

THE HYDRATION OF SUPER ALUMINOUS CEMENT AND THE MECHANICAL STRENGTH DEVELOPMENT

^{1, 2}Cristina STANCU, ²Nicolae ANGELESCU, ²Vasile BRATU

¹CEPROCIM S.A., Romania, ²VALAHIA University of Targoviste, Romania
e-mail: cristina.ionita@ceprocim.ro, nicolae.angelescu@yahoo.com

Abstract. The use of super aluminous cement based on mineralogical compounds whose refractoriness is high as possible, is economically and technologically desirable. However, with increasing of the alumina content in the composition of mineralogical compounds from the aluminous cements, their reactivity towards water decreases.

Therefore, this paper aims to monitoring the evolution in time of development the mechanical strength of aluminous cement based on mineralogical compounds with highly refractoriness properties: CA, CA₂ and CA₆ at ambient temperature.

For this we will monitor the evolution in time of the anhydrous mineralogical compounds hydration and their transformations from metastable forms into stable forms using X-ray diffraction and their influences on the development of mechanical strength.

Keywords: mechanical strength, super aluminous cement, highly refractory compound, calcium monoaluminate, calcium dialuminate, calcium hexa aluminate.

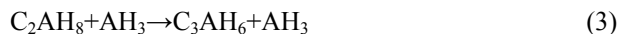
1. INTRODUCTION

The nature of hydrated phases of calcium aluminates are determined by the anhydrous composition. Thus, as the ratio CaO/ Al₂O₃ in aluminates calcium is increased, the basicity of calcium aluminates is higher and increases the speed of interaction with water, but in the same direction the refractoriness of calcium aluminates decrease [1, 2].

The hydration products of calcium aluminates are calcium hydro aluminates well crystallized (CAH₁₀, C₂AH₈) as pseudo-hexagonal, cubic (C₃AH₆) or gelic (Al(OH)₃) [3].

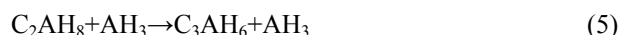
Following the interaction of calcium aluminates toward water, they form different initial hydrated compounds (CAH₁₀, C₂AH₈) which are thermodynamically metastable and will transform in the same stable form (C₃AH₆).

Regarding the calcium monoaluminate, CA, following its interaction with water will form initial CAH₁₀, which transform into C₂AH₈ and then into C₃AH₆ thermodynamically stable form, see reactions 1 to 3:



Solubility of the hydrated phases change with temperature, but the most sensitive is CAH₁₀. At temperatures below 20⁰C, it is initially formed a gel containing CAH₁₀, from which resulting the monocalcium hydro-aluminate crystalline. If the hydration occurs at temperatures around 20⁰C results and dicalcium hydro-aluminate, C₂AH₈, and the originally formed CAH₁₀ transforms with more or less speed into dicalcium hydro-aluminate with release of aluminium hydroxide. At 50⁰C, the supra-saturation is higher only in C₃AH₆ that rapidly forms [4, 5, 6].

The hydration of CA₂ is a slow process, but basically the same reaction products as in the hydration of CA are form, C₂AH₈ and C₃AH₆ [6]:



(Abbreviations: C = CaO; A = Al₂O₃; H = H₂O; S= SiO₂)

Although reactions 1 to 5 are not stoichiometric, such representation gives a better perspective on the hydration processes occurring at the interaction with water of the calcium aluminates.

The factors that influencing the speed of interaction with water of the super aluminous cement are mainly: ambient temperature, humidity, mineralogical composition of cement and storage time.

2. EXPERIMENTAL CONDITIONS

In order to characterize the super aluminous cements of interest in this paper, it will be presented before the chemical composition determined by classical chemical methods and mineralogical composition highlighted by X ray diffraction for each type of cement.

However, before starting to characterize these types of cements, they must be identified in the CaO-Al₂O₃ binary system shown in Figure 1.

The point noted in Figure 1 by C1 corresponds to the mineralogical composition of super aluminous cement based on CA₂ and CA₆. The C2 point corresponds to the mineralogical composition of super aluminous cement based on CA₂. Regarding the location of industrially super aluminous cement composition, it is known only the fact that it can be located in CA and CA₂ subsystem.

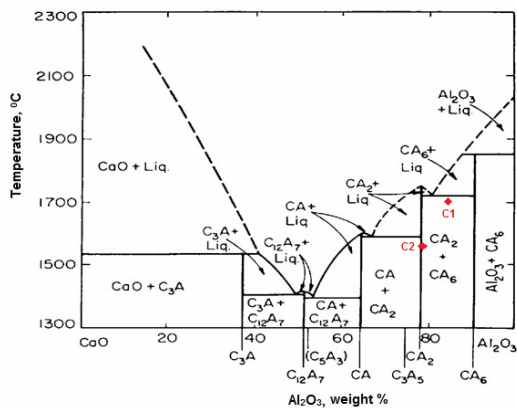


Figure 1. Phase diagram of CaO-Al₂O₃ system

In Table 1 it is presented the oxide composition of ordinary and experimental super aluminous cements.

Table 1. Chemical composition of super aluminous cements

Cement types	Al ₂ O ₃ , %	CaO, %	SiO ₂ , %	Fe ₂ O ₃ , %	Alkalis, %	SO ₃ , %	MgO, %	CaO free, %
CA ₆ +CA ₂	85.33	14.24	0.15	0.12	0.03	0.00	0.13	0.00
CA ₂	74.56	25.15	0.10	0.09	0.02	0.00	0.08	0.00
CA+CA ₂	80.75	17.00	0.35	0.20	0.70	0.27	0.47	0.00

It can be seen from Table 1 that all three cements have an alumina content exceeding 70%, threshold limit value considered for an aluminous cement to be used in making refractory's used in applications that can be used at very high temperatures. These types of cements are called super aluminous cements.

In the Figures 2 to 4 are presented the X-ray diffraction spectrum of cements used in the experiments presented here in order to show that the composition corresponds to the chosen propose.

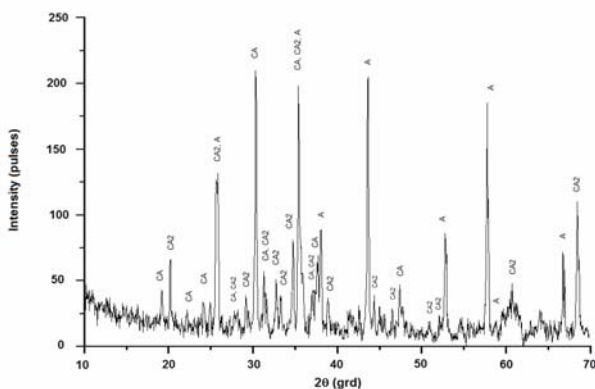


Figure 2. X-ray diffraction spectrum of super aluminous cement based on CA and CA₂

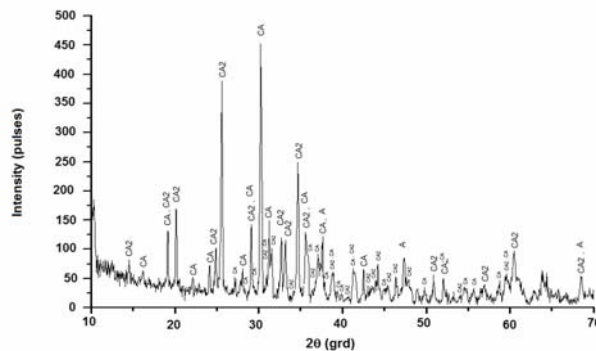


Figure 3. X-ray diffraction spectrum of super aluminous cement based on CA₂

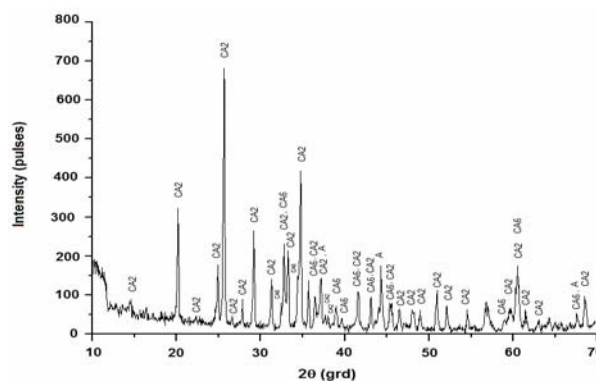


Figure 4. X ray diffraction spectrum of super aluminous cement based CA₆ and CA₂

The data from Figure 2 shows that in the experimental super aluminous cement sample was formed the mineralogical compounds wanted: CA₆ (2.4780Å, 2.6230Å, 2.1090Å) and CA₂ (3.5000, 2.5990Å, 4.4400Å).

Analyzing the shape and the intensity of the peaks corresponding to the experimental super aluminous cement presented in Figure 3 can be seen that in the analyzed sample was formed the mineralogical compound wanted: CA₂ (3.5000Å, 2.5990Å, 4.4400Å), corresponding to the composite selected from CaO-Al₂O₃ phase diagram for these cement. Because the chosen composition is very close to the CA-CA₂ subsystem and the formation of the CA is thermodynamically favored, its presence is met in the sample, but the quantity in which is present is low.

Along with these compounds, in both experimental cements was also found unreacted Al₂O₃ (2.0650Å, 2.5230Å, 1.5900Å) from the raw mix.

Comparing the peaks intensity of industrially super aluminous cement, figure 4, with those of literature, the following mineralogical compounds were identified: CA (2.9625Å, 4.6672Å, 2.5132Å) and CA₂ (3.5000, 2.5990Å, 4.4400Å), together with A (2.0650Å, 2.5230Å, 1.5900Å).

Well defined peaks of alumina from the composition of ordinary super aluminous cements is explained by the fact that usually the one obtained in industrially have the composition corrected by adding alumina. This explains the data of oxide analysis presented in Table 1.

3. RESULTS AND DISCUSSIONS

The particle size distribution was achieved for experimental super aluminous cements by taken a representative sample after heat treatment and grinding the clinkers. Regarding industrially super aluminous cements based on CA and CA₂, a representative sample was taken directly from the container supply.

The Figures 5 - 7 show the size distribution for all super aluminous cements used in this paper.

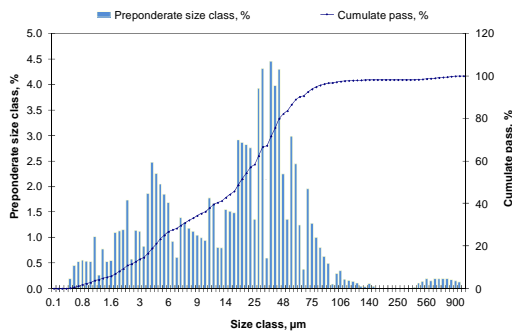


Figure 5. Size distribution of experimental super aluminous cement based on CA₂ and CA₆

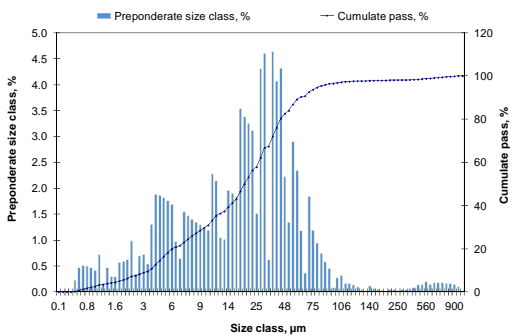


Figure 6. Size distribution of experimental super aluminous cement based on CA₂

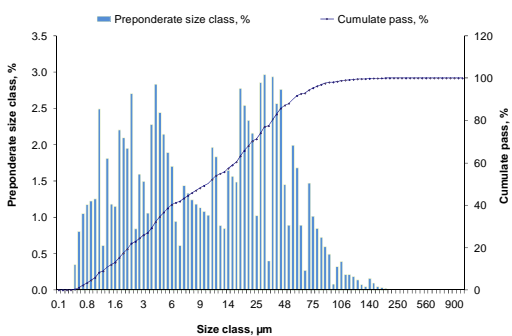


Figure 7. Size distribution of industrially super aluminous cement based on CA and CA₂

Analysing the size distribution of super aluminous cements it can be seen that a large proportion of grain size classes do not exceed the maximum size of 100μm. However, further analysis of particle size distribution characteristic parameters obtained base on Figures 5 - 7 are presented in Table 2.

Table 2. Maximum size grains of super aluminous cements for different values of cumulative pass

Cement types	Parameter	Cumulative pass, %	Size class, μm
CA ₂ +CA ₆	d ₁₀	10	2.3
	d ₅₀	50	20.0
	d ₉₀	90	63.0
CA ₂	d ₁₀	10	3.2
	d ₅₀	50	20.0
	d ₉₀	90	63.0
CA+CA ₂	d ₁₀	10	1.40
	d ₅₀	50	10.00
	d ₉₀	90	55.00

As can be seen from Table 2 most cement grains have a maximum diameter of 63.0μm for the experimental cements based on CA₂ and CA₆ and respectively based on CA₂ and maximum 55.0μm for the industrially super aluminous cement based on CA and CA₂. This is encouraging for the next investigation to be made, because this shows that the cements present an advanced fine grinding and because of that the reactivity will be good.

If it compares the size distribution of the two experimental cements can be observed that they are very similar. This is easily observed seen the parameters d₁₀, d₅₀ and d₉₀ (d = diameter of the grains for a given level of cumulative pass).

To understand the reactivity toward water of anhydrous super aluminous cements, have made determinations of mechanical strength and X-ray diffraction analysis on hardened cement pastes after different hydration periods: 1 day, 3 days, 7 days and 28 days .

Need to mention that in the all cases, the cement pastes were prepared using water of normal consistency and the pastes were kept until terms of tests in water at a temperature of 20⁰C.

The Figures 8 - 10 show the X-ray diffraction spectrum of pastes made by super aluminous cement at the hydration periods mentioned above.

28 days. The cement specimens were kept in water at 20°C.

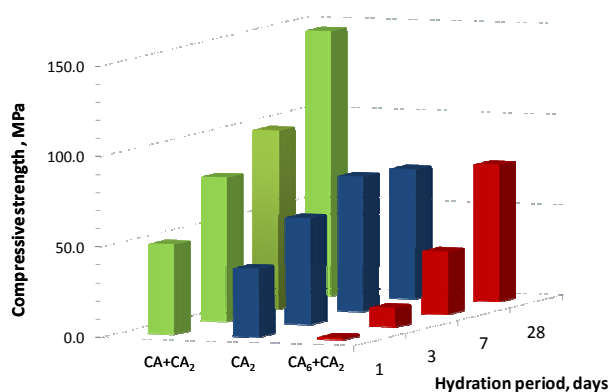


Figure 11. Compressive strength of the cement pastes at different hydration periods

As it expected, the compressive strength evolves in time. It was recorded at short hydration periods low strength values, but at long hydration periods strength values improve, see Figure 11. It should be noted that the values recorded for super aluminous cements based on compounds with higher refractoriness, CA₂ and CA₆, were anticipated from the moment of that the mineralogical composition was chosen. However, the resistance to high temperature makes these cements interesting to aim improvement of compressive strength values at ambient temperature.

As shown in Figure 11 the values recorded at longer hydration periods (28 days) are compared in the cases of experimental cements based on CA₂ and CA₆ and based on CA₂, that since the time evolution of cement contains CA₆ was slower, in time, the reactive mineralogical compound toward water - CA₂ hydrates. These findings are confirmed by the evolution of anhydrous compounds hydration obtained by X-ray diffraction spectrum.

In terms of compressive strength development of cement based on CA₂, this is higher at short terms of hydration (1 day and 3 days) and at the 28 days term to have the same compressive strength at the 7 days term. This suggests that the interaction with water of this cement took place more quickly and stable hydrate forms are formed faster than the cement with higher refractoriness.

4. CONCLUSIONS

Data from the investigation conducted in this paper makes a possible opening to further investigations on super aluminous cement based on compounds with higher refractoriness, CA₂ and CA₆.

Samples of experimental super aluminous cements based on CA₂ and CA₆ and respectively based on CA₂ and industrially super aluminous cements based on CA and CA₂ were compared in terms of reactivity to water. For it was made determinations of mechanical strength and X-

ray diffraction analysis on samples at hydration periods of 1 day, 3 days, 7 days and 28 days.

Data obtained showed that the experimental cements based on mineralogical compounds with lower basicity have compressive strength lower than industrially cement base on more reactive mineralogical compounds. This was in accordance with the data obtained from X-ray diffraction spectrum.

However, because these compounds have reactivity to water, a possible activation/ acceleration of this interaction could make it possible to increase the speed of interaction with water, with positive effects on mechanical strength.

5. ACKNOWLEDGEMENT

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