

THE EFFECT OF POTASSIUM OXIDE K_2O ON THE PURITY OF C_3A

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Abstract

The article is devoted to the study of the preparation and stabilization of pure cubic phase of tricalcium aluminate C_3A . The findings from the literature and several experimental trials have been summarized. Based on these findings, the synthesis of C_3A was realized, and high purity of this mineral was achieved. Furthermore, the influence of foreign ions, mainly in the form of potassium oxide K_2O combined with Na_2O in the form of sodium oxide on the crystal structure was investigated. The transformation of the cubic phase of C_3A into an orthorhombic phase was observed when the amount of these ions in the structure was changed.

Keywords

Potassium oxide, tricalcium aluminate, C_3A , clinker, high purity, crystal structure

1 INTRODUCTION

Tricalcium aluminate C_3A is one of the four main minerals of Portland clinker. It is found in the clinker as part of the liquid phase and subsequently the interstitial mass of the clinker and acts as a flux during firing. Together with C_4AF , it forms 22 to 28% of the melt in the clinker. This melt is essential for the formation of Belite C_2S and subsequently Alite C_3S minerals. These minerals bring short-term and long-term strength parameters to the hydrated system. Milled Portland cement reacts very rapidly with water and hardens. This phenomenon is known as "flash hardening" and is caused by the very high reactivity of C_3A (present in the clinker) with water. This phenomenon must be prevented by the addition of a hardening retardant in the form of gypsum $CaSO_4 \cdot 2H_2O$ at 2 to 5% of the clinker content [1], [2].

The matter of hardening regulation is based on the immediate formation of ettringite $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, which, in a thin layer, covers the grain of tricalcium aluminate, delaying its hydration for a sufficient time. Hydration of C_3A then continues only when Ca^{2+} ions, formed during hydration of Alite C_3S , are released into the system to form additional ettringite particles. The ettringite produced in this way is referred to as primary ettringite because it is formed in the early hydration phase when the cement structure is just forming [2], [3], [4].

In Portland clinker, C_3A occurs in a stable state. Its existential region is below 1542 °C, so that complete crystallization can occur on cooling. Since Portland clinker cools very rapidly to preserve Alite C_3S and Belite C_2S , C_3A becomes part of the glass like phase [1], [3]. Tricalcium aluminate, despite its significant advantages, is also a major cause of reduced resistance of cement to aggressive environments [4].

The mechanism of entry of foreign ions into the structure and the subsequent polymorphic modification of C_3A itself can be simplistically defined as the replacement of one mole of CaO by one mole of Na_2O . This means the replacement of one calcium ion by two sodium ions. In each cell of the C_3A structure there are eight sites on the triaxial planes into which additional foreign atoms can intercorporate. Since the atomic radius sizes of Ca^{2+} and Na^+ ions are comparable being 192 and 185 pycnometers, respectively, it is almost certain that Na^+ ions enter the sites in the structure [3], [5]. Because the Na^+ ion is smaller than the Ca^{2+} ion, when it is replaced, the space is not filled, so the crystal structure begins to change, deform, and reshape. This causes the symmetrical cubic lattice to become less symmetrical and adopt an orthorhombic structure K_2O , on the other hand, is poorly soluble in C_3A , and crystalline mixtures with added K_2O appear cubic by X-ray diffraction. However, in the presence of sodium, the solubility of potassium increases and hence its presence should help to convert the cubic polymorphic phase into an orthorhombic one [4], [5], [6].

This topic is highly relevant recently because developments in cement production are increasingly influenced by environmental and economic factors. For this reason, it is very important to know in detail all the mineralogical processes of transformation of each polymorphic modification of each clinker mineral.

These minerals determine a very high proportion of the final physical properties of the produced clinker. In practice, they are never found in pure form but are contaminated with other chemical elements [5], [6].

These contaminanats may partially change their basic properties such as melting point or transition to other modifications, and this may alter the properties of the final product [5]. This paper deals with the investigation of the effect of varying the amount of potassium oxide by subsequent milling of the raw material mixture and firing at 1350 °C, followed by soaking for 120 min on the formation of polymorphic C₃A phases.

2 METHODOLOGY

The following raw materials were used for the preparation of the raw material powder mixture; calcium carbonate CaCO₃ (p.a. 99.7%), aluminum oxide Al₂O₃ (p.a. 98.5%), potassium carbonate anhydrous K₂CO₃ (p.a. 99.0%) and sodium carbonate anhydrous Na₂CO₃ (p.a. 99.0%) from the manufacturer Penta. The calcium carbonate was calcined to calcium oxide in a furnace at 900 °C with 60 minutes soaking to prevent volumetric changes during then subsequent heating of the sample. The composition of the raw material mixture for the preparation of tricalcium aluminate is given in the following Tab. 1.

Tab. 1 Chemical composition of the raw material mixture in grams and % per 15 g of the resulting C3A.

C ₃ A Label	CaCO ₃ [g]	Al ₂ O ₃ [g]	Na ₂ CO ₃ [g]	Na ₂ O [%]	Na ₂ O [g]	K ₂ O [%]	K ₂ CO ₃ [g]	K ₂ O [g]
0.5% K₂O + 1.5% Na₂O	22.395	7.605	0.7695	1.5	0.45	0.5	0.2201	0.15
0.5% K₂O + 4.0% Na₂O	22.395	7.605	2.0521	4.0	1.20	0.5	0.2201	0.15
0.5% K₂O + 6.0% Na₂O	22.395	7.605	3.0781	6.0	1.80	0.5	0.2201	0.15
1.0% K₂O + 1.5% Na₂O	22.395	7.605	0.7695	1.5	0.45	1.0	0.4401	0.30
1.0% K₂O + 4.0% Na₂O	22.395	7.605	2.0521	4.0	1.20	1.0	0.4401	0.30
1.0% K₂O + 6.0% Na₂O	22.395	7.605	3.0781	6.0	1.80	1.0	0.4401	0.30
1.5% K₂O + 1.5% Na₂O	22.395	7.605	0.7695	1.5	0.45	1.5	0.6602	0.45
1.5% K₂O + 4.0% Na₂O	22.395	7.605	2.0521	4.0	1.20	1.5	0.6602	0.45
1.5% K₂O + 6.0% Na₂O	22.395	7.605	3.0781	6.0	1.80	1.5	0.6602	0.45

The raw materials were weighed individually on a laboratory scale Radwag PS 600.3Y, then homogenized by wet milling in the presence of water 0.2 dm³ in a PULVERISETTE 6 planetary mill at 350 rpm. A 0.5 dm³ agate grinding bowl with 25 agate grinding balls of spherical shape with a diameter of 20 mm was used. Agate was chosen to prevent contamination of the sample with iron oxides, which are released during grinding in a steel bowl with steel grinding bodies. The grinding time was set at 30 minutes. The grinding of the material is mainly through the high-energy impact of the grinding balls.

The collected samples were dried in a Binder C 170 laboratory dryer at 105 °C for 24 hours. During the drying process, nodules with diameters ranging from 10–15 mm were formed spontaneously.

These nodules were placed in platinum crucibles with 80 g volume capacity. The filled platinum crucibles were placed in the laboratory chamber of a high temperature supercantal furnace Classic 2017S at 22 °C. The firing was carried out in two steps. First, the sample was heated to a selected temperature of 900 °C with 60 min soaking to remove CO₂ from the raw materials to prevent volume changes when the sample is heated further and to ensure better reactivity in the solid phase. Then, the temperature was increased to a 1350 °C at a rate of 8 °C /min and soaked 120 minutes in two experiments. After soaking, the platinum crucibles were removed (one piece at a time) and then spontaneously cooled to the laboratory temperature. The sample preparation for the Rietveld method was carried out in a RS 200 vibrating disc mill at 900 rpm for 20 sec. Subsequently, the sample was placed in sealed PE bags or PP airtight capsules with silica gel to prevent it from reacting with air moisture.

These samples were then evaluated by XRD analysis on an XRD PANalatical Empyrean, $\lambda = 1.540598$ for K λ 1 radiation, Cu – anode, voltage 45 kV, and current 40 mA; with a diffraction angle of 2 θ ranging from 5° to 80° with a step of 0.01°. Qualitative evaluation of the diffractograms to determine the individual monoclinic phases was performed using HighScore plus software (3.0e, PANalytical B.V., Netherlands) with the ICSD database (released in 2012). Quantification was performed using the Rietveld method employing the fundamental parameter approach was used to identify the individual phases and perform their quantification.

3 RESULTS

Firings were performed with an intermediate step at 900 °C for calcination with the main soaking at temperature of 1350 °C. The results were obtained after 120 min of soaking at this temperature. This soaking duration was chosen due to reactivations of the Mayenite and free lime CaO, which were detected during XRD analysis of each soaked sample. These results can be seen in Tab. 2, Furthermore, Na and K ions were intentionally added to the C₃A structure. This treatment was carried out using Na₂CO₃ and K₂CO₃ during the preparation of the raw C₃A meal.

Tab. 2 Evaluation of the Rietveld method for samples with different firing times and different K₂O and Na₂O contents.

n	Input of Na ₂ O [%]	Input of K ₂ O [%]	Cubic C ₃ A [%]	Ortho. C ₃ A [%]	C ₃ A [%]	Content of Mayenite [%]	Content of Free Lime CaO [%]	Sum of con. [%]
1	1.5	0.5	94.5	2.5	97.0	1.2	1.8	100.0
2	1.5	1.0	83.5	6.3	89.8	3.3	6.9	100.0
3	1.5	1.5	86.5	4.0	90.5	2.7	6.8	100.0
4	4.0	0.5	10.9	79.3	90.2	3.8	6.0	100.0
5	4.0	1.0	6.6	76.3	82.9	4.8	12.3	100.0
6	4.0	1.5	3.0	75.5	78.5	8.5	13.0	100.0
7	6.0	0.5	2.0	86.4	88.4	3.3	8.3	100.0
8	6.0	1.0	1.5	81.6	83.1	0.4	16.5	100.0
9	6.0	1.5	0.6	77.2	77.8	0.7	21.5	100.0

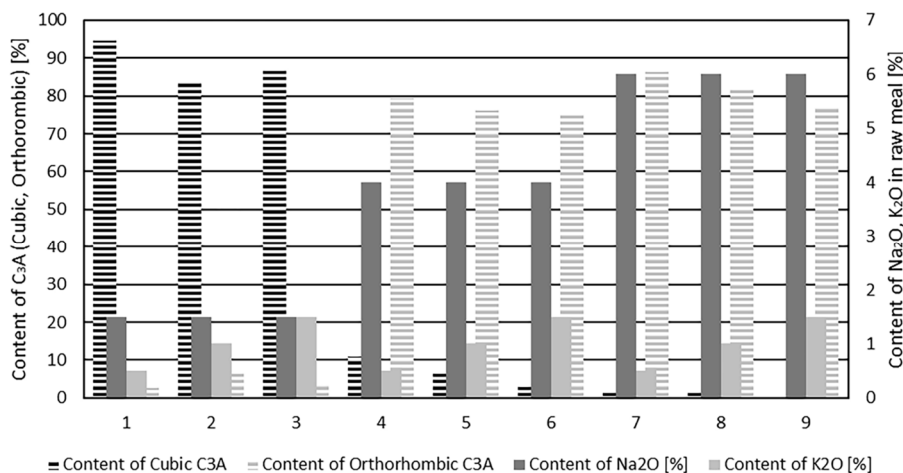


Fig. 1 Graphic evaluation of the individual content components.

According to the results in Tab. 2 and its graphical representation in Fig. 1, increasing the addition of K₂O from 0.0% to 1.5% has no effect on the change of crystal structures. In all cases, the structure changes significantly only with increasing Na₂O content. It can be concluded that with increasing Na₂O content, the cubic form of C₃A progressively changes to the orthorhombic form. From the measured results, it is not possible to determine exactly at what wt. % of Na₂O the cubic structure changes to orthorhombic. The quantification and analysis of measured sample results were performed by the Rietveld method in HighScore plus software (3.0e, PANalytical B.V., Netherlands) with the ICSD database (released in 2012).

4 DISCUSSION

In two independent experiments, it was investigated whether the extension of the soaking duration influences the formation of C₃A. These experiments showed that for a given sample preparation mechanism, a longer isothermal

hold time is not beneficial. Therefore, the inability to react free lime CaO and Mayenite is most likely due to insufficient preparation and homogenization of the raw meal.

The effect of foreign ions on the structure of C₃A was consistent with the results from the literature were confirmed, where sodium ions were shown to transfer into the structure from sodium oxide Na₂O. It was proven that with increasing content of Na⁺ ions, the crystal structure change from cubic C₃A to orthorhombic C₃A. It was also shown that potassium ions from Potassium Oxide K₂O at given concentrations have no significant effect on the crystal structure transformation. It was also demonstrated by these experiments that as the content of foreign impurities in the form of K⁺ and Na⁺ cations in the samples increases, it provides the conditions for the formation of a completely new phase.

The mechanism of this new phase can be attributed to the reaction when the cations react with Al₂O₃. Therefore, with increasing amounts of foreign ions, the amount of free lime CaO also increases. For samples prepared in this way, the question arises whether they are still C₃A.

5 CONCLUSION

This paper focused on investigating the effect of the amount of impurities in the form of K⁺ and Na⁺ cations on the formation and transformation of the internal structure of C₃A with two-step calcining and a main calcination temperature of 1350 °C with 120-min soaking duration. Laboratory-prepared C₃A was obtained by mechanochemical solid phase activation reaction and based on the results obtained, and it can be concluded:

- Preparation of various modifications of C₃A with different mineral composition has been designed.
- Experimentally prepared C₃A were analysed and evaluated by Rietveld method to assess the purity of C₃A mineral, and its phase composition.
- The phase composition of the different structures on this mineral was determined and the effect of foreign ions on the crystal structure was also described.
- Further research in the field of tricalcium aluminate C₃A should be concerned with expanding and intensifying the number of experiments as well as repeating the experiments.
- In future studies, the issue of impurities in the form of sodium oxide Na₂O should be investigated. It would also be good to achieve a higher degree of milling and homogenization of the raw meal to ensure a higher degree of reactivity of the final C₃A.

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