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# Hydration of ordinary Portland cement and calcium sulfoaluminate cement blends

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ABSTRACT

Ordinary Portland cement (OPC) and calcium sulfoaluminate (CSA) cement are two chemically different hydraulic binders. OPC and CSA cement blends can be used to adjust the binder properties for specific applications. The first part of this article compares the compressive strength and hydration products of three blends (85–15, 70–30 and 40–60% of OPC–CSA cement) using two different OPC. CSA cement percentage modifies the hardening speed as well as the hydration mechanisms (hydrates nature and quantity). The composition of OPC has also a significant influence even for the lowest OPC proportion (40% of OPC). In the second part, investigations based on compressive strength and calorimetry analysis indicate that OPC free lime is a key parameter.



## 1. Introduction

OPC is the hydraulic binder, obtained from limestone and clay, traditionally used for building and civil engineering construction. Though widespread, OPC production emits around 5% of the worldwide carbon dioxide ($CO_2$) man made emissions [1].

Firstly developed in the sixties, various CSA cements (calcium sulfoaluminate – belitic sulfoaluminate – ferrosulfoaluminate) have been produced mainly in China [2]. Depending on their application, these CSA cements contain the compound named ye'elimite or Klein's salt ($C_4A_3\overline{S}$) and also variable proportions of belite ($C_2S$), calcium aluminate (CA), mayenite ($C_{12}A_7$) or brownmillerite ($C_4AF$). CSA cements have many advantages and are for example used for their shorter setting time, their high hardening speed, their glass fiber compatibility or, by addition; their ability to improve Portland cements dimensional stability [3–5].

In this article, the major compound of the CSA clinker used is ye'elimite and belite is the secondary component. This clinker is obtained by burning limestone, a source of aluminum (bauxite, recycled materials) and calcium sulfate resulting in a clinker which is further blended with a suitable amount of calcium sulfate. During its production, this kind of CSA clinker releases less $CO_2$ than OPC clinker for essentially two reasons: the clinkerization temperature is around 1250 °C (1450 °C for OPC clinker) and the limestone percentage is lower. However the cost of this special clinker is higher than OPC mainly due to the higher aluminum proportion (a more expensive material).

Blends of OPC and CSA cements can potentially be used to combine their advantages and to control specific properties such as expansion or setting time. For example, theses blends have been used in United State (type K cements (ASTM C 845 – 04)) since the sixties in order to produce shrinkage compensated or expansive cements as well as in Japan [6–9]. In these cements, OPC is blended with a mixture containing mainly CSA cement, calcium sulfate (as anhydrite: $C\overline{S}$) and calcium hydroxide (CH). Expansion mechanisms are complex phenomenon linked to ettringite ($C_6A\overline{S}_3H_{32}$) formation discussed in many articles [10–17].

Ye'elimite ($C_4A_3\overline{S}$) hydration products depend on sulfate and lime quantities. In the presence of calcium hydroxide and sulfate, ye'elimite leads to ettringite ($C_6A\overline{S}_3H_{32}$) formation (reaction 1). Without calcium hydroxide, ye'elimite hydration forms ettringite and gibbsite ($AH_3$) (reaction 2), or monosulfoaluminate ($C_4A\overline{S}H_{12}$) and gibbsite in the absence of sulfate (reaction 3). In absence of sulfate but with calcium hydroxide, gibbsite and/or hydrogarnet ($C_3AH_6$) and a solid solution ($C_3A$. ½$C\overline{S}$. ½CA. Hx) have also been reported [18].

$$C_4A_3\overline{S} + 8\ C\overline{S} + 6CH + 90\ H \rightarrow 3\ C_6A\overline{S}_3H_{32} \quad (1)$$

$$C_4A_3\overline{S} + 2\ C\overline{S} + 38\ H \rightarrow C_6A\overline{S}_3H_{32} + 2\ AH_3 \quad (2)$$

$$C_4A_3\overline{S} + 18\ H \rightarrow C_4A\overline{S}H_{12} + 2\ AH_3 \quad (3)$$

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Reactions 1 and 2 show that lime can modify the nature and quantities of hydrates. Lime also changes the ye'elimite hydration rate [19]. In blends of OPC and CSA cement, calcium hydroxide can be (i) directly added to the binder, (ii) brought by OPC (free lime) or (iii) produced during OPC hydration (portlandite). Hence OPC composition can be important because it can change the free lime percentage as well as the portlandite quantity over hydration.

In blends of OPC and CSA cement containing a high proportion of CSA cement (50% and more), OPC hydration mainly occurs after several hydration days [20,21]. Alite ($C_3S$) hydration (OPC main component) produces strätlingite ($C_2ASH_8$) and portlandite (reaction 4). Alite can also generate the formation of C–S–H gel and portlandite as in OPC alone or blended with a low CSA cement proportion. OPC also contains $C_3A$ and its hydration leads to ettringite formation (reaction 5).

$$C_3S + AH_3 + 6H \rightarrow C_2ASH_8 + CH \quad (4)$$

$$C_3A + 3\ C\overline{S} + 32H \rightarrow C_6A\overline{S}_3H_{32} \quad (5)$$

If the quantity of calcium sulfate is insufficient, $C_3A$ can also form monosulfoaluminate. In the absence of calcium sulfate, $C_3A$ forms unstable calcium aluminate hydrates (as $C_4AH_{13}$) and then stable hydrogarnet hydrate ($C_3AH_6$). The change of OPC origin modifies the percentages of $C_3S$ and $C_3A$ and therefore the hydrates and quantities formed.

The five reactions previously described are not exhaustive. Indeed OPC and CSA cement secondary components such as belite ($C_2S$), brownmillerite ($C_4AF$) or mayenite ($C_{12}A_7$) can have also an impact. However, these reactions show that OPC composition can have an important impact on OPC and CSA cement blends. In the first part of this article, OPC composition impact is studied on three OPC–CSA cement blends (85–15, 70–30 and 40–60% of OPC–CSA cement) with two different OPCs (one grey and the other white). In the second part, complementary compressive strength and isothermal heat conduction calorimetric tests on other OPCs indicate the fundamental role of free lime.

After describing the materials and methods used, the results are detailed. The discussion gives an interpretation of the data and proposes an explanation of the results.

## 2. Materials

In this study, CSA cement is a mixture of a milled CSA clinker and a milled natural anhydrite. The CSA clinker used is a commercial binder (ALIPRE) produced by Italcementi Group with recycles materials (as aluminum sources) at a clinkering temperature below 1300 °C.

In the first part of the article, two OPCs (European standard: CEM I 52.5) are used (one grey (G) and the other white (W)). In the second part, three others OPCs (European standard: CEM I 52.5) (G2, G3 and G4) are employed as well as calcium hydroxide (CH). Density, Blaine surface, chemical and mineralogical compositions of those materials are described in Tables 1 and 2. It is important to note that the free lime content of three OPCs (G, G2 and G3) are similar (free lime percentage: 0.8–1.0%) and lower than the two other OPCs (W and G4) (free lime percentage: 2.0–2.1%). Moreover, two cements (G2 and G3) have similar composition but a very different Blaine surface (3900 and 4500 g/cm$^3$). CSA cement is mainly composed of two hydraulic phases: ye'elimite (65%) and belite (10%). Properties and hydration of cements and mortars based on similar CSA cement, in terms of ye'elimite and belite proportions (65% and 21% [22] or 53% and 18% [23] or 54% and 19% [24] respectively) have already been investigated. Fluorellestadite (11%) formation in CSA clinker is linked to fluorine in raw materials used for CSA clinker production. This mineral formation in white OPC and its structure have already been described [25]. In white OPC, it is unreactive during 90 days of hydration [26]. Assemblages containing ye'elimite and fluorellestadite have also already been described [27].

Table 3 shows CSA cement (clinker and anhydrite) and OPC percentage in the three OPC–CSA cement mixtures used in this study. Anhydrite percentage was calculated to obtain a blend (OPC, CSA clinker and anhydrite) where ye'elimite hydration (reaction 2) and tricalcium aluminate hydration (reaction 6) should form mainly ettringite ($SO_3/Al_2O_3$ molar ratio is always higher than 1). Details of anhydrite percentage choice are described in Appendix A.

In this article, blends are referenced with G (or G2, G3 and G4) for mixtures containing grey OPC and W for those containing white OPC. G and W can be followed by the percentage of CSA cement (15%, 30% or 60%). For example, a sample named "G2-60" corresponds to the blend containing 40% of a grey OPC number 2 mixed with 60% of CSA cement.

## 3. Methods

### 3.1. Mortars

Three prismatic samples of 4 × 4 × 16 cm were made with 450 g of cement (OPC and CSA cement blend), 1350 g of sand (EN 196-1) and 225 g of water (water/cement (w/c) ratio of 0.5). Even if the OPC setting is accelerated by addition of CSA cement, the mortars workability (20 min for 60% of CSA cement) allows molds preparation without admixtures. Mortar curing conditions depend on the CSA percentage (Table 4). Note that mixtures containing

**Table 1**
OPC. CSA clinker and anhydrite chemical analysis by X-ray fluorescence and free lime measurements [12] (in weight percentages) as well as Blaine surface and density.

| | G | W | G2 | G3 | G4 | CSA clinker | Anhydrite | Lime |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 20.0 | 22.0 | 19.8 | 19.9 | 19.7 | 6.2 | 2.7 | 0.6 |
| $Al_2O_3$ | 4.8 | 4.2 | 4.2 | 4.4 | 4.8 | 31.5 | 0.8 | 0.2 |
| $Fe_2O_3$ | 3.1 | 0.3 | 2.2 | 2.1 | 3.2 | 1.2 | 0.3 | 0.1 |
| $TiO_2$ | 0.2 | 0.2 | 0.2 | 0.2 | 0.3 | 0.5 | – | – |
| MnO | – | – | – | – | 0.1 | 0.2 | – | – |
| CaO | 63.3 | 66.8 | 63.1 | 63.2 | 63.4 | 39.7 | 38.4 | 73.3 |
| MgO | 2.8 | 0.6 | 3.7 | 3.8 | 0.7 | 3.9 | 1.8 | 0.6 |
| $SO_3$ | 3.4 | 2.7 | 2.8 | 3.3 | 3.2 | 13.9 | 51.6 | 0.3 |
| $K_2O$ | 0.5 | 0.1 | 0.7 | 0.7 | 0.7 | 0.4 | 0.2 | – |
| $Na_2O$ | 0.2 | – | 0.1 | 0.1 | 0.3 | 0.7 | 0.2 | – |
| $P_2O_5$ | 0.2 | 0.1 | 0.2 | 0.4 | 0.3 | 0.1 | – | – |
| SrO | 0.1 | 0.2 | – | – | 0.1 | 0.4 | 0.2 | – |
| Ignition loss (%) | 1.2 | 3.0 | 2.5 | 1.7 | 2.5 | 0.1 | 4.3 | 25.1 |
| Free lime | 0.8 | 2.1 | 1.0 | 1.0 | 2.0 | 0.2 | – | – |
| Blaine (cm$^2$/g) | 4440 | 4390 | 3920 | 4900 | 4710 | 4120 | 4580 | – |
| Density | 3.18 | 3.08 | 3.13 | 3.14 | 3.14 | 2.84 | 2.95 | – |