305.0
P00-15	242.0	257.0	258.0	245.0
P00-20	NA	NA	249.2	230.0
P00-30	210.0	225.0	230.3	212.0
P01-15	131.0	233.0	222.0	220.0
P01-30	NA	NA	191.5	201.0
P05-15	NA	NA	NA	190.0
P05-20	NA	NA	NA	180.0
P05-30	NA	NA	NA	160.0
P10-15	NA	NA	NA	175.0
P10-20	NA	NA	NA	160.0
P10-30	NA	NA	NA	140.0

Note : NA = Not Analysis

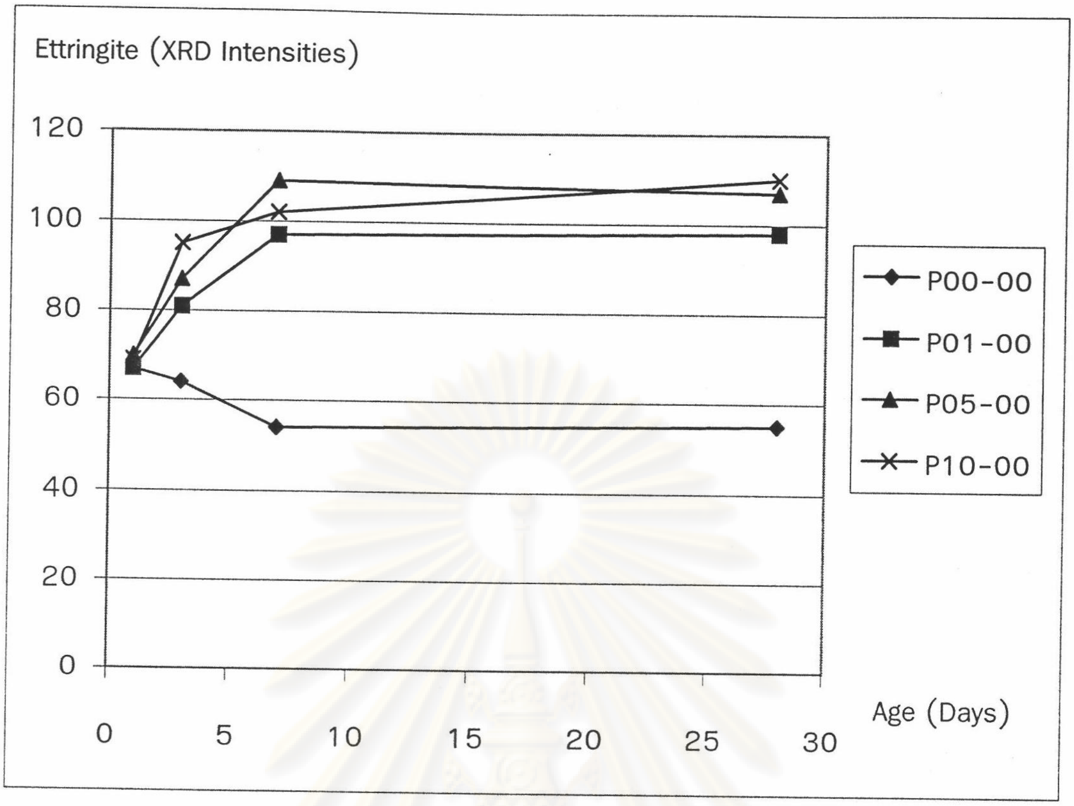


Fig. 4.7 Ettringite from XRD test by time

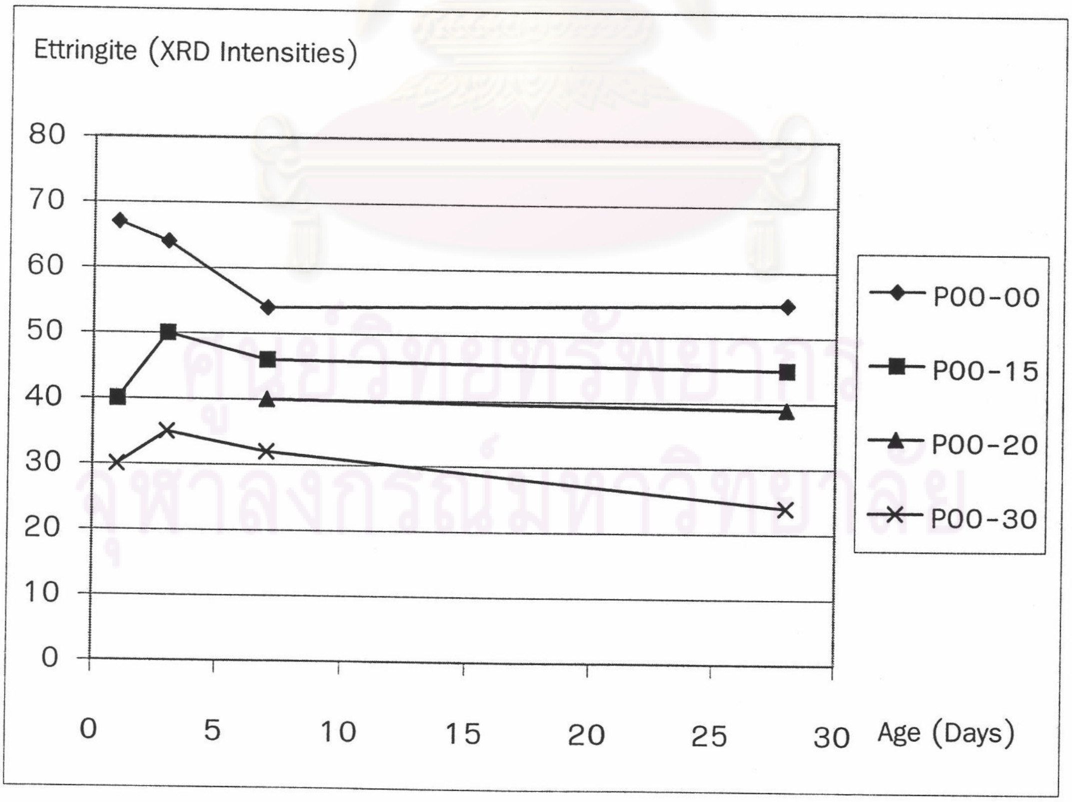


Fig. 4.8 Ettringite from XRD Test by Time

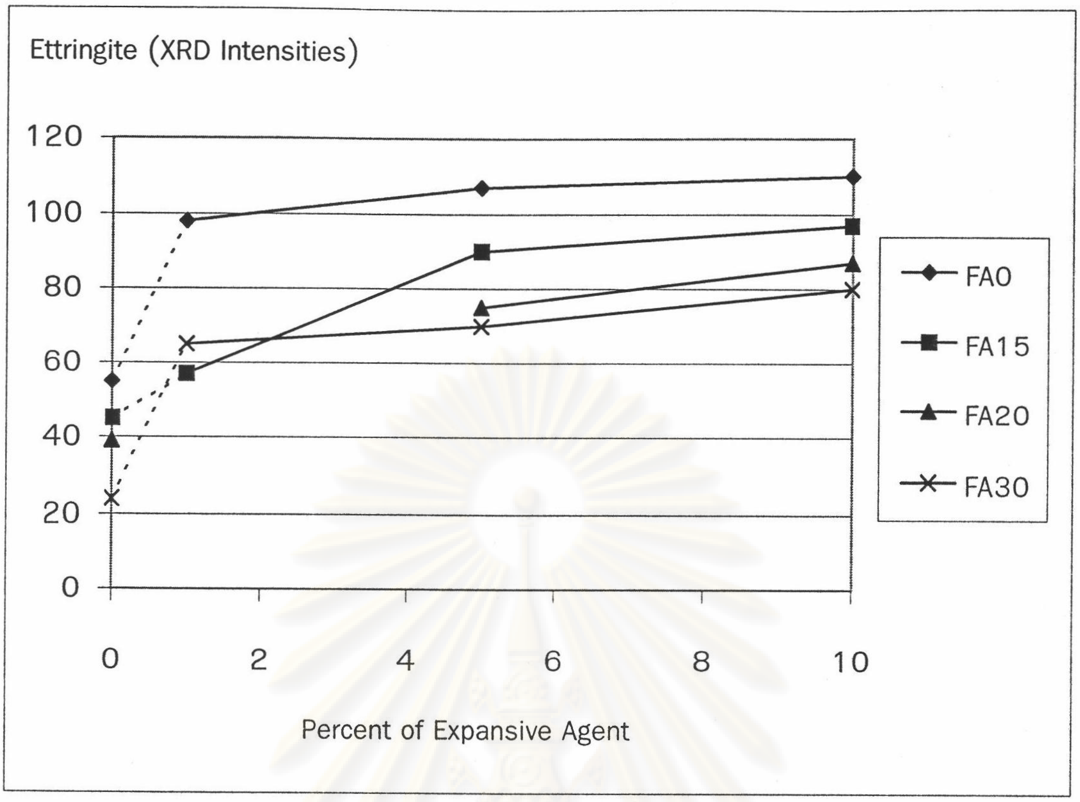


Fig. 4.9 Ettringite from XRD test by expansive agent

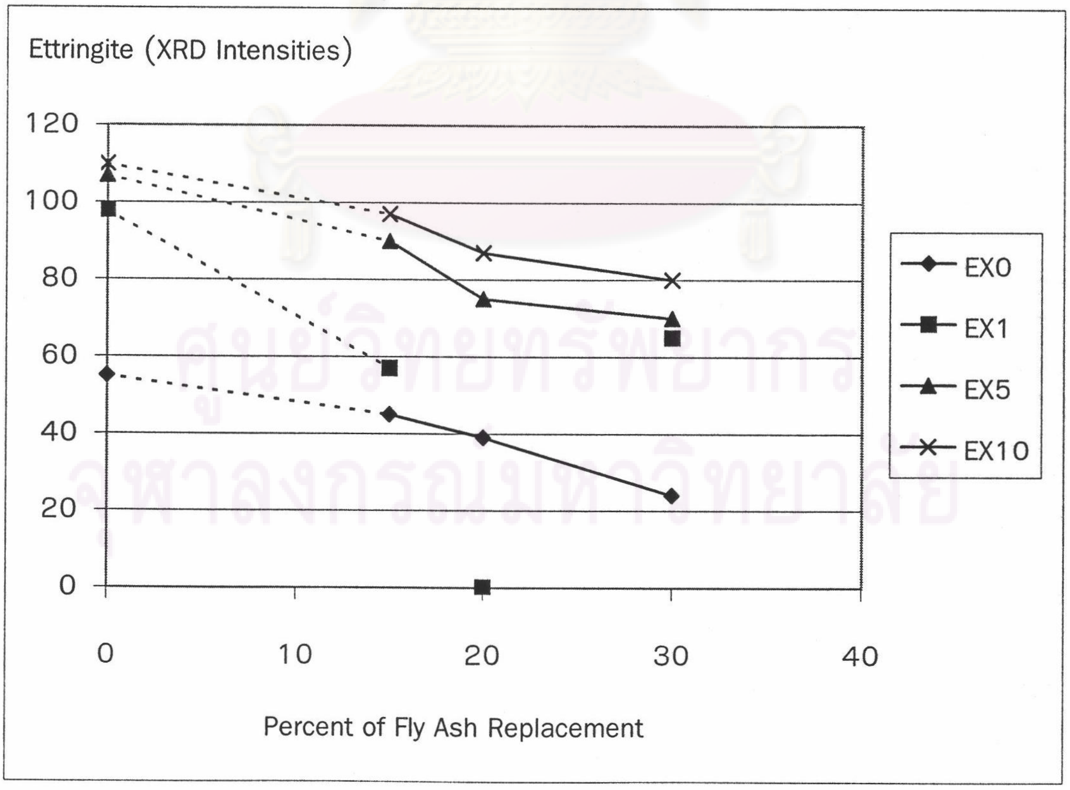


Fig. 4.10 Ettringite from XRD test by Fly Ash replacement

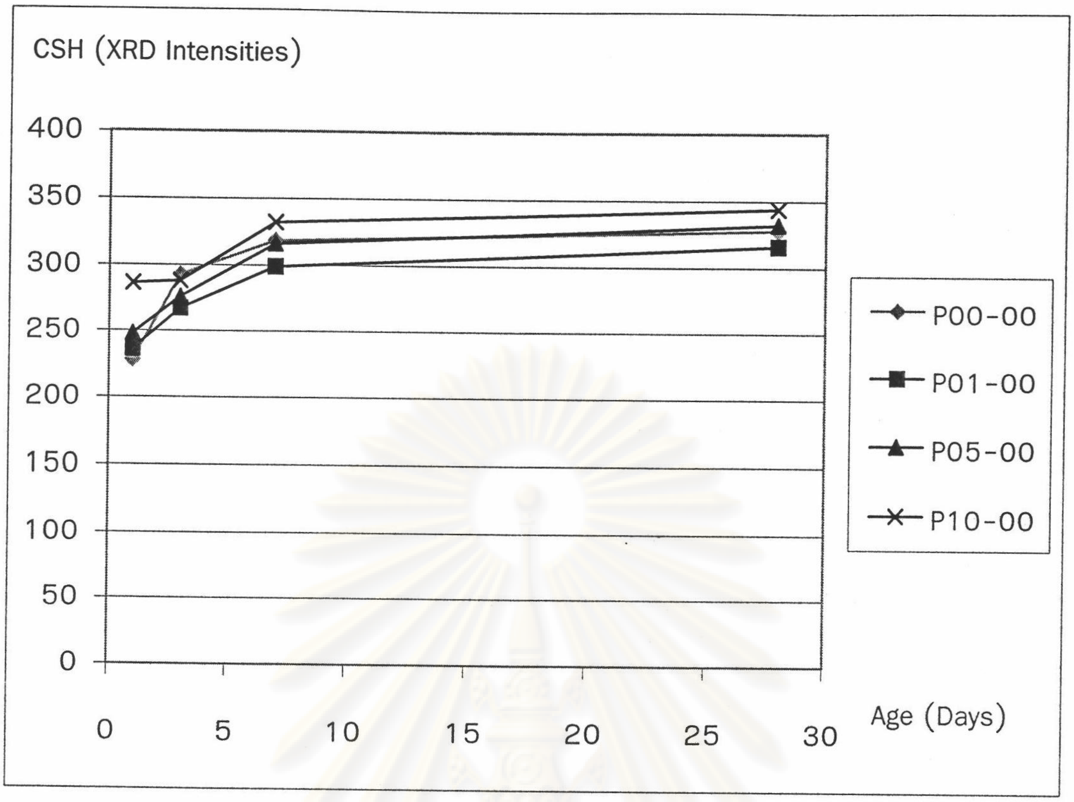


Fig. 4.11 Calcium silicate hydrate from XRD test by time

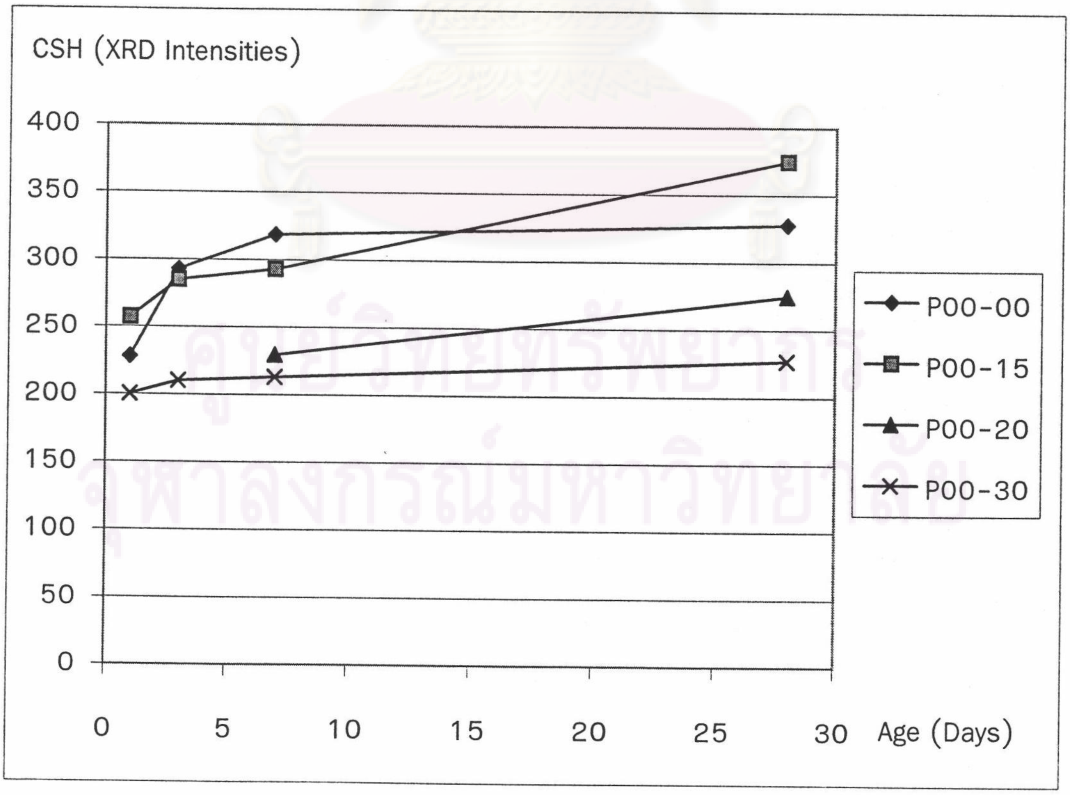


Fig. 4.12 Calcium silicate hydrate from XRD test by time

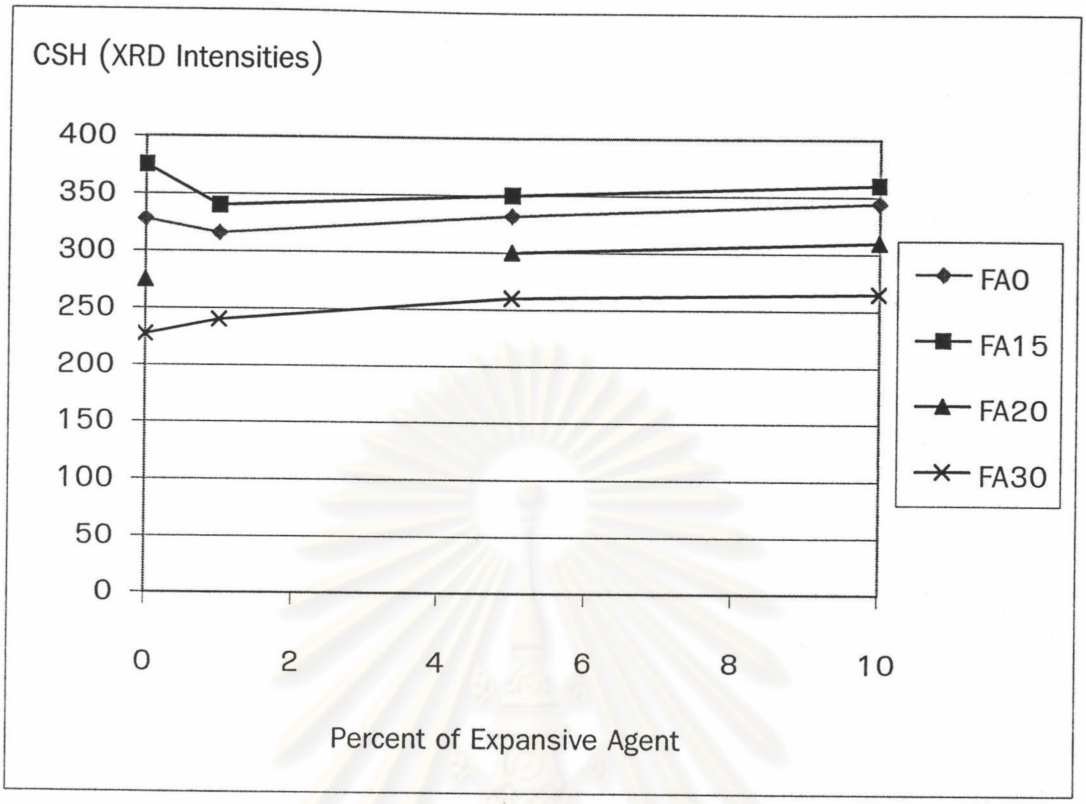


Fig. 4.13 CSH from XRD test by expansive agent

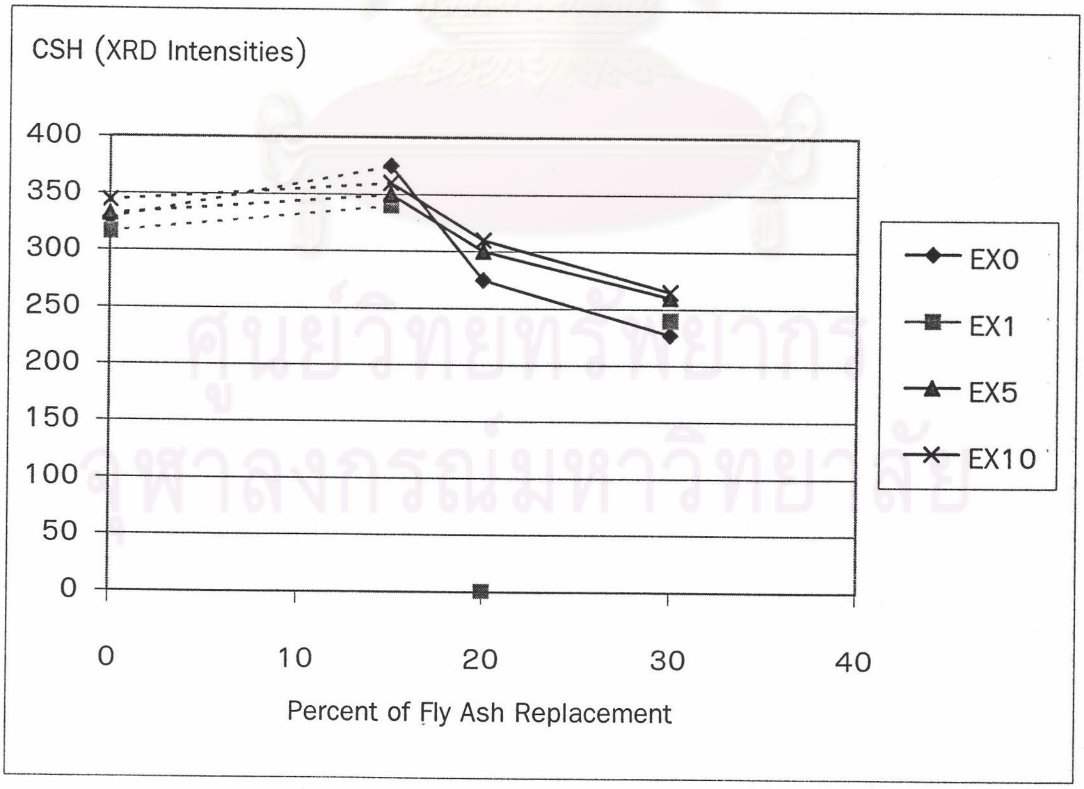


Fig. 4.14 CSH from XRD test by fly ash replacement

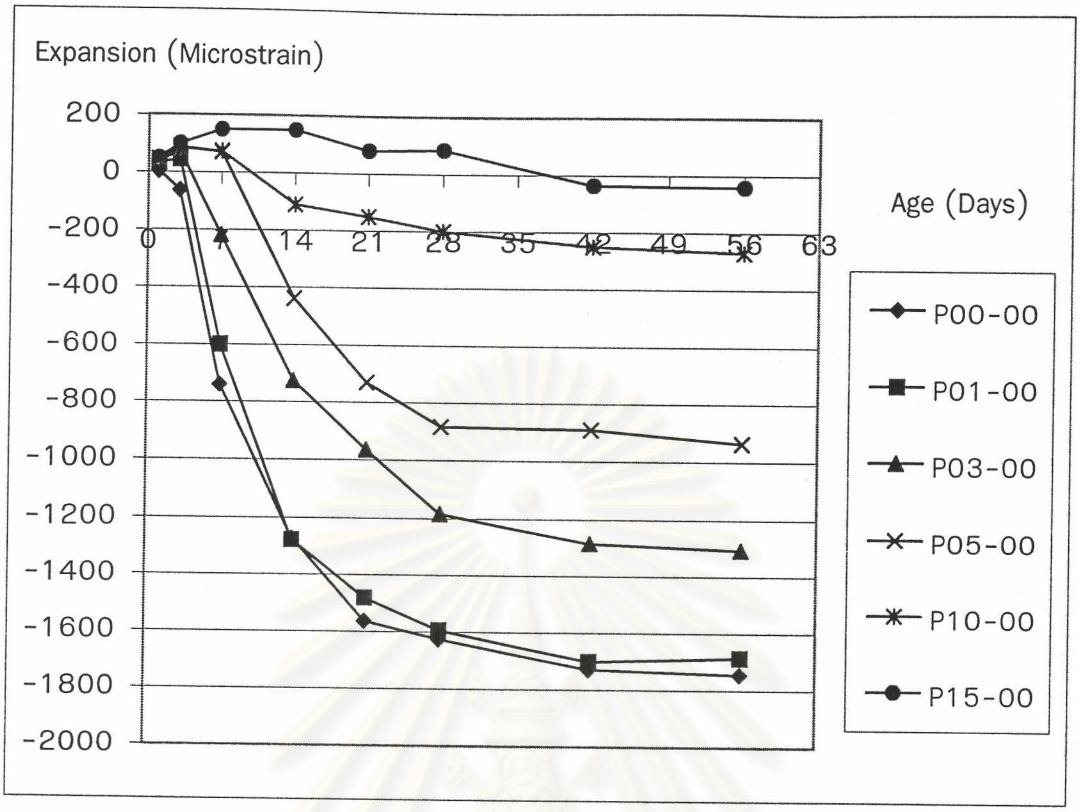


Fig. 4.15 Shrinkage of shrinkage compensating cement paste

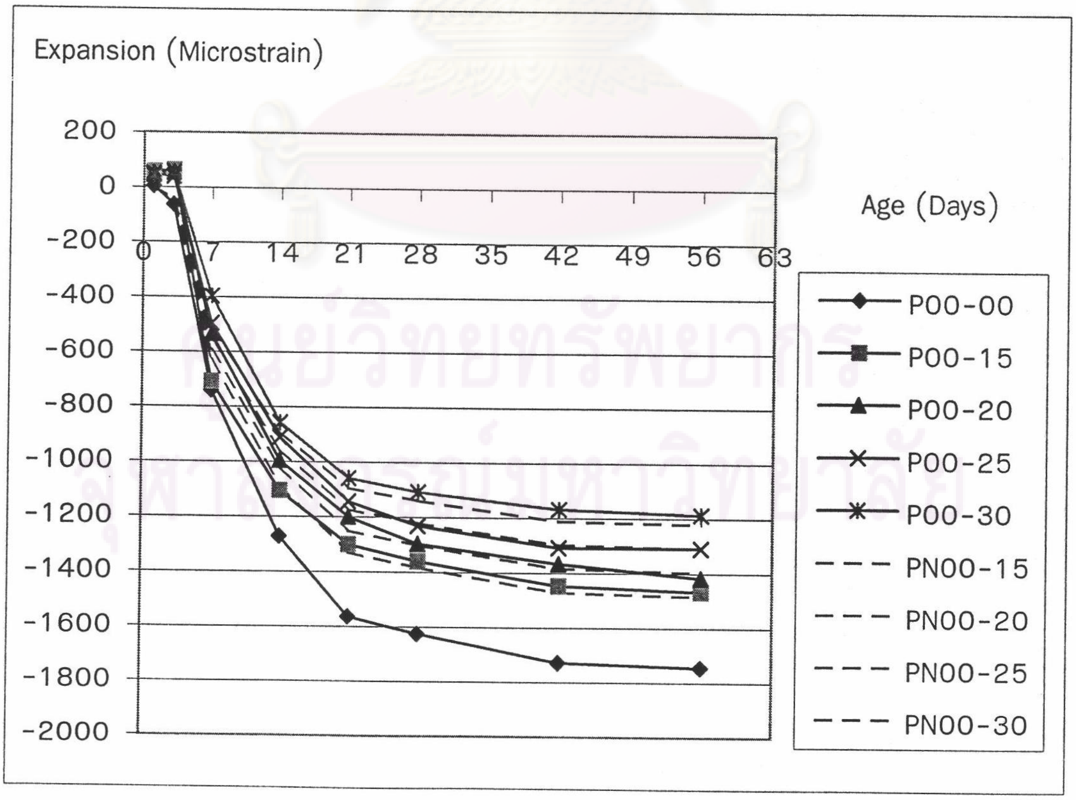


Fig. 4.16 Effects of fly ash in cement paste

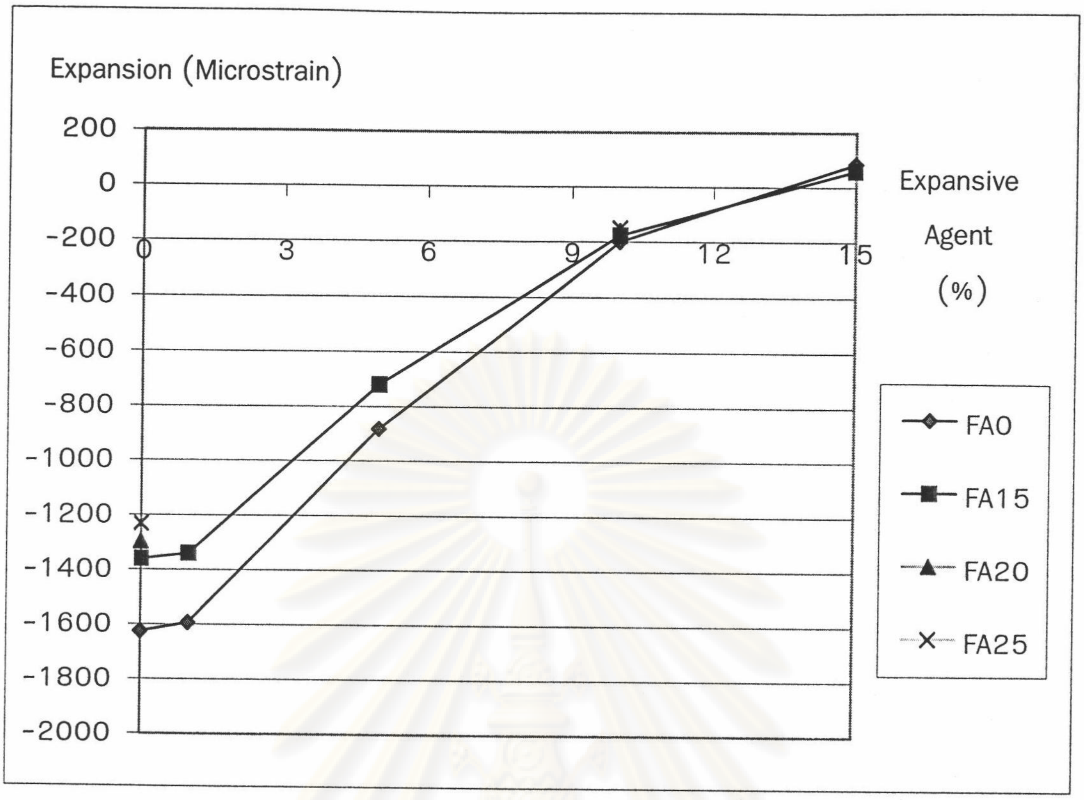


Fig. 4.17 Shrinkage of cement paste by expansive agent

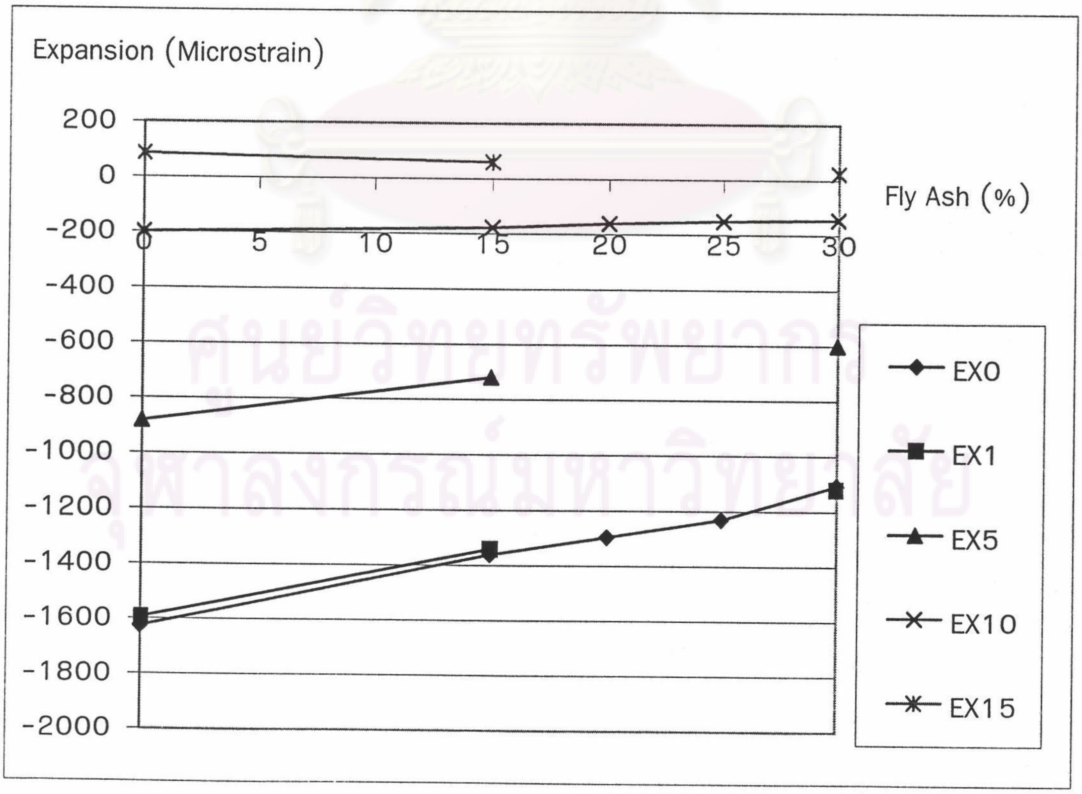


Fig. 4.18 Shrinkage of cement paste by fly ash

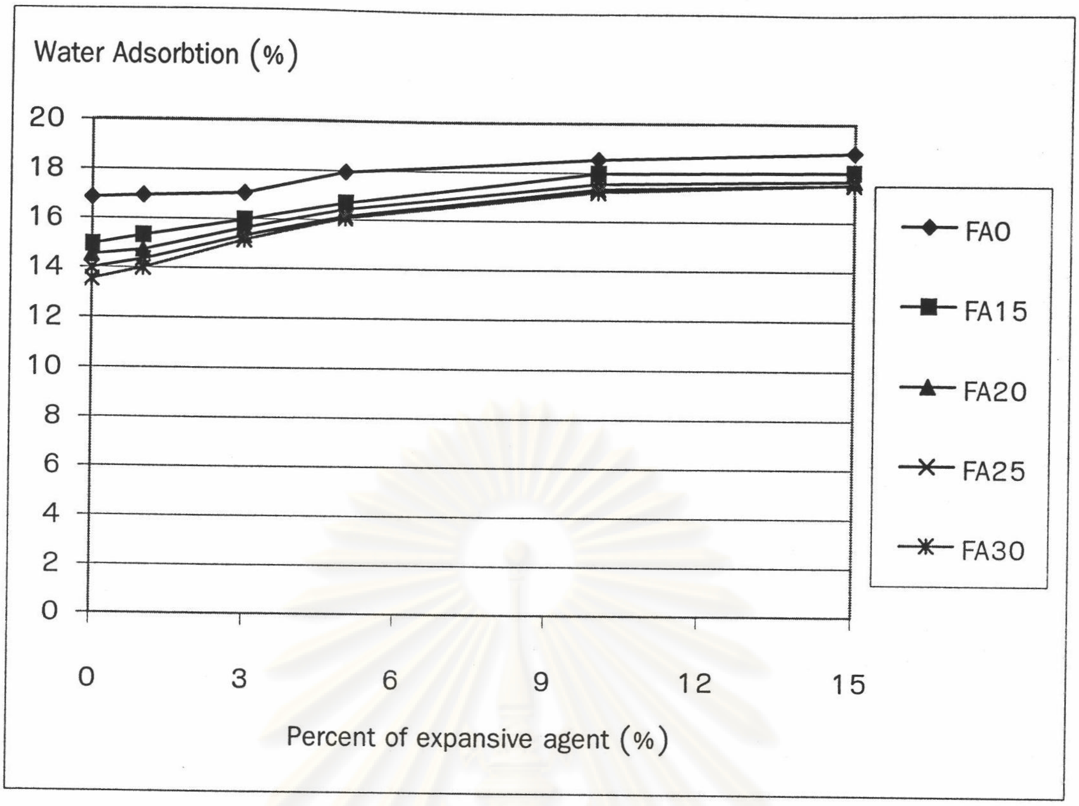


Fig. 4.19 Water adsorbtion of cement paste by expansive agent

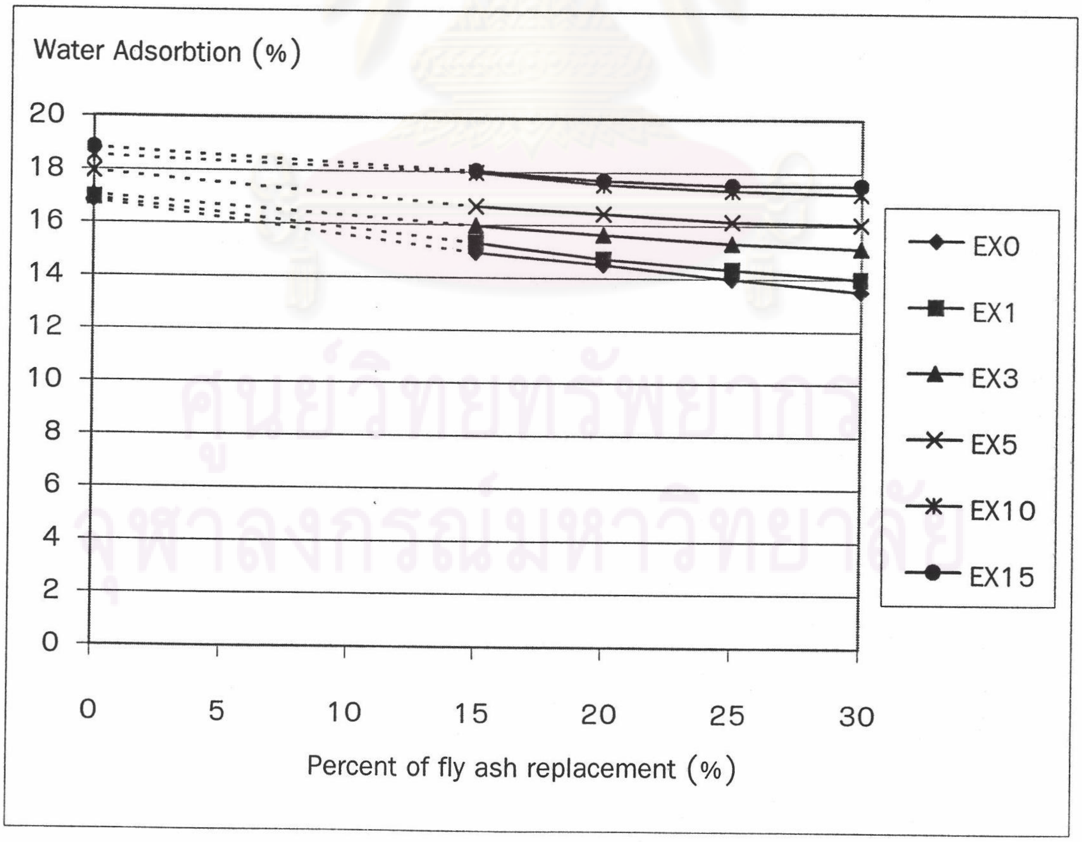


Fig. 4.20 Water adsorbtion of cement paste by percent of fly ash

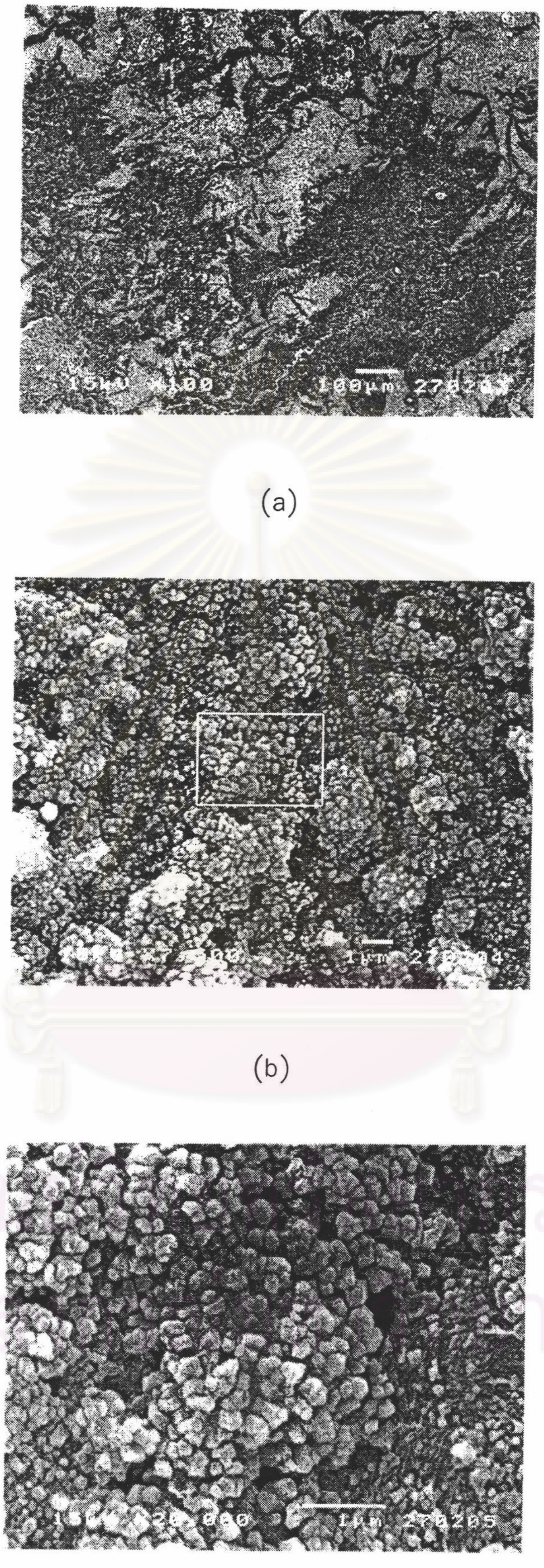


Fig. 4.21 SEM of ordinary portland cement paste at 1 day

(a)

(b)

(c)

Fig. 4.22 SEM of ordinary portland cement paste at 7 day

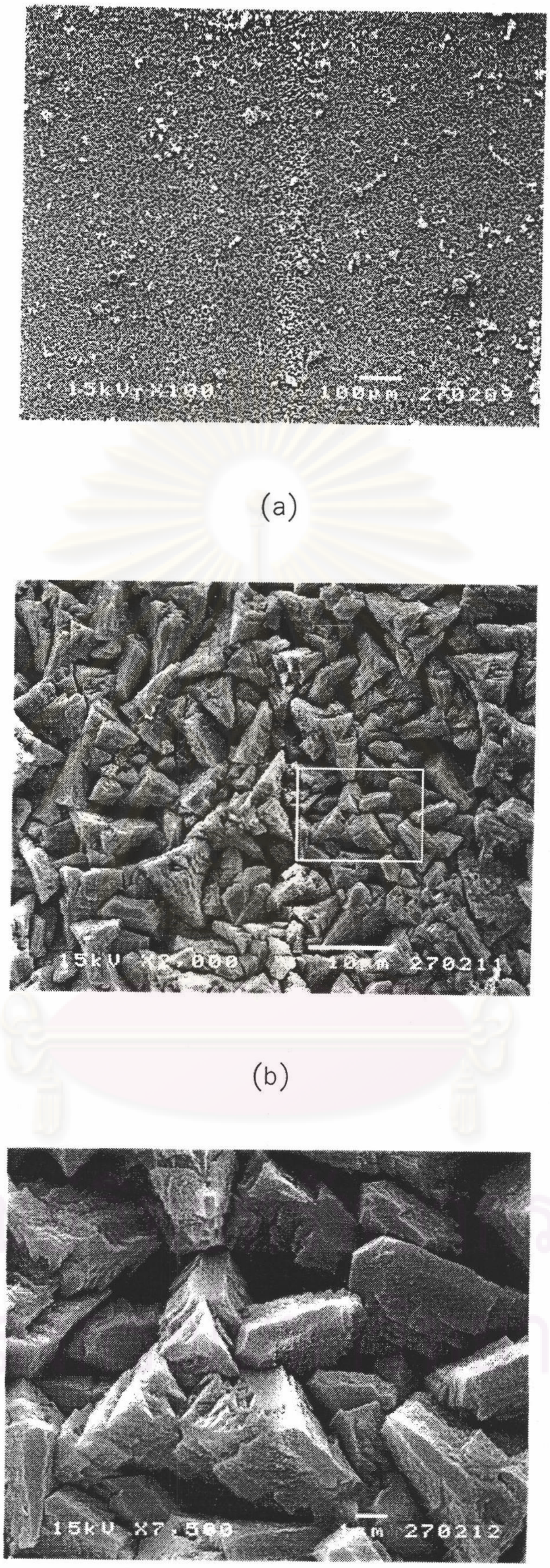
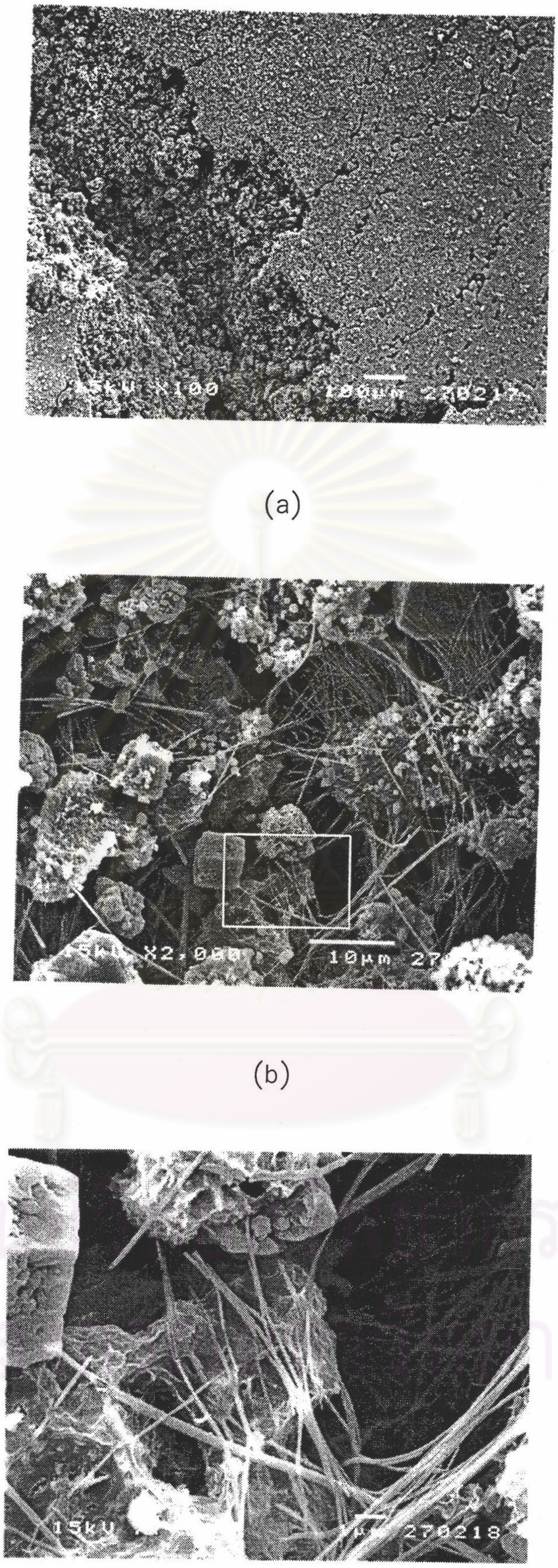


Fig. 4.23 SEM of ordinary portland cement paste at 28 day

Fig. 4.24 SEM of portland cement paste with expansive agent at 1 day

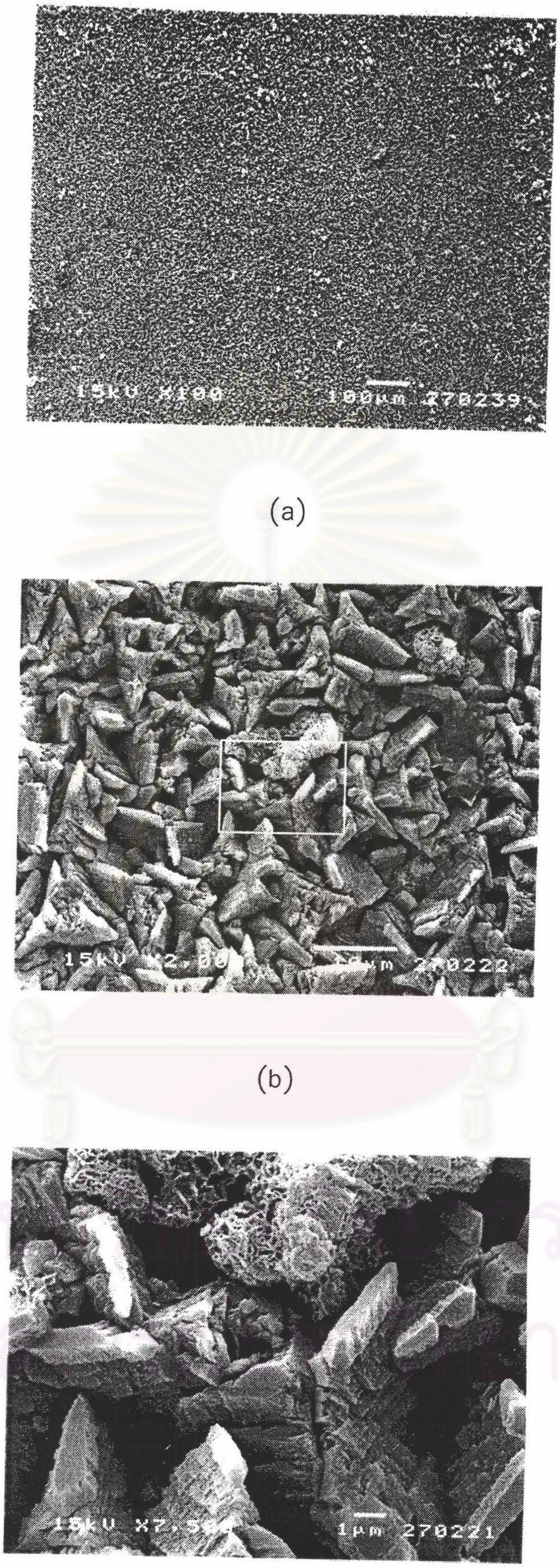


(a)

(b)

(c)

Fig. 4.25 SEM of portland cement paste with expansive agent at 7 day

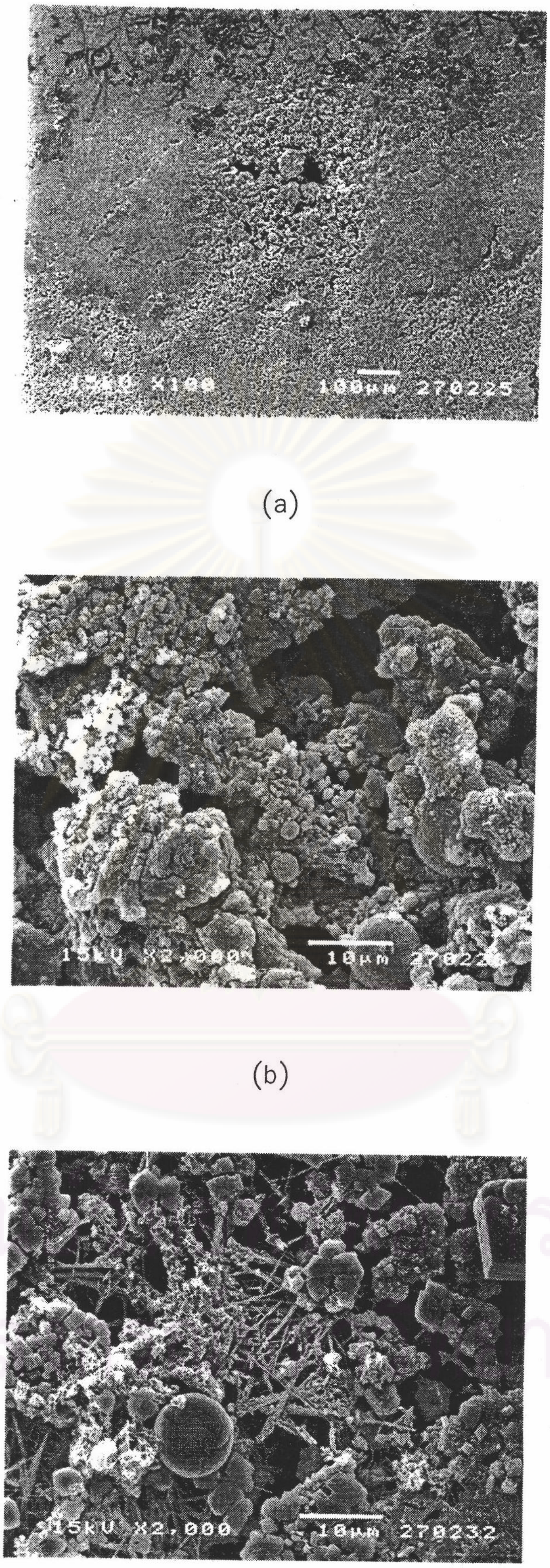


(a)

(b)

(c)

Fig. 4.26 SEM of portland cement paste with expansive agent at 28 day

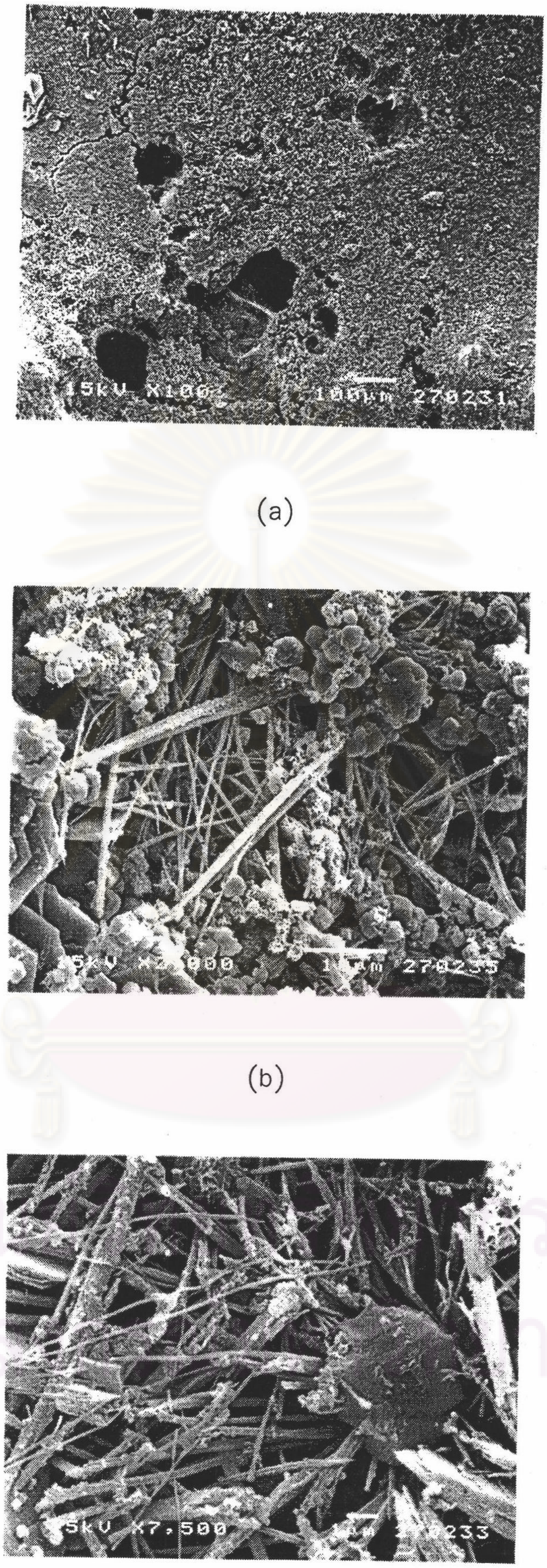


(a)

(b)

(c)

Fig 4.27 SEM of portland cement paste with expansive agent and fly ash at 1 day

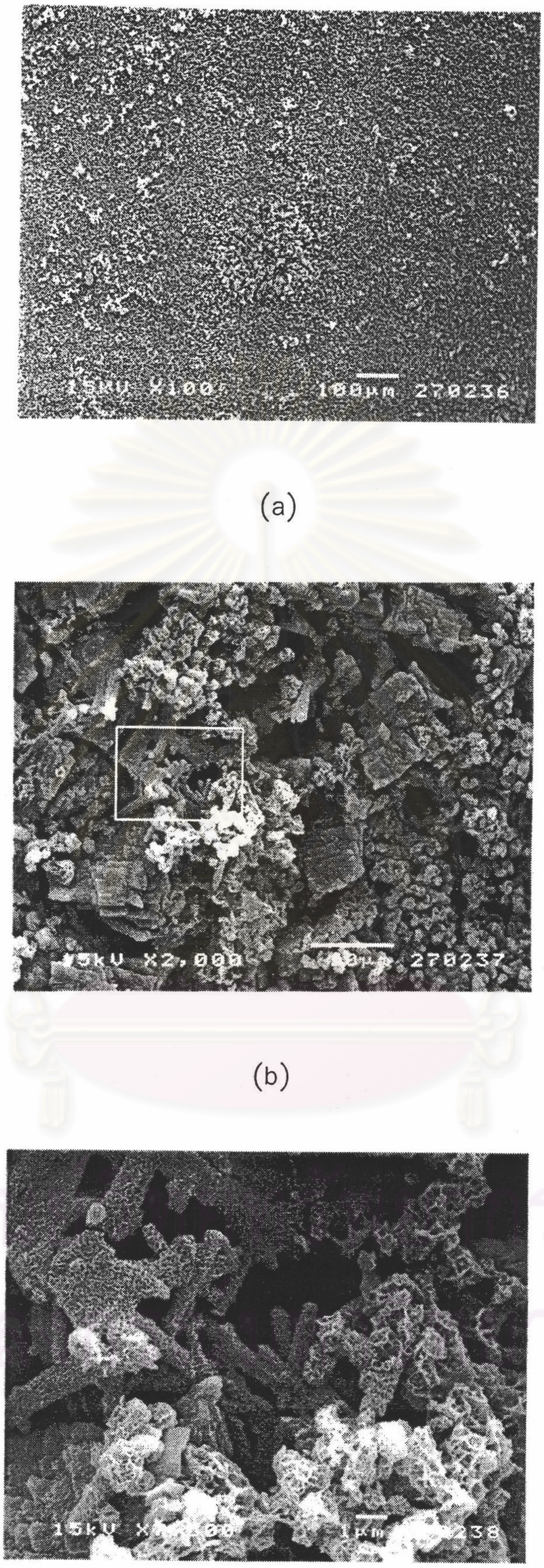


(a)

(b)

(c)

Fig 4.28 SEM of portland cement paste with expansive agent and fly ash at 7 day



(a)

(b)

(c)

Fig 4.29 SEM of portland cement paste with expansive agent and fly ash at 28 day

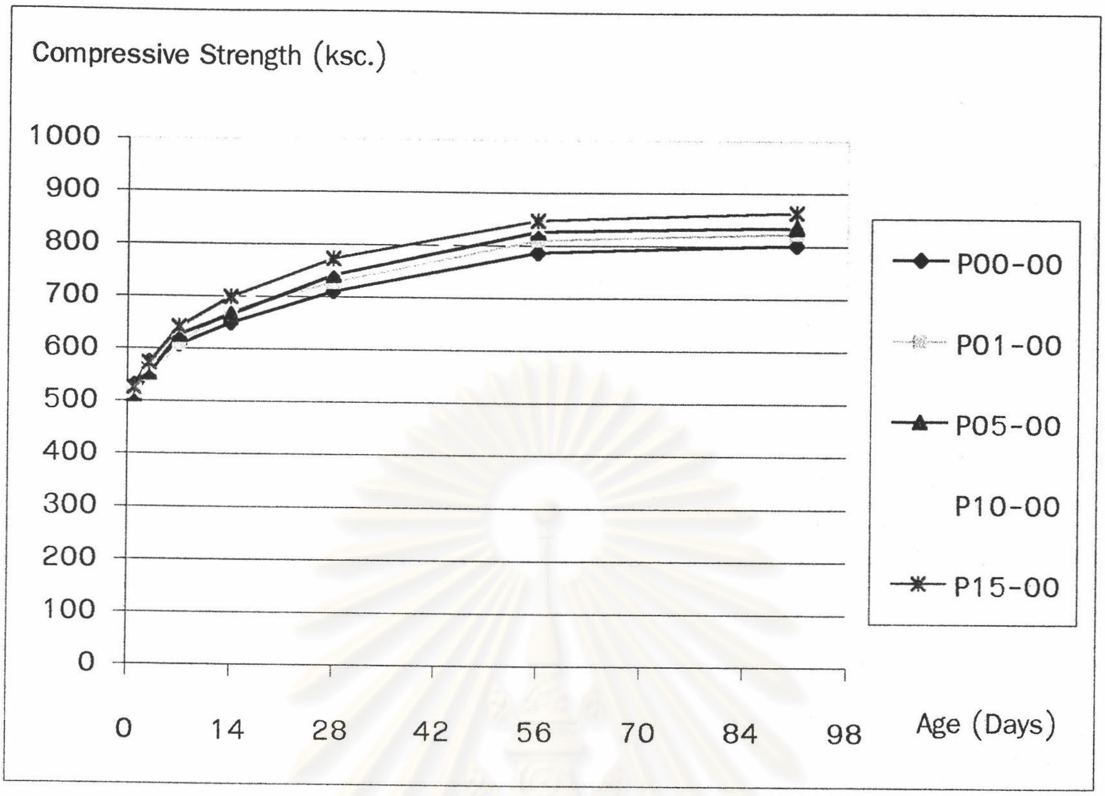


Fig. 4.30 Compressive strength by time

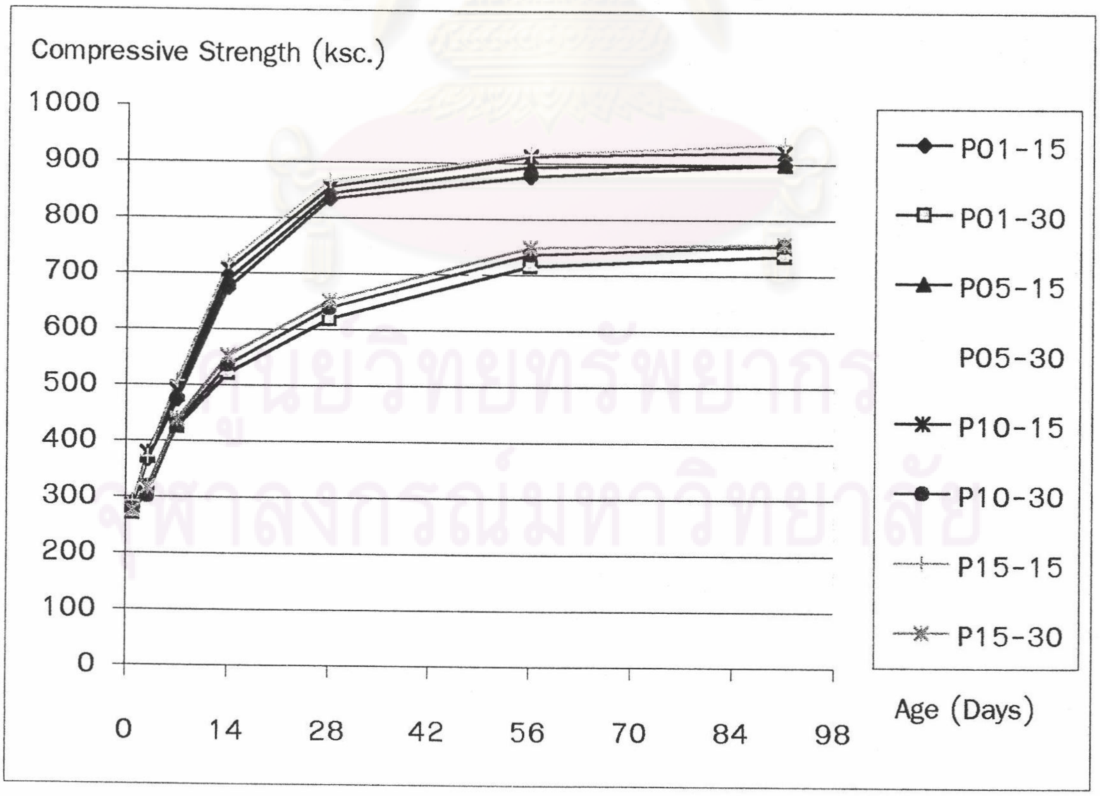


Fig. 4.31 Compressive strength of cement paste by fly ash

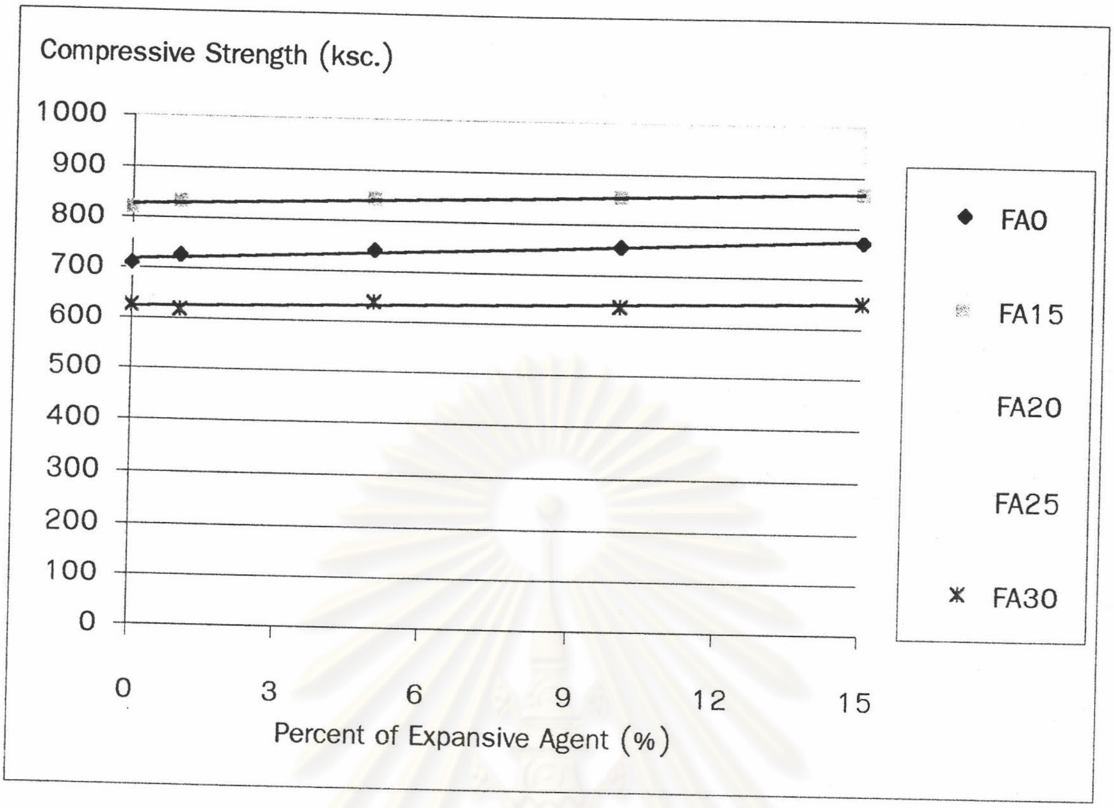


Fig. 4.32 Compressive strength of cement paste by expansive agent

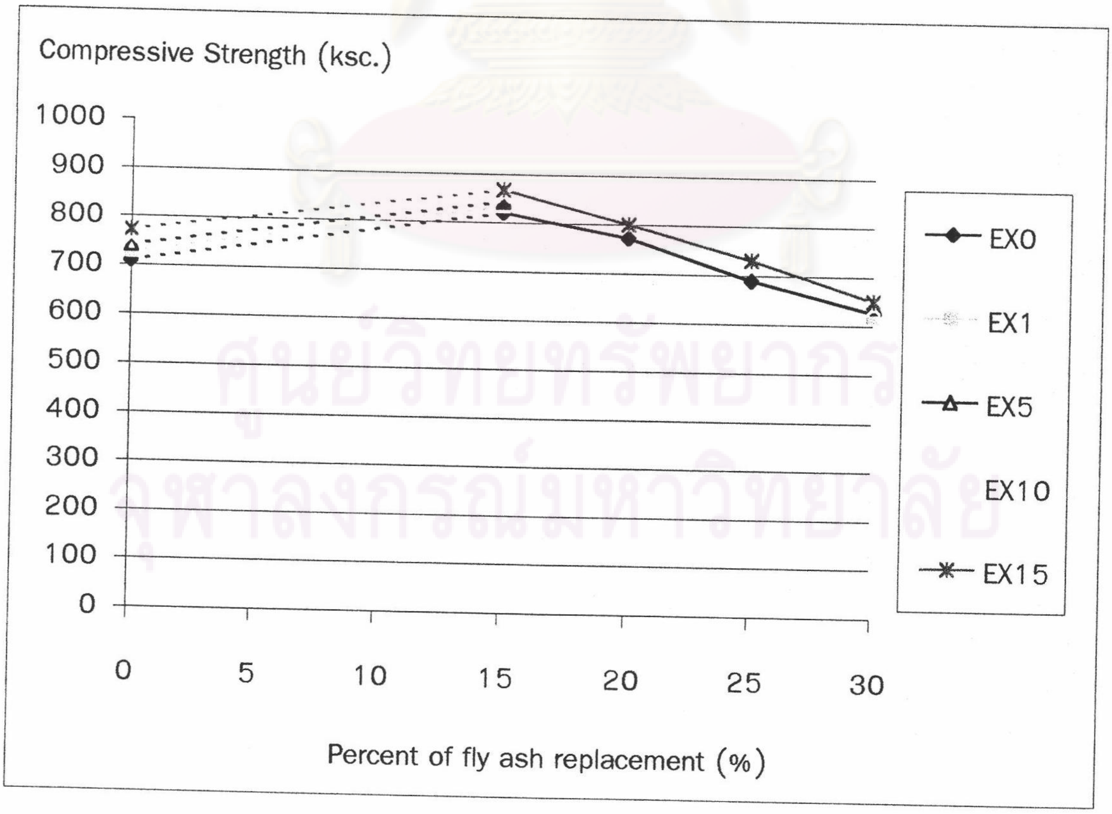


Fig. 4.33 Compressive strength of cement paste by fly ash at 28 day

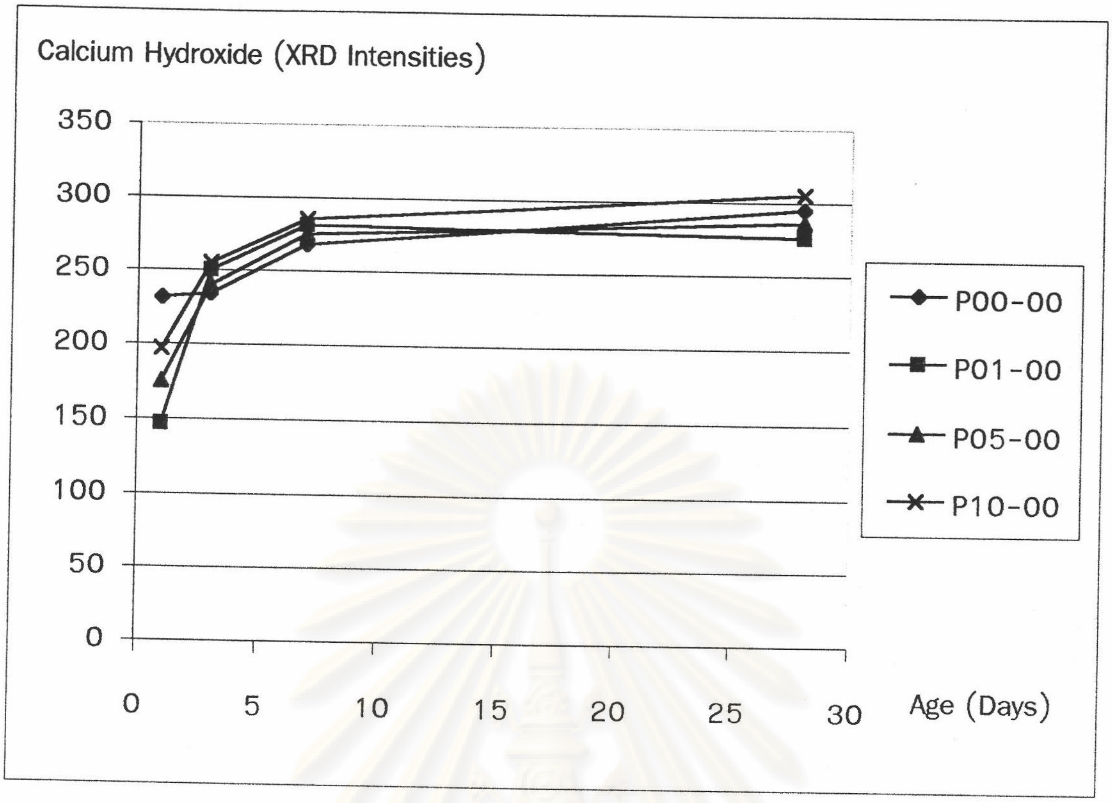


Fig. 4.34 Calcium hydroxide from XRD test by time

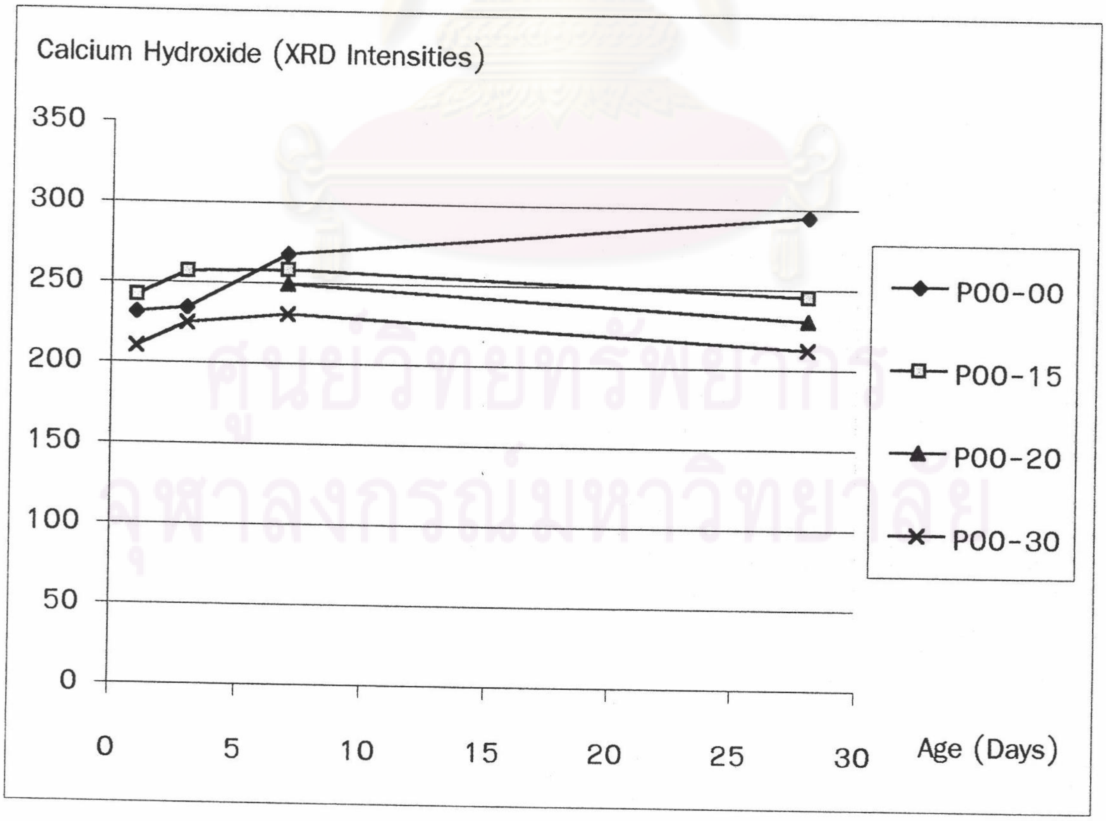


Fig. 4.35 Calcium hydroxide from XRD test by time

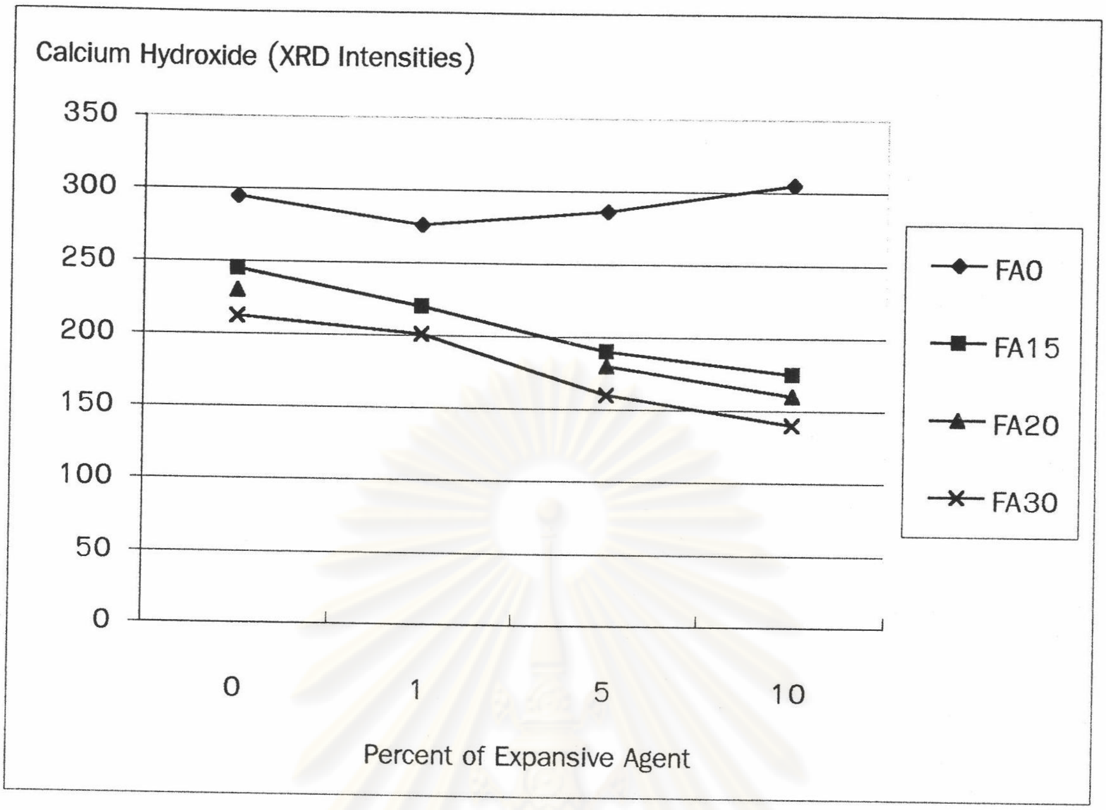


Fig. 4.36 Calcium hydroxide from XRD test by expansive agent

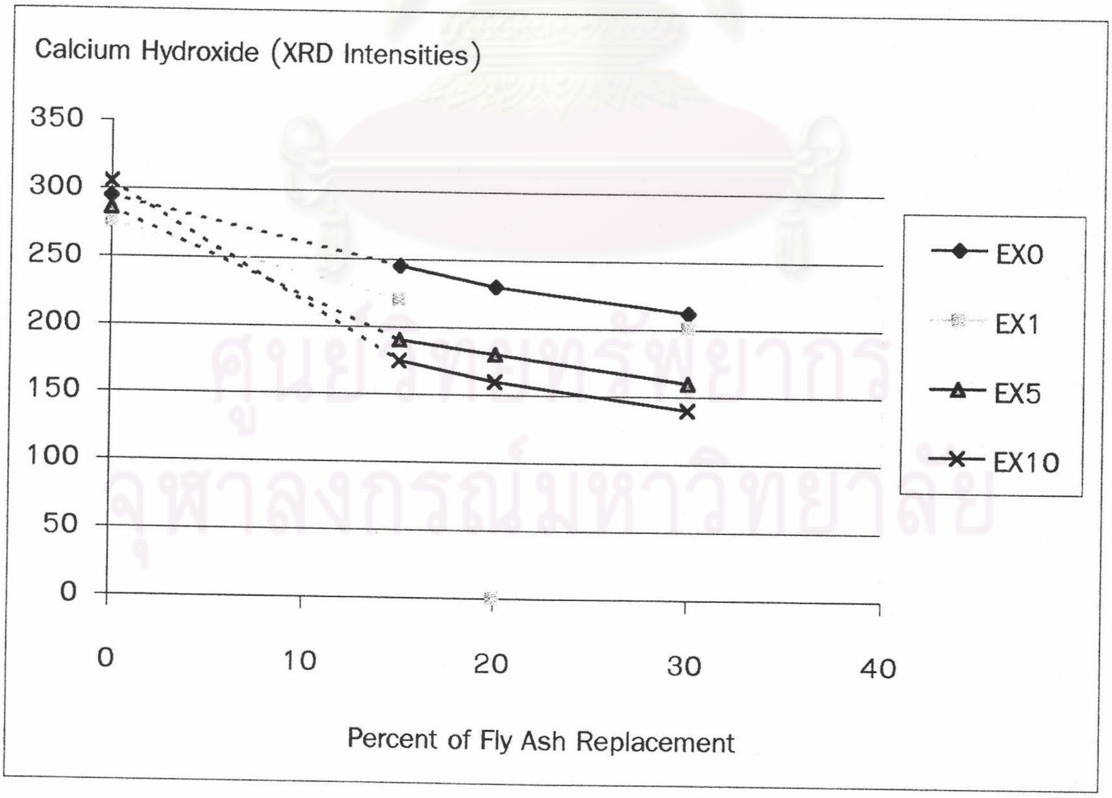


Fig. 4.37 Calcium hydroxide from XRD test by fly ash replacement

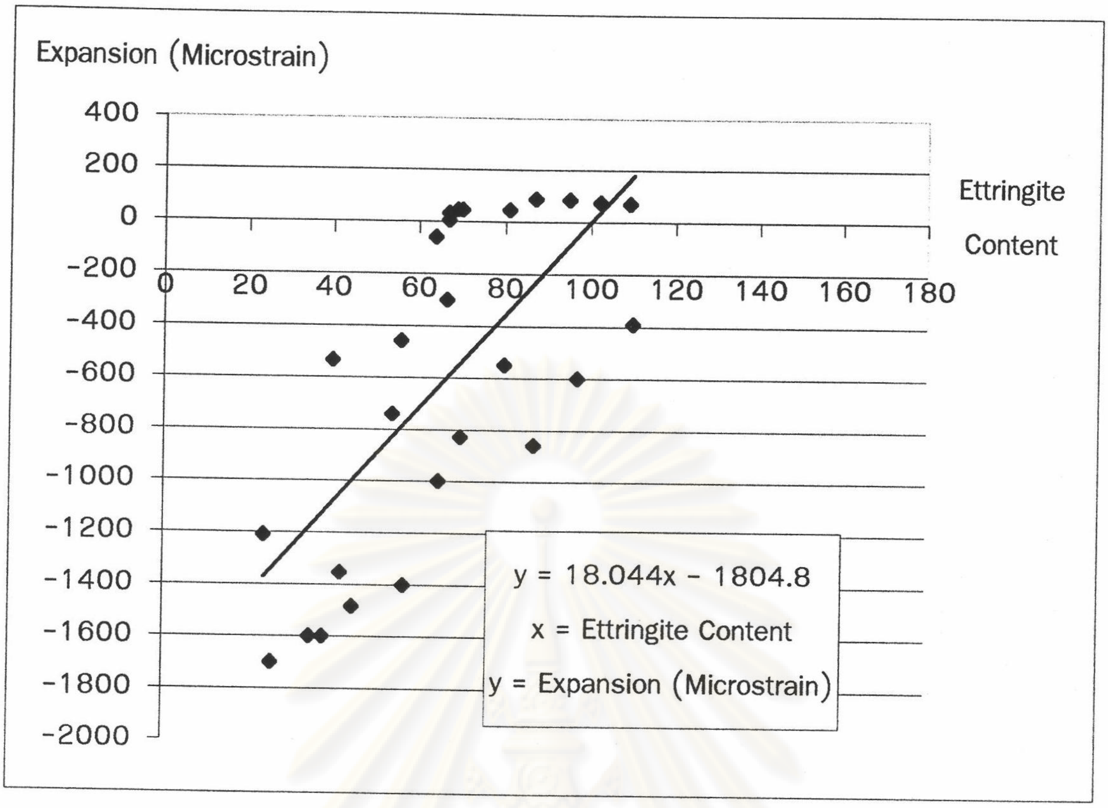


Fig. 4.38 The amount of ettringite with shrinkage of cement paste

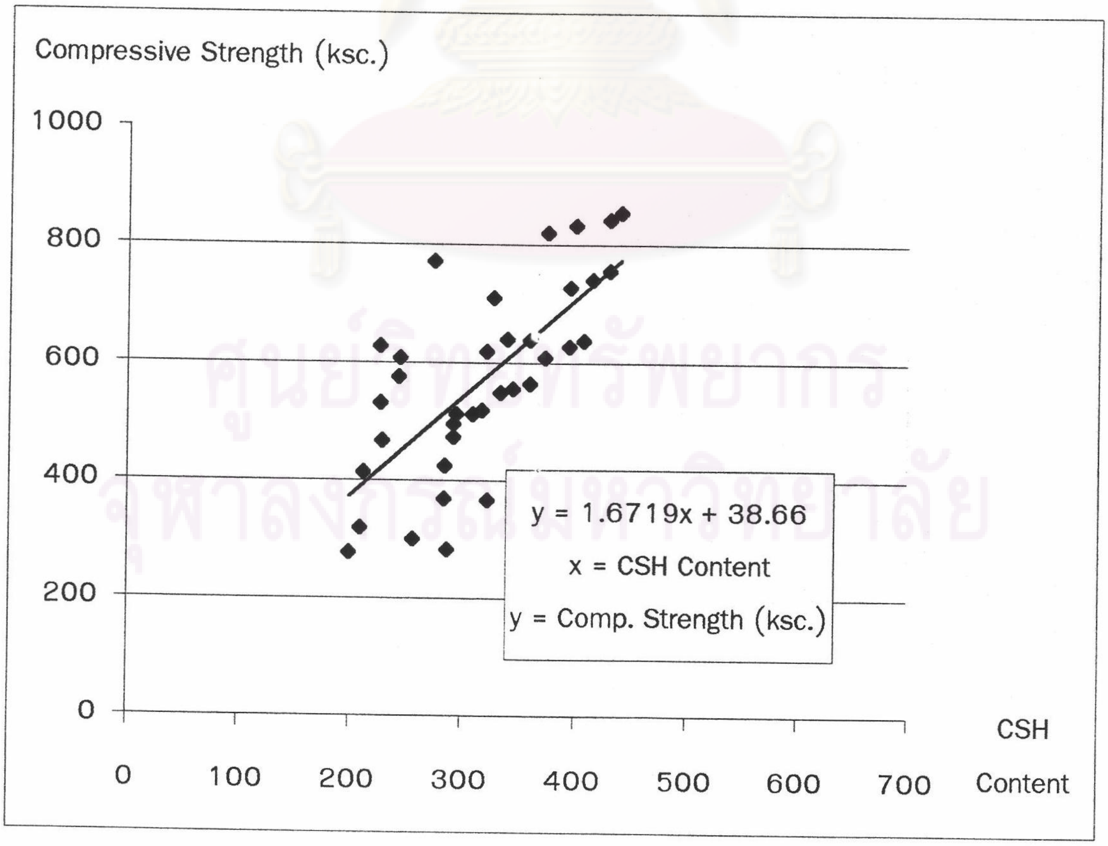


Fig. 4.39 The amount of CSH with compressive strength of cement paste

Fig. 4.40 Cement Paste Mixer

Fig. 4.41 Specimen for measuring drying shrinkage

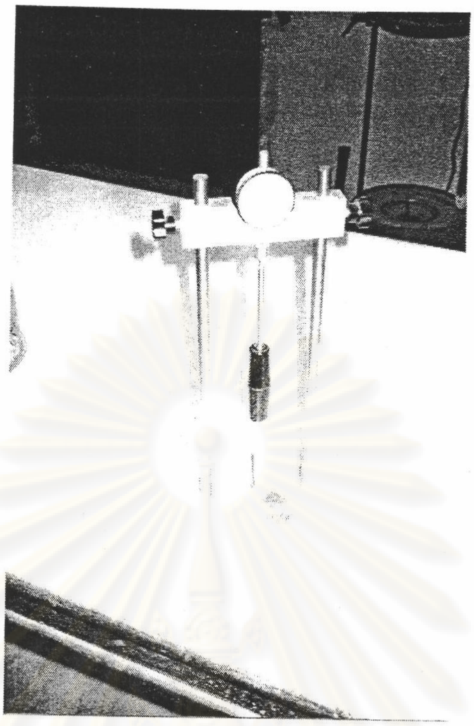


Fig. 4.42 Borletti length comparator

Fig. 4.43 Measuring of drying shrinkage

Fig. 4.44 Specimen for drying shrinkage test

Fig. 4.45 Compressive strength test

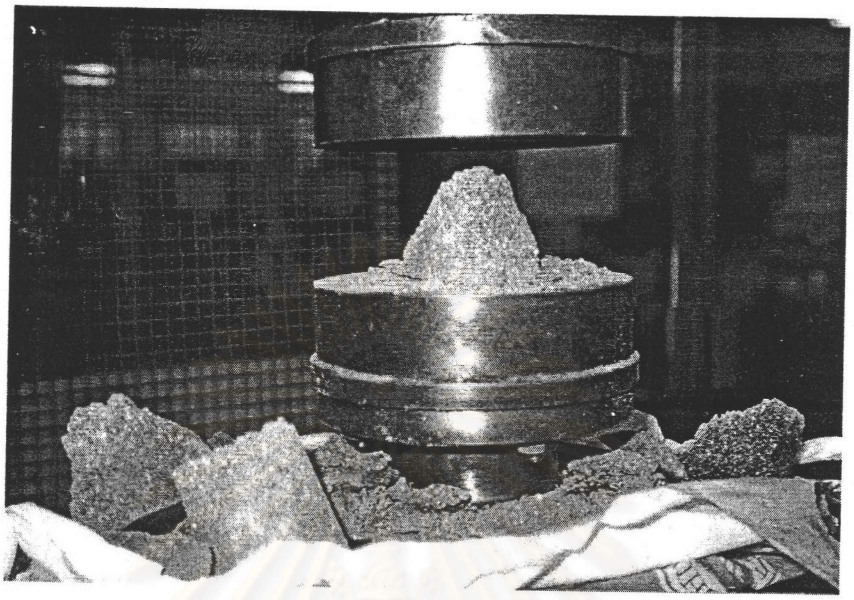


Fig. 4.46 Compressive strength test

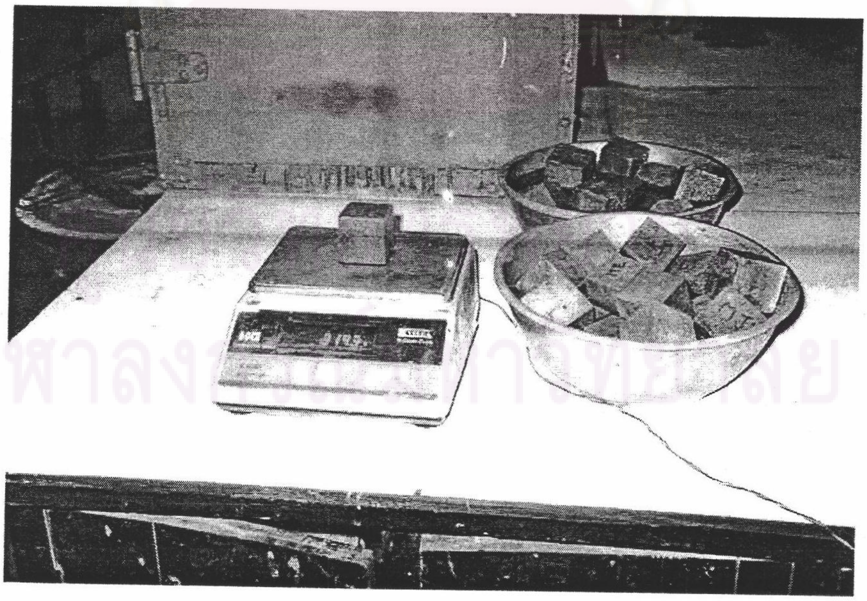


Fig. 4.47 Test of water adsorbtion