

CHAPTER 3.

DEVELOPMENT OF EXPANSIVE AGENT

The principal difficulty with the use of concrete is its shrinkage during the hardening process. Shrinkage compensating cement or non-shrink cement is a cement which increases in volume after setting and during hardening. It is used extensively to eliminate or minimize cracking caused by drying shrinkage. Normally, shrinkage compensating cement consists of a mixture of portland cement, expansive agent in the form of sulphotoaluminate cement and fly ash to improve its concrete properties.

The setting and hardening of concrete is the result of the hydration reaction that takes place between cement and water. The products of hydration reaction in hydrated cement paste are various and have different properties. When portland cement disperses in water, the needle shaped crystals of calcium sulphotoaluminate hydrate (Ettringite) are first formed. Later, a large prismatic crystals of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and very small fibrous crystals of calcium silicate hydrate (CSH) begin to fill the empty space.

The calcium silicate hydrate phase makes up 50–60% of the volume of solids in a completely hydrated cement paste. CSH is the most important factor in determining the shrinkage and strength of the paste due to the formation of a solid bond network. But loss of water in interlayer of CSH causes shrinkage in the paste. Calcium hydroxide contributes 20–25% of the volume of solids. The strength of calcium hydroxide is much lower than CSH because of the van der Waals forces which are limited due to less surface area. And it has an adverse effect on chemical durability.

Calcium sulphotoaluminate (Ettringite) occupies 10–15% of solid volume in ordinary hydrated cement paste. 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 takes the form of long slender needles, typically 10x0.5 micrometer. This needle-like crystal can grow to fill up the space. When this crystal is impeded by solid material, ettringite can develop pressures, as high as 240 MPa., at the point where growth has been stopped. This mechanism makes concrete expansion.

The expansive mechanism of calcium sulphoaluminate can be used beneficially to induce a compressive pre-stress of sufficient magnitude to compensate for drying shrinkage. The expansion can be controlled by adjusting the amount of the expansive agent in the form of calcium sulphoaluminate.

3.1 CHEMICAL COMPOSITION AS RAW MATERIALS

The chemical compositions of ordinary portland cement are composed of 4 main compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). It is not possible to determine the amounts of each compound by direct chemical analysis, oxide analysis is carried out instead. The chemical compositions is calculated from the oxide proportions using equations developed by Bogue.

According to ASTM C-150, ordinary portland cement type I will have C_3S 45-55%, C_2S 20-30%, C_3A 8-12% and C_4AF 6-10%. The amount of the main chemical composition is plotted in figure 3.1. High early strength portland cement type III will have C_3S 50-65%, C_2S 15-25%, C_3A 8-14% and C_4AF 6-10%. Sulfate resistant portland cement will have C_3S 40-50%, C_2S 25-35%, C_3A 0-4% and C_4AF 10-20%. These chemical compositions contribute to concrete's properties.

The calcium silicate in set portland cement provides most of the strength development. Tricalcium silicate (C_3S) provides most of the early strength and dicalcium silicate (C_2S) provides strength in later age. But both C_3S and C_2S contribute equally to ultimate strength. The strength development is shown in figure 3.2.

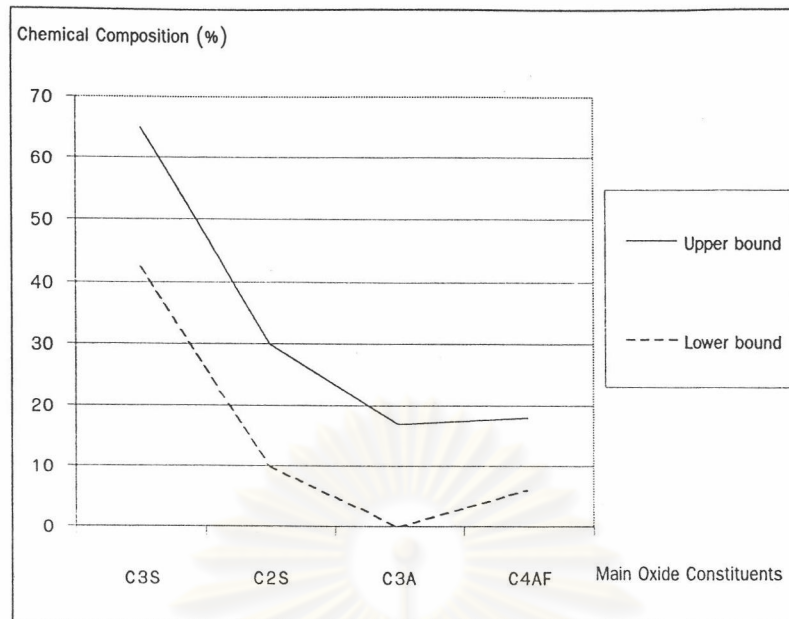


Fig. 3.1 Chemical proportion of ordinary portland cement.

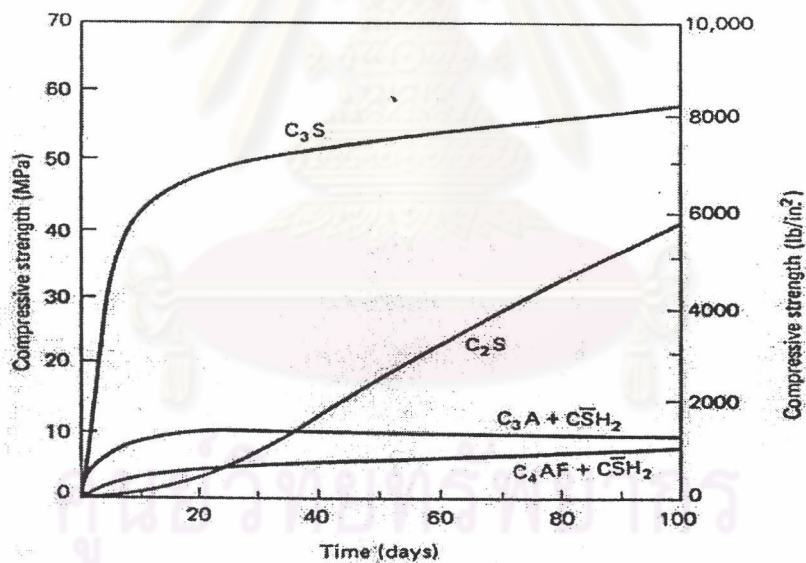


Fig. 3.2 Strength development in the pastes of pure cement compounds.

The expansion of concrete is controlled by the formation of ettringite in set portland cement which is produced from the hydration reaction of calcium sulfoaluminate (C_4A_3S) in expansive agent and tricalcium aluminate (C_3A) in portland cement. The expansive characteristic of C_4A_3S is shown in fig. 3.3. This expansive agent (calcium sulfoaluminate) is manufactured under oxidising conditions of ions. The formation of

ettringite requires calcium, sulphate and aluminate ions as sources of chemical reaction in an aqueous phase.

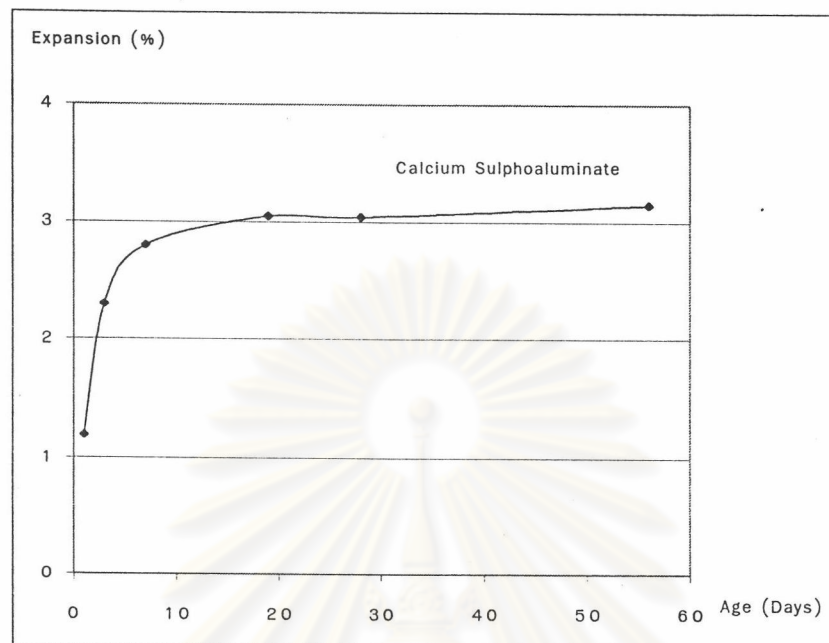


Fig. 3.3 Expansion of C_4A_3S in cement.

From the basic chemical theoretical approach described in chapter 2 (equation 2.16, p.25), the amount of ettringite required to compensate cement shrinkage of OPC depends on the chemical composition in portland cement. In portland cement type I 100 g., the maximum C_3S is 55% and the maximum C_2S is 30% then the amount of CSH calculated from hydration reaction is approximate 26.2 cm^3 (71 g.). The volume of water adsorbed in the pores and the surface of CSH that can be removed from paste is approximately 32 cm^3 . The volume of ettringite must be compensated in equal magnitude 32 cm^3 . Then the amount of calcium sulphoaluminate required in cement compensation is 4 cm^3 (10%). This calculation is based on an assumption of $w/c = 0.32$ at normal condition concrete.

If C_3S is 45% and C_2S is 20% (Minimum content in cement) then the amount of CSH calculated from hydration reaction is approximately 22 cm^3 (54 g.). The volume of water adsorbed in the pores and surface of CSH that can be removed from paste is approximately 29 cm^3 . The volume of ettringite must be compensated in equal magnitude 29 cm^3 . Then the amount of calcium sulphoaluminate required in cement

compensation is 4 cm^3 (8%). This calculation is based on an assumption of $w/c = 0.32$ at normal condition concrete.

From the chemical calculation, fig. 3.4 shows the upper and lower bound of chemical compound of ordinary portland cement with an expansive agent. Aluminium and sulphate in this cement is of greater quantity than in ordinary portland cement because expansive agent is a source to supply both aluminium and sulphate to form ettringite.

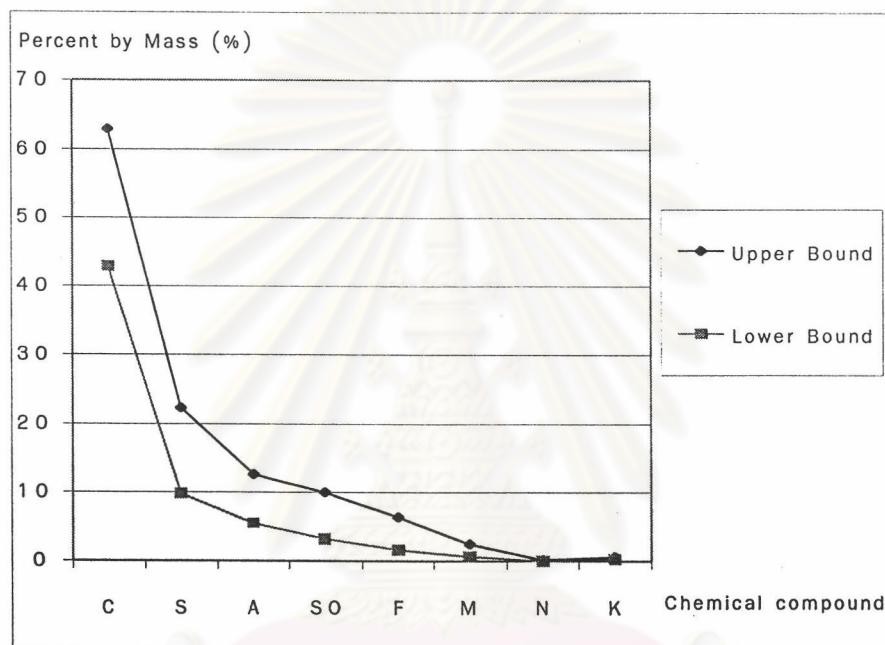


Fig. 3.4 Upper and lower bound of chemical compound in shrinkage compensating cement.

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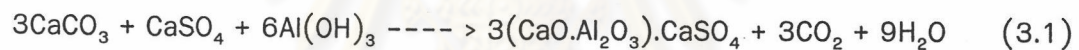
3.2 CHEMICAL REACTION TO PRODUCE AN EXPANSIVE AGENT AND PROCESS

3.2.1 CHEMICAL REACTION

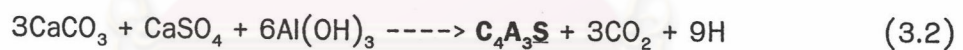
The expansive mechanism of hydrated cement occurs due to the formation of ettringite. Calcium sulphoaluminate from the expansive agent and tricalcium aluminate from portland cement are sources to supply the chemical constituent for the hydration reaction of ettringite ($C_6AS_3H_{32}$).

From literatures review^{(1),(4),(7),(9)}, calcium sulphoaluminate $3(CaO.Al_2O_3).CaSO_4$ or C_4A_3S is produced from a mixture of calcium, alumina and sulphate ion in an aqueous phase. Raw materials to produce an expansive agent are bauxite, chalk, kaolin, slaked lime and gypsum but the chemical reaction is not fully investigated.

The chemical reaction to produce an expansive agent in the form of calcium sulphoaluminate is shown in equations 3.1 and 3.2 ;



or simple form ;

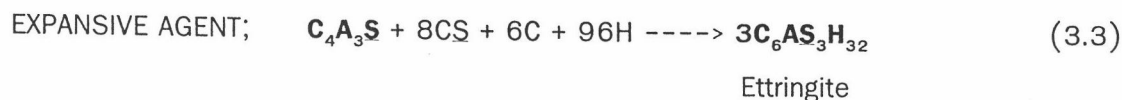


Mass 300 g. 136 g. 468 g. ----> 904 g.

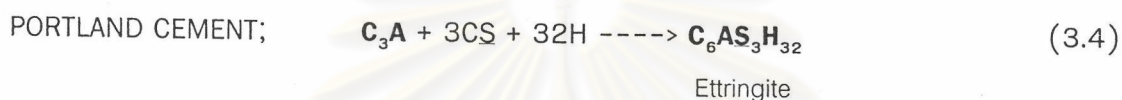
Equation 3.2 shows that 300 g. of calcium carbonate, 136 g. of calcium sulphate and 468 g. of aluminium hydroxide will produce 904 g. of calcium sulfoaluminate.

This reaction requires a high temperature. The temperature for sintering is 1,200–1,400°C. This temperature is lower than the fusion temperature of High Alumina Cement (>1,600°C) and lower than the calcination temperature of ordinary portland cement (1,450°C).

Mixing calcium sulfoaluminate in portland cement and water will produce a large amount of ettringite. This hydration reaction is shown in equation 3.3. and it should be noted that this reaction is quick setting and prone to suffer rapid slump loss.



Tricalcium aluminate (C_3A) in ordinary portland cement also provides ettringite. In ordinary portland cement the hydration of C_3A involves reactions with sulfate ions which are supplied by the dissolution of gypsum. The reaction is written in equation 3.4.



Ettringite is a stable hydration product only while there is a supply of sulfate available. If the sulfate is all consumed before the C_3A has complete hydration, the ettringite will be transformed to tetracalcium aluminate monosulfate-12 hydrate or monosulfoaluminate ($\text{C}_3\text{A}.\text{CS}.\text{H}_{12}$). If this phase is brought into contact with a new source of sulfate ions, then ettringite can be formed once again.

3.2.2 PROCESS

Calcium Carbonate, calcium sulphate and aluminium hydroxide were blended together in a correct stoichiometric ratio and placed in a crucible. Then the mixture was dried in an oven for 2 hours. A powdered mixture was burn in the furnace at various temperatures ranging from 1,100-1,400°C for 1-4 hrs.

As the temperature increased (at 100°C), there was little or no change in the raw materials, however the moisture in the mixture was removed. When the temperature increased up to 600°C, a loose paste formed but there was no obvious chemical changes occurring in the raw materials. But when the temperature reached 800°C, chemical changes were observed. Gypsum was converted to anhydrate and calcium carbonate was converted to calcium oxide, continuously heated to a high temperature of 1,400°C, the raw materials became clinker, and pale green-blue clinker was obtained.

The sequence of the formation of this phase during the sintering process is shown in figure 3.5⁽¹¹⁾.

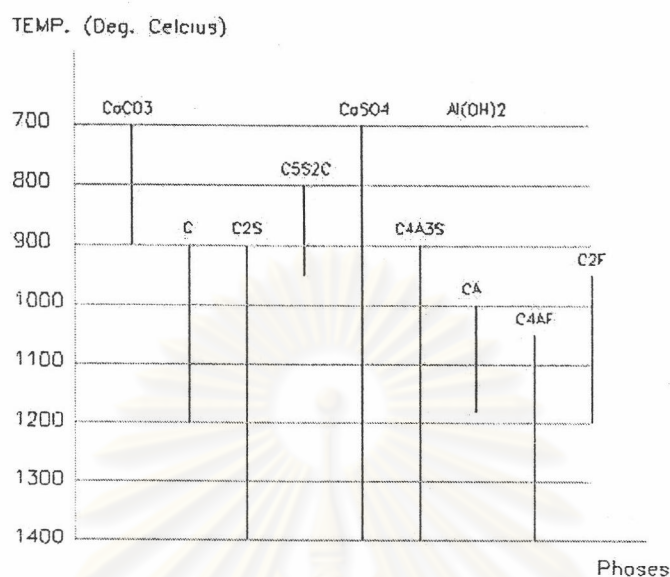


Fig. 3.5 Sequence of the formation of phases during the sintering.

The sintering product was ground to a fineness of $3,700 \text{ cm}^2/\text{g}$. without any supplementary addition of gypsum. The chemical composition of the products was examined by XRD.

3.3 TESTS RESULTS AND EVALUATION OF THE PRODUCT

X-ray diffraction method is a method to estimate the compound content of the sintered product. The result pattern obtained from a x-ray photograph or diffractogram of a substance consists of many varying intensity lines. These results show a trace (peak) of diffracted energy versus the angle turned by the specimen. The diffracted energy for a selected reflection is compared with a standard preparation of the substance to estimate the 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 XRD peak of standard $\text{C}_4\text{A}_3\text{S}$ specimen shows a significant peak at $23.7^\circ 2\theta$. The chemical composition of products was qualitatively identified by X-Ray Diffraction Analysis are shown in Figure 3.6.

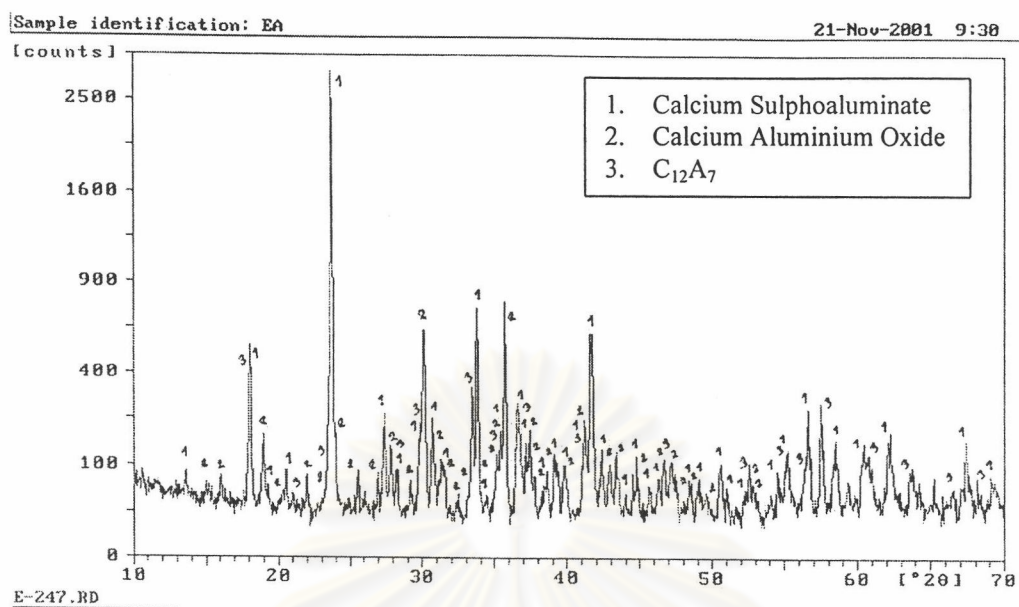


Fig. 3.6 XRD results of calcium sulphoaluminate products.

Table 3.1 Intensities of XRD results at 23.7°.

| Temperature (Deg. Celsius) | Sintered Time (Hr.) | Peak Intensities |
|-------------------------------|------------------------|---------------------|
| 1100 | 4 | 1058 |
| 1200 | 4 | 3015 |
| 1300 | 4 | 6891 |
| 1400 | 0.5 | 15 |
| | 1 | 186 |
| | 1.5 | 1258 |
| | 2 | 2258 |
| | 3 | 6548 |
| | 4 | 8496 |
| | 4.5 | 8769 |

Table 3.1 shows the peak intensities at 2θ of sintered product. The intensities are related to the amount of calcium sulphoaluminate compared with standard intensities. Figure 3.7 shows the peak intensities of calcium sulphoaluminate at temperatures varying from $1,100^{\circ}\text{C}$ to $1,400^{\circ}\text{C}$. Test results from XRD show that calcium sulphoaluminate is formed at $1,100^{\circ}\text{C}$. And the largest amount of calcium sulphoaluminate is formed at $1,400^{\circ}\text{C}$. Figure 3.8 shows the relation between peak intensities of calcium sulphoaluminate by sintered time. These results show that after 3 hrs. calcium sulphoaluminate will form rapidly, and starts to gradually form after 4 hrs.

The optimum process, in a cost and chemical reaction, to produce an expansive agent is to burn raw materials at high temperature for 3–4 hours.

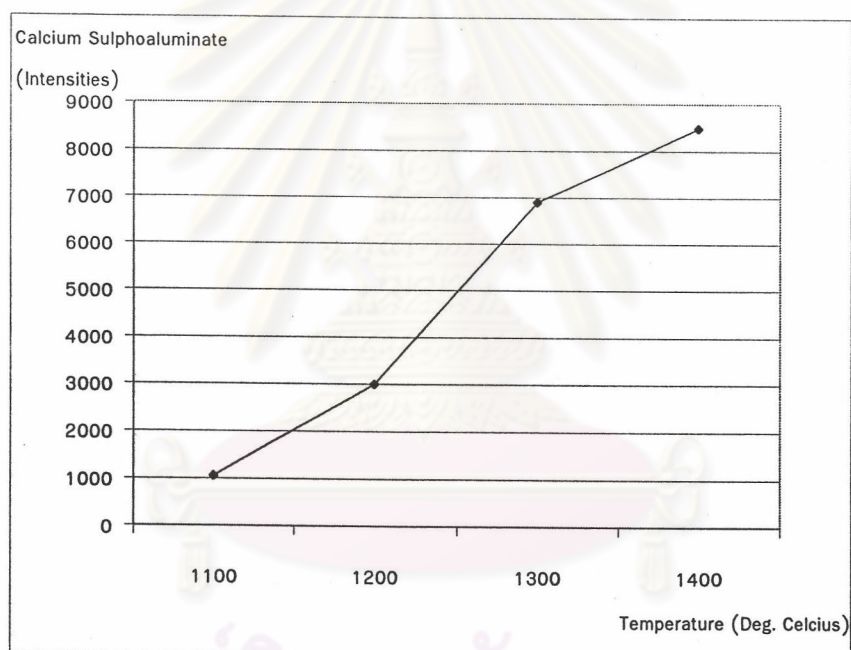


Fig. 3.7 Peak Intensities of calcium sulphoaluminate at various temperature.

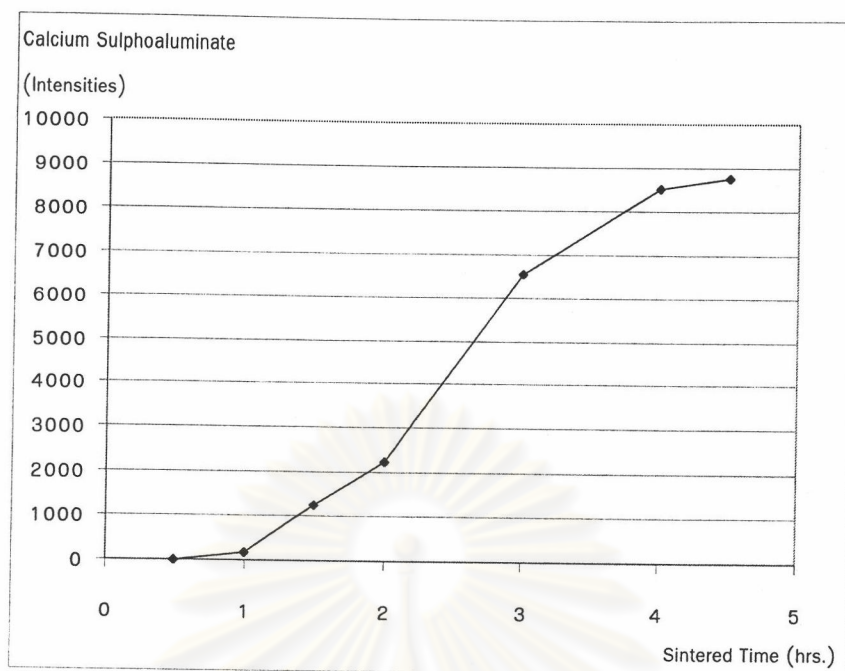


Fig. 3.8 Peak Intensities of Calcium Sulphoaluminate by Sintered Time

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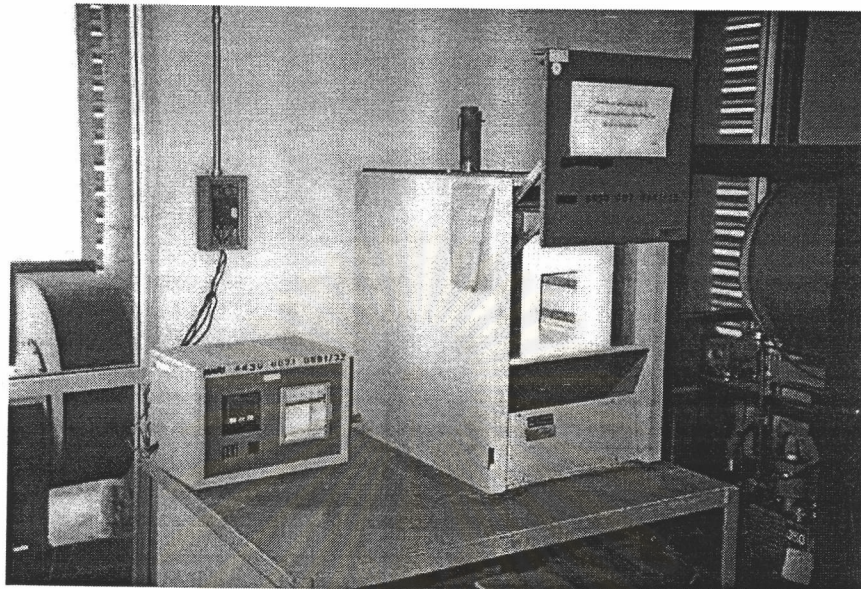


Fig. 3.9 Cobolite Furnance

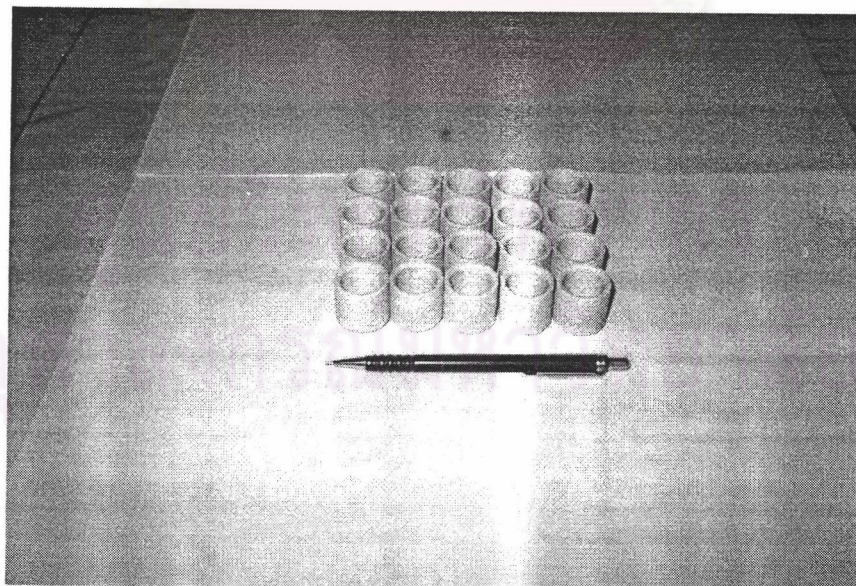


Fig. 3.10 Crucible



Fig. 3.11 Calcium Sulphoaluminate

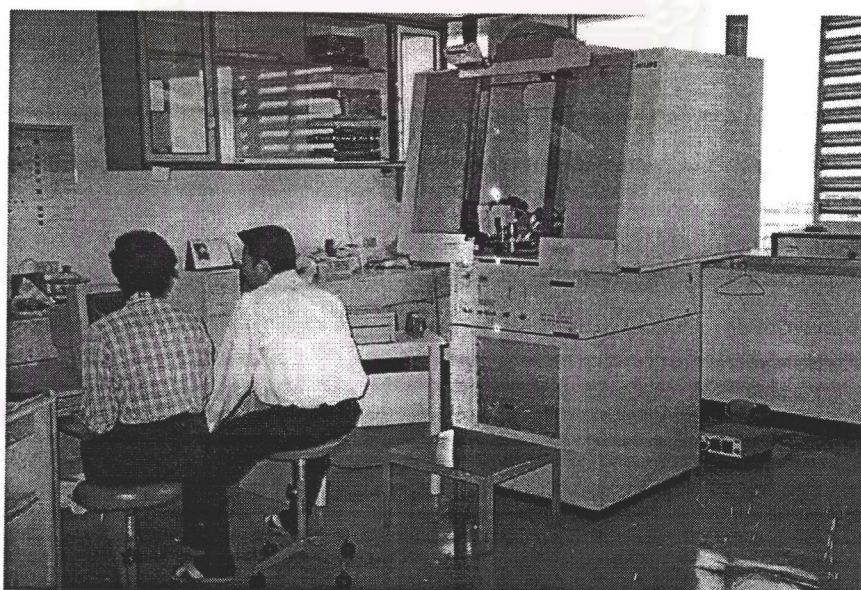


Fig. 3.12 Philips PW 3020 X-Ray Diffractometer
(Metallurgy and Materials Science Research)

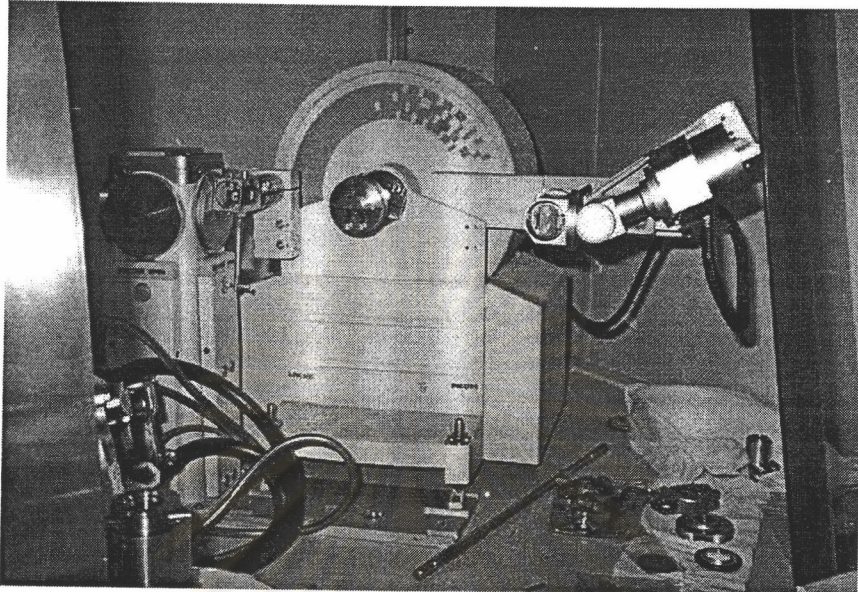


Fig. 3.13 Philips PW 3020 X-Ray Diffractometer
(Metallurgy and Materials Science Research)

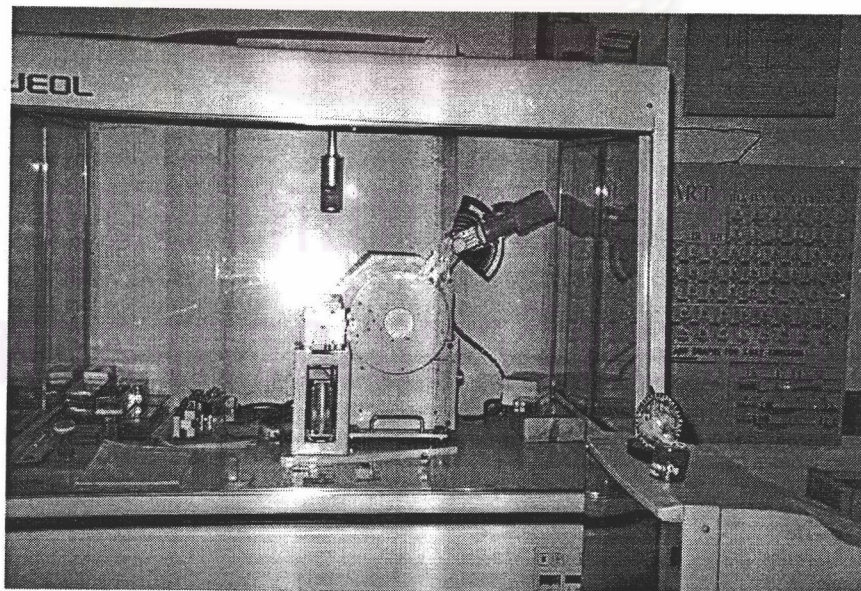


Fig. 3.14 JEOL JDX 8030 X-Ray Diffractometer
(Scientific and Technology Research Equipment Centre)

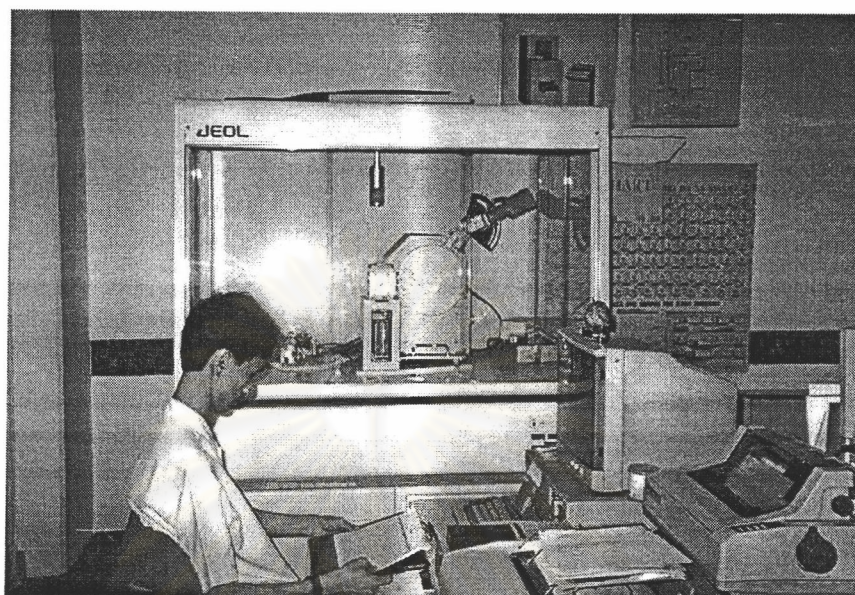


Fig. 3.15 JEOL JDX 8030 X-Ray Diffractometer
(Scientific and Technology Research Equipment Centre)

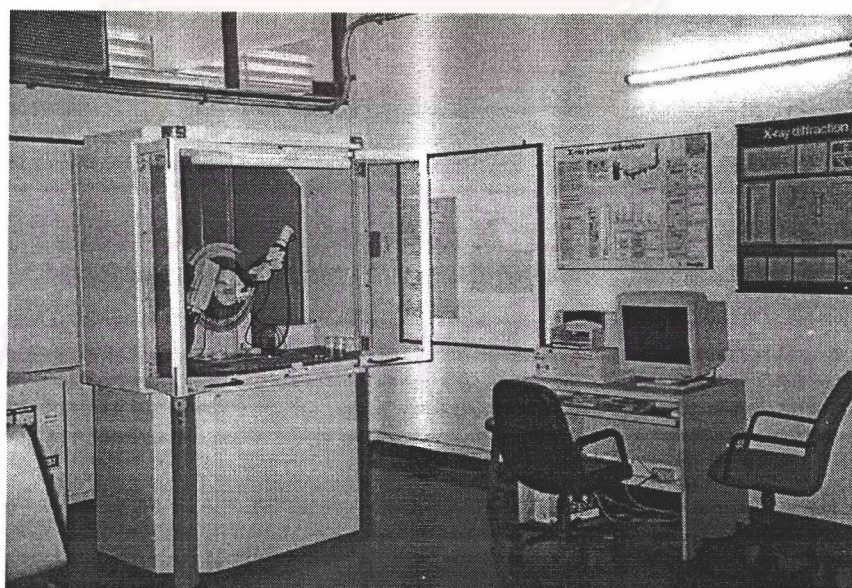


Fig. 3.16 D8 Advance X-Ray Diffractometer
(Faculty of Science, Chulalongkorn University)

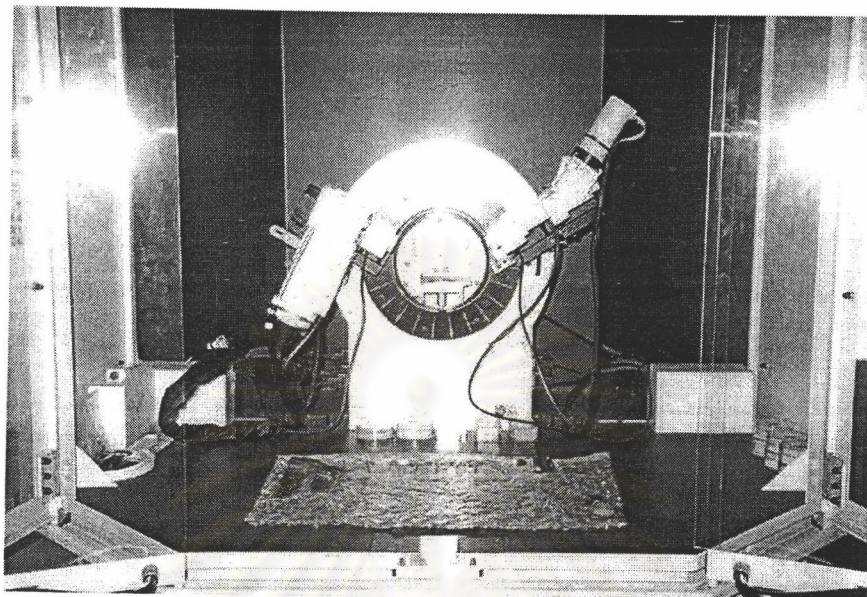


Fig. 3.17 D8 Advance X-Ray Diffractometer
(Faculty of Science, Chulalongkorn University)



Fig. 3.18 SEM Sample

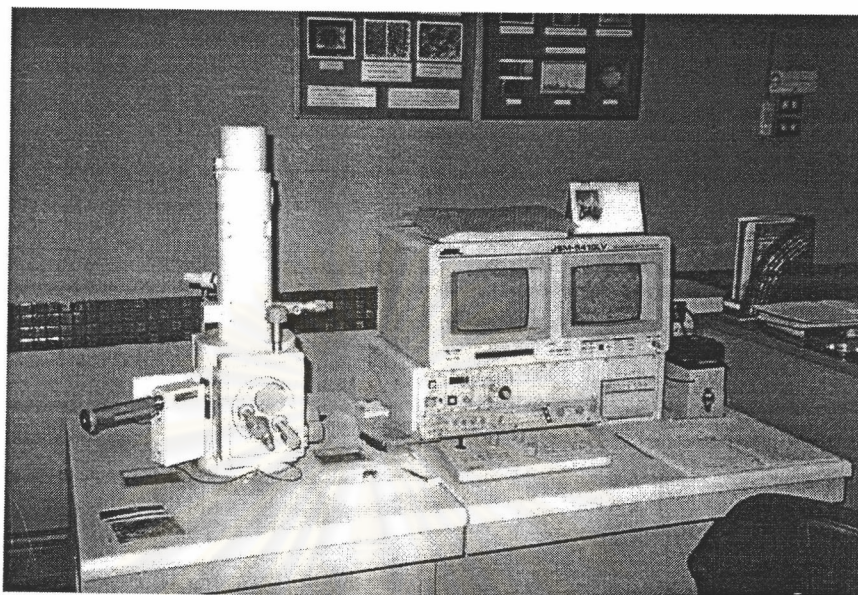


Fig. 3.19 Scanning Electron Microscope
(Scientific and Technology Research Equipment Centre)

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