

# INVESTIGATING THE LINEAR EXPANSION, SET, AND STRENGTH BEHAVIORS OF THE BINARY MIXTURE; PORTLAND CEMENT CLINKER-GYPSUM

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**Abstract:** The linear expansion, early-age compressive strength and setting times of the binary mixtures of gypsum and Portland cement clinkers of relatively low  $C_3A$ -contents were investigated. For this reason, type 1, 2, and 5 of Portland cement-clinkers were selected and a number of binary mixtures were designed. At relatively lower percentages of gypsum (about 5%), the early strength behavior is improved. Results obtained for compressive strength of mixtures with 5% gypsum confirm the possibility of achieving 28- and 90-day compressive strengths up to values higher than 100 MPa and 130 MPa, respectively. At relatively higher percentages of gypsum (more than 25%), excessive expansion caused by ettringite formation results in the formation of micro-cracks effectively weakening the strength behavior. The work suggests that type S expansive cements could be produced from Portland cement clinkers of relatively low  $C_3A$ -contents.

**Keywords:** Portland cement; Gypsum; Linear expansion; Compressive strength

## 1. INTRODUCTION

The reactions of cement compounds with water are accompanied by a small volume contraction of the system, which appears in the plastic-paste period. After achieving certain strength in the paste, further reaction of anhydrous grains with water gives a volume increase or expansion which is typical for samples cured in water. This is followed by a paste porosity decrease which in turn leads to higher compressive strengths [1-3]. The strength of the hardened cement paste therefore depends on the internal structure of which usually characterized by the size and the shape of hydration products and their compression density [4]. At the hardening stage, the formation of the crystallo-hydrates such as: Portlandite ( $Ca(OH)_2$ ), Ettringite ( $C_3A \cdot 3\bar{C}\bar{S} \cdot 32H_2O$ ), and sometimes Brucite ( $Mg(OH)_2$ ) may cause self stressing in the micro-structure of the hardened cement paste and a subsequent expansion. Ettringite ( $C_3A \cdot 3\bar{C}\bar{S} \cdot 32H_2O$ ) is formed in the hydration reaction of a variety of inorganic binders [4-8].

The formation of limited amounts of this phase could be useful, whereas excessive amount of which may cause undesirable expansion and cracking of the hardened paste. In some expansive cements, the

controlled-formation of ettringite results in desired expansive stresses leading to a better strength behavior, i.e. self-stressed expansive cements [4-8].

In cases where drying shrinkage due to loss of free or physical water is equal to the expansion during water curing, the hardened cement paste shows no volume changes; such cement is called shrinkage-compensated expansive cement [1, 2]. It has also been recognized that there does not exist a simple proportionality between the amount of ettringite formed and the extent of expansion, and in some cementitious systems even large amounts of this phase may cause only insignificant volume changes [7]. A majority of practical expansive cements have depended on the modification of a Portland cement in such a way as to increase the formation of ettringite [9, 10]. The ettringite formed by the through-solution reactions has no expansive action in cement paste, whereas the topochemical reaction of anhydrous  $C_3A$  with water-soluble gypsum leads to a considerable increase in volume [2, 11]. Observations by scanning electron microscopy however reveal early-age ettringite formation by through-solution reactions [12]. Based on experimental results, four different hypotheses have been proposed for

expansion due to delayed ettringite formation [12]. These hypotheses include;

1. Pressure of crystallization due to anisotropic growth of crystals
2. Crystallization in situ of the anhydrous phases into the hydrated product
3. Absorption of water by colloidal ettringite
4. Expansion due to osmotic pressure phenomena

The control of the process of crystallohydrates formation by creating appropriate conditions for fixing their amount and time of crystallization is the basis for the technology of expansive-cement production.

Blends of calcium aluminate-rich materials, calcium sulfates and water are known to produce ettringite, a hydrate that may form long needle-like crystals. The expansive effect of ettringite formation from the addition of calcium sulfates and materials rich in phases, like CA,  $C_4A_3\bar{S}$  or  $C_3A$ , has been utilized to compensate shrinkage in Portland cements [13].

According to the ACI standards, there are three types of Portland cement-based expansive cements designated by the letters of K, M, and S [1, 14, 15]:

- Type K: Portland cement, anhydrous calcium alumino-sulfate, calcium sulfate, free lime.
- Type M: Portland cement, calcium-aluminate cement, calcium sulfate.
- Type S: High  $C_3A$  Portland cement, calcium sulfate.

As seen, type K and M are not binary systems and include a few more constituents in addition to Portland cement and calcium sulfate. Very few

published results are available for type S expansive cements. In 1966, Gustaferro, Greening, and Klieger [16] deduced from published work on sulfate resistance [17] that Portland cement with high  $C_3A$  content could be modified to expansive cement by raising the  $SO_3$  content sufficiently. Later Klieger and Greening [18] reported the results obtained on cement with  $C_3A$  content up to 17.1%.

The increased expansion observed in cements containing relatively higher amounts of calcium sulfate may be explained by the corresponding increase in the ettringite formation [19-22]. In this research work, results of expansion tests, set, and strength behaviors on binary mixtures of Portland cement-clinker and gypsum or Portland cement with very high contents of  $SO_3$  are described. The point is that these cements cannot be regarded as type S expansive cements, because their  $C_3A$  content are too low. The sulfate contents of the mixtures however are increased to quite very high amounts to accelerate the ettringite formation reactions. Mixtures of very high gypsum proportions, i.e. gypsum based binary mixtures, were also included in the study to see any possible set and strength behaviors.

## 2. EXPERIMENTAL

### 2. 1. Materials

Enough samples of Portland cement clinkers including types 1, 2, and 5 were prepared. The clinker samples were separately ground in a laboratory ball mill to attain a specific surface area of  $285 \text{ m}^2/\text{kg}$ . The chemical and mineralogical phase compositions of these



Fig. 1. X-ray diffraction pattern of natural gypsum

**Table 1.** Chemical composition of Portland cement clinkers

	Type 1 Portland Cement Clinker	Type 2 Portland Cement Clinker	Type 5 Portland Cement Clinker
<b>SiO<sub>2</sub></b>	21.88	22.50	22.50
<b>Al<sub>2</sub>O<sub>3</sub></b>	5.56	5.13	4.08
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.18	4.04	4.53
<b>CaO</b>	64.73	64.23	65.36
<b>MgO</b>	2.30	1.85	1.80
<b>LOI</b>	0.18	0.12	0.17
<b>Free-CaO</b>	0.85	1.25	1.16
<b>LSF</b>	92.05	88.13	91.65
<b>SM</b>	2.34	2.45	2.61
<b>AM</b>	1.48	1.27	0.90

**Table 2.** Potential phase composition of Portland cement clinkers according to Bogue's formulas

	Type 1 Portland Cement Clinker	Type 2 Portland Cement Clinker	Type 5 Portland Cement Clinker
<b>C<sub>3</sub>S</b>	54.37	50.19	61.14
<b>C<sub>2</sub>S</b>	21.78	26.72	18.45
<b>C<sub>3</sub>A</b>	8.30	6.76	3.15
<b>C<sub>4</sub>AF</b>	11.58	12.29	13.78

clinkers are listed in Table 1 and 2, respectively. The calcium sulfate used to prepare the binary mixtures was natural gypsum with 98.8% purity and as seen in fig. 1, mostly in the form of dihydrate. The natural gypsum was also ground in the same laboratory ball mill to attain the same fineness, i.e. nearly 285 m<sup>2</sup>/kg.

## 2. 2. Specimens Preparation

Twelve different mixtures were designed from proportioned combinations of ground Portland cement clinkers and ground gypsum. Table 3 shows the weight-proportions of the mixtures. The prepared mixtures were then completely homogenized using a domestic grinder of the type SANA SCG-3001 and grinding each mixture

separately for 2 minutes. Water-to-dry binder ratio was kept constant at 0.30 for all the mixtures. After adding water and mixing manually for 3 minutes, the pastes were formed into specimens of 20x20x100 mm<sup>3</sup> in size, and the moulds were placed at an ambient of more than 95% relative humidity at 25 °C, for 24 hours. The moulds were then opened and the specimens were immersed in water at 25 °C until the time of testing.

## 2. 3. Test Procedure

At the ages of 25, 40, 55, 70, and 90 days, the linear expansion of the wet specimens were determined using a 0.02 mm accurate digital caliper. For each mixture and at each time, three specimens were used and the average of the three

**Table 3.** Weight proportions of the constituents of the mixtures

Mixture No.	Type 1 Portland Cement Clinker	Type 2 Portland Cement Clinker	Type 5 Portland Cement Clinker	Gypsum
1	95	-	-	5
2	75	-	-	25
3	50	-	-	50
4	25	-	-	75
5	-	95	-	5
6	-	75	-	25
7	-	50	-	50
8	-	25	-	75
9	-	-	95	5
10	-	-	75	25
11	-	-	50	50
12	-	-	75	75

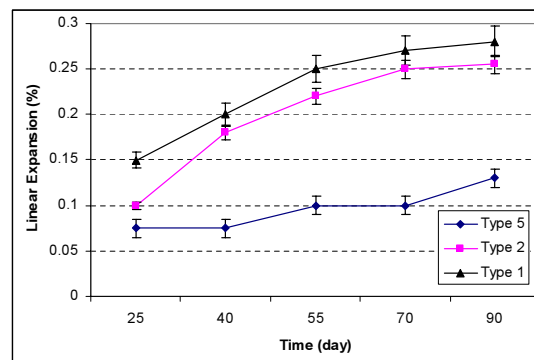
measurements was recorded as the result of linear expansion. The set and strength behaviors of the mixtures were studied by measuring the initial and final setting times in accordance with ASTM standard C 191-82 [23] and the 14, 28, 60, and 90 day compressive strengths. For each mixture, three specimens were used for determining compressive strength. X-ray diffractometry (XRD, Philips Expert System) and scanning electron microscopy (SEM, Philips XL30) along with electron probe microanalysis (EPMA) were the principal laboratory techniques used to study the phase composition and the morphology of the mixtures exhibiting the minimum and the maximum linear expansions. The X-ray diffraction patterns of the powdered samples were recorded on a Philips Expert diffractometer using CuK $\alpha$  radiation. The tests were run in the range of 4–8° at a scanning rate of 2°/min, with a deliverance slit of 1°, an anti-scatter slit of 1° and a receiving slit of 0.01 mm. For SEM studies, a number of specimens were cut into halves to expose internal regions. Halves with suitable fracture surfaces were then selected for SEM studies. The selected halves were coated with gold after being dried at 90 °C for 24 h. SEM

studies were done with secondary electrons at a voltage of 20.0 kV.

### 3. RESULTS AND DISCUSSION

#### 3. 1. Linear Expansion

Figures 2 to 5 show linear expansion of the test specimens. As seen, linear expansion increases with time in all mixtures. In mixtures based on



**Fig. 2.** Linear expansion versus time for mixtures with 5% gypsum replacement



Fig. 3. Linear expansion versus time for mixtures with 25% gypsum replacement



Fig. 4. Linear expansion versus time for mixtures with 50% gypsum replacement

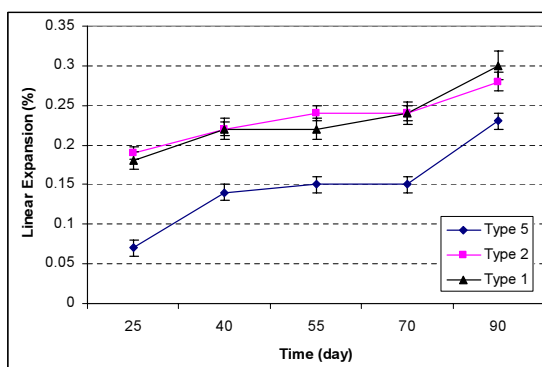


Fig. 5. Linear expansion versus time for mixtures with 75% gypsum replacement

type 5 Portland cement clinker and up to 25% replacement by gypsum, 90 day linear expansion of test specimens increases with gypsum. At higher percentages of replacement however, linear expansion decreases steeply (see fig. 6).

As seen in figure 6, for mixtures based on type 1 and 2 Portland cement clinkers the maximum 90-day linear expansion occurs at 50% replacement by gypsum. In these mixtures also, with increasing the percentage of replacement the 90-day linear expansion increases at first and then decreases showing a maximum. The maximum 90 day linear expansion in these mixtures lies somewhere between 50% and 75% gypsum. Therefore in all the mixtures depending on  $C_3A$ -content of Portland cement clinker, the 90-day linear expansion increases to a maximum value with increasing gypsum percentage and then decreases at higher percentages. The decrease in 90 day linear expansion at relatively high

percentages of gypsum could be attributed to the amount of ettringite formed. It is well known that the amount of expansion strongly depends on the amount of ettringite formed. On the other hand, formation of ettringite depends on the concentration of the reactants including tricalcium aluminate and calcium-sulfate so that decreasing the concentration of one or both of them results in a decrease in the expansion. Therefore, at relatively high percentages of gypsum, the 90 day linear expansion decreases due to decrease in the concentration of tricalcium aluminate with time.

Attempts were made by X-ray diffractometry to determine the phase composition of mixtures exhibiting the minimum and the maximum linear expansions, i.e. mixture based on type 5 Portland cement clinker with 5% gypsum and mixture based on type 1 Portland cement clinker with 50% gypsum, respectively. The corresponding X-ray



Fig. 6. 90-day linear expansion versus gypsum replacement percentage

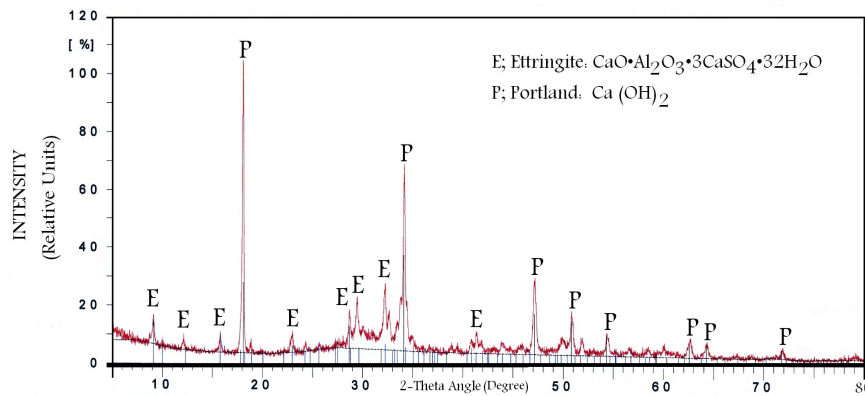


Fig. 7. X-ray diffraction pattern of 90-day hardened paste of mixture exhibiting minimum linear expansion (type 5 Portland cement with 5 percent gypsum replacement)

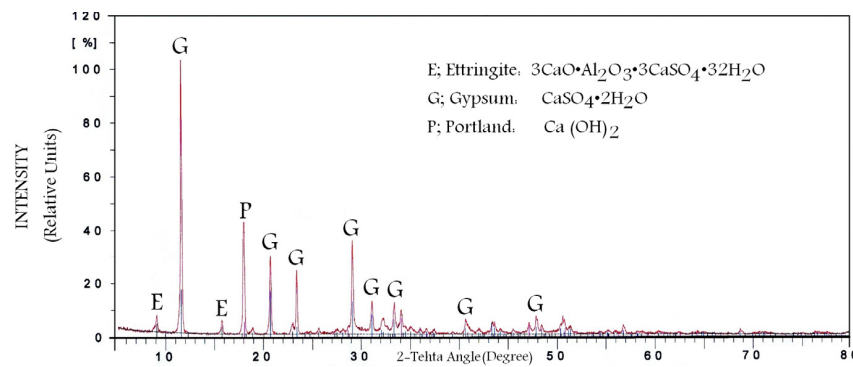


Fig. 8. X-ray diffraction pattern of 90-day hardened paste of mixture exhibiting maximum linear expansion (type 1 Portland cement with 50 percent gypsum replacement)

diffraction patterns are shown in figures 7 and 8. As seen, the only crystalline phases include Portlandite, ettringite, and gypsum with no evidence from the other existing and usually detectable hydration products, even in the mixture exhibiting the minimum linear expansion. It is well known that internal stresses originating from the progression of hydration reactions could effectively change the hydration products from crystalline to amorphous state. Increasing the gypsum content therefore enhances the internal stresses and the expansion caused by ettringite formation which in turn could completely transform hydration products to amorphous state.

### 3. 2. Setting Times and Compressive Strengths

Compressive strengths of the mixtures at four ages of 14, 28, 60, and 90 days are shown in figures

9-16. It is well experienced that at relatively lower percentages of gypsum (about 5%), the early mechanical behavior is improved by both mechanisms of filling effect and pore volume

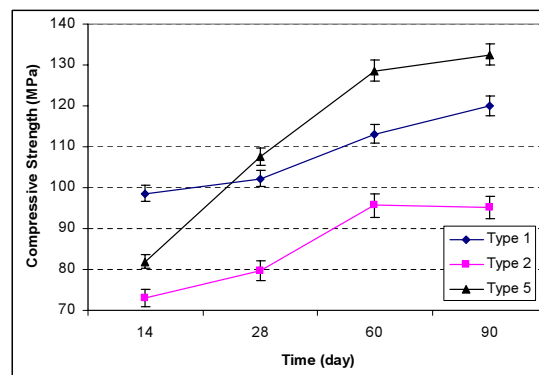


Fig. 9. Compressive strength versus time for mixtures with 5% gypsum replacement

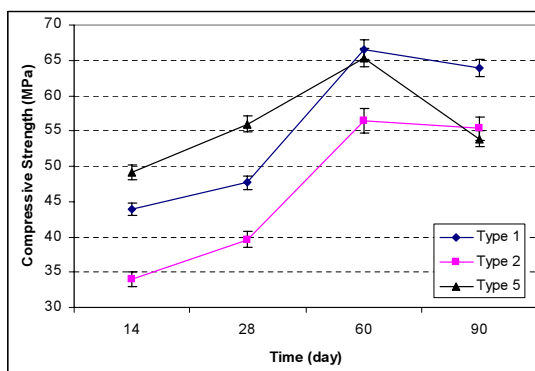


Fig. 10. Compressive strength versus time for mixtures with 25% gypsum replacement

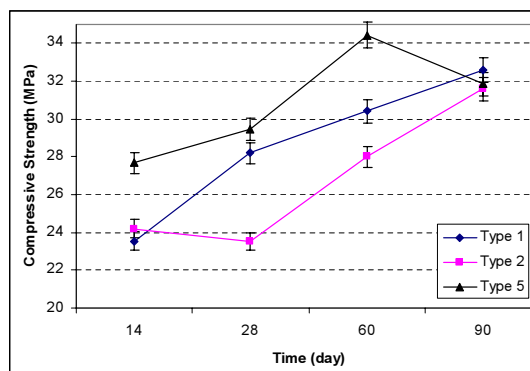


Fig. 11. Compressive strength versus time for mixtures with 50% gypsum replacement

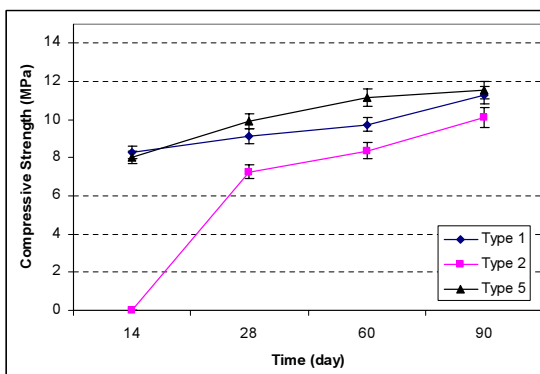


Fig. 12. Compressive strength versus time for mixtures with 75% gypsum replacement

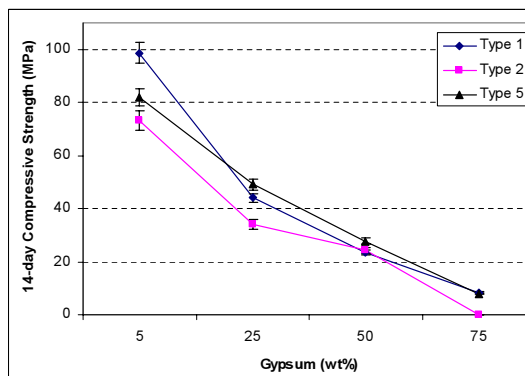


Fig. 13. 14-day compressive strength versus gypsum replacement percentage

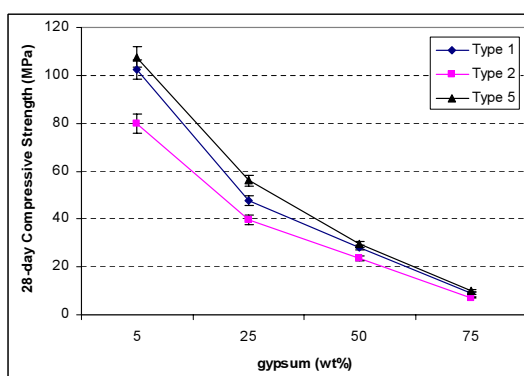


Fig. 14. 28-day compressive strength versus gypsum replacement percentage

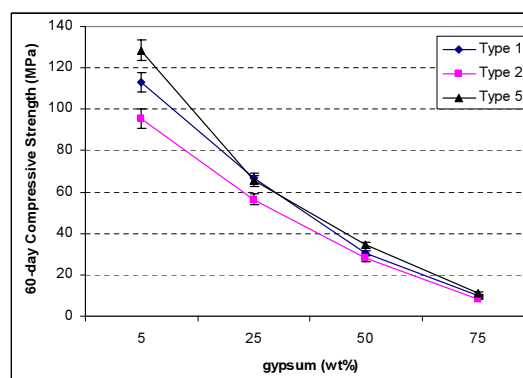


Fig. 15. 60-day compressive strength versus gypsum replacement percentage

reduction due to favorable expansion caused by ettringite formation [5]. At relatively higher percentages of gypsum replacement (i.e. more than 5%), as seen in figures 10 to 16, increasing the

percentage of gypsum weakens the strength behavior in all the systems and at all the four ages.

All mixtures containing 5% gypsum exhibit quite good strength behaviors showing

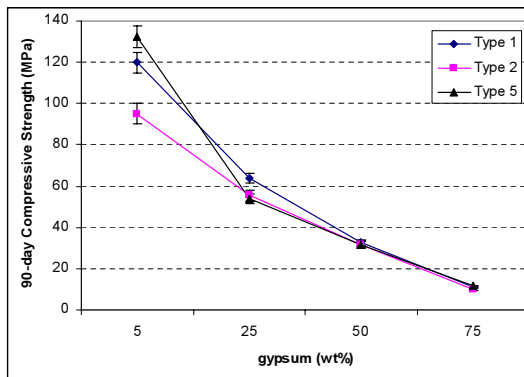


Fig. 16. 90-day compressive strength versus gypsum replacement percentage

continuous strength gain up to the 90th day of curing in water (fig. 9). Results obtained for compressive strength of mixtures containing 5% gypsum confirm the possibility of achieving 28- and 90-day compressive strengths up to values higher than 100 MPa and 130 MPa, respectively. At relatively higher gypsum percentages (about 25% and more), compressive strength increases to a maximum at first and then slowly decreases with time. Such a decrease in compressive strength is due to excessive expansion producing disintegrating stresses in the microstructure of the test specimens. These stresses not only change the crystalline state of the hydration products to amorphous state more effectively, but also could result in the formation of micro-cracks. Gypsum percentages higher than 50% will change the nature of the mixtures from Portland cement-based to a non-binding material-

based, i.e. gypsum-based. The strength behavior of such mixtures therefore reduces significantly.

Figures 17 and 18 show the resulting changes in both initial and final setting times due to increase in gypsum percentage. As seen in all the mixtures, setting time increases with increasing gypsum percentage. In other words at a constant  $C_3A$ -content, any increase in the gypsum content of Portland cements could effectively lengthen the setting times. This is because increasing the percentage of gypsum results in the formation of higher amount of ettringite which provides a hindering effect on hydration reactions. On the other hand, at any percentage of gypsum, mixtures of higher  $C_3A$ -content exhibit shorter setting times. It should be considered that increasing the  $C_3A$ -content of mixtures not only results in the formation of higher amounts of ettringite, but also could result in the formation of some calcium-alumino-hydrates shortening the setting times.

### 3. 3. Scanning Electron Microscopy

Investigations done by scanning electron microscopy clearly confirm that microstructure of the 90-day hardened paste of the mixture exhibiting minimum linear expansion consists of mostly amorphous masses with a very few crystalline structures (fig. 19). These few crystalline structures are Portlandite crystals as revealed by X-ray diffraction pattern (fig. 7) and results obtained by EDAX using ZAF correction. In addition to the crystals of Portlandite, the X-ray diffraction pattern shown in figure 7 proves



Fig. 17. Initial setting time versus percentage of gypsum replacement

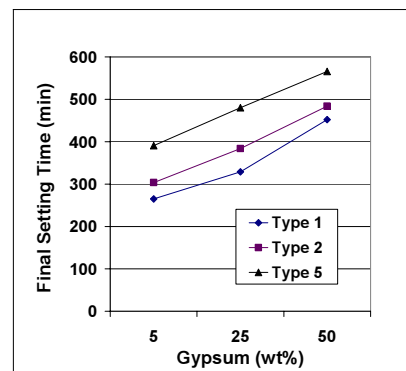
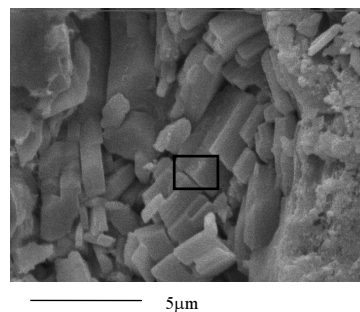


Fig. 18. Final setting time versus percentage of gypsum replacement





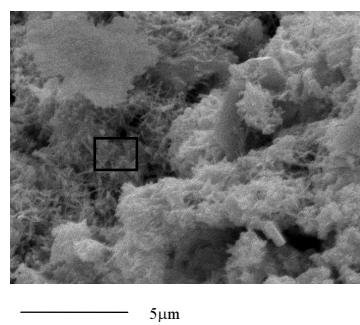
**Fig. 19.** Portlandite crystals in the hardened paste of mixture exhibiting minimum expansion, EDAX analysis (wt %); CaO: 86.12, SO<sub>3</sub>: 2.43, Fe<sub>2</sub>O<sub>3</sub>: 3.67



**Fig. 20.** Gypsum crystals in the hardened paste of mixture exhibiting maximum expansion, EDAX analysis (wt %); CaO: 42.50, SO<sub>3</sub>: 38.15, Al<sub>2</sub>O<sub>3</sub>: 3.21, SiO<sub>2</sub>: 6.14



**Fig. 21.** Probable presence of very fine needle-like ettringite crystals, EDAX analysis (wt %); CaO: 62.78, SO<sub>3</sub>: 8.83, Al<sub>2</sub>O<sub>3</sub>: 3.05, SiO<sub>2</sub>: 18.16



**Fig. 22.** Needle-like ettringite crystals along with a micro-crack, EDAX analysis (wt %); CaO :66.97, SO<sub>3</sub> : 9.15, Al<sub>2</sub>O<sub>3</sub> : 5.26, SiO<sub>2</sub>: 8.48

the presence of ettringite crystals.

In the case of the mixture exhibiting maximum linear expansion, observations done by scanning electron microscope indicated the presence of considerably more crystalline content in the microstructure of its 90-day hardened paste. Figure 20 shows a SEM-image taken from the predominant crystalline phase. The results of analysis done by EDAX show that the predominant crystalline phase is the non-reacted gypsum present in the mixture. The X-ray diffraction pattern shown in figure 8 also confirms the same conclusion.

Two of the mixtures including type 5 Portland cement clinker containing 5% gypsum and exhibiting the maximum 90-day compressive strength (i.e.  $\approx 130$  MPa, fig. 9), and type 5 Portland cement clinker containing 25% gypsum, showing an abrupt decrease in 90-day compressive strength (fig. 10), were selected and attempts were made to detect needle-like ettringite crystals and any probable micro-crack

in their microstructures.

In the case of mixture exhibiting maximum 90-day compressive strength, it was quite difficult to observe ettringite crystals. Figure 21 shows a SEM-image taken from part of its microstructure consisting of probably a few ettringite crystals. The chemical composition of the area obtained by EDAX shows an amount of sulfate probably due to the presence of ettringite crystals.

For mixture showing an abrupt decrease in its 90-day compressive strength, the situation was quite different. Presence of needle-like ettringite crystals and micro-cracks was clearly obvious. Figure 22 presents a SEM-image taken from part of its microstructure showing a relatively large collection of ettringite crystals along with a macro-crack very likely due to disintegrating internal stresses. The chemical composition obtained by EDAX shows a considerable amount of sulfate very probably due to the presence of ettringite crystals.

According to the results obtained, it is suggested that induced expansions may not only balance the

early age contraction, both thermal and drying, but also result in beneficial internal stresses strengthening mechanical properties. The work also suggested that the general conclusions may be applicable to type S expansive cements and these cements could also be produced from Portland cement clinkers of relatively low  $C_3A$ -contents.

#### 4. CONCLUSIONS

In binary mixtures of type 5 Portland cement clinker containing about 3%  $C_3A$  and gypsum, the maximum 90-day linear expansion, i.e. nearly 0.30%, occurs at a gypsum proportion of about 25% by weight. For binary mixtures based on gypsum and type 1 and 2 Portland cement clinkers containing approximately 8 and 6.5%  $C_3A$  respectively, the maximum 90-day linear expansion occurs at a gypsum percentage about 50%. At relatively higher percentage of gypsum, i.e. more than 50%, the 90-day linear expansion decreases due to decrease in the concentration of tricalcium aluminate with time.

Early-age strength behavior of Portland cements could be effectively improved by gypsum, if added at relatively lower percentages of replacement about 5%. Favorable expansion caused by controlled ettringite formation could result in 28- and 90-day compressive strengths up to 100 and 130 MPa respectively.

The work also suggested that the general conclusions may be applicable to type S expansive cements and these cements could also be produced from Portland cement clinkers of relatively low  $C_3A$ -contents.

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