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STUDY ON HYDRATION AND STRENGTHENING OF HIGH ALUMINA CEMENTS

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Abstract. *Refractory concretes based on aluminous cements are used with great success in areas where high temperatures are required. The mineralogical composition of the high alumina cement is the main factor which gives the physical and mechanical properties at high temperatures of refractory monolithic materials.*
It is therefore desirable to use high alumina cements based on mineralogical compounds with high refractoriness, because in the end those beneficial properties can be found in the final product - refractory concrete.
The aim of this paper is to design, realize and characterize different compositions of high alumina cements based on mineralogical compounds with the highest refractory from the CaO-Al_2O_3 binary system (i.e. CA, CA_2, and CA_6), and to find ways of hydraulic activation of calcium hexa aluminate, also.

Keywords: *calcium monoaluminate, calcium dialuminate, calcium hexa aluminate, activated hydration, mechanical strength, additive, highly refractory compound.*

1. INTRODUCTION

The main mineralogical constituents of high alumina cement that have hydraulic activity and which are important for the manufacture of refractory concretes are: monocalcium monoaluminate (CA) and monocalcium dialuminate (CA_2) which, by hydration, develop mechanical strength.
To achieve a refractory concrete that can be used at very high temperature, it must be use high refractory hydraulic binders such as high alumina cement with a content of alumina ≥ 70%. An alternative technological option that can have the same result, and which it is showed in this paper, is to design a binder matrix whose value of molar ratio Al_2O_3/CaO is higher than the one corresponding to monocalcium dialuminate [1, 2].
The types of binder matrix (high alumina cements) used in this papers are base on CA6 and CA2, on CA2, CA and closer to stoichiometric CA2 (an industrial Alcoa cement).
But once the value of molar ratio Al2O3/CaO is increasing the interaction with water of the mineralogical compounds is decreasing together with it the mechanical strength decreasing, too. But in the calcium aluminates series, the refractoriness increases with the basicity decrease and enrichment in alumina as follows: C12A7<CA<CA2<CA6. The mineralogical compound with the highest refractoriness from the calcium aluminates series is CA6, whose Al2O3/CaO molar ratio is 6:1. However, due to the fact that with the enrichment in alumina of the mineralogical compound the hydraulic activity decreases dramatically, the presence of CA6 was avoided [2]. To counteract this deficiency it can be use some additives with activation of hydration properties for CA_6. From the great variety of high alumina cement activation of hydration must be chose the one that improve the physical and mechanical properties at room temperature and which do not affect refractoriness. One such activation of hydration is calcium sulfoaluminate. The data from literature indicates that it presence can enable interaction with water of high alumina cement, especially of the high refractory mineralogical compounds: CA2 and CA6 [3, 4].

2. MATERIALS

The raw materials used to made high alumina cements on CA_6 and CA_2 and, respectively, based on CA_2, were reactive alumina (Al_2O_3 content = 99.50%) and calcium carbonate ($CaCO_3$ content = 99.70%).

The raw materials used to made calcium sulphoaluminate, the activator of interaction with water for CA_6 and CA_2, were reactive alumina (Al_2O_3 content = 99.50%), calcium carbonate ($CaCO_3$ content = 99.70%) and dehydrate calcium sulphate ($CaSO_4 \cdot 2H_2O$ content = 99.98%).

In order to achieve the high alumina clinkers, which by grinding were obtained cements based on CA_2 and CA_6 and respectively based only on CA_2, we used the CaO-

Al_2O_3 binary system to choose the composition of mixtures of raw materials and heat treatment temperatures.
For increasing the molar ratio Al_2O_3/CaO form high alumina cement based on CA and CA_2 was used reactive alumina.

The high alumina cements based on high refractory compound were characterized in parallel with the additivated samples and with the increasing Al_2O_3/CaO molar ratio samples. The percent in which the additive (calcium sulphoaluminate - $C_4A_3\check{S}$) was added to the cement is 5%. The Al_2O_3/CaO molar ratio was 4.0 for the high alumina cement based on the usual cement with molar ratio Al_2O_3/CaO = 2.5 with addition of alumina (see Table 1).

Table 1. Oxide composition of high alumina cements

Cement type	Al2O3 (%)	CaO (%)	SiO2 (%)	Fe2O3 (%)	Alkalis (%)	SO3 (%)	MgO (%)	CaO free, (%)
CA6+ CA2	85.33	14.24	0.15	0.12	0.03	0.00	0.13	0.00
CA2	77.60	22.20	0.10	0.09	0.02	0.00	0.08	0.00
CA+CA2	70.91	27.89	0.22	0.20	0.21	0.30	0.27	0.00

3. EXPERIMENTAL CONDITIONS

Before starting to characterize these types of cements, they must to be identified in the CaO-Al_2O_3 binary system characteristic to the super aluminous cement, shown in Figure 1.

The point shown in Figure 1 by C1 corresponds to the mineralogical composition of super aluminous cement based on CA_2 and CA_6 and C_2 point corresponds to the mineralogical composition of super aluminous cement based on CA_2. Regarding the location of industrially super aluminous cement composition, it is known only the fact that it can be located in CA - CA_2 subsystem.

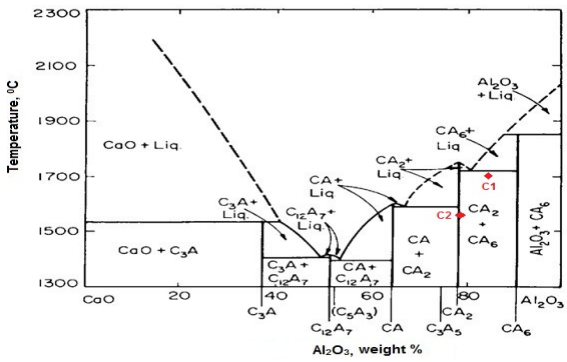


Figure 1. Phase diagram of CaO-Al2O3 system

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 use in making refractory's used in applications that can be use at very high temperatures.
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.

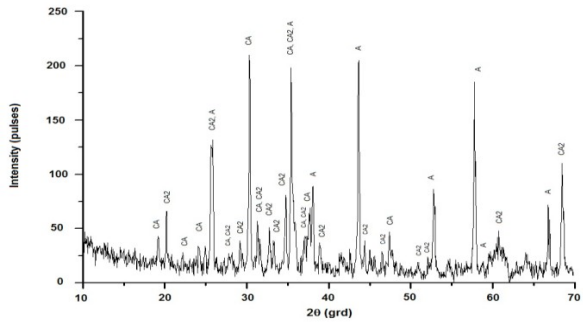


Figure 2. X-ray diffraction spectrum of super aluminous cement based on CA and CA_2

Analyzing the peak intensity of ordinary super aluminous cement, the following mineralogical compounds were identified: CA (2.9625Å, 4.6672Å, 2.5132Å) and CA_2 (3.5000, 2.5990Å, 4.4400Å), together with A (2.0650Å, 2.5230Å, 1.5900Å).

Well defined peaks of alumina presence 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, thus explaining the high alumina content obtained by chemical analysis which does not correspond to the place in CaO-Al_2O_3 binary system.

Analyzing the shape and intensity of the peaks corresponding X-ray diffraction spectrum of the experimental super aluminous cements presented in Figures 3 and 4, it can be seen that in the analyzed samples were formed the mineralogical compounds wanted: CA_6 (2.4780Å, 2.6230Å, 2.1090Å) and/or CA_2 (3.5000, 2.5990Å, 4.4400Å), corresponding to the composite selected from CaO-Al_2O_3 phase diagram for these cements. Along with these compounds was also found unreacted alumina (2.0650Å, 2.5230Å, 1.5900Å) from the raw mix.

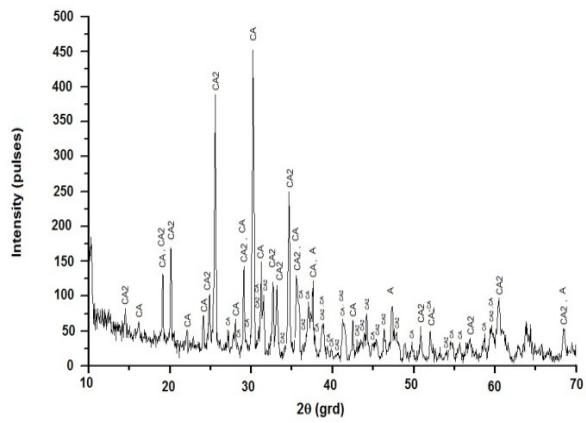


Figure 3. X-ray diffraction spectrum of super

aluminous cement based on CA_2

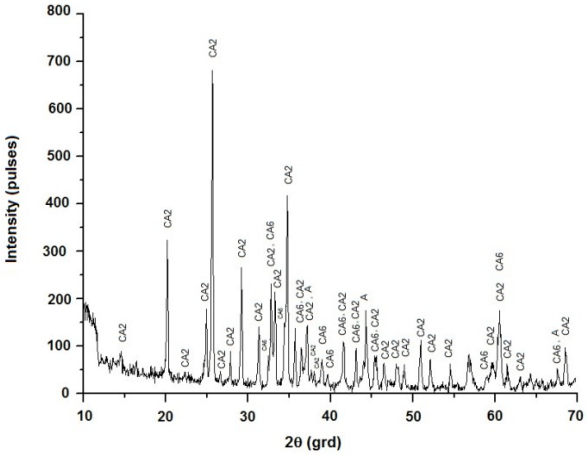


Figure 4. X ray diffraction spectrum of super aluminous cement based CA_6 and CA_2

4. RESULTS AND DISCUSSIONS

For a better understanding of the properties of the new high alumina cements, the results obtained after the physical and mechanical characterisation will be presented versus the ones obtained on the same cements but with 5% additive and with the one with addition of alumina, see Table 2 for characterisation at normal conditions and Table 3 for characterisation after exposure at high temperature.

Regarding the water content for standard consistency for the high alumina cements types studied in this paper is correlated with specific surface area and complies with the recommended values (see [5, 6, 7]).

Setting time of high alumina cements is related with the mineralogical composition. As it was anticipated from the moment of choosing the compositions of sintered alumina cement based on CA_2 and CA_6, the initial setting time and final setting time are much longer than those of high alumina cement based on CA_2 that has a higher basicity.

With the addition of 5% $C_4A_3\check{S}$ the initial and final setting times of high alumina cement were significantly shortened, Table 2. The initial setting time was reduced by approx. 63% - 64% and final setting time was reduced by approx. 80 - 84% for both high alumina cements with additive versus the samples without additives.

The values of compressive strength obtained for high alumina cement based on CA_2 and CA with molar ratio Al_2O_3/CaO = 2.5 are high, even at low hydration time. This was expected because in the composition of this cement are found mineralogical compounds with high reactivity towards water.

The presence of reactive alumina lead to a very low improving of the compressive strength is attributed, probably, to the increased of workability and/or to the surface activity of the particles of alumina with positive consequence in the strength structures.

Table 2. Physical and mechanical properties of high alumina cements at 20^0C

Cement type	Blaine specific surface area	Water content for standard consist	Setting time		Compressive strength			
			initial	final	Terms of hydration			
					1 day	3 days	7 days	28 days
	(cm^2/g)	(%)	(min)	(min)	(MPa)	(MPa)	(MPa)	(MPa)
CA2+CA6	3490	28.0	415	1200	2	11	35	75
(CA2+CA6)+5% C4A3Š	*	28.0	150	240	3	22	49	80
CA2	3210	28.0	320	960	38	59	72	76
CA2+5% C4A3Š	*	28.0	120	150	41	67	81	88
CA + CA2 with Al2O3/C	4370	36.0	135	210	75	94	103	107
CA + CA2 with Al2O3/C	*	36.0	135	210	76	96	114	115

* It assumes to be the same as the cement of whose composition we try to improve.

The compressive strength values of high alumina cements (Table 3) showed a strong influence to the temperature treatment at which they were exposed.

Table 3. Mechanical properties of high alumina cements after exposure at high temperature

Cement type	Compressive strength (MPa)						
	110°C	600 °C	800 °C	1000 °C °	1200 °C	1400 °C	1600 °C
CA_2+CA_6	75	74	71	67	65	121	130
(CA_2+CA_6)+5% $C_4A_3\check{S}$	80	70	67	65	62	103	111
CA_2	76	70	68	64	63	91	98
CA_2+5% $C_4A_3\check{S}$	87	69	65	60	59	84	90
CA + CA_2 with molar ratio Al_2O_3/CaO = 2.5	107	80	65	57	63	100	73
CA + CA_2 with molar ratio Al_2O_3/CaO = 4,0	115	86	83	76	80	113	102

All high alumina cements showed a decrease in compressive strength in the temperature range 110°C - (1000°C) 1200°C, due to structural reorganization that occurs in the critical temperature range. Instead in the range 1000°C (1200°C) - 1600°C, the values of compressive strength are improved than those recorded in the critical temperature range, this being due to the formation of ceramic binding between mineralogical

compounds present at high temperature.
The decrease in compressive strength was higher for samples with additive, comparing to the one without additive, explained by the stronger hydration of the samples with additive. In the case on high alumina cement based CA and CA_2 with molar ratio Al_2O_3/CaO = 4.0, the increase of compressive strength was higher than that reported to the strength values of cement without addition of alumina. Those increased values of compressisive strength were explained by XRD and SEM.

The XRD helped to identify the mineralogical compounds presented in cement samples exposed to high temperatures, thus explaining the good behavior of the samples. After the exposure at 1600°C representative samples from all cements were exposure at XRD. The characteristic mineralogical components of every cement samples are presented in Table 4.

Table 4. Diffraction lines of specific mineralogical components from high alumina cements after exposure at 1600 ^{0}C

Cement type	Calcium alumina			
	CA_6	CA_2	CA	A
CA_2+CA_6	+++	+++	+	-
(CA_2+CA_6)+5% $C_4A_3Š$	+++	+++	+	-
CA_2	-	+++	+	-
CA_2+5% $C_4A_3Š$	-	+++	+	-
CA + CA_2 with molar ratio Al_2O_3/CaO = 2.5	-	+++	++	-
CA + CA_2 with molar ratio Al_2O_3/CaO = 4,0	+	+++	++	-

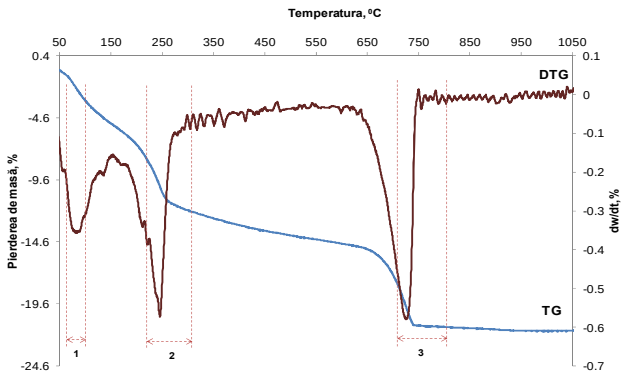
The XRD of the samples highlight the presence of CA_2 in all high alumina cements, very well crystallized and the presence of CA_6 only in cements based on CA_2 and CA_6 and, at the same time - in a smaller amount in the sample in which the molar ratio Al_2O_3/CaO was increased. This fact is due to the movement of the composition from the CA-CA_2 subsystem to the CA_2-CA_6 subsystem for the cement with increase molar ratio Al_2O_3/CaO. The crystallization of CA_6, although is not very good, was favoured by high temperature and oxide composition of the sample, thus explaining the good mechanical behaviour of this sample at high temperature.

The presence of additive was not detected after heat treatment at 1600°C, due to its low stability at temperatures higher than 1450°C.

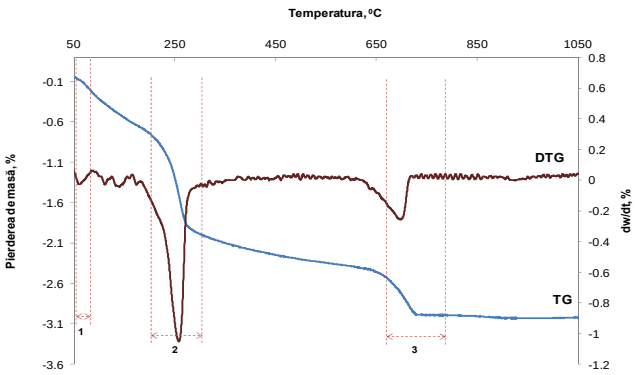
The samples under investigation by thermogravimetric analysis are samples of super aluminous cements hydrated for 3 days. Hydrated cement samples for 3 days were dried before tests achievement for 3 hours in desiccator on calcium chloride, because traces of water that could be in samples to not influence the tests.

Figure 5 presents the results of thermogravimetric investigations up to 1100°C obtained for super aluminous cements. Looking at Figure 5 we can see that with increasing temperature the mass loss is higher. These effects can be highlighted by DTG curve. It can be seen that first effect occurs around 70°C. This mass loss can be attributed to the existence of the water physical bound and of hydrated metastable compounds (C_2AH_8 – in the case of all cements or CAH_{10} - in the case of ordinary super aluminous cement) transformations in stable hydrated compounds (C_3AH_6).

The intensity of this effect is higher for super aluminous cements based on CA and CA_2 and for the one based on CA_2. This because these cements presents more reactive mineralogical compounds in higher amounts than the one based on CA_2 and CA_6, because in this cement only one compound shows reactivity towards water. This does not mean that it does not present mass lose, but as it intensity is lower.



a)



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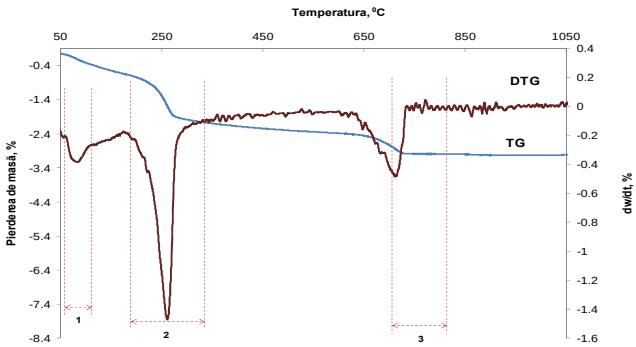


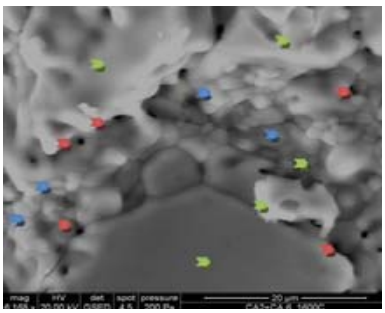
c)

Figure 5. Thermogravimetric analysis of super aluminous cements: a) CA şi CA_2; b) CA_2 şi CA_6; c) CA_2

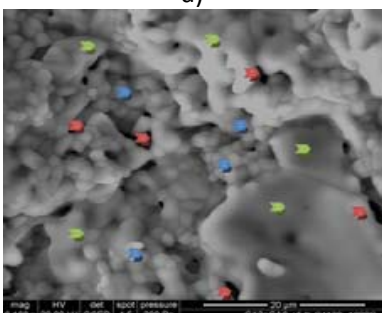
The second area of mass loss occurs in the temperature range 180 - 280°C, where take place the partial dehydration of C_2AH_8, C_3AH_6 and AH_3. Data from the literature indicate that in this temperature range the dehydration of C_3AH_6 goes to $C_3AH_{1.5}$, of C_2AH_8 to C_2AH_4 and of AH_3 to A [2, 8, 9, 10, 11], thus explained the mass loss and the high peak intensity from the curve DTG.

Regarding the third temperature range in which take place significant mass loss, this is included in the temperature range 600 - 730°C. This temperature range corresponds to complete dehydration of the hydration products, with the formation of $C_{12}A_7$ and CA, followed at 1000°C only CA and CA_2 to be meet.

In Figure 6 are presented the electron micrographs of the high alumina cements after the exposure at 1600°C. The SEM performed on samples exposed to 1600°C comes to support both compressive strength values of cement samples and mineralogical compounds identified by XRD.



a)



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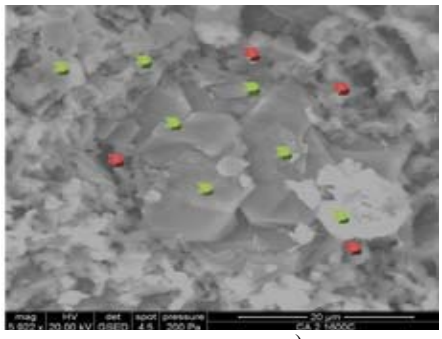

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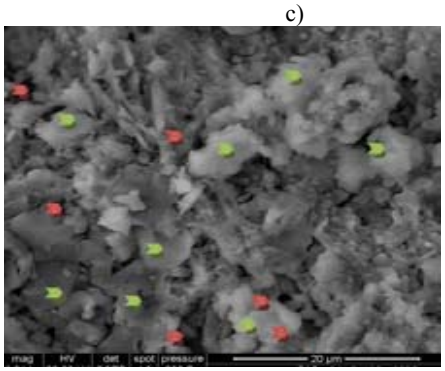

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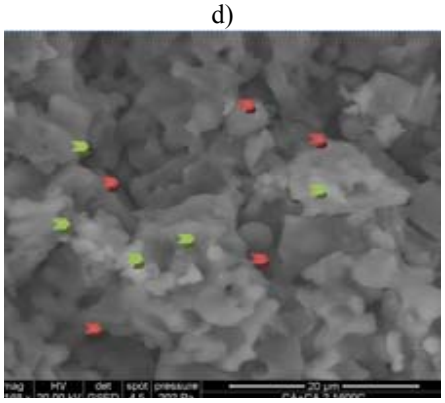

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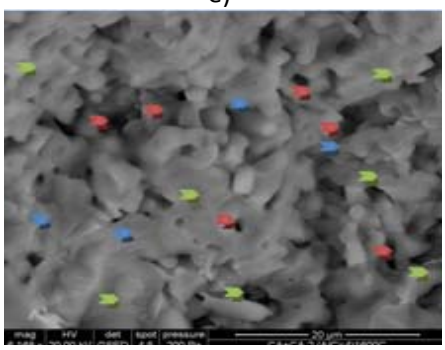

f)

Legend: CA2 crystals; CA6 crystals; Pores

Figure. 6. Electron micrographs of the high alumina cements based on: a) CA2 and CA6, without additive; b) CA2 and CA6, with 5% C4A3Š additive; c) CA2, without additive; d) CA2, with 5% C4A3Š additive; e) CA and CA2 with molar ratio Al2O3/CaO = 2.5; f) CA and CA2 with molar ratio Al2O3/CaO = 4.0 after the exposure at 1600°C

It can be seen from Figure 6 that high alumina cement samples without additives shows better defined crystals ranging from 1 µm up to 40 µm for the sample base on

CA_2 and CA_6 [*Fig. 6 a)*], and from 1 µm up to 20 µm for the sample base on CA_2 [*Fig. 1 c)*], lower porosity than the samples without additives [Fig. 6 *b)* and *c)*], this is due to the fact that this additive is not stable at high temperatures, although it presence at normal temperature (during hydration) was favorable.

The electronic micrograph of high alumina cement with molar ratio Al_2O_3/CaO = 4.0 [*Fig. 6 f)*] revealed a structure composed of small crystals, between 1 µm and 10 µm belonging to CA, CA_2 and maybe CA_6, well defined, forming a well-densified ceramic body.
Regarding the porosity of the sample, it is composed of a number of pores not very high and pore sizes go up to max. 5 µm. Compared with the structure of high alumina cement with molar ratio Al_2O_3/CaO = 2.5 without alumina [*Fig. 6 e)*], the structure of high alumina cement with molar ratio Al_2O_3/CaO = 4.0 is more compact and well crystallized due to mineralogical composition.

5. CONCLUSIONS

After the different investigations made on the high alumina cement based on high refractory calcium aluminous compounds we drown the following conclusions:

1. Using a hydration activator lead to improved structural and mechanical behavior of high alumina cements based on highly refractory mineralogical compounds at room temperature while maintaining the good behavior at high temperature of the base cements.
2. The high alumina cements based on high refractory mineralogical compounds such as CA2 and CA6 presented a very good structural and mechanical behavior after heat treatment at high temperature, if the normal hydration has been activated.
3. Once the molar ratio Al2O3/CaO of the high alumina cement was increase the value of compressive strength after the exposure at high temperature were increased because in the sample was found CA2 and CA6, formed by recrystallization.
4. The presence of C4A3Š was favorable at normal temperature, especially for the cements with low interaction with water, thus obtaining an increase of mechanical strengths. After heat treatment at 1600°C, due to its low stability was not detected anymore.

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