Crystallization process in the preparation of the tetracalcium ferroaluminate

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Abstract. The study of the origin, stability and properties of various calcium silicate polymorphs is important for a better understanding of the processes involved in the production of Portland clinker. At the same time, the synthetic pure clinker phases can serve in further investigations, such as hydration or the effects of plasticisers. The aim of this article is to prepare the pure phase of tetracalcium ferroaluminate and to observe the crystallization process based on the calculation of the size of the crystallite using the simplest method, the Scherrer's equation. Based on the results of the X-Ray analysis, the temperature of 1350 °C with a soaking time of 3 hours is sufficient to produce the tetracalcium ferroaluminate pure phase. This firing mode is also characterized by a very good development of the crystalline structure.

1. Introduction

Portland cement is a complex product made from very simple and abundant materials: limestone and clay (or shale). Very precise proportions of these two basic materials have to be mixed with some additions to create a raw meal with a precise chemical composition. Usually, Portland cement raw meal is heated up to a temperature of about 1450 °C. The chemical composition of the raw feed is adjusted to obtain the formation of four minerals that react with water to create bonds: tricalcium silicate C₃S, dicalcium silicate C₂S, tricalcium aluminate C₃A and tetracalcium ferroaluminate C₄AF. The first two minerals constitute the silicate phase of Portland cement, and the tricalcium aluminate and tetracalcium ferroaluminate its aluminous phase also called the interstitial phase, because in the burning zone this part of the clinker reaches a more or less viscous state that bonds together the two silicate phases [1,2,3]. Alite content is by far the most common in currently produced Portland clinker. Except for brownmillerite, all major clinker minerals show strong polymorphism. The composition of the raw material and the setting of firing parameters are the most influential factors that determine the final phase composition of clinker [4,5].

Due to previous unsuccessful attempts to synthesize the pure C₄AF phase, the work deals with optimization the manufacturing process, verifying purity and monitoring the crystallization process in the C₄AF production process. The previous failure occurred in attempts to synthesize C₄AF using the Wesselsky-Jensen method [6] mainly due to the selected firing mode.

Therefore, nine different firing modes have been tried to find the best possible firing method. At the same time, much more emphasis was placed on precision in the early stage of the preparation of the raw material mixture when the homogenization time was extended and the medium used in the process of milling the raw material mixture in the planetary mill PULVERISETTE 6 was changed.
Pressing of the pellets, were replaced by the spontaneously formed pellets after drying from wet suspension with 10 mm in diameter, which were directly dosed into the platinum crucibles for solid state reaction [7,8].

2. Materials and methods

The Wesselsky-Jensen method was used to prepare tetracalcium ferroaluminate. This method indicated the molar ratio of used raw materials. Calcium carbonate CaCO₃ (p.a. 99,8%), aluminum oxide Al₂O₃ (p.a. 99,0%) and iron oxide Fe₂O₃ (p.a. 99,8%) were used to prepare a tetracalcium ferroaluminate. The raw material mixture was homogenized with the water in a Pulverisette 6 planetary mill for 10 minutes at 400 rpm. Fritsch planetary ball mill Pulverisette 6 in a bowl with the volume of 0.5 dm³ was used. The bowl was filled by 25 steel grinding balls with 20 mm in diameter. The comminution of the material takes place primarily through the high-energy impact of the grinding balls. The grinding bowl, containing the grinding balls and the material to be ground, rotates around its own axis on the main disk whilst rotating rapidly in the opposite direction. Centrifugal force causes the 3ground sample material and the grinding balls to separate from the inner wall of the grinding bowl. The grinding balls then cross the bowl at high speed and further grind the sample material by impact against the opposite wall. The homogenized raw material mixture was dried in a Binder C170 laboratory dryer for 24 hours.

The spontaneously formed pellets with 10 mm in diameter were directly dosed to platinum crucibles.

Superkhantal High temperature furnace Classic 2017S was used for solid state reaction. Solid state reaction was carried out at 3 temperatures: 1350, 1400 and 1450 °C with 3 soaking times: 1, 3 and 5 hours. At the end of each firing mode, the platinum crucibles were removed from the furnace and immediately cooled down with air flow. The samples were adjusted by milling to X-Ray analysis. At first, the samples were milled in a RS 200 vibratory disc mill for 30 seconds at 900 rpm. The Vibratory Disc Mill RS 200 comminutes by impact and friction. The grinding set is firmly attached to the vibration plate with a quick-action lever. The plate with the grinding set is subjected to circular horizontal vibrations. The centrifugal force acting on the grinding rings in the dish results in extreme pressure. Impact and frictional forces acting on the sample produced analytical fineness in 1-3 minutes. The circular vibrations are produced by a frequency controlled 1.5 kW 3-phase motor.

The material was further milled with isopropyl alcohol in McCrone Micronising Mill to complete sample preparation for X-Ray analysis.

Phase composition control was performed by X-ray analysis on Panalytical Empyrean XRD with Cu-Kα as the radiation source, λ=1.540598 for Kα1, accelerating voltage 45 kV, beam current 40 Ma, diffraction angle 2θ in the range from 5° to 80° with a step scan of 0.01°.

Input values were obtained to determine the effect of the firing temperature and the soaking time on the evolution of C₄AF crystallites. The crystallite size was evaluated on selected diffractive lines at appropriately selected crystallographic planes that had a major crystallographic direction. Two distinct crystallographic planes were selected. They are determined by the Miller Index "hkl": 200 and 411, which were shown on the diffraction pattern at angles of: 20: 50.4 and 33.7°. Calculation of the size of crystallites was based on the measurement of FWHM (full width of half maximum). The measurement of FWHM was carried out using the HIGHSCORE PLUS program. The FWHM values were obtained in the program HIGHSCORE PLUS for selected diffraction lines. From the list of peaks and their FWHM, the data for the lines that responded to the Kα2 radiation were deleted. The instrument extension was set to the LaB₆ standard (lanthanum hexaborite). LaB₆ is considered to be a fully crystalline material in which the size of crystallites is theoretically equal to infinity. Diffraction lines of LaB₆ were determined in the same positions as the selected diffraction lines in the same way in the HIGHSCORE PLUS program. The size of the crystallite was evaluated by the modified Scherrer equation [9]:
for the $\lambda = 1.540598$ for the Cu cathode and the Scherrer constant $K = 0.94$, crystallite size values were obtained without device extension.

The last step was scanning on the scanning electron microscope TESCAN MIRA3 XMU. Three samples were selected, which were prepared using a colloidal graphite solution in isopropyl alcohol and a rotary pump pumped by a carbon sputter.

3. Results
Figure 1 shows brownmillerite samples removed from the laboratory furnace and cooled down by air flow for individual temperatures and soaking times.

Figure 1. Brownmillerite samples removed from the laboratory furnace.

C₄AF was sintered at temperatures of 1300, 1350 and 1400 °C with soaking times of 3 hours. There are colour differences from the picture between samples. Samples sintered at 1300 °C are brown to rust in colour, while samples sintered at higher temperatures are gray to black. For samples sintered at temperature of 1400 °C a greater amount of gloss can be observed. The gloss of the sample is more intense with longer soaking time.

The quality control of the mineralogical composition of prepared tetracalcium ferroaluminates were performed by X-Ray analysis, the scans of which are shown in Figure 2.

Figure 2. X-Ray diffraction patterns of C₄AF (B-Brownmillerit, N-Ca₁₂Al₁₄O₃₂).
At a firing temperature of 1300 °C, impurities in the form of a mineral from the group Ca$_{12}$Al$_{14}$O$_{32}$ are identified on the diffraction pattern. A temperature of 1350 °C is already sufficient to fully crystallize C$_4$AF. Therefore, the temperature of 1400 °C is no longer necessary in terms of material quality.

For the clarity of the resulting crystallite size values, 3D graphs were constructed to express the dependence of crystallite size on firing temperature and soaking time, which are shown in Figure 3.

![Figure 3](image_url)

**Figure 3.** Graphical representation of the influence of the temperature and the soaking time on the size of C$_4$AF crystallites in crystallographic planes 200 and 411.
The trend of changing the size of the crystallites is very similar in both selected crystallographic planes. The most significant changes in crystallinity occur at a temperature of 1350 °C with soaking time of 3 hours.

The grain shape was evaluated by optical microscopy. The Figure 4 shows C₄AF images at 3 different temperatures with soaking of 3 hours.

![C₄AF electron microscope scans (A-1300/3hour, B-1350/3hour, C-1400/3hour).](image)

4. Discussion

The article deals with the preparation and monitoring of the influence of temperature and soaking time on the C₄AF crystallization process.

Based on the results of the X-Ray analysis, it can be stated that the temperature of 1300 °C even with 5 hours of soaking time was insufficient to fully crystallize the material, because the residues with a different mineralogical composition are identified on the diffraction patterns. At a temperature of 1350 °C with soaking time of 3 hours, the pure C₄AF phase has already been prepared and thus a temperature of 1400 °C was no longer necessary in terms of firing mode.

The simplest Scherrer-method was used to evaluate the effect of the firing process on the crystallization of the tetracalcium ferroaluminate. The trend in the development of C₄AF crystallites can be considered very similar in both selected crystallographic planes. In general, the higher the firing temperature and the soaking time, the higher the crystallite size. The most significant changes in the size of crystallites occur at a temperature of 1350 °C with 3 hours in both crystallographic planes. This temperature and soak result in a continuous increase in crystallite size to 180 nm in the crystallographic plane 200 and to 256 nm in the 411 plane. With increasing soaking time, there is only a slight increase in crystallite size to 183 nm in plane 200 and 313 nm in the 411 plane. Consideration should also be given to the fact that values above 200 nm are the limits of the applicability of the method and the device extension. Electron microscopy images also confirmed the trend in C₄AF crystal structure development. At a firing temperature of 1300 °C, the crystalline structure is relatively fine with small crystals, while at 1350 °C it reaches the top and large C₄AF crystals are observed in the scan. Conversely, at 1400 °C, the surface appears to be sintered.

5. Conclusion

Nine different firing modes have been tried to obtain the most advantageous or optimal C₄AF firing process. After evaluating the results of X-Ray analysis and scanning electron microscopy, firing at a temperature of 1350 °C (with a heating rate of 8 °C/minute) with soaking time of 3 hours seems to be the most suitable firing process to obtain a pure material. Samples synthesized by this firing process were shown as the desired pure C₄AF phase in the X-ray analysis. Firing at higher temperatures and
longer soaking times was therefore unnesessary. At lower temperature, impurities in the form of \( \text{Ca}_{12}\text{Al}_{14}\text{O}_{32} \) occurred in the mineral. The firing at 1350 °C with 3 hours of soak also showed a very good development of the crystal structure, where the magnitude of the crystallites reached values of about 180 nm, which was also confirmed by electron microscope images.

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