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Special Cement Additives Using Ettringite Formation

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Special cement additives or admixtures are widely used in cement material to control various characters such as fluidity, setting, hardening, strength development, and shrinkage for improvement of molding capability, properties and durability. Special cement additives based on calcium sulfoaluminate show various functions such as quick hardening, high strength development, and shrinkage compensation. These functions are fulfilled by controlling the reaction of ettringite formation during the cement hydration. Ettringite is a hydrate sulfate consists of calcium and aluminum and forms by hydration of calcium aluminate and calcium sulfate in cement material. Quick hardening property is achieved by formation of ettringite at early stage of cement hydration. High strength is achieved by formation of very fine ettringite crystals filling vacant spaces of hydrated cement structure. Shrinkage compensation or expansive property is produced by formation of large and rod-like-grain ettringite crystals at later stage of cement hydration.
Key words: Special cement additive, Ettringite, Calcium sulfoaluminate,

1. INTRODUCTION

Cement material, in a broad sense, is explained as hydrated materials based on inorganic powder. Having a very long history, cement materials tend to be regarded as an old and conventional material. However, it has been changed and improved especially in these days due to the drastic change in society and life style, demanding new applications in cement material.

One of the developments in cement material is an application of admixtures or additives to improve forming capability, properties, and durability. The word "admixture" is usually applied for organic and liquid material and used for adding less than 1% of cement by weight. On the other hand, the word "additive" is usually applied for inorganic fine powder and additive content is larger than admixture such as several percent or even few tenth percent.

Special cement additives based on calcium sulfoaluminate showing quick hardening, high strength, and shrinkage compensation or expansive properties by controlling the reaction of ettringite formation is widely used in many application in civil engineering.

This paper reports the formation of ettringite in cement materials and mechanism of function fulfilled by special cement additives based on calcium sulfoaluminate.

2. ETTRINGITE IN CEMENT MATERIAL

The general formula of ettringite is;
$[Ca_3Al(OH)_6 \cdot 12H_2O]_2 \cdot (SO_4)_3 \cdot 2H_2O$, or
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$. One molecule of ettringite contains 32 water molecules, which are about 46% of ettringite by weight.

Crystal structure of ettringite is shown in Fig. 1 [1]. Three calcium atoms and twelve water molecules form one unit, and in the unit, four water molecules are arranged in outside of each calcium atom. These units are connected by Al atoms and placed in order. Furthermore, these units are bonded with several SO_4^{2-} ions and water molecules and forms needle like crystal.

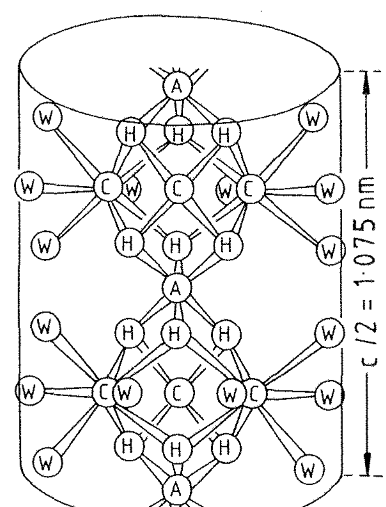

Fig. 1 Crystal structure of ettringite.
Part of a single column in (1120) projection;
A = Al, C = Ca, H = O of an OH group, W = O of an H_2O molecule. Hydrogen atoms are omitted.

Figure 2 shows the SEM (Scanning Electron Microscope) observation of ettringite synthesized by reaction of calcium hydroxide and aluminum sulfate in water. Needle like structure or rod-like grain with high aspect ratio is observed.

In cement material, ettringite is formed by a hydration of calcium aluminate and calcium sulfate which both are components in Portland cement. Similar to Fig. 2, ettringite with needle like structure is often observed in cement material. The reaction is as follows,

$$3CaO \cdot Al_2O_3 + 3\ CaSO_4 \cdot 2H_2O + 26\ H_2O$$
$$\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

Ettringite has been regarded as a bacillus in cement material as it induces excessive expansion and cracks in cement products. Special cement additives based on calcium sulfoaluminate overcome the drawback by controlling the reaction of ettringite formation.

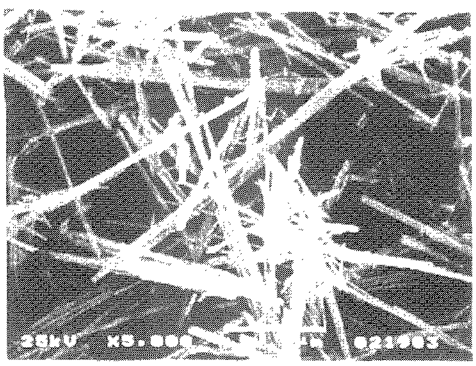

Fig. 2 SEM observation of ettringite.

3. FORMATION OF ETTRINGITE BY SPECIAL CEMENT ADDITIVES

By adding special cement additives in cement, and controlling the period of ettringite formation in combination with cement hydration, quick hardening, high strength, and expansive properties are achieved. Relationship between age and ettringite formation together with cement hydration is illustrated in Fig. 3 [2, 3].

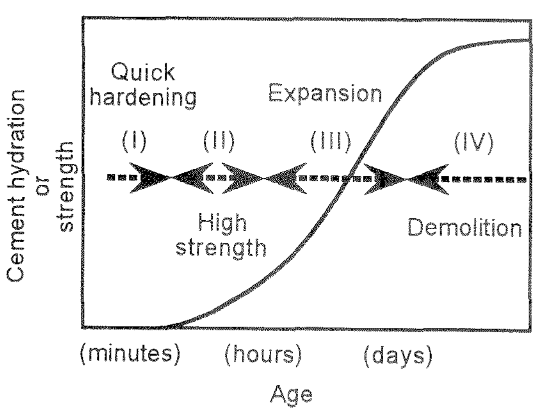

Fig. 3 Period of ettringite formation and property obtained by special cement additives.

Quick hardening property is achieved by formation of ettringite at early stage of cement hydration, in the range of minutes. Expansive property is achieved by formation of ettringite crystals at later stage of cement hydration, in the range of days. Demolition occurs at the last stage when the ettringite forms in fully hardened cement material. High strength property is suggested to achieve by formation of ettringite at intermediate stage of other two properties.

Figure 4 shows the experimental result of relationship between ettringite formation and the time elapsed of cement paste with three types of special cement additives, namely quick hardening additive (DENKA ES), expansive additive (DENKA CSA#20), and high strength additive (DENKA Σ1000). Additive content of each special cement additive was set to 10% of cement powder by weight and water to cement ratio (W/C) was set to 50%. The amount of ettringite was evaluated by X-ray diffraction measurement of powder sample, comparing the main peak of ettringite and peak of TiO_2 mixed in powder sample as a comparison.

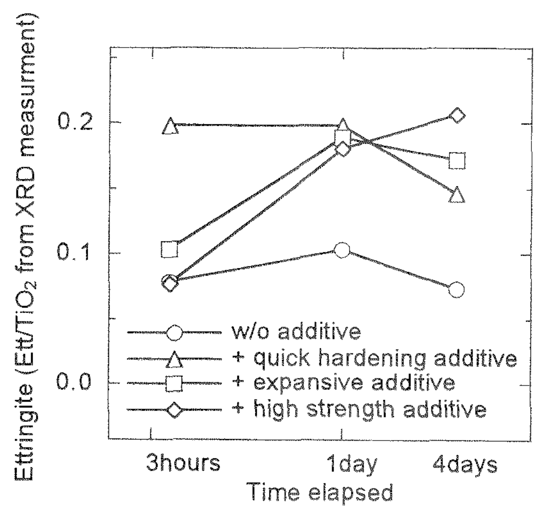

Fig. 4 Relationship between ettringite formation and the time elapsed of cement paste with special cement additives.
additive content: C x 10wt%, W/C=50%

Ettringite content of cement paste without special cement additive is nearly the same during the evaluation. Cement paste with quick hardening additive results in higher ettringite content after 3 hours compared with other pastes. At the time elapsed of one day, higher ettringite content is observed with cement pastes with additives compared with the cement paste without additive. The ettringite formation of cement paste with expansive additive and high strength additive are nearly the same.

SEM observation on cement pastes with additives after one day are shown in Fig. 5. In the cement paste with expansive additive, larger ettringite crystals are observed compared with the other cement pastes. From the evaluation of ettringite content and microstructure, expansion is considered to occur by large ettringite crystals pressing against hydrated cement structure and forming a microstructure with fine pores. On the other hand, high strength is considered to achieve by formation of very fine ettringite crystals filling vacant spaces of hydrated cement structure.

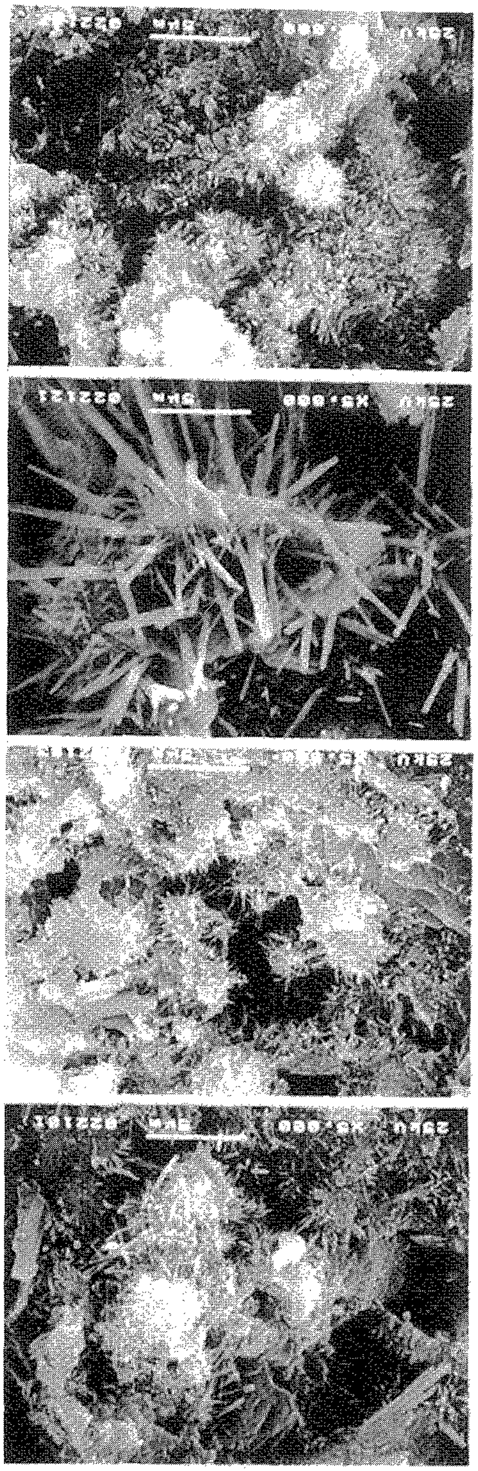

Fig. 5 SEM observation of cement pastes with special cement additives after 1 day.
(A) cement, (B) + quick hardening additive, (C) + expansive additive, (D) + high strength additive.

Chemical compositions of these special cement additives are shown in Table I. Calcium, aluminum, and sulfur are the main component in these special cement additives. Figure 6 shows the relationship between the chemical composition and the property achieved by the special cement additives. Quick hardening property is achieved by special cement additive with chemical composition of higher Al_2O_3 content than the other two. High strength is achieved by higher SO_3 content, and expansive property is achieved by higher CaO content, respectively.

Table I Chemical composition of special cement additives.

	Quick hardening additive	Expansive additive	High strength additive
ig.loss	0.3	0.3	1.3
SiO_2	1.2	1.4	15.4
Al_2O_3	20.6	15.0	3.8
Fe_2O_3	0.6	0.5	0.4
CaO	45.5	52.4	34.0
MgO	0.3	1.5	0.5
SO_3	30.4	28.0	44.0
Na_2O	0.03	0.05	0.16
K_2O	0.13	0.06	0.19

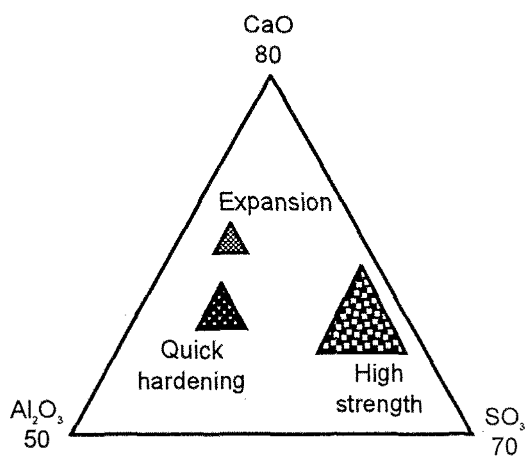

Fig. 6 Chemical composition of special cement additives and properties.

4. QUICK HARDENING ADDITIVE

Quick hardening additive is used in many applications, such as soil stabilization, shotcrete, hardening of industrial waste, repair of concrete structures and so on.

Combination of calcium aluminate and calcium sulfate is well-known special cement additive used in practical application [4]. Amorphous calcium aluminate with calcium to aluminum ratio of 12/7 is known to show superior quick hardening property [5, 6, 7, 8].

Figure 7 shows the compressive strength of mortar containing quick hardening additive. Mortar with quick hardening additive results in sufficient strength from 3 hours.

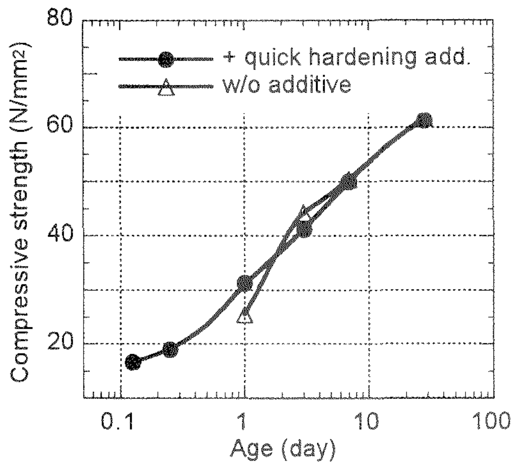

Fig. 7 Compressive strength of mortar with quick hardening additive.

5. HIGH STRENGTH ADDITIVE

High strength additive is used in application of concrete products such as pole, pile, and Hume pipe. It is also used in concrete structure such as shore protection, dam, and traffic road.

In application of concrete products, high strength additive can abbreviate autoclave curing and leads to both time saving and cost saving. High strength additive consist of mainly anhydrite is widely used nowadays [9, 10].

Figure 8 shows the relationship between additive content of high strength additive and compressive strength of concrete at various age. The concrete was steam cured at 80 °C for 4 hours. Additive content of 13% by cement results in about 35 N/mm^2 higher compressive strength after 28 days.

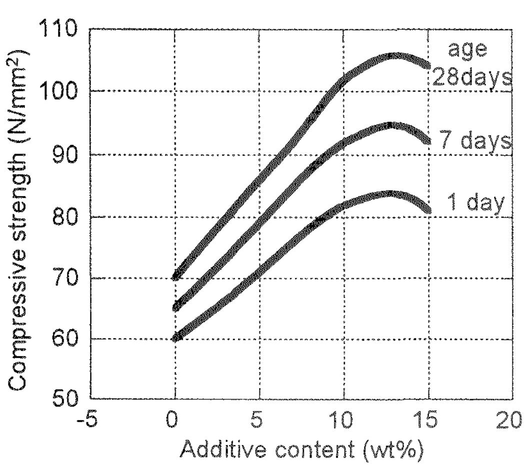

Fig. 8 Compressive strength of concrete with high strength additive.

Cement 486 kg/m^3, Superplasticizer 7.2 kg/m^3
W/C = 29%, s/a = 38%

6. EXPANSIVE ADDITIVE

Expansive additive is used to compensate shrinkage of concrete or to produce self-stressing concrete. Expansive additives containing hauyne and free lime are now placed on the market [11].

Figure 9 shows the expansive property of mortar with expansive additive compared with mortar without additive. Mortar with expansive additive shows increasing expansion during the first 7 days, and the expansion remains even after 28 days.

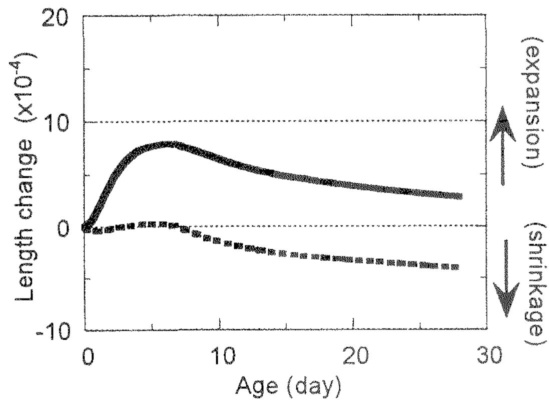

Fig. 9 Length change of mortar as a function of age.
▪▪▪▪▪▪▪▪ mortar without additive
━━━━ mortar with expansive additive (C x 10%)

7. SUMMARY

Special cement additives based on calcium sulfoaluminate show various functions such as quick hardening, high strength development, and shrinkage compensation. Controlling the reaction of ettringite formation during the cement hydration fulfills these functions.

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