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A POSSIBILITY OF SYNTHESIS OF HIGH-ALUMINA CEMENTS FROM DIFFERENT RAW MATERIALS

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Abstract: Calcium aluminate cements with high Al_2O_3 content are synthesized from different raw materials. Raw materials used in the synthesis include: lime, tricalcium aluminate hexahydrate, aluminum hydroxide and sodium aluminate solution. The preparation of raw material mixture for sintering was performed in two ways: the first method of preparation of a raw material mixture was by mixing powdered components ($Al(OH)_3$ and CaO, $Al(OH)_3$ and $3CaO \cdot Al_2O_3 \cdot 6H_2O$), another method included stirring into the liquid phase ($NaAlO_2$, CaO and Al $(OH)_3$) for a certain period of time at the temperature of 90°C, whereby the obtained solid phase was used as raw material for sintering. Chemical and mineralogical analysis (XRD) were performed on the cements obtained in synthesis. Based on chemical analysis it was concluded that the cements obtained were CAC 70 and CAC 80, as the Al_2O_3 content in these cements ranged from 70 to 75.37% for the first type, while the second type had a range of 77-79%. XRD analysis showed that the dominated minerals in cement CAC 70 were CaO• Al_2O_3 and CaO • $2Al_2O_3$, and in cement CAC 80, mineral CaO • $2Al_2O_3$, which is consistent with the findings published on these cements.
Keywords: Calcium aluminate cements; tricalcium aluminate hexahydrate; aluminum hydroxide; lime; sodium aluminate solution.

1. INTRODUCTION

Aluminate cements or calcium aluminate cements (CAC) are binding materials which fall into the category of special cements. The important difference in chemical and mineralogical composition when compared with silicate cements has resulted in the occurrence of a series of advantageous properties of aluminate cements.

The properties making them more desirable compared to silicate cements are the following: rapid hardening in the air and under the water, the ability of intensive hardening at lower temperatures, fire resistance, chemical stability, etc. Their greatest application is in the manufacture of fireproof materials. They are used in the construction of bridges, dams, fast road repairs, jet grouting (the process of cement coating application), etc. Due to their chemical stability, aluminate cements have ever more significant application in tamping of oil and gas rigs [1,2].

Basic raw materials for the manufacture of aluminate cements include bauxite and limestone (or possibly quicklime), which are used in different mass proportions depending on the type of cement. Production of aluminate cements with a high content of aluminium oxide involves the use of technical aluminium oxide and limestone as raw materials. It can be produced by using two different methods: sintering of the raw material mixture in rotary, tunnel and chamber kilns and by melting in electric and blast kilns. The choice of the method mainly depends on the chemical composition of bauxite and the type of the heat aggregate applied [3,4].

Aluminate clinker is characterized by the presence of different types of minerals: $CaO \cdot Al_2O_3$ (or CA), $3CaO \cdot Al_2O_3$ (C_3A), $CaO \cdot 2Al_2O_3$ (CA_2), $CaO \cdot 6Al_2O_3$ (CA_6), $12CaO \cdot 7Al_2O_3$ ($C_{12}A_7$) or $5CaO \cdot 3Al_2O_3$ (C_5A_3) and $3CaO \cdot 5Al_2O_3$ (C_3A_5). The presence of these minerals depends primarily on the content of CaO and Al_2O_3 in the starting raw material, as well as on the ways the most important stages

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in the manufacture of cement are carried out: the process of sintering (or melting) and the process of cooling of the obtained clinker. The most important mineral component of aluminate cements is monocalcium aluminate ($CaO \cdot Al_2O_3$), which makes for rapid hardening and hydration of aluminate cements. Its content in the cement is over 45%. Tricalcium aluminate ($3CaO \cdot Al_2O_3$) reacts rapidly with water and contributes to early hardening of cement. Twelve calcium seven aluminate ($12CaO \cdot 7Al_2O_3$) is present in small quantities and does not contribute to the hardness of cement, however it hardens more rapidly than monocalcium cement. Unlike the minerals stated above, calcium hexaaluminate ($CaO \cdot 6Al_2O_3$) is an inert material when it comes to mutual action on water, because it does not hydrate. Its presence reduces the hardness of the cement rock. High alumina cements are characterized by the presence of CA and CA_2, whereas the aluminate cements with the content of Al_2O_3 lower 50 % are characterized by CA and $C_{12}A_7$ [1-4].

Aluminate cements are classified into groups according to the content of Al_2O_3 (Table 1.), namely there are the following types: CAC 40, CAC 50, CAC 70 and CAC 80. Chemical content of CaO, SiO_2 and Fe_2O_3 also has a large effect on the properties of the final product.

The following table shows the classification of aluminate cements depending on the content of Al_2O_3 in the cement.

Table 1. Classification of calcium aluminate cement depending of the content of aluminium oxide

Type	%Al_2O_3	%CaO	%Fe_2O_3	%SiO_2	Colour
CAC 40	37-42	36-40	11-17	3-8	Dark grey
CAC 50	49-52	39-42	1,0-1,5	5-8	Light grey
CAC 70	68-75	25-30	0-0,5	0-0,5	White
CAC 80	78-82	17-19	0-0,2	0-0,3	white

2. EXPERIMENTALS

High aluminate cement was synthesized from various raw materials in the laboratory. The starting raw materials for the synthesis included the following: technical aluminium hydroxide, lime, sodium aluminate solution and tricalcium hydroaluminate. The raw material mixture for the production of aluminate clinker was prepared by using two different methods.

The first method involves the production of aluminate clinker starting from powdery raw materials using sintering: synthesis I (technical aluminium hydroxide and lime), synthesis II and synthesis III (technical aluminium hydroxide and tricalcium hydroaluminate).

The second method of preparation of the raw material mixture involves mixing of raw materials in the liquid phase in appropriate conditions. In the syntheses IV, V and VI, a suspension was obtained by mixing aluminate solution with finely ground lime and technical aluminium hydroxide. At first aluminate solution is mixed with lime for a certain period of time (synthesis IV- 1 hour, synthesis V – 2 hours and synthesis VI -1 hour) at the temperature of 90°C in the 1000 cm^3 reaction vessel. Aluminium hydroxide is added to obtained suspension. The suspension obtained in that way is separated from the liquid phase by filtration. The washed solid phase is dried and then annealed at the temperature of 1430°C, for 30 minutes.

The clinker obtained is then cooled and ground in a ball mill to the granulation size of 200 μm and subjected to chemical and mineralogical analysis.

Characterization of the starting raw materials and the obtained CAC involves the use of the following methods of analysis: volumetric method, gravimetric method, absorption spectrophotometry (for chemical analysis), laser determination of particle size and X-ray diffraction for the determination of mineralogical composition of the obtained cement.

3. RESULTS AND DISCUSSION

Technical aluminium hydroxide used in the syntheses has characteristics that satisfy the following conditions: % Al_2O_3 min 64,0; % SiO_2 max 0,015; %Fe_2O_3 max 0,02; %Na_2O_{uk} max 0,3; %CaO max 0,02; %W(105°C) max 10,0 and loss in ignition at 1000°C max 35 %. Tricalcium hydroaluminate used in syntheses I and III has the following chemical composition: Al_2O_3 = 24,70%, CaO= 44,00%, Fe_2O_3=0,11%, SiO_2=0,32%, TiO_2=0,06%, MgO=0,74%, Na_2O_{uk}=0,06% and loss in ignition at 1000°C 29,74% (Figure 1 and Figure 2).

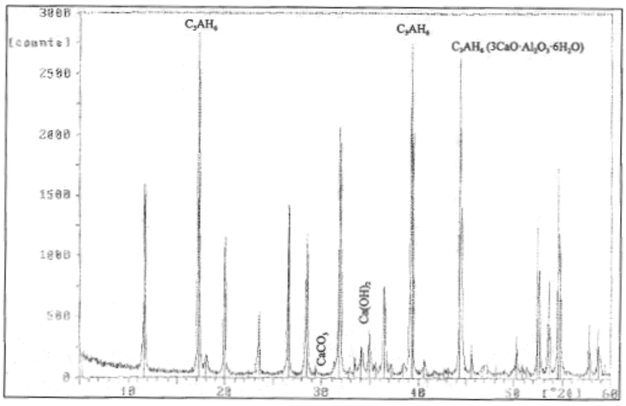

Figure 1. Difractogram of tricalcium hydroaluminate dried at 105 °C

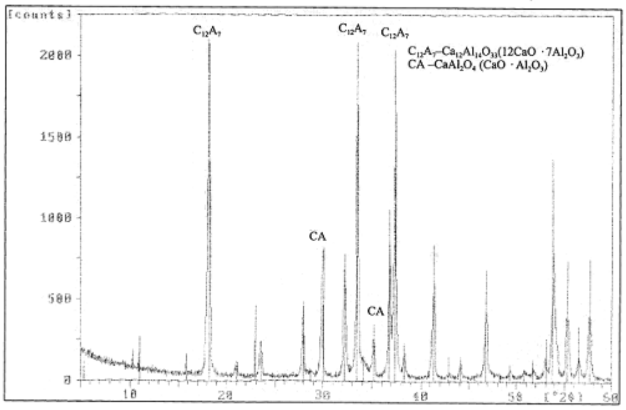

Figure 2. Difractogram of tricalcium hydroaluminate annealed at 1000 °C

In synthesis I, aluminate clinker was prepared by sintering at 1430°C, from powdery raw materials, by mixing 109.4 g of aluminium hydroxide (chemical content of Al_2O_3 in aluminium hydroxide is 64%) with 40 g of lime (with 75% CaO_{akt}).

Synthesis II was also carried out from powdery raw materials, by mixing 10 g of tricalcium hydroaluminate with 16.96 g of aluminium hydroxide and then by sintering at 1430°C.

Synthesis III involved mixing 10 g of tricalcium hydroaluminate with 25.6 g of aluminium hydroxide which was also sintered at 1430°C.

In syntheses IV and V the procedure ran in the following way: the first suspension was prepared by mixing 500 cm^3 of aluminate solution (Al_2O_3= 159,89 g/dm^3, Na_2O_k= 160,43 g/dm^3), 86,80g of lime (with 76,04% CaO_{akt}) with 254 g of aluminium hydroxide(Al_2O_3= 64%) at 90°C for different periods of time. Synthesis IV lasted for 1 hour, whereas synthesis V lasted for 2 hours. Separated and dried solid phase was sintered for 30 minutes, just as in the syntheses I, II and III, at 1430°C.

Synthesis VI involved firstly the preparation of the suspension by mixing 500 cm^3 of aluminate solution (Al_2O_3=223,64 g/dm^3, Na_2O_k= 219,33 g/dm^3), 81,55 g of lime (ca 80,93% CaO_{akt}) and 439,26 g of aluminium hydroxide (Al_2O_3= 64%) at 90°C for one hour. Filtration separated and dried solid phase was sintered at the temperature of 1430°C

After cooling of the clinker obtained by sintering, chemical (Table 2.) and mineralogical analyses were carried out.

The chemical analysis (Table 2.) of the obtained clinkers, aluminate cements produced in syntheses I, II, IV and V can be classified according to the content of aluminium oxide as CAC 70, whereas syntheses III and VI produced CAC 80.

Syntheses I and II, from powdery components and synthesis IV, produce clinkers with approximately the same granulometric compositions, unlike synthesis V, which produces clinker with smaller average diameter of particles and residue on the sieve +80μm. This indicates that prolonging of the reaction time in the suspension (syntheses IV and V) resulted in the decrease of the average diameter of particle.

Syntheses III and VI also produce clinkers with the same granulometric composition.

Starting from powdery components in synthesis I, mineralogical analysis (Figure 3) shows that the clinker contains minerals CA and CA_2, which are typical of high alumina cements.

Table 2. Chemical analysis of aluminate clinker obtained from different raw materials

	$\%Al_2O_3$	%CaO	$\%Fe_2O_3$	$\%SiO_2$	$\%Na_2O_{uk}$	$d_s50\%$ (μm)	+80μm (%)
SYNTHESIS I	75,37	23,80	0,1	0,2	-	39,9	9,2
SYNTHESIS II	72,53	26,60	0,1	0,05	0,28	39,8	9,3
SYNTHESIS III	78,91	20,30	0,08	0,05	0,29	31,2	7,6
SYNTHESIS IV	70,80	28,1	0,032	0,02	0,26	39,6	7,5
SYNTHESIS V	70,74	28,26	0,036	0.022	0,24	34,6	5,5
SYNTHESIS VI	76,94	22,75	0,032	0,019	0,3	30,2	7,6

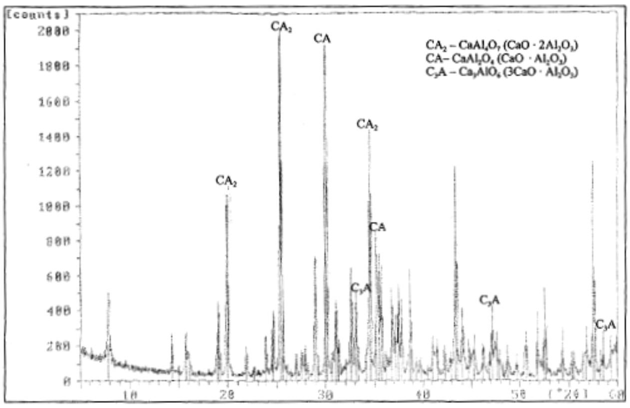

Figure 3. Difractogram of aluminate clinker obtained by synthesis I

Synthesis II (Figure 4) produces aluminate clinker with a complex mineralogical composition which is characterized by the presence of complex calcium aluminate minerals: $C_{12}A_7$, C_5A_3 and C_3A_5, apart from the presence of basic minerals CA and CA_2.

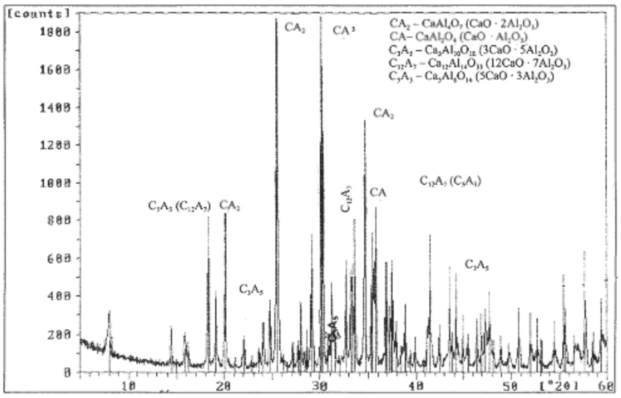

Figure 4. Difractogram of aluminate clinker obtained by synthesis II

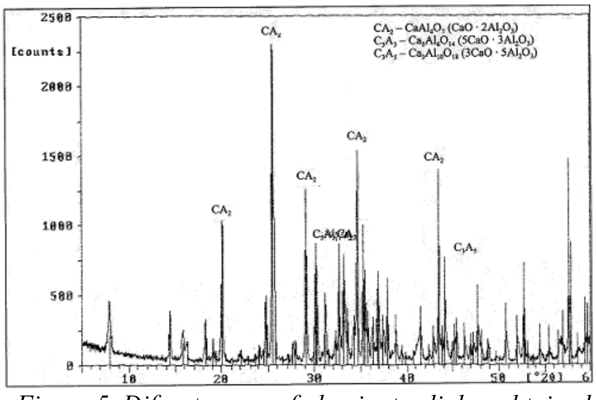

Figure 5. Difractogram of aluminate clinker obtained from synthesis III

Clinker obtained in synthesis III (Figure 5) contains mainly CA_2 mineral as well as C_3A_5. Mineralogical analysis (Figure 6 and 7) of the clinker obtained from synthesis IV and V, the prevailing minerals are CA and CA_2. The prolonging of time in synthesis V does not cause significant changes in mineralogical composition. Synthesis VI (Figure 8) produces the dominant mineral CA_2. X-ray structural analysis shows that the dominant minerals in the cement CAC 70 are $CaO\cdot Al_2O_3$ and $CaO\cdot 2Al_2O_3$, whereas in CAC 80, the dominant mineral is $CaO\cdot 2Al_2O_3$, which is consistent with the findings published on these cements.

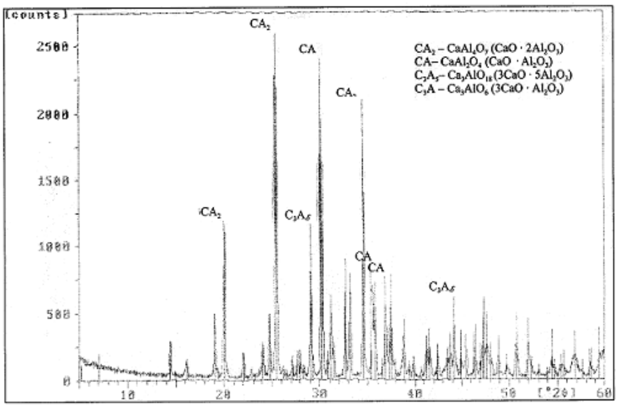

Figure 6. Difractogram of aluminate clinker obtained by synthesis IV

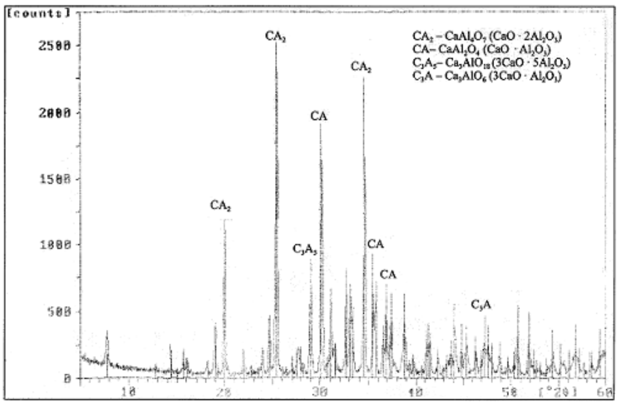

Figure 7. Difractogram of aluminate clinker obtained by synthesis V

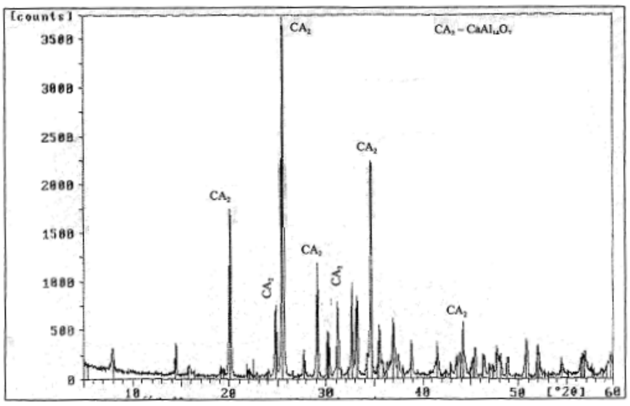

Figure 8. Difractogram of aluminate clinker obtained by synthesis VI

4. CONCLUSION

From chemical analysis of the obtained aluminate clinkers it can be concluded that the obtained cements are CAC 70 and CAC 80, because the content of Al_2O_3 in these cements for the first type ranges from 70 to75,37%, and for the second type 77-79%.

The results obtained indicate that aluminate cement CAC 70 can also be produced starting from aluminate solution, lime and aluminium hydroxide (syntheses IV and V), first by reaction in the liquid phase and then by sintering of the obtained solid phase at 1430°C. Moreover, the synthesis of this solution can also be carried out by sintering aluminium hydroxide and tricalcium hydroaluminate (synthesis II) at 1430°C, which is confirmed by the presence of CA mineral in the obtained clinkers.

An XRD analysis shows that CAC 80 cement can be obtained starting from aluminate solution, lime and aluminium hydroxide (synthesis VI) first by reaction in the liquid phase and then by sintering of the obtained solid phase at 1430°C, as well as by sintering aluminium hydroxide and tricalcium hydroaluminate (synthesis III).

All the above stated leads to a conclusion that high alumina cements can be synthesized not only by using the usual method of preparation from aluminium hydroxide and lime, but also from aluminate solution, lime and aluminium hydroxide, as well as from aluminium hydroxide and tricalcium hydroaluminate.

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МОГУЋНОСТ СИНТЕЗЕ ВИСОКОАЛУМИНАТНИХ ЦЕМЕНАТА ИЗ РАЗЛИЧИТИХ СИРОВИНА

Сажетак: Калцијум-алуминатни цементи (CAC) са високим садржајем Al_2O_3 су синтетисани из различитих сировина. За њихову синтезу коришћене су следеће сировине: креч, трикалцијум-хидроалуминат, алуминијум-хидроксид и натријум-алуминатни раствор. Припрема сировинске смеше за синтеровање вршена је на два начина. Први начин припреме сировинске смеше је мешањем прашкастих компоненти ($Al(OH)_3$ и CaO, $Al(OH)_3$ и $3CaO\cdot Al_2O_3\cdot 6H_2O$). Други начин припреме сировинске смеше је мешањем у течној фази ($NaAlO_2$, CaO и Al $(OH)_3$) одређено време на температури 90 °C, где је добијена чврста фаза коришћене као сировина за синтеровање. Добијеним цементима рађена је хемијска и минералошка (XRD) анализа. На основу хемијске анализе констатовано је да су добијени цементи CAC 70 и CAC 80, јер se садржај Al_2O_3 у тим цементима, за први тип, кретао 70–75,37%, а у другом типу 77–79%. XRD анализа показала је да у цементу CAC 70 доминирају минерали $CaO\cdot Al_2O_3$ и $CaO\cdot 2Al_2O_3$, а у цементу CAC 80, доминира минерал $CaO\cdot 2Al_2O_3$, што је у сагласности са литературним сазнањима о тим цементима.

Кључне ријечи: калцијум-алуминатни цементи; трикалцијум-хидроалуминат; натријум-алуминатни раствор; алуминијум-хидроксид; креч.