

EFFECT OF PREPARATION PROCESS ON PURITY OF TRICALCIUM ALUMINATE

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ABSTRACT. In the realm of cement production, traditional fuels are steadily giving way to alternative sources. While this shift yields economic and ecological advantages, it introduces notable technological challenges. Specifically, there is an escalation in certain chemical elements, leading to variability in the mineralogical composition. This variability is subsequently manifested in the characteristics of Portland clinker. It becomes imperative, therefore, to synthesize pure clinker minerals. This synthesis is essential for both understanding their behavior in industrially manufactured cement and creating analytical standards for mineral identification through XRD. The primary focus of the research is on the production of pure tricalcium aluminate, a key clinker mineral, within laboratory conditions. A direct laboratory methodology involving solid-phase synthesis is used. The investigation meticulously tracks the impact of homogenizing the raw material mixture on the resultant mineral's purity. To achieve this, a high-speed Pulverisette 6 planetary mill is utilized along with two types of grinding bodies. A corundum grinding capsule with corundum grinding bodies is employed to prevent contamination by foreign ions. Simultaneously, a highly efficient steel grinding capsule with steel grinding bodies is utilized. The raw material mixture is then subjected to sintering at six different temperatures ranging from 1 200 to 1 450 °C, and the purity of the produced mineral is quantified using Rietveld analysis. Laser granulometry results indicate a strikingly similar comminution of the raw material in both grinding cases. Iron contamination, as revealed by XRF analysis, is minimal, accounting for only 0.21 %. The purity of 97.6 % C_3A , is achieved at 1 450 °C using a steel grinding capsule, with 2.4 % unreacted lime. Conversely, when using a corundum capsule, a purity of 93.6 % is achieved, accompanied by residues of 2.2 % mayenite and 3.8 % lime. This discrepancy may be attributed to an insufficient degree of raw material comminution in the corundum capsule. Intriguingly, a slight iron contamination during the grinding of the raw material mixture exerts a positive influence on purity. In this case, iron acts as a flux, fostering a more favorable reaction of the mineral mayenite. This multifaceted exploration enhances our understanding of clinker mineral synthesis, offering insights into optimizing purity based on grinding methods, sintering temperatures, and the impact of minor contaminants.

KEYWORDS: Tricalcium aluminate, synthesis, contamination, Rietveld analysis.

1. INTRODUCTION

Tricalcium aluminate C_3A is one of the main components of Portland clinker. C_3A acts as a melt during clinker production and is part of the liquid phase during firing. In the prepared clinker, it becomes part of the interfacial substance. Together with C_4AF , it forms most of the 22 to 28 % of the clinker melt that is essential for the formation of other clinker minerals such as alite C_3S and belite C_2S , which are the main minerals that bring the cement parameters. Ordinary Portland clinker contains 8 to 11 % of C_3A . In cement, the role of C_3A is related to the kinetics of cement hydration. 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 chemicals. A better understanding of all the mechanisms involved in C_3A formation and hydration requires the ability to prepare pure C_3A . [1]

There are several different procedures for the preparation of tricalcium aluminate by the solid-state syn-

thesis, but they all involve the following steps:

- Preparation of raw materials: raw materials such as limestone and corundum are usually first ground into small particles.
- Mixing the raw materials: the ground materials are then mixed in the correct proportions to ensure that the final product contains the correct amount of calcium and aluminium.
- Processing of the mixture.
- Drying and firing: the resulting mass is then dried and fired at high temperature to become a solid tricalcium aluminate [2].

The synthesis of tricalcium aluminate by the solid-state synthesis means that tricalcium aluminate is produced directly from solid materials without the use of liquid solvents. This method is often used to produce large quantities of tricalcium aluminate and to achieve high purity and quality of the final product. Solid synthesis is carried out using a mixture of

calcium oxide (CaO) and aluminium oxide (Al_2O_3) in a molar ratio of 3:1, which is then calcined at a temperature of around 1 100–1 200 °C for 2–3 hours. This process leads to the formation of tricalcium aluminate in crystalline form [3, 4].

Coprecipitation is a process in which two or more elements or compounds are precipitated as a solid crystal under specific conditions such as temperature and pH. In addition, C_3A and cement mixtures containing C_3A can be modified by the addition of various additives such as calcium oxide (CaO), silicates or carbonates. These additives can alter the properties of the cement, such as hydration (i.e. the reaction of the cement with water), setting, strength and resistance to chemicals. Modifications to C_3A and cement mixtures can also be made by various processes, such as changing the temperature or pressure during manufacture [5]. This topic is very relevant lately 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.

2. MATERIAL AND METHODS

To produce cubic tricalcium aluminate, calcium carbonate (p.a. purity, 99.7 %) and aluminium oxide (p.a. purity 99.5 %) were used in an amount corresponding to the molar ratio of C_3A or 3 moles of CaO and 1 mole of Al_2O_3 , see Table 1 (Chemical composition of the raw material mixture).

The homogenisation of the raw materials was carried out by high-speed milling in a laboratory planetary mill Frisch Pulverisette 6. Distilled water was added to the raw material mixture at a powder/water ratio of 0.8. Two distinct grinding capsules made of different materials were chosen. First half of the raw material powder was homogenized in a steel-bodied capsule with 25 steel milling bodies for 15 minutes at 500 rpm.

The second half of the raw material powder was homogenized in a corundum capsule with 25 corundum milling bodies for 30 minutes at 350 rpm. The reason for the choice of two different materials is possible iron contamination during abrasion of the grinding capsule and the ground material. However, it was also checked if grinding in a corundum capsule achieve the desired degree of comminution as a steel capsule. Possible iron contamination will be verified by XRF analysis. The degree of comminution of the raw meal will be verified by laser granulometry by Malvern Paralytical Mastersizer 2000. After milling, the raw material powder was left to dry into nodules 10–15 mm in diameter were formed spontaneously in a laboratory dryer at 105 °C for 24 hours. In the next step, a series of two-phase sintering's were carried out from both prepared raw material flours. In the first stage of sintering, calcination occurs at 900 °C with soaking time of 60 minutes. In the second sintering stage, the

actual solid phase synthesis takes place. The sintering temperatures were chosen in the range in range between 1 200–1 450 °C. The purity of the prepared products was verified by X-ray analysis.

	CaCO_3	Al_2O_3	H_2O
C_3A cubic	111.124	37.736	120.000
	Ca/Al=1.500		H ₂ O/ C_3A =0.8

TABLE 1. Chemical composition of the raw material mixture in grams and relevant ratios.

3. RESULTS AND DISCUSSION

XRF analysis of the raw material powders was carried out due to possible iron contamination during milling in the steel capsule. According to the results, it can be seen that the iron contamination is minimal, specifically 0.21 %. The complete results are shown in Table 2.

The results of the laser granulometry, which was performed after the XRF evaluation see Figure 1, show that the particle size distribution of the powder milled in the steel capsule for 15 minutes and in the corundum capsule for 30 minutes is almost identical. However, the steel capsule ground meal has a higher particle size distribution in the range of 10 to 100 μm .

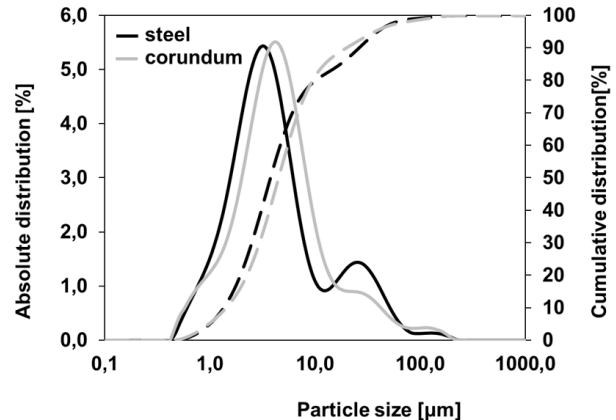
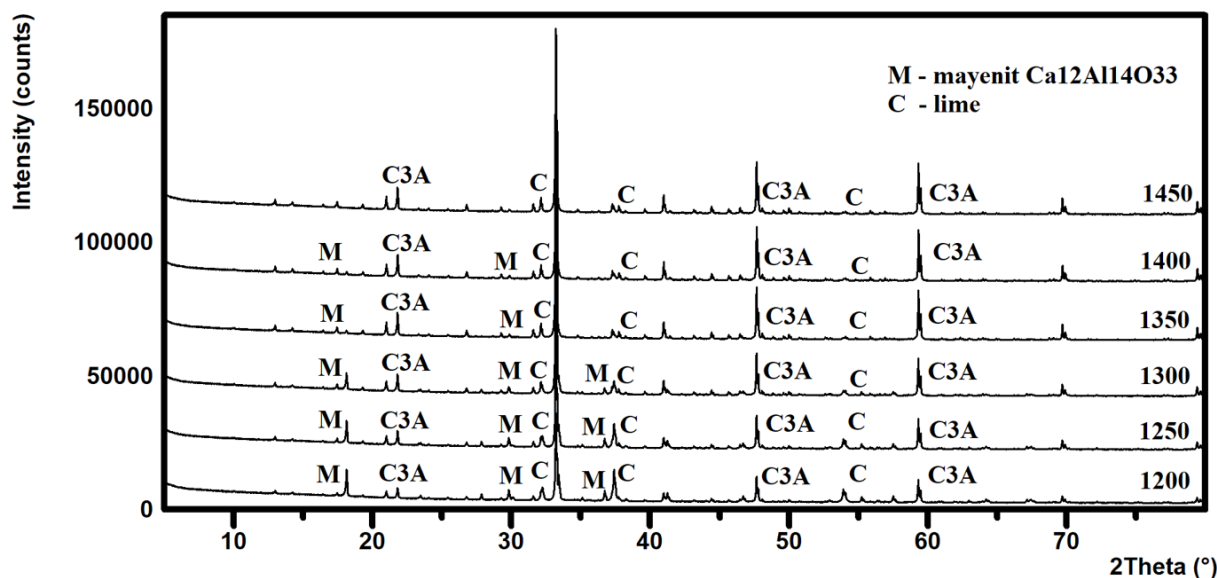


FIGURE 1. Particle size distribution (PSD) of raw material mixture after milling in Pulverisette 6.

The evaluation of the samples by XRD analysis, which were milling in a steel and corundum capsule and underwent a two-phase sintering first at 900 °C with a soaking time of 60 min. The samples were then subjected to a second sintering at 1 200, 1 250, 1 300, 1 350, 1 400 and 1 450 °C. From the diffractograms, increasing the firing temperature influences the formation of C_3A . As shown in the detail images, with increasing temperature the intensity at $18.1^\circ 2\theta$ angle decreases indicating the decrease of the mineral mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (M) and the intensity increase of the peak at $17.4^\circ 2\theta$ indicating an increase in the amount of C_3A mineral.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O ₃	K ₂ O	SO ₃	TiO ₂	MnO	Sum.
steel	0.0	36.522	0.21	63.268	0.0	0.0	0.0	0.0	0.0	0.0	100.0
corundum	0.0	37.109	0.0	62.891	0.0	0.0	0.0	0.0	0.0	0.0	100.0

TABLE 2. XRF analysis: chemical composition of raw material mixture after milling.

FIGURE 2. XRD analysis of C₃A (steel capsule).

The X-ray diffraction patterns show that the purest C₃A was formed at 1450 °C, however, the lime CaO and the mineral mayenite are still present in the sample; the inability of these components to react is probably due to insufficient comminution of the corundum component of the raw material. The mineral mayenite is more evident on samples milled in a corundum grinding capsule.

Quantification by the Rietveld method was performed in HighScore Plus version 3.0.5. Table 3 and Table 4 show the results of the first batch of sintered samples.

The Rietveld method confirmed that C₃A reaches the highest purity at 1450 °C, however, as already known from Figure 2 and Figure 3 of the XRD analysis, mayenite and free lime are also present in the samples. These partially reacted minerals are found in greater quantities in the samples that were milled in the corundum capsule. This is likely due to the slight iron contamination proven above by XRF analysis, this iron contamination in this case acting as a melting medium that helped to react the remaining mayenite.

Managed to demonstrate that the difference in results when grinding in a corundum and steel capsule is minimal, as iron contamination is only 0.21 %.

Furthermore, it was found that during the preparation of cubic C₃A, the purity of this mineral increases with the firing temperature, the highest purity was achieved by the mineral C₃A at 1450 °C in the sample

	C ₃ A	Ca ₁₂ Al ₁₄ O ₃₃	CaO	Al ₂ O ₃
1200 °C	55.4	24.2	19.3	1.1
1250 °C	66.5	19.3	13.2	1.0
1300 °C	78.3	13.9	7.3	0.5
1350 °C	95.5	1.5	2.6	0.4
1400 °C	94.4	2.4	3.1	0.0
1450 °C	97.6	0.0	2.4	0.0

TABLE 3. Rietveld analysis: mineral composition (steel capsule).

	C ₃ A	Ca ₁₂ Al ₁₄ O ₃₃	CaO	Al ₂ O ₃
1200 °C	49.2	31.4	18	1.4
1250 °C	59.3	26.6	12.6	1.5
1300 °C	71.3	20.4	7.9	0.4
1350 °C	94.8	3.6	1.2	0.4
1400 °C	94.5	3.4	1.6	0.5
1450 °C	93.6	2.2	3.8	0.4

TABLE 4. Rietveld analysis: mineral composition (corundum capsule).

that was ground in a steel capsule. Here, iron as a flux most likely helped to achieve a C₃A purity of 97.6 % according to the Rietveld method.

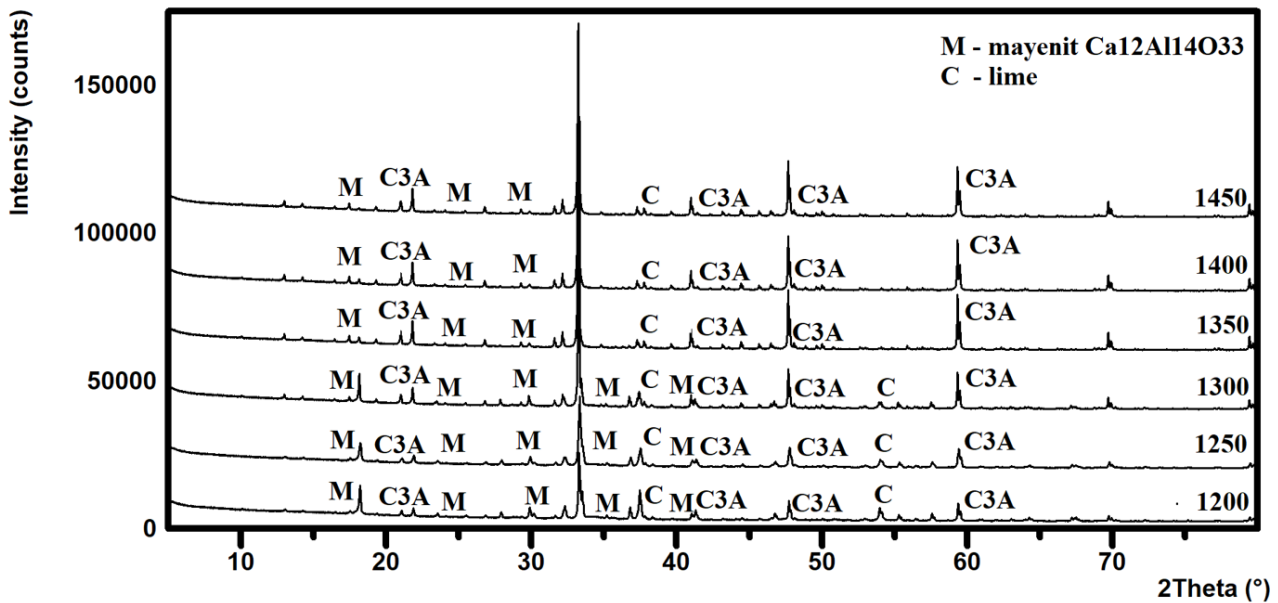


FIGURE 3. XRD analysis of C₃A (corundum capsule).

4. CONCLUSION

- Laser granulometry results showed similar comminution of the raw material in both cases of grinding.
- Iron contamination based on XRF analysis was minimal at only 0.21 %.
- The highest purity of 97.6 % C₃A was achieved at a temperature of 1 450 °C when grinding in a steel capsule, with 2.4 % representing unreacted lime.
- Grinding in a corundum capsule resulted in a purity of 93.6 %, with a residue of the mineral mayenite of 2.2 % and lime of 3.8 %. This may be attributed to insufficient comminution in the corundum capsule.
- Slight iron contamination during grinding had a positive effect on purity, as iron acted as a flux, improving the reaction of the mineral mayenite.

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