INFLUENCE OF CALIUM SULFATE ON SOME PROPERTIES OF TERNARY ETTRINGITE BINDER

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Abstract: *The research in the field of cementitious materials has brought towards many non-traditional binder systems. One of these systems, a ternary binder composed of calcium aluminate cement (CAC), ordinary Portland cement (OPC), and calcium sulfate (C\$Hx), called ettringite binder, offers a possibility of very rapid development in mechanical strength. In this research, 18 different ternary mixtures were tested with two types of calcium sulfate, i.e. anhydrite and hemihydrate.*

The results show that the type of C\$Hx affects the setting time significantly, and the effect of anhydrite on final setting time of binder is more pronounced when compared to those of binder containing hemihydrate. Generally, compressive strength of the binder containing anhydrite is higher at the ages of 3 and 6 hours but after 1 day it gets lower compressive strength compared to that of the binder containing hemihydrate. The optimal mixture using ettringite binder in this research contains 20% cement CEM I, 50% calcium aluminate cement and 30% calcium sulfate. The binder can obtain compressive strength of 20-30 MPa after 3h, 30-40 MPa after 1 day and 50-60 MPa after 28 days of hydration.

Keywords: *Early compressive strength; setting time; ettringite binder; anhydrite; hemihydrate.*

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1. Introduction

As the most used construction material in the world, the need for new, improved and better binder is an ever-present goal for many of us involved in the R&D field. This has brought engineers all disciplines to develop innovative types of cement, concrete and even placement methods [1]. In parallel, one of the recent cementitious materials exhibiting interesting properties is a ternary binder called ettringite binder which composes of Calcium Aluminate Cement (CAC), Ordinary Portland Cement (OPC), and Calcium Sulfate ($C\$H_x$) [2-4].

The main advantage of the ternary binder of OPC-CAC-$C\$H_x$ is the rapid hydration that leads to extremely rapid development of mechanical strength. The combination of this binder with special additives distinguishes itself from Portland cement by rapid setting and hardening, shrinkage compensation [5,6]. This feature is obtained by the production of large amount of early ettringite during the hydration process [3,7]. Despite this interesting advantage, ettringite can also cause problems; for example, when too much ettringite is produced, uncontrolled expansion occurs which can ruin a poorly proportioned matrix [8-11]. The best way to control the expansion is to limit the sulfate content available for ettringite formation [11]. The sulfate content must be enough to form large amount of ettringite but not too much to cause uncontrolled expansion of the matrix.

The hydration of an ettringite binder containing calcium aluminate cement (CAC) and calcium sulfate ($C\$H_x$) induces ettringite ($C_6A\$_3H_{32}$) and aluminum hydroxide (AH_3) as follows [5]:

$$3CA + 3C\$H_x + (38 - 3x)H \rightarrow C_6A\$_3H_{32} + 2AH_3 \quad (1)$$

$$3CA2 + 3C\$H_x + (47 - 3x)\ H \rightarrow C_6A\$_3H_{32} + 5AH_3 \quad (2)$$

$$C_3S + H \rightarrow C_3S_2H_3 + CH \quad (3)$$

$$CA + 3C\$H_x + 2CH + (34 - 3x)H \rightarrow C_6A\$_3H_{32} \quad (4)$$

$$CA_2 + 6C\$H_x + 5CH + (59 - 6x)H \rightarrow 2C_6A\$_3H_{32} \quad (5)$$

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The previous studies [7,12] investigating binary binder composed of CAC and calcium sulfate (different types: anhydrite and hemihydrate) have shown that the different dissolution properties of calcium sulfates produce different hydrates, which inevitably lead to the difference in compressive strength development. The kinetic of hydration varies significantly depending on the type and the amount of calcium sulfate used and the major constituent, i.e. OPC or CAC. Thus, the objective of this study is to investigate the influence of the different amount and source of calcium sulfate on some properties of a CAC-OPC-CH_x$ ternary binder system. The result will contribute more knowledge to the application of this new binder in construction such as for repair and rehabilitation of buildings, for ground support (mining and tunneling) in order to increase workers' safety and productivity…

2. Materials and methods

2.1 Materials

The ettringite binder in this study consists of a calcium aluminate cement (CAC), a Portland cement (PC) and a calcium sulfate. The calcium sulfate is natural anhydrite (A) or hemihydrate (P). The amount of C_3S, C_2S, C_3A, C_4AF, and gypsum in Portland cement CEM I were 71.5%, 14.05%, 11.6%, 0.5% and 4.3%, respectively; the content of CA and CA2 of CAC were 57.7% and 37.5%, respectively, which was determined by the Rietveld quantitative phase analyses. The chemical composition of these raw materials is shown in Table 1.

Table 1. *Chemical composition of raw materials in binder*

Raw material	Principal oxides, wt%										
	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	TiO_2	K_2O	Na_2O	SO_3	MnO	L.O.I
CAC	69.68	29.78	0.26	0.16	0.15	0.04	-	0.23	0.27	0.01	-
CEM I	5.30	67.28	20.22	0.20	1.02	0.18	0.26	0.20	2.63	0.06	-
Hemihydrate	-	38.70	0.27	0.03	0.1	0.003	-	-	52.40	-	8.4
Anhydrite	-	42.69	-	0.07	0.05	0.002	-	-	56.83	0.006	3.9

2.2 Mixed design

In this paper, the sand/binder ratio of 3.0 and the water/binder ratio of 0.4 were fixed for all the mixtures. The samples were named as A1 to A9 for mixtures containing anhydrite (Table 2) and as H1 to H9 for mixtures containing hemihydrate (Table 3) based on the different types of C$Hx as well as the amount of the CAC, PC in the binder.

The goal of this research is to identify the optimal proportion in terms of high early compressive strength and absence of strength deterioration in later ages. To enable the casting of the samples, and accelerate the hardening of the binder, a polycarboxylate based superplasticizer and a small amount of a retarder and an accelerator were used.

2.3 Experimental methods

The setting time of pastes was determined according to EN 196-3. Mortar samples (40mm×40mm×160 mm) were fabricated for compressive strength of binder. For each mixture, 6 molds were cast for the evaluation of the compressive strength comply with EN 196-1.

Because of the fast setting of most ternary binder, samples were demolded after 2h of hydration and cured under endogenous condition at 20±2°C for compression testing after periods of 3h, 6h, 1d, 3d, 7d, and 28d.

After compression test, the solid fractions of the mortar were crushed and immediately immersed in acetone for two days to stop the hydration of the binder. Thereafter, the samples were placed in a desiccator to remove the acetone. The specimens were then ground with particles size smaller than 100 µm for XRD analysis to determine the major hydration products.

3. Results and discussion

3.1 Setting time of pastes using ettringite binder

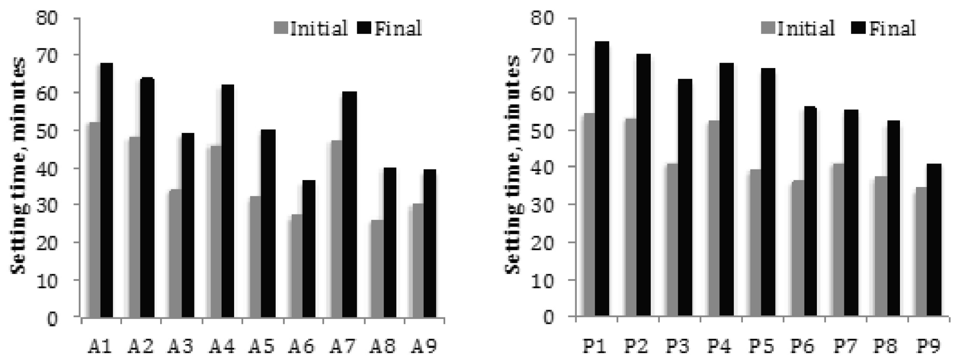
Setting time plays an important role in the construction industry since they directly influence on the workability of mortar and concrete mixtures. Initial and final setting times of the ternary system are shown in the Tables 2, 3 and Fig. 1 as follows:

Table 2. *Results of setting time of ettringite binder containing anhydrite*

Sample	Mixes containing anhydrite			Setting time, minutes	
	CEM I	CAC	C$	Initial	Final
A1	10	80	10	52	68
A2	10	70	20	48	64
A3	10	60	30	34	49
A4	20	70	10	46	62
A5	20	60	20	32	50
A6	20	50	30	27	36
A7	30	60	10	47	60
A8	30	50	20	26	40
A9	30	40	30	30	39

Table 3. *Results of setting time of ettringite binder containing hemihydrate alpha*

Sample	Mixes containing hemihydrate alpha			Setting time, minutes	
	CEM I	CAC	C$H0.5	Initial	Final
P1	10	80	10	54	73
P2	10	70	20	53	70
P3	10	60	30	41	63
P4	20	70	10	52	68
P5	20	60	20	39	66
P6	20	50	30	36	56
P7	30	60	10	41	55
P8	30	50	20	37	52
P9	30	40	30	34	41



a) Mixtures containing anhydrite *b) Mixtures containing hemihydrate*

Figure 1. *Setting time of ettringite binder containing different types of calcium sulfate*

In general, both initial and final setting times are shortened when the amount of cement CEM I and calcium sulfate increases. The setting time of pastes containing anhydrite is faster and the effect of anhydrite on final setting time is more pronounced than those of pastes containing hemihydrate. This can be attributed to the fact that anhydrite is less soluble than hemihydrate at early time, which cannot supply enough alumina to prohibit the rapid setting of C_3A in PC. Otherwise, some researches [13-15] have proved that in the presence of the admixture, which accelerates the nucleation rate of AH_3, the formation rate of AH_3 will control the duration of the induction period. Therefore, the setting time of ettringite binder containing anhydrite is faster due to the higher rate of AH_3 formation.

3.2 Compressive strength development

In this part, 18 different ettringite ternary mortars were made in which only the composition of binder is changed (Tables 2 and Table 3). The results of compressive strength of the binder containing anhydrite calcium sulfate or hemihydrate calcium sulfate are presented in Table 4 or Table 5, respectively. Figs. 2 and 3 show the comparison of the compressive strength of samples containing the different amount of cement and with different types of calcium sulfate.

It can be seen from these results that at a same amount of CAC and CEM I, the development of compressive strength of binders containing anhydrite are much faster than those of binders containing hemihydrate. For example, the compressive strength development of the A1, A2, A3 binders from 6 to 24 hours is nearly twice that of the P1, P2, P3 binders. However, the trend begins to reverse after 24h of hydration where the compressive strength development of mortars containing hemihydrate is higher than that of binders containing anhydrite.

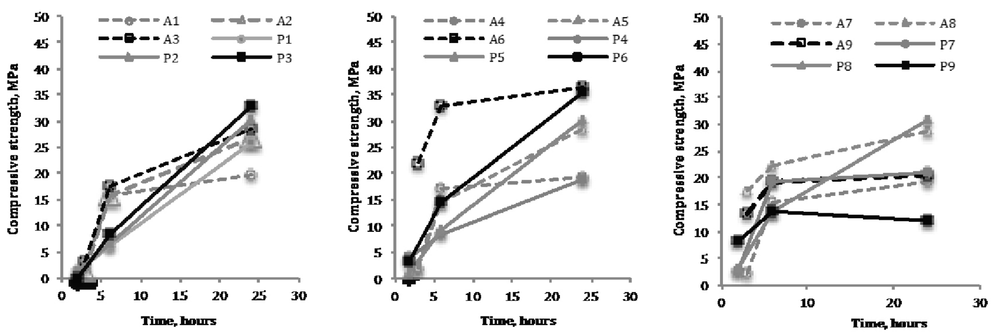
It is noted that the maximum compressive strength of the P9 binder containing 30% can be obtained after 6h of hydration, then decreasing from 13.6 MPa at 6h to 11.9 MPa at 24h. Meanwhile the compression strength of A9 binder containing 30% anhydrite is still increasing continuously. Therefore, the amount of hemihydrate should be used less than 30%.

Table 4. *Results of compressive strength of ettringite binder containing anhydrite*

Sample	Compressive strength of binder containing anhydrite with time, MPa					
	3h	6h	1 day	3 days	7 days	28 days
A1	2.1	15.6	19.6	20.2	21.7	25.8
A2	1.2	15.7	26.8	27.6	27.4	29.3
A3	2.9	17.5	28.3	33.7	38.5	43.6
A4	2.0	17.2	19.4	20.4	22.7	23.9
A5	2.2	14.3	28.4	29.6	30.9	31.3
A6	22.1	32.7	36.6	38	41.2	49.2
A7	2.1	15.3	19.4	22.8	28.9	33.2
A8	17.5	22.1	28.9	31.8	33.2	35.3
A9	13.2	19.5	20.8	12.1	7.3	12.4

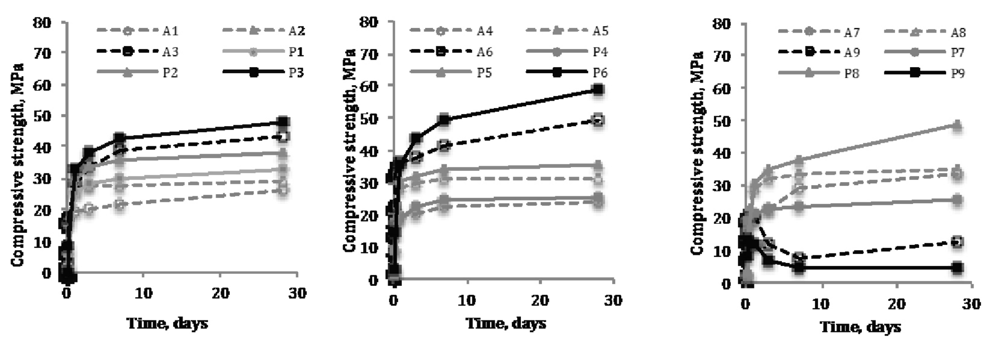
Table 5. *Results of compressive strength of ettringite binder containing hemihydrate*

Sample	Compressive strength of binder containing hemihydrate with time, MPa					
	3h	6h	1 day	3 days	7 days	28 days
P1	1.2	6.1	25.7	28.4	30.1	32.8
P2	1.4	6.5	30.2	33.4	35.8	37.9
P3	0	8.2	32.7	37.9	42.2	48.1
P4	3.8	8.4	18.9	22.1	24.7	25.1
P5	1.1	9.4	30.2	32.1	34.3	35.6
P6	3.2	14.4	35.5	43.6	49.3	58.9
P7	2.7	19.4	21.1	22.5	23.3	25.6
P8	3.0	13.9	30.8	34.8	38.2	48.6
P9	8.1	13.6	11.9	6.7	4.5	4.8



a) Samples using 10% CEM I *b) Samples using 20% CEM I* *c) Samples using 30% CEM I*

Figure 2. *Compressive strength of ettringite binders using different types of calcium sulfate during the first 24h of hydration*



a) Samples using 10% CEM I *b) Samples using 20% CEM I* *c) Samples using 30% CEM I*

Figure 3. *Compressive strength of ettringite binders using different types of calcium sulfate up to 28 days*

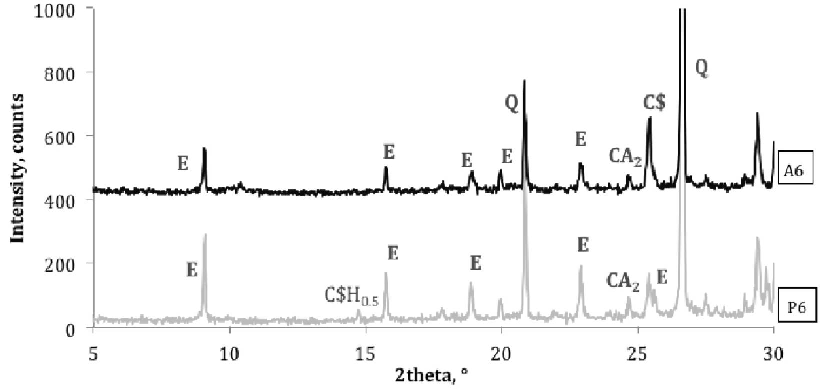


Figure 4. *XRD pattern of the A6 and P6 ettringite binders after 3 hours of hydration*

The results of compressive strength of all ternary binders at later ages are presented in Fig. 3. In contrast to early ages, the compressive strength of binder containing hemihydrate is much higher than that of binder containing anhydrite with the same proportion, i.e. from 5-15 MPa, depending on the amount of CAC and CEM I in binder. After 1 day of hydration, compressive strength of the A9 binder starts decreasing. Therefore, in both cases of A9 and P9 binders, local expansion can be easily occurred due to the ettringite formed too much and caused the cracking stress inside the binder matrix. To minimize this risk, the binder using not more than 30% calcium sulfate should be selected, and the optimal proportion in this research contains 20% CEM I, 50% CAC and 30% calcium sulfate in binder (the A6 and P6 binders).

To understand the hydration product formed in the two optimal ettringite binders, the XRD analysis of 3 hour hardened mortar was carried out and presented in Fig. 4.

As expected, the intensity of the main peak of ettringite at 2θ of 9.07°, 15.7°, 18.8° of binder containing hemihydrate is higher than that of binder containing anhydrite. It means that the amount of ettringite in P6 binder is lager than that in A6 binder. It is also observed that there is still a sharp peak of binder containing anhydrite at 25.5°, but the intensity of the peak at 14.7° of binder containing hemihydrate is very small. The lower solubility of anhydrite (as compared with hemihydrate) reduces the rate of the ettringite formation process, thus, the higher value of the intensity of ettringite XRD pattern at 9.07° is recorded after 3h of hydration for binder containing hemihydrate.

The results also show that the $CaO.Al_2O_3$ (CA) is totally consumed but $CaO.2Al_2O_3$ (CA_2) still exists in the binder. This could be explained by the fact that the solubility and activity of CA_2 is very low especially within the first 48 hours [16].

4. Conclusion

The objective of this paper was to study on the influence of different calcium sulfate types on some properties of ettringite binder. Some conclusions can be drawn from the results of this study:

- The setting time of ettringite binders in this research is very short, about 30-55 minutes for initial setting time and 40-75 minutes for final setting time. The pastes containing anhydrite have a shorter setting time when compared to those containing hemihydrate.

- The compressive strength development of binder containing anhydrite is faster than that of binder containing hemihydrate during the first 24 hours. It can obtain 36 MPa for 24 hours and even up to 50 MPa for 28 days for binder containing anhydrite and 60MPa for binder containing hemihydrate.

- The amount of calcium sulfate used in the ettringite binder should be limited less than 30% due to the uncontrolled expansion in the binder caused, which may lead to cracks.

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