Preparation of triclinic alite with short soakings in a small experimental high-temperature furnace

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Abstract. The article deals with a laboratory preparation of triclinic modification of clinker mineral tricalcium silicate. A substantial part of the article is devoted to the technology and technique of firing a sample of tricalcium silicate, which would in the future allow the study of the development of the crystal lattice structure of this clinker mineral at short isothermal durations, in the order of minutes. As part of the research, a small high-temperature experimental furnace was designed and constructed. Based on the results, we can express the suitability and applicability of this furnace for the study of the formation of triclinic tricalcium silicate at short soakings.

1. Introduction

The current main problem of the industrial cement productions is the variability of their mineralogical composition. This depends on the presence of impurities from the raw materials or fuel and the firing process. The process of synthesis of clinker minerals becomes a decisive factor that determines their subsequent behaviour in industrially produced cements. To characterize and possibly influence the variability of the mineralogical composition of clinker, it is necessary to study the influence of various polymorphs of clinker minerals on the properties of industrially produced clinkers, especially from a chemical and structural point of view [1-3].

In general, more than twenty minerals can be identified in clinker, but only four of them are considered important, namely tricalcium silicate (C_3S, alite), dicalcium silicate (C_2S, belite), tricalcium aluminate (C_3A) and tetra calcium aluminate ferrite (C_4AF). Due to their characteristic properties, each of these minerals influences the specific properties of individual cements. Except for C_4AF, all major clinker minerals show strong polymorphism [4-5].

Most of the standard methods used for laboratory preparation of clinker minerals are relatively time consuming. The composition of the raw material mixture and the setting of the combustion parameters are among the main factors that determine the final composition of the clinker.

The article deals with the study of the course of triclinic alite formation during short soakings. The aim is to assess the suitability of the proposed small experimental high-temperature furnace and its applicability for this purpose.

2. Materials and methods

Two raw materials in chemical purity p.a. were used to prepare triclinic alite, namely calcium carbonate (p.a. 99.0%, Penta) and silica (99.9%, Lachner). The raw materials were dosed in an amount corresponding to the molar ratio for alite in the percentages of 73.6% CaO and 26.3% SiO_2.

The raw material mixture was homogenized by wet milling in the presence of water in a PULVERISETTE 6 planetary mill at a milling speed of 500 rpm for 30 minutes. A 500 ml grinding capsule with 25 pieces of agate grinding balls with a diameter of 20 mm was used.

The wet milling slurry was then dried in a Binder C 170 laboratory oven at 105 °C for 24 hours. The material thus prepared was used to produce tablets for the alite firing itself.

2.1. Preparation of tablets

Samples for firing were prepared from powdered raw material mixture, which was compressed into a cylindrical hole, from which, after compression, cylindrical tablets with a hollow centre were made. This hollow centre serves for hanging the sample on the weld of a thermocouple used to insert the tablet into the furnace.

A custom-made compression mold was used to prepare the tablets, see figure 1a. The mold with a shaped piston was made of hardened steel and ground with high precision to prevent it from seizing up and losing weight. This allows for accurate weighing. By pushing the material to the stop, a constant bulk density of the molding was maintained.

The bulk density of the tablet mentioned in literature [7] is 1.8 g/cm^3 based on which the weight to produce the tablet has been optimized. The production of the tablet itself took place by means of a compression roller using oil and graphite, which was then placed in a hand press, where compression was performed to a constant volume of the tablet.

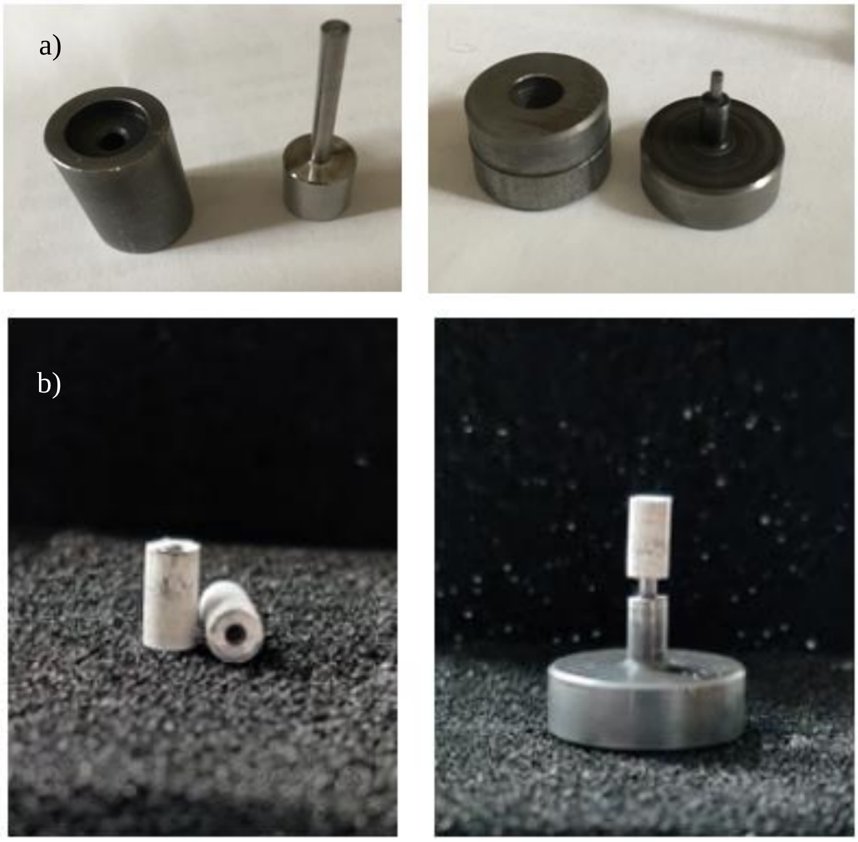


Figure 1. a) tablet mold; b) made tablet for firing.

2.2. Firing

The firing took place in an electric resistance furnace with a manipulator, which is suitable for firing substances in which reactions take place in the solid phase or with only a partial proportion of the melt. The firing cycle is fully automated, which guarantees high reproducibility of heat treatment and precise adherence to firing parameters.

The sample was placed in a well in the oven cap when the selected oven temperature was reached and stabilized. Then the soaking time of the sample in the furnace was set on the control unit panel. The ejection of the thermocouple weld with a small sample hole occurs after one turn of the crank.

The thermocouple lifted the sample and the cap opened. The closure of the cap occurs after the return of the thermocouple with the sample to the centre of the heating zone of the furnace. After the firing time has elapsed, the shutter opened, and the sample is ejected on the thermocouple to the upper position. After ejection, the cap is closed and the thermocouple leaves the sample in the cap well, where air flows from the fan.

The tablets prepared by an optimized method were subjected to firing in an experimental furnace at a temperature of 1500 °C and with soaking times calculated from the insertion of the sample into the oven at 5, 10, 15 and 20 minutes, with addition of 60 s to warm up the sample.

The XRD analysis was performed with a multifunctional diffractometer XRD Empyrean PANanalytical with Cu anode; Kα was used as the radiation source with para meters of 5° to 90° with a scan-step of 0.01°. The ICSD database (released 2012) was used to qualitatively analyse the diffraction patterns. HighScore plus software was used to identify the individual phases.

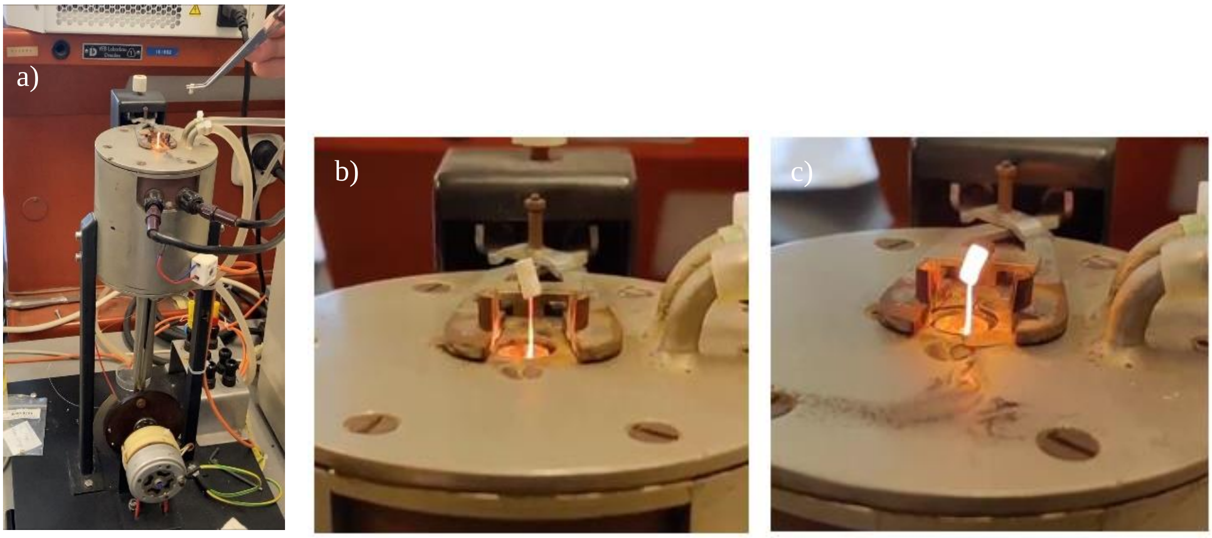


Figure 2. a) high-temperature furnace with manipulator; b) tablet before firing; c) tablet after firing.

3. Results and discussion

The article deals with the study of the progress of alite formation during short soaking times. The aim of this article is to assess the suitability of the proposed small experimental high-temperature furnace and its applicability for this purpose.

3.1. Preparation of tablets

For the first sample preparation, the value of bulk density was taken from the literature, namely 1.8 g/cm^3. The weight of the batch was calculated to be 58 mg. The pouring into the press roller took place at once and the sample was compacted. The pressed tablet could not be removed without damage. Compaction occurred only in the upper part the lower part disintegrated during handling.

Subsequently, the optimization took place in steps. The weight of the batch and bulk density were increased. The individual weights for the samples are given in table 1.

For sample no. 2, the weighing was optimized, the pressing rod and the inner part of the roller were rubbed with oil to prevent the sample from sticking and so that there was no problem during removal. The filling process was optimized and divided into 3rd phases; each poured layer was compacted with a pressing rod. After filling and pressing, the sample was not strong enough, the lower part disintegrated during gentle handling and the batch was glued to the walls of the pressing device.

After further optimization, sample no. 3, the weight and the method of sample separation were increased. The press roller and rod were coated with a combination of oil and hard graphite. The batch was poured in the same way as previous.

Finally, the whole procedure was optimized as follows. The amount of sample was weighed to 73 mg. The material was ground, without additional compaction, and soft graphite was applied to the press. This sample was sufficiently strong and did not disintegrate during handling. With such a procedure, it was possible to repeatedly form 30 pellets without breaking them, see figure 1.

Table 1. Density and weight of individual samples when optimizing tablets for firing.

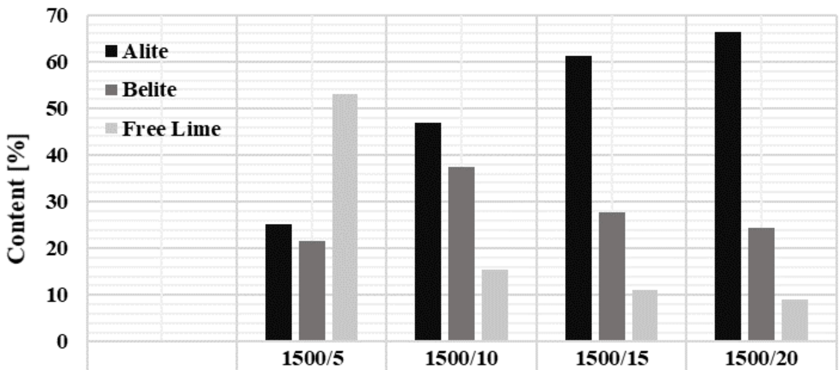
Sample no.	Weight [mg]	Bulk density [g/cm3]	Result
1	58	1.878	x
2	65	2.034	x
3	70	2.191	x
4	75	2.347	x
5	73	2.285	✓

Weighing 73 mg ($CaCO_3$, SiO_2) for an assumed density of 2.285 g/cm^3. Separating agent soft graphite in combination with oil. Filling process continuously, slowly with simultaneous cellaring, pressing to constant volume to the stop.

3.2. Firing

The prepared tablets were fired in an experimental furnace at a temperature of 1500 °C and soaking times of 5, 10, 15 and 20 minutes. The proposed tablet, prepared by an optimized method, has been shown to be reliable and works very well for firing in a small experimental high-temperature furnace. The manipulator in the oven repeatedly picks it up, inserts it into the furnace and pushes it back out. The tablet does not disintegrate during insertion, firing and removal from the furnace and does not tend to explode or crack.

By XRD analysis using the Rietveld quantitative method, in addition to the main mineral alite, mineral residues such as free lime and belite were also identified in the fired samples, see Fig. 3.



	1500/5	1500/10	1500/15	1500/20
■ Alite	25.29	46.92	61.32	66.43
■ Belite	21.59	37.53	27.63	24.4
■ Free Lime	53.12	15.55	11.04	9.17

Temperature/soaking

Figure 3. Graphical representation of the mineral content during firing.

Based on the results, we can observe an increase in the alite mineral content with increasing firing time. After 5 minutes the alite content in the formula is 25.29%, while after 20 minutes its content increases to 66.43%. With increasing firing time and the related increasing alite content, the free lime content gradually decreases, from 53.12% after 5 minutes to 9.17% after 20 minutes of firing. This is due to the saturation of the mineral belite and its gradual conversion to alite. This is illustrated by the decreasing content of belite, which is gradually transformed into alite, which is confirmed by the results of optical phase analysis, see figure 4.

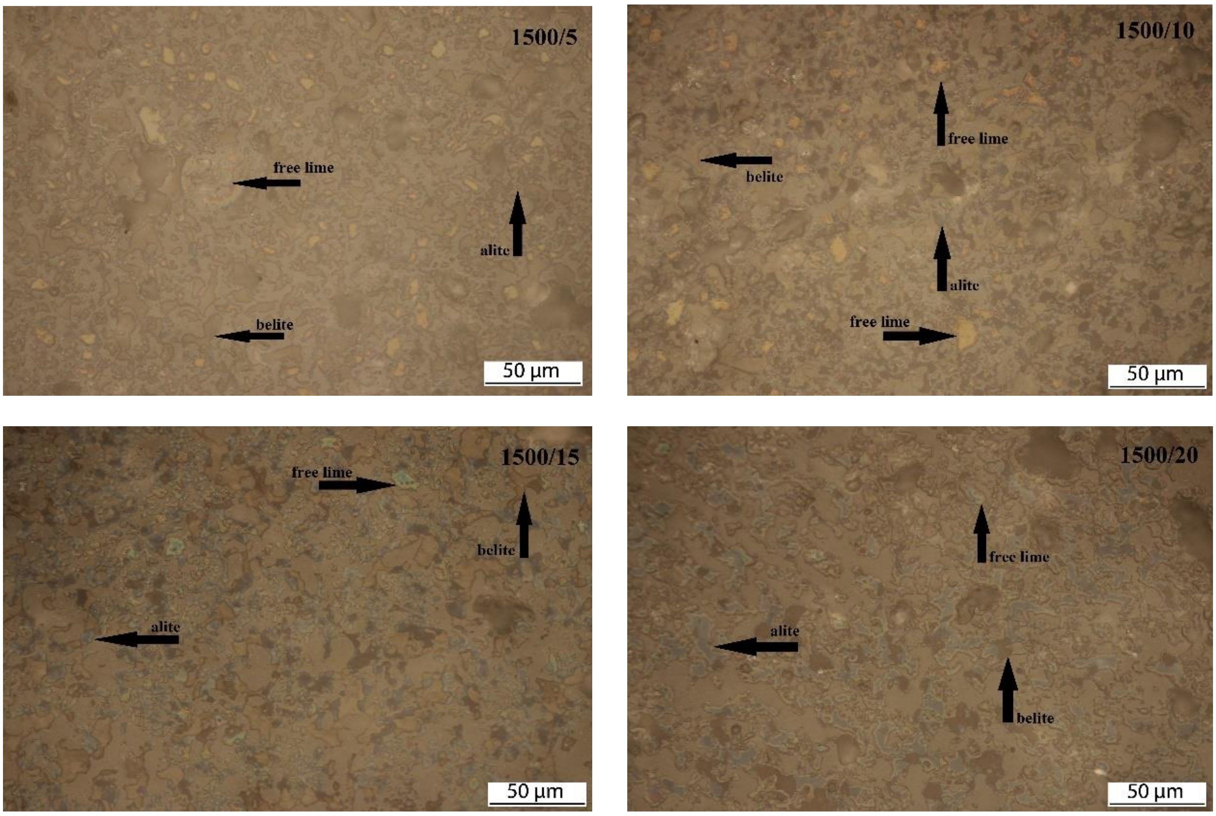


Figure 4. Optical phase analysis.

After only 5 minutes of firing, we can observe small nuclei of alite in the images from the optical phase analysis. As the alite crystals grow, the belite content disappears and the free lime content gradually decreases.

4. Conclusion

The article deals with laboratory preparation of triclinic modification of clinker mineral tricalcium silicate. A substantial part of the article is devoted to the technology and technique of firing tricalcium silicate at short soaking times. A furnace that requires special sample preparation was selected and designed. Therefore, a tablet preparation procedure was designed and optimized, making it possible to repeatedly prepare identical tablets with precise parameters for this type of oven. The resulting tablet weight was 73 mg at a density of 2.285 g/cm^3, which was compressed to a constant volume using an oil and graphite compression roller and a hand press. The firing of the tablet in a furnace with a manipulator using short firing times took place under identical conditions and the obtained results show that all processes take place very quickly. The used furnace with a manipulator is therefore suitable and usable for the study of the course of triclinic alite formation at short soaking times.

5. References

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