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Long-term strength and porosity of mortars based on ettringite binder

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Abstract. Ettringite binder is widely used in mortars for technical applications such as patching mortars, self-leveling screeds, repair mortars thanks to their fast hardening ability and high early strength. However, depending on the amount and types of raw materials used in the composition, the properties of these types of binder have different behaviors at early-age and at long term. In this work, the influence of the nature and dosage of calcium sulfate in ettringite binder on the long-term strength of mortar in different curing conditions was determined. The results showed that the increase of calcium sulfate content in ettringite binder from 10–25 % improves the strength of mortars regardless of the calcium sulfate nature. In all curing conditions (endogenous, drying, outdoor), the strength of ettringite mortars with anhydrite is smaller than that of mortars containing hemihydrate. There is no major difference in the porosity of the mortars in different types of curing conditions before 28 days. However, after 28 days the porosity of mortar in drying condition is about 2–3 % higher than that of the mortars in endogenous and outdoor conditions.

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1. Introduction

Within the last few decades, ettringite-based binders are used in applications that require a high compressive strength in a very short period of time to minimize construction times and disruption to the traveling public or user [1–5]. The binder system containing Portland cement (OPC), calcium aluminate cement (CAC) and calcium sulphate ($C\$H_x$) is often used when fast setting and hardening and high early strength development are required [5–7].

An ettringite binder is mainly based on the reaction between a calcium aluminate cement (CAC) and a calcium sulfate (C$Hx), which lead to the formation of ettringite ($C_6A\$_3H_{32}$), aluminum hydroxide ($AH_3$):

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

$$3\ CA_2 + 3\ C\$H_x + (47\text{-}3x)\ H \rightarrow C_6A\$_3H_{32} + 5\ AH_3 \quad (2)$$

$$C_{12}A_7 + 12\ C\$H_x + (137\text{-}12x)\ H \rightarrow 4\ C_6A\$_3H_{32} + 3\ AH_3 \quad (3)$$

The rate of the reactions in the mixture in the fresh state is dependent on the ratio CAC/C$Hx, the nature of the calcium sulfate and the presence or absence of admixtures [8, 9]. The setting time of ettringite-based binder is close to that of OPC, typically around 3 hours, but their hardening rate is in the range of 10 MPa to 20 MPa (compressive strength) per hour from setting. This rapidity is compatible with applications that require compressive strength from 10 MPa to 30 MPa after 4h to 6h. Therefore, ettringite-based binders from ternary system (CAC – C$Hx – OPC) can be used in self-leveling mortars for underlayments and overlayments, screeds and repairing mortar, etc. [10, 11].

This combination with special additives makes a fast curing and drying possible, as well as shrinkage compensation of the cured mortar [12]. The mechanism is in many cases caused by ettringite formation, which is provided by blending CAC with calcium sulfates such as anhydrite, hemihydrate, gypsum or mixes thereof [13–15]. The calcium sulfate sources may vary in reactivity and have a large impact on the mechanical properties [16–18]. Although there are several papers on the study of these systems at early ages in the literature [19, 20], there appears to be a complete lack of studies about these systems as they reach older ages [21]. The carbonation of the ettringite binder was also studied, this process depends on weather conditions and occurs more or less quickly depending on several factors, especially the concentration of CO_2 in the weather [22–25].

The aim of this work is to clarify the influence of the nature and dosage of calcium sulfate in ettringite binder on the long-term strength and porosity of ettringite mortar in different curing conditions.

2. Materials and Methods

2.1. Materials

The binder of ettringite mortar consists of the calcium aluminate cement (CAC), Portland cement (CEM I) and 2 types of calcium sulfate: anhydrite (A) or hemihydrate α (P). 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 – 42.5	5.30	67.28	20.22	0.20	1.02	0.18	0.26	0.20	2.63	0.06	–
Hemihydrate *α*	–	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

The skeleton of ettringite mortars is composed of silica sand, slag and limestone fillers, whose average particle size is given in Table 2:

Table 2. Average particle size of the granular skeleton.

Raw material	Average diameter, D50 (µm)
Silica sand	88.19
Slag	11.95
Limestone fillers	13.17

2.2. Formulation of ettringite mortars

The formulation selected for studying ettringite mortars based on CAC and C$$H_x$ is presented in Table 3. In order to grasp the influence of the nature of C$$H_x$ (hemihydrate α or anhydrite) and the CAC/C$$H_x$ ratio (75CAC/25C$$H_x$ or 90CAC/10C$$H_x$), the amount of each raw material was kept constant excepting for the nature of C$$H_x$ and CAC/C$$H_x$ ratio.

Table 3. Formulation of ettringite-based mortars in the research.

Raw materials		Percentage composition of raw materials, %	
		75CAC/25C$$H_x$	90CAC/10C$$H_x$
SKELETON	CAC	24.26	29.11
	C$$H_x$	8.09	3.23
	CEM I – 42.5	3.97	3.97
	Silica sand Carbonate powder Slag	33.41	33.41
ADJUVANTS	Superplastifier Viscosity agent Anti-shrinkage agent	5.46	5.46
Retarder + Accelerator		0.238	0.238
Water		24.57	24.57
Water/Solid (W/S)		0.326	0.326

Total	100	100

2.3. Research methods

2.3.1. Experimental conditions

The hydration process and structure of material, in general, depend on both the constituents and the conditions of casting and curing (temperature, humidity) where the material is hydrated versus time. In this study, the durability versus time of mortar based on ettringite binders in different curing conditions was investigated. The test protocol is as follows: after casting, the specimens are kept in endogenous condition for 24 hours (20 °C, Relative humidity – HR 100 %), then the mortar specimens are demoulded and stored in three different conditions:

- In endogenous condition (ENDO): the specimens were stored in sealed bags and placed in an air-conditioned room at 20 °C, 50 % RH.
- In drying condition (SEC): the specimens were placed in a temperature-controlled room at 20 °C and humidity 50 % RH.
- In outdoor condition (INT): the specimens were placed outdoors, their surfaces exposed to environment. Therefore, climatic conditions involve irregular changes of temperature and relative humidity (diurnal cycles, seasonal cycles, precipitation, and carbonation).

At desired age, the strength and porosity of ettringite mortars would be tested to evaluate the durability versus time of ettringite binders in different curing conditions.

2.3.2. Compressive strength and flexural strength

The freshly mixed mortars were cast into 40 mm×40 mm×160 mm mold for compressive strength and 3 point flexural strength tests. After 24 h, these specimens were unmolded and kept in three curing conditions mentioned above. The strength tests of ettringite mortars were performed at 1, 28, 90 and 330 days.

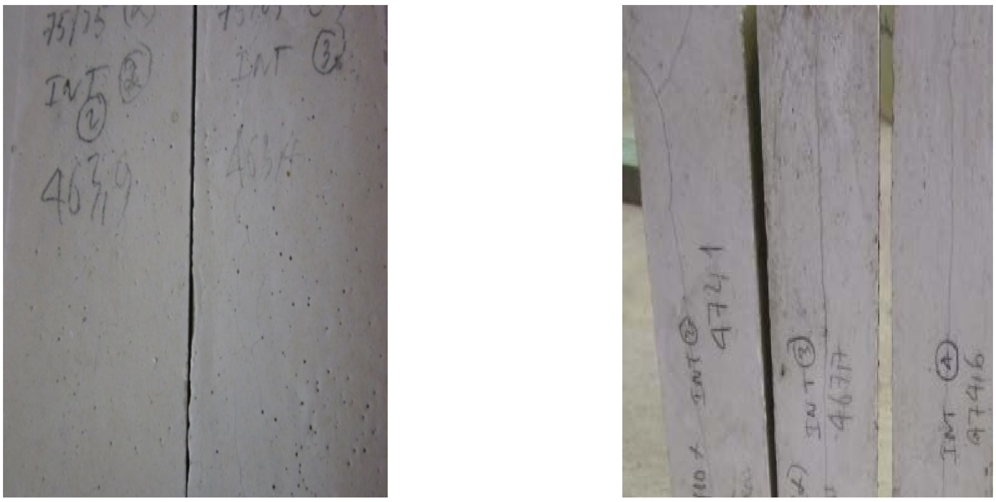
2.3.3. Mercury intrusion porosimetry test

Porosity was measured on fragments in the center of specimens (40×40×160 mm), which were first stopped hydration by grinding the samples of ettringite mortars at the required ages and putting the pieces obtained in an acetone bath for 2 days then filtered in a Buchner and placed in a dryer for 2 days to extract excess acetone and limit carbonation.

3. Results and Discussion

3.1. Observation of ettringite mortars

The main objective of this study is to investigate the influence of the curing conditions on the appearance of mortar using ettringite binder after a long-term weathering. Fig. 1 shows the surface of the mortars under outdoor exposure for 330 days.



a) 75CAC/25P **b) 75CAC/25A**

c) 90CAC/10P

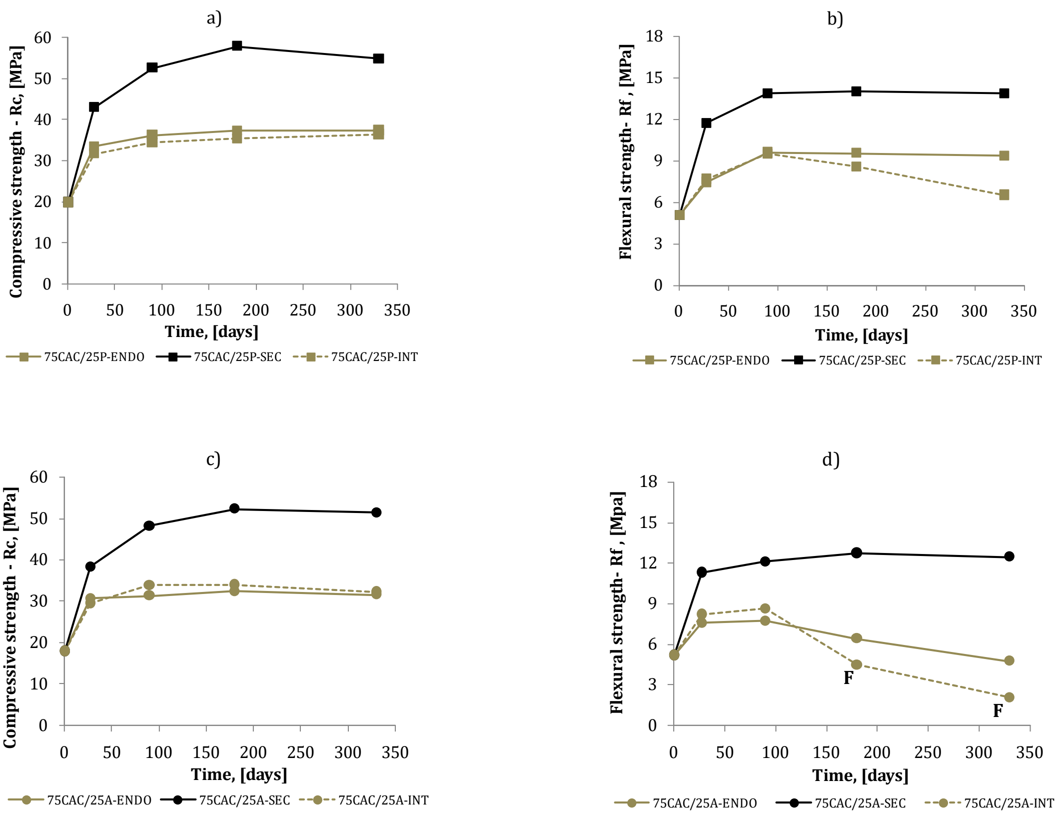
d) 90CAC/10A

Figure 1. Surface of the ettringite mortars after 330 days outdoors exposure.

The results showed that cracks appeared at all the specimens except the composition 75CAC/25P. Meanwhile, the surfaces of mortars in endogenous condition or in drying condition are almost undamaged. It seemed that the cycle 'absorption – evaporation' of water in mortars occurs repeatedly due to outdoor weather conditions and is accompanied by dimensional variations that lead to local stresses causing cracks in the mortar structure.

3.2. Impact of curing conditions on the mechanical strength

Mechanical behavior is a very important property for construction materials. The results of compressive strength and flexural strength of the 4 compositions from 1 day to 330 days are shown in the Fig. 2:



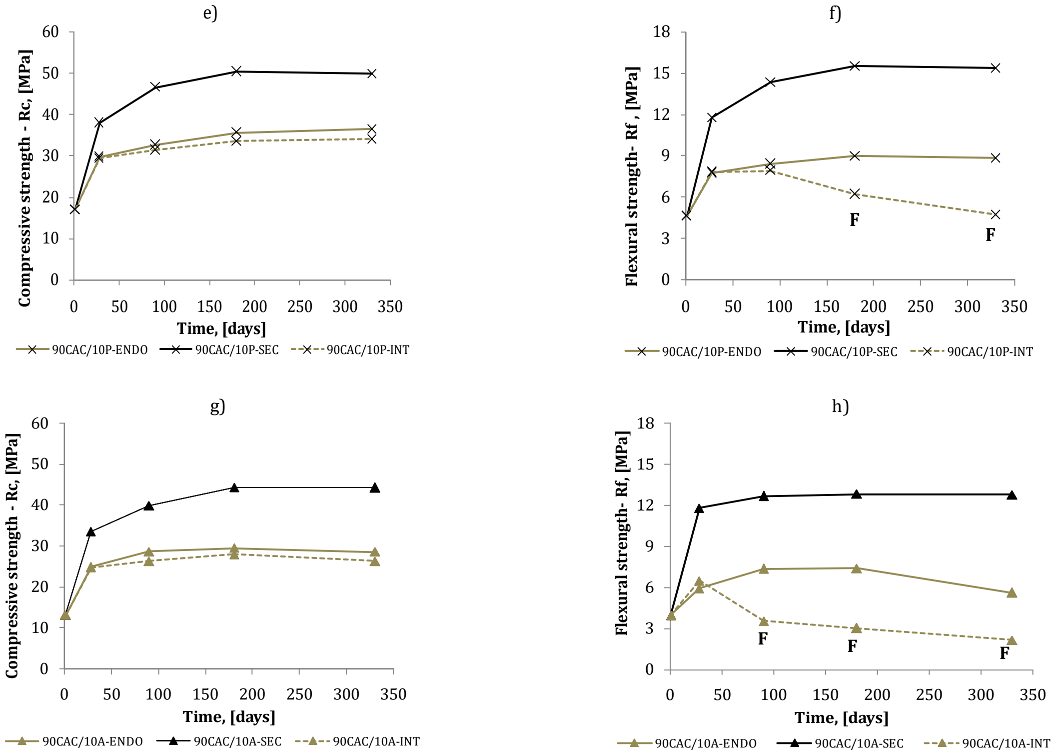


Figure 2. Strength of ettringite mortars in different curing conditions:
a) Compressive strength – 75CAC/25P; b) Flexural strength – 75CAC/25P;
c) Compressive strength 75CAC/25A; d) Flexural strength – 75CAC/25A;
e) Compressive strength – 90CAC/10P; f) Flexural strength – 90CAC/10P;
g) Compressive strength – 90CAC/10A; h) Flexural strength – 90CAC/10A.

The results in the Fig. 2 suggest that whatever the curing conditions, the compressive strength increases continuously versus time. Indeed, the compressive strength increases rapidly during the first 28 days then progress slowly. The strength of the composition 75CAC/25P is always more important than that of the other three compositions. In the contrast, the composition 90CAC/10A has the lowest strength, whereas the strengths of compositions 90CAC/10P and 75CAC/25A have the same values.

In the endogenous condition, except for composition 90CAC/10A, all samples achieved compressive strength above 30 MPa. For the flexural strength, it raises in the similar manner as compressive strength except for the compositions containing anhydrite: From 180 days, the flexural strength of the compositions containing anhydrite begin to decrease, the drop of flexural strengths is difficult to understand because there was no obvious evidence about the decrease in compressive strength.

In drying condition, the strength increases sharply during the first 28 days; then from 28 days until 180 days, it still continues increasing slightly and achieves the values higher than that in endogenous condition. The compositions with hemihydrate have flexural strength of about 15 MPa while compositions using anhydrite only achive about 12 MPa. Meanwhile, the compressive strength of samples 75CAC/25C$H achieve 50–60 MPa, but samples 90CAC/10C$H only have compressive strength of 40–50 MPa.

The strength of the 4 compositions cured outdoors in Fig. 2 also indicated clearly the influence of weathering processes on ettringite mortars in the research. The result shows that the compressive strength of the outdoor-exposed mortars evolves in the similar way as other curing conditions (endogenous or drying condition) in the following order:

$$R_c\ (75CAC/25P) > R_c\ (75CAC/25A) \approx R_c\ (90CAC/10P) > R_c\ (90CAC/10A).$$

This trend of strength development is consistent with research results in the literature [16]. However, there is a drop in long-term flexural strength (the letter F in Fig. 2b, d, f, h is for cases of the micro-cracks visible). These micro-cracks are observed from 90 days for composition 90CAC/10A, 180 days for the compositions 90CAC/10P and 75CAC/25A. With the composition 75CAC/25P, a small decrease in flexural strength was remarked but there was no crack detected on the specimen surface. There may be micro-cracks in its structure.

3.3. Impact of curing conditions on the porosity of ettringite mortars

Porosity is one of the basic factors influencing durability of mortar and concrete. Fig. 3 shows the porosity of the 4 compositions at different curing conditions:

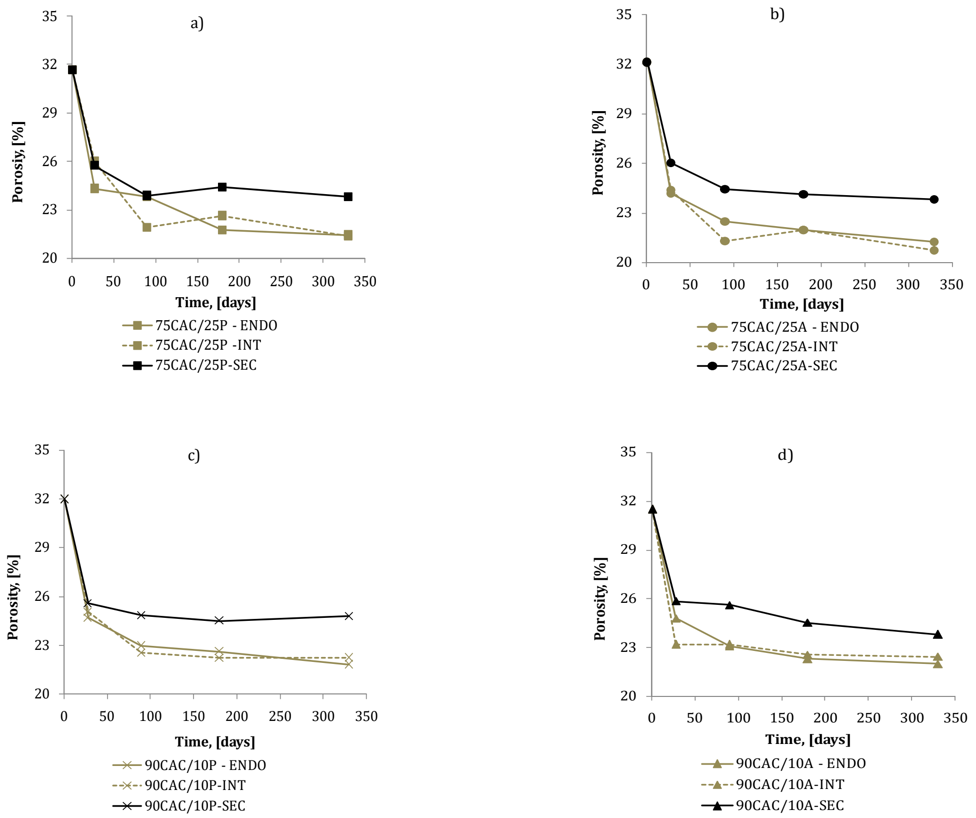


Figure 3. Evolution of the ettringite mortar porosity depending on the curing conditions: a) Composition 75CAC/25P; b) Composition 75CAC/25A; c) Composition 90CAC/10P; d) Composition 90CAC/10A.

The results indicated that there is no major difference on the porosity of the mortars in endogenous condition and outdoor exposure condition. This is explained by the fact that the water is always supplied for hydration when it rains for outdoor weathering specimens. Meanwhile, for the samples in drying condition (air-conditioned room at 20 °C, HR 50 %) the specimens are not rehydrated. Before 28 days, only the water at the surface of mortar specimens evaporates, so the difference in porosity between the different types of curing condition is not significant. However, after 28 days the porosity of mortar in drying condition is higher than that of the mortars in endogenous and outdoor condition about 2–3 % due to the evaporation of water in specimens, which becomes important. Besides, the main hydrates containing many water molecules (ettringite or carboaluminate) can lose a few water molecules in its formula because of a long-term drying period [26].

4. Conclusions

The study on long-term mechanical property and porosity of ettringite mortars leads to some key conclusions:

1. After 330 days, the surface of mortars in endogenous condition or in drying condition is still in good condition. In the contrast, the mortars stored outdoor have been discovered some micro-cracks on the surface. This phenomenon is more remarked on the compositions containing anhydrite.

2. Whatever the curing conditions, the compressive strength increases rapidly during the first 28 days but slightly at long-term age. The strength of the compositions containing hemihydrate is better than the strength of the compositions containing anhydrite.

3. The compressive strength of the specimens stored outdoors is the less important but still close to that in endogenous condition and the decrease in flexural strength maybe due to micro-cracks in the structure. The strength of mortar in drying condition is higher than that in endogenous condition or in outdoor condition although the porosity of mortar in drying condition is higher.

4. The difference of porosity at early age between the different types of curing condition is not significant. However, at later age after 28 days, the porosity of mortar in drying condition is higher than that of the mortars in endogenous and outdoor condition about 2–3 %.

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