Contribution of calcium aluminates to the water resistance of hydrated calcium sulfates

Tien Dung Nguyen¹ and Jean Ambroise²

¹National University of Civil Engineering, Vietnam
²Institut National des Sciences Appliquées de Lyon (INSA Lyon), France

E-mail: dungnt1@nuce.edu.vn

Abstract. The water sensitivity of calcium sulphate materials has been known for a long time. In a humid atmosphere, plaster elements can become veiled under the action of their own weight because a low water uptake of 3% by mass can cause a drop in compressive strength of 50%. The low water resistance of calcium sulfates limits the applications of these materials to decorative elements or interior coatings despite their strengths compared to other construction materials: good fire resistance, low CO₂ emission and low production cost. The objective of our research work is to evaluate the insensitivity of calcium sulfates to water by ettringitic binders containing calcium aluminates cement (CAC). Four types of calcium sulfates have been studied: natural gypsum, hemihydrate-α, hemihydrate-β, and synthetic anhydrite. In this research, only the majority binders of calcium sulfates will be studied: [70%, 80% of Calcium sulfates with 30%, 20% of CAC]. The experiments results have shown that in high-calcium sulphate binders (≥ 70%), CAC helps reduce the water sensitivity of binders regardless of the nature of calcium sulphate by decreasing the total porosity, which leads to an increase in mechanical strengths; and reducing the connectivity of the pores, which contributes to reducing the entry of water and its movements into the material and consequently, reducing the degradation of the test pieces during immersion tests in the water.

1. Introduction

Calcium sulfates (gypsum, hemihydrates and anhydrite) are economical materials that are found in abundance in nature and in industrial by-products. The different characteristics of these forms of calcium sulphate are presented in Table 1. They also have interesting properties for the construction industry: good acoustic and thermal insulation; low CO₂ emission and low production cost [1].

However, their use is quite limited because of a high solubility, which leads in wet conditions to dissolution and therefore the degradation of this type of material [2]. In a humid atmosphere, plaster elements can become veiled under the action of their own weight because a low water uptake of 3% by mass can cause a drop in compressive strength of 50% [3]. According to Badens’s research, from 80% relative humidity, the Young modulus of hydrated calcium sulfate sample decreased significantly [4].

The degradation of calcium sulfates is due to their high solubility. However, the mechanical degradation of gypsum, the hydration product of the hemihydrate, is not due solely to the dissolution of the gypsum in water. It is explained by an increase in the thickness of the layers of water between the gypsum crystals which leads to a decrease in the intrinsic surface cohesion and consequently promotes sliding between the crystals and lower the mechanical resistance of the calcium sulfate base mixtures [5] [6].
### Table 1. Phases du système CaO – SO₃ – H₂O [1]

| Hydration level | Designation                        | Symbol | Crystal form | Thermodynamic stability |
|-----------------|------------------------------------|--------|--------------|-------------------------|
| Anhydrite (CaSO₄) | Anhydrite obtained at high temperature | A-I    | Cubique      | > 1180°C                |
|                 | Anhydrite insoluble                | A-II   | Rhombique    | < 1180°C                |
|                 | α-Anhydrite soluble                | A-III α| Hexagonal    | Metastable              |
|                 | β-Anhydrite soluble                | A-III β|             |                         |
| Hemihydrate (CaSO₄.1/2H₂O) | α-Hemihydrate                | α – HH | Orthorhombic | Metastable              |
|                 | β-Hemihydrate                  | β – HH |             |                         |
| Di-hydrate (CaSO₄.2H₂O) | Di-hydrate (gypsum)            | DH     | Monoclinic   | < 45°C                  |

Since the 1990s, several studies have been carried out to reduce the sensitivity of calcium sulfates to water. This research was oriented along two lines of investigation. The first is to make calcium sulfates insoluble by adding an “insoluble” protective layer around the grains of calcium sulfate. The second approach consists in reducing the proportion of calcium sulphate in the material by reacting the calcium sulphates with additives such as slag, fly ash and metakaolin, or cements of the OPC type (Portland cement) or CȘA (sulfoaluminous cement).

The evaluation of the water sensitivity of calcium sulfates is based on a main indicator: the mechanical resistance after immersion in water. The addition of Portland cement alone leads to a significant expansion linked to the formation of ettringite with consequent deterioration of the gypsum–cement mixture [7]. Research into the water repellency of calcium sulfates with additives reveals that with 10% slag, the water resistance of gypsum-based mixtures improves. On the other hand, the mechanical performance at a young age is poor because of the slow reaction of slag with calcium sulfates [8]. The association [cement - addition] seems interesting for insensitizing calcium sulfates to water. The maximum dosage of calcium sulfate which maintains performance after testing to assess sensitivity to water, is 75% ([9] [10]).

The ability to desensitize calcium sulfates to water with ettringitic binders was studied in the thesis of Kuryatnyk T. (2007) with interesting results. The hydration of the calcium sulphate / sulfoaluminous clinker (CȘA) mixtures which leads to the formation of ettringite and aluminum hydroxide makes it possible to reduce the water sensitivity of calcium sulphates: no drop in resistance after immersion in water which has not been renewed in the thesis of Kuryatnyk T. A decrease in the water solubility of calcium sulfates 11.1 g/l for the 100% β plaster mixture, 2.4 g/l, 1.8 g/l and 1.2 g/l for the mixture with 30%, 50% and 70% CȘA was also observed [11].

Different from Kuryatnyk’s thesis, only the majority of calcium sulfate binders will be studied: 70% and 80% and instead of sulfoaluminous cement, CAC will be used in this research.

### 2. Materials properties and experimental techniques

**2.1. Materials properties**

The physical parameters of calcium sulfates and CAC with the presence of the specific surfaces and the mean diameter D₅₀ are presented in Table 2.

### Table 2. Physical properties of materials

| Specifications | CAC | Gypsum | Hemi α | Hemi β | Anhydrite |
|----------------|-----|--------|--------|--------|-----------|
| Specific density (g/cm³) | 3.19 | 2.30  | 2.75   | 2.60   | 2.86      |
Specific surface Blaine \((\text{cm}^2/\text{g})\) 3180 5474 3120 7180 3240
BET \((\text{m}^2/\text{g})\) 0.83 2.1 0.98 3.03 0.99
Average diameter \((\mu\text{m})\) 44 16 33 19 39

Chemical analysis results of CAC and four type of calcium sulfates are shown in the Table 3.

### Table 3. Chemical analysis of materials

|       | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | FeO\textsubscript{3} | CaO | MgO | K\textsubscript{2}O | Na\textsubscript{2}O | SO\textsubscript{3} | TiO\textsubscript{2} | MnO | P\textsubscript{2}O\textsubscript{5} |
|-------|---------------------|---------------------------------|---------------------|-----|-----|-----------------|------------------|-----------------|-----------------|-----|-----------------|
| Gypsum | 0.55                | 0.11                           | 0.05                | 33.1| 0.47 | <1.d            | <1.d             | 43.6            | 0.008          | 0.002| <1.d            |
| Hemi α | 0.27                | <1.d                           | 0.03                | 38.7| 0.1  | <1.d            | <1.d             | 52.4            | 0.003          | <1.d | <1.d            |
| Hemi β | 0.22                | <1.d                           | <1.d                | 38.7| 0.11 | <1.d            | <1.d             | 52.0            | 0.004          | <1.d | <1.d            |
| Anhydrite | <1.d                 | 0.05                           | 0.06                | 41.6| 0.07 | 0.01            | 0.03             | 57.8            | 0.013          | 0.0023| <1.d            |
| CAC    | 4.15                | 15.96                          | 37.19               | 0.60| 0.1  | 0.06            | 0.10             | 1.88            | 0.35           | 0.27 |                 |

2.2. Specimens preparation

The composition of the mortars is shown in Table 4. The water/binder \((\text{W/B})\) ration for gypsum, anhydrite and hemihydrate \(\alpha\) mixtures is 0.5. For mixtures with hemihydrate \(\beta\), it is equal to 0.8. The \(\text{W/B}\) are chosen to ensure the same consistency of mixtures [calcium sulphate / CAC]. The binder portion consists of calcium sulphate and CAC, the proportions of which are shown in Table 5.

### Table 4. Composition of mortars \((\text{in g})\)

| Nature of calcium sulfate | Sand | Binder | Water | Water/Binder |
|---------------------------|------|--------|-------|--------------|
| Gypsum, Anhydrite, Hemihydrate \(\alpha\)| 1350 | 450    | 225   | 0.5          |
| Hemihydrate \(\beta\)     | 1350 | 450    | 360   | 0.8          |

### Table 5. Compositions of binders \([\text{calcium sulfate / CAC}]\) \((\text{en g})\)

| Components | Ratio calcium sulfate / CAC |
|------------|-----------------------------|
| Calcium Sulfate | 80/20                      |
| CAC         | 70/30                       |

All binders, except anhydrite binders, are delayed with a retarder: PE retarder which is a degraded protein used as a plaster retarder. Its dosage is set at 0.044% of the total weight of binder, or 0.2g.

2.3. Experimental techniques

The experimental techniques used in this work are of two types: macroscopic characterization methods and methods of microstructure analysis.

The macroscopic characterization methods will allow us to assess the sensitivity to water of mixtures [calcium sulfates / CAC]. The tests will be carried out on mortar. The evaluation indicators will be as follows:

- Measurement of mechanical resistance at 28 days;
- Mercury porosity measurement;
- Surface dissolution by immersion in water;

After casting, the test samples \((4\times4\times16\text{cm})\) are kept in a waterproof bag for up to 28 days. They are then immersed in demineralized water (Fig. 1).
The test specimens being immersed in water for 28 days are weighed daily to determine their water absorption capacity. This capacity is represented by the coefficient $\alpha$:

$$\alpha = \frac{\Delta P_i}{P_0} \times 100\% = \frac{P_i - P_0}{P_0} \times 100\%$$  

(1)

In which, $P_i$: Mass of test sample at i days under water
$P_0$: Mass of test sample before immersion

If the test pieces do not degrade, the coefficient $\alpha$ increases and if the test pieces are saturated, the $\alpha$ is constant. The decrease in the absorption coefficient over time means that the test pieces physically degrade.

- Degradation of mechanical performance after accelerated aging:

Three series of test samples made of binders based on calcium sulphates are poured and demolded 24 hours after the start of mixing and stored in sealed bags. These samples came out of the waterproof bags at 28 days.
- The 1st serie is dried for 24 hours at 20°C and 50% relative humidity. After drying, the 3 samples are tested for bending and compression strength.
- The 2nd serie is kept in water. The bending and compression tests are carried out after 28 days of storage of the samples in water followed by 24 hours of drying at 20°C and 50% relative humidity.
- The 3rd serie is subjected to 28 immersion-drying cycles. Each cycle consists of 8 hours of drying in the oven at 35°C and 16 hours of immersion in water at 20°C. After these 28 cycles, the samples are dried for 24 hours at 20°C and 50% relative humidity and then passed to bending and compression tests.

3. Results and discussion

3.1. Mechanical strengths
The mechanical strengths of the calcium sulphate / CAC mixtures are shown in Figure 5.

Increased compressive strengths as a function of the CAC dosage are recorded for all calcium sulphate mixtures. Increased compressive strengths of mixtures [gypsum, hemi-hydrate $\alpha$ and anhydrite / CAC] are identical. The increase in compressive strength as a function of increasing CAC dosage is about 1. For hemi-hydrate $\beta$ mixtures, this increase is 0.43. The lower increase is due to the higher W/B rate: 0.8 instead of 0.5 for mixtures with other calcium sulfates.

The influence of the W/B was measured by lowering the water content to 0.5 using a polycarbocylate superplasticizer. In Figure 2, we observe that the mechanical strengths based on the hemihydrate $\beta$ mixtures increase considerably. Compared with the mixtures based on hemihydrate $\alpha$, the resistances are slightly lower, but the increase based on the CAC dosage is identical.
3.2. Mercury porosity measurement

Porosity is an important parameter that determines the strength, durability of calcium sulphate mixtures [12]. Figure 3 shows the evolution of the total porosity as a function of the CAC dosage in the various calcium sulphate mixtures. The porosity decreases with increasing amount of CAC in the mixture regardless of the nature of calcium sulphate.

With α and β hemihydrates, when 20% CAC was added, there was no significant decrease in total porosity. At the same water content W/B = 0.5, two porosity families are observed: mixtures [natural gypsum or synthetic anhydrite / CAC] and [hemihydrate α or β / CAC]. These results are consistent with the evolution of compressive strength as a function of the CAC dosage.

For all mixtures [calcium sulfate / CAC], there is a correlation between the total porosity and the compressive strength (Figure 4). The decrease in porosity, linked to the increase in the dosage of CAC, leads to an increase in mechanical resistance.

At the same mixing rate, W/B = 0.5, there is a linear relationship between the compressive strength and the total porosity of the mixtures [calcium sulphate / CAC] with a coefficient of determination R² = 0.98.
3.3. Physical degradation – Dissolution of sulfates

The results of the evolution of the weight of the test samples of the mixtures [calcium sulphate / CAC] are presented in Figure 5.

If we analyze the evolution curves of the weights of the test specimens in 100% hemihydrates $\alpha$ and $\beta$, Figure 5 - (c) and (d), the degradation is identical. Weight stability is recorded until the 14th day of immersion and then an acceleration of the degradation between 14 and 28 days with a degradation rate of the same order of magnitude: 4.3% for the hemihydrate $\alpha$ and 4.9% for the $\beta$ hemihydrate.

With mixtures containing 20% CAC, the degradation rates are between 0.8% and 1.6%. The highest rate is measured with natural gypsum. Increasing the CAC dosage from 20% to 30% does not change the degradation kinetics, except for synthetic anhydrite (Figure 5 - b). Recall that with anhydrite, at a dosage of 30% CAC, the highest microporosity is recorded.

In all cases, contrary to what is observed with the $\alpha$ and $\beta$ hemihydrates, there is no acceleration of the degradation during 28 days of immersion.

![Figure 5. Degradation by dissolution of test samples of mixtures [calcium sulfate/CAC]](image)
3.4. Degradation of mechanical performance after accelerated aging

The accelerated aging test protocol was presented in 2.3. In summary, two types of aging were applied: 28 days of immersion in water (at 20°C) and 28 immersion cycles (in water at 20°C) - drying (in the oven at 35°C).

The results of the compressive strength of the mixtures [calcium sulphates / CAC] after 28 days, 28 days of immersion and 28 immersion-drying cycles are presented in Figure 6.

Overall, there is no collapse of the resistances on all the mixtures whatever the nature of the calcium sulphate and the calcium sulphate / CAC ratio.

Aside from the mixture [α hemihydrate / CAC] under immersion conditions, the evolution curves of compressive strengths according to the CAC dosage of mortars having undergone immersion-drying cycles or having been submerged are superimposed or parallel to the curves of evolution of the compressive strengths according to the CAC dosage obtained at 28 days.

With all the mixtures [calcium sulphates / CAC], there is a drop in compressive strength of around 2 Mpa. The increase in the dosage of CAC, from 20% to 30%, leads to an increase in resistance. However, it has no influence on the resistance drop after the accelerated aging tests.

Figure 6. Compressive strength after accelerated aging test of mixtures [calcium sulfate/CAC]
4. Conclusions

To conclude, the addition of 20% and 30% of calcium aluminate cement (CAC) improves the water resistance of the binders whatever the nature of the calcium sulphate. The greater the dosage of CAC in calcium sulphate based mixtures, the greater the mechanical resistance at 28 days. The gain in resistance is less marked with the β hemihydrate because of the high mixing rate. The increase in the dosage CAC, from 20% to 30%, leads to a reduction in the total porosity on all the mixtures whatever the nature of calcium sulphate. In terms of resistance degradation, a drop in resistance of 2 Mpa is recorded after 28 days of immersion and 28 immersion-drying cycles on all mixtures and regardless of the dosage of CAC cement (20% and 30%). Concerning the durability of calcium sulphate / CAC mixtures, no drop in resistance is recorded on the test pieces kept in the laboratory at 20 ° C, 50% relative humidity which was not the case for the sulphate mixtures of calcium / sulfoaluminous cement studied in the thesis of Kuryatnyk T. (2007).

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