



Formation and hydration of C_3S prepared by microwave and conventional sintering

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Abstract

A microwave sintering method was used to prepare C_3S from precipitated $CaCO_3$, Ludox (SiO_2), and $Al(OH)_3$ or Fe_2O_3 . Brunauer-Emmett-Teller (BET), X-ray diffraction, scanning electron microscopy, and calorimetry were used to characterize the sintered samples. The results indicate that heating rate played a very important role in C_3S formation in conventional sintering. Microwave sintering resulted in improved formation of C_3S compared to conventional sintering, even at the same heating rates. After sintering at $1500^\circ C$ samples prepared using microwaves were still porous, with a specific surface area of about $0.4\text{ m}^2/\text{g}$. Microwave formation of C_3S was achieved at temperatures as low as $1350^\circ C$ when using Al_2O_3 additions. The use of Fe_2O_3 as an additive was not as effective in promoting C_3S formation as expected. Microwave effects on sintering as well as the sintering setup are also discussed in this paper. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Microwave sintering; Tricalcium silicate; X-ray diffraction; Calorimetry

1. Introduction

In 1983, Quéméneur, et al. reported the feasibility of using microwaves to process Portland cement clinker [1]. In recent years others have reported the use of microwave clinkering [2–4] to form a variety of cements. In the Portland cement clinker system there are many components that are helpful to C_3S formation because the melt phase occurs at high temperature, promoting ion diffusion. The microwave energy absorptions [5] of the pure oxides of the elements that make up Portland cement clinker have been characterized. However, the behavior of complex systems such as those found in cement clinkering especially involving solid-state reactions is less well characterized. Conventional preparation of C_3S requires a high sintering temperature and long holding time [6] due to the low ion diffusion rates for solid-state reactions. The goal of the study described here was to lower the required sintering temperature and to reduce the holding time.

Typically using a multimode microwave cavity for sintering causes problems with unstable temperature measurement due to energy discharges, as well as the nonuniformity in sintering due to localized heating. In our work, we have attempted to make some improvements in these areas.

2. Methods

2.1. Starting materials

Precipitated $CaCO_3$ and colloidal SiO_2 (Ludox, $SiO_2 = 40\%$) were used for C_3S production. $Al(OH)_3$ and Fe_2O_3 were used in small amounts. On an as-sintered basis the additives were used as follows:

No. 1 series: $Al_2O_3 = 0.85\%$

No. 2 series: $Al_2O_3 = 0.5, 1.0, 1.5, \text{ and } 2.0\%$

No. 3 series: $Fe_2O_3 = 0.5, 1.0, 1.5, \text{ and } 2.0\%$

2.2. Sample preparation

The starting materials were put into a plastic beaker and hand-mixed for about 20 min. The doughy mixture then was put into a foil container, vibrated, and then dried at $105^\circ C$ for ~ 4 h. The dried “cake” was cut into the desired dimensions.

2.3. Microwave and conventional sintering setup

The microwave sintering setup has been described elsewhere [2]. A high heating rate electrical furnace was used to obtain average heating rates of 41 to $56^\circ C/\text{min}$. A general purpose electrical furnace was also used for conventional sintering at an average heating rate of $\sim 8^\circ C/\text{min}$. A type S thermocouple wrapped with platinum foil and well grounded was used to monitor the temperature in the microwave chamber. The holding time at maximum temperature was 10 min for all samples.

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Conventional cement notation is used throughout.

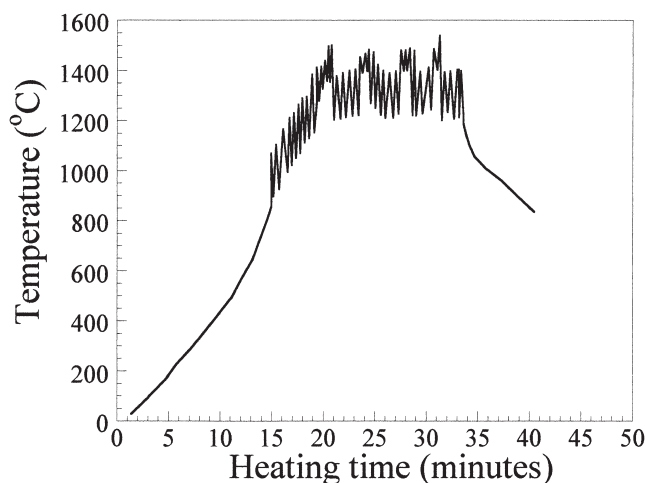


Fig. 1. Temperature curve in discharge.

3. Results and discussion

3.1. Microwave sintering process improvements

Discharge is often encountered when sintering in a multi-mode cavity. The effect of the discharge phenomenon on temperature measurement when using a thermocouple is illustrated in Fig. 1, which shows that the discharge causes the thermocouple readout to fluctuate. When discharge is severe, it causes damage to the sintering packet and thermocouple. In order to overcome this problem the following steps must be taken:

1. Optimize the mass of the sample [7].
2. Expose the sample directly to the microwave field (no crucible).
3. Carefully align the sintering packet (and sample) along the vertical axis of the microwave cavity.
4. Ground the thermocouple.
5. Optimize the heating rate.

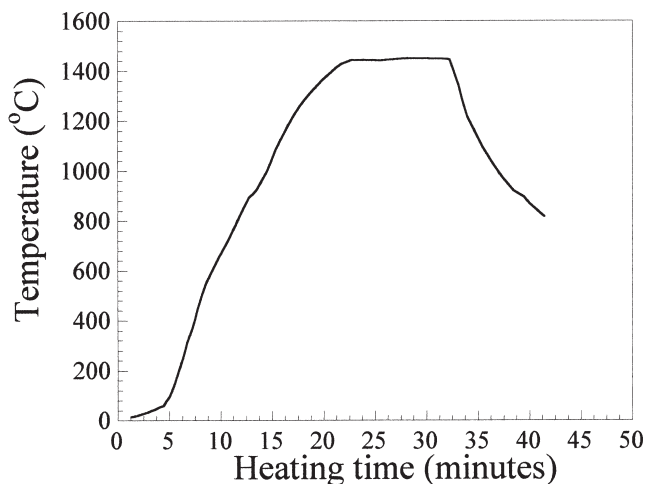


Fig. 2. Improved temperature curve.

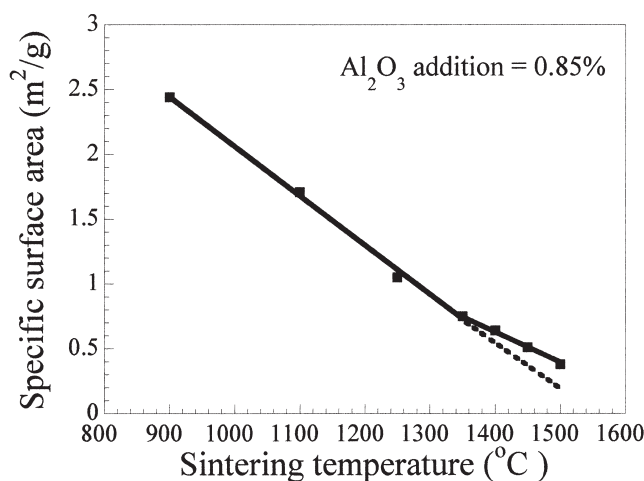


Fig. 3. No. 1 series surface area development with sintering temperature.

With the above measures the discharge was eliminated, as shown by the improved sintering temperature curve in Fig. 2.

3.2. Sintered surface area development

A MonoSorb Surface Area Analyzer (model MS-12, a product of Quantachrome, Boynton Beach, FL, USA) was used for Brunauer-Emmett-Teller (BET) surface area measurements.

Fig. 3 shows the surface area development in the first series (0.85% Al_2O_3 addition). The change in BET surface area was apparently linear with increasing temperature up to 1350°C. In the system C_3S - C_2S - C_3A , the lowest temperature at which a liquid can be expected to form is 1455°C. When the liquid forms, the surface area should decrease quickly. There was no noticeable change due to the formation of liquid observed in our samples, suggesting that the changes occurring were due to solid-state reactions. The samples were

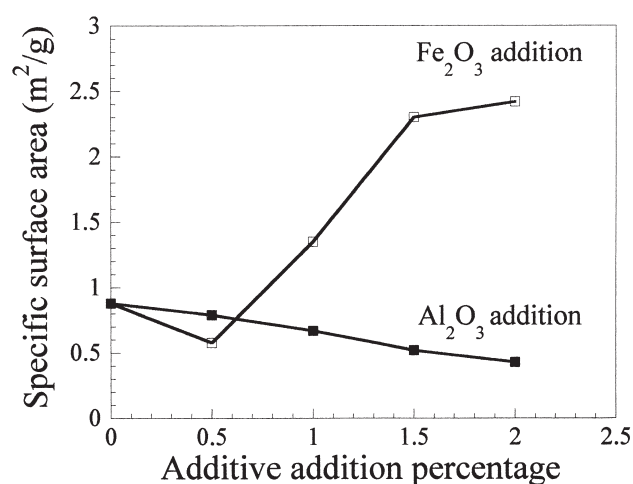


Fig. 4. No. 2 and 3 series surface area development with additive addition.

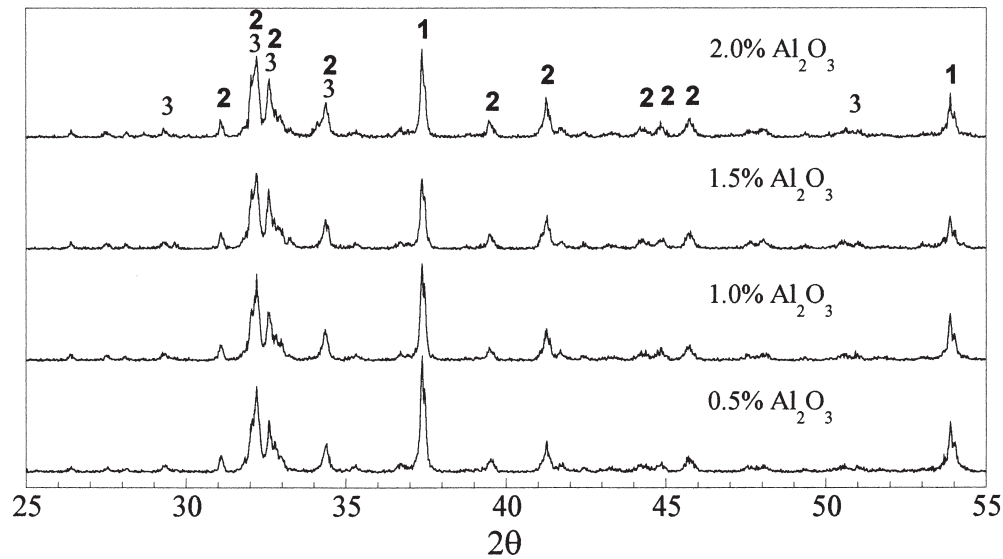


Fig. 5. Conventional, 1400°C (8°C/min). (3) C_3S , (2) β - C_2S , (1) CaO .

found to be porous even when sintered in microwave at 1500°C. The surface area was much higher (about 0.4 m²/g) than that of commercial clinker.

Fig. 4 shows the surface area development of No. 2 and 3 series of samples that were microwave sintered at 1350°C. As the content of Al_2O_3 was increased, the surface area decreased while the Fe_2O_3 addition had an opposite effect.

3.3. Phase composition

A Scintag PAD V diffractometer (Cupertino, CA, USA) in conjunction with a computerized calculation program was used for X-ray diffraction (XRD) phase characterization. $Cu K\alpha$, $\lambda = 1.54059 \text{ \AA}$ and a scanning rate of $2^\circ(2\theta)/$

min were applied. Sample size was controlled at 0.25 g to minimize sample-to-sample variations.

3.3.1. Conventional sintering

Fig. 5 shows the XRD patterns of No. 2 series of samples sintered with an average heating rate of 8°C/min. In this set of samples, only β - C_2S and CaO were detected. In the C_3S - C_2S - C_3A system the liquid phase appears only at a temperatures of 1455°C or higher, making it difficult to form C_3S at lower temperatures.

Fig. 6 and Fig. 7 show the XRD patterns of No. 2 series samples sintered conventionally at higher heating rates. In both situations C_3S formed. It should be noted that the heating rate was even more important than the final sintering

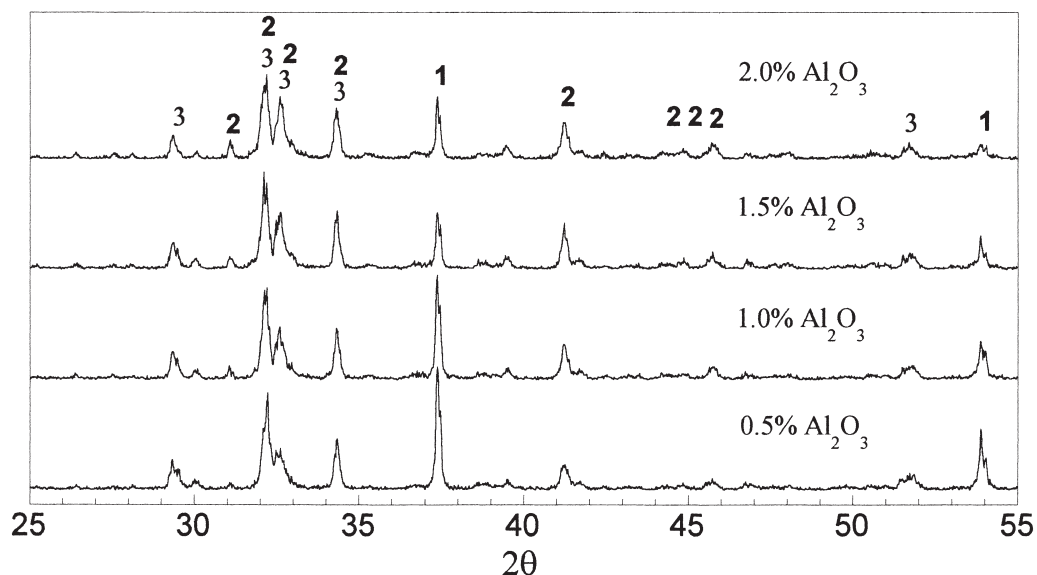


Fig. 6. Conventional, 1450°C (41°C/min). (3) C_3S , (2) β - C_2S , (1) CaO .

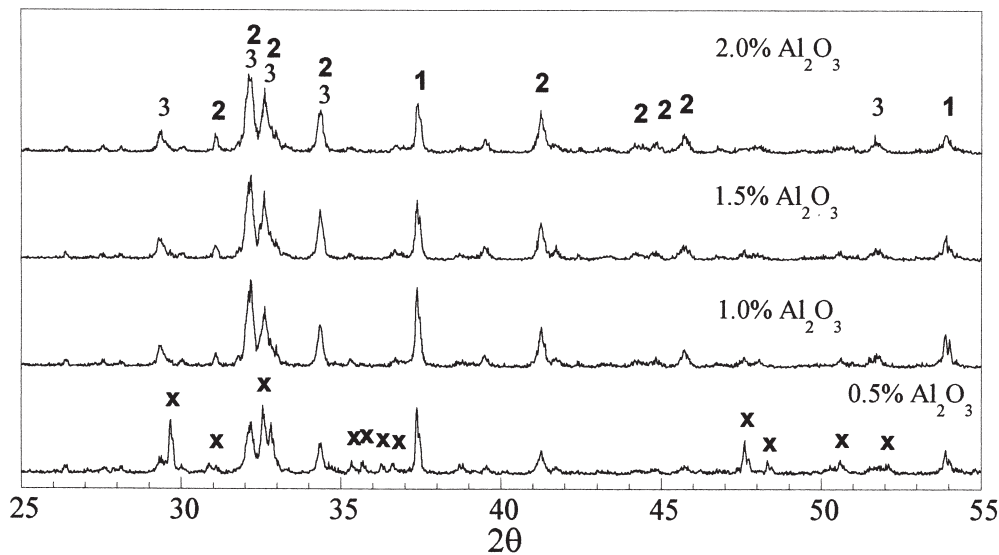


Fig. 7. Conventional, 1400°C (56°C/min). (3) C_3S , (2) β - C_2S , (1) CaO , (x) γ - C_2S .

temperature since the CaO content (intensity) was less at 56°C per minute (Fig. 7) than at 41°C per minute (Fig. 6). But with higher heating rate and lower additive addition ($Al_2O_3 = 0.50\%$), the sample had a higher surface area and β - C_2S changed to γ - C_2S as shown in Fig. 7 (bottom curve).

3.3.2. Microwave sintering

Figs. 8, 9, and 10 show the XRD patterns of No. 2 series of samples; when sintered at 1300°C the samples contained C_3S .

As the sintering temperature was raised, the CaO content was reduced, and C_3S content increased. But the dramatic

development occurred at 1350°C. It should be noted that even at 1300°C the microwave-sintered samples contained less CaO compared with samples conventionally sintered at 1400°C or higher, showing the advantage of microwave sintering. The other characteristic was that the identical peak of C_3S ($d = 3.04 \text{ \AA}$) was widened, indicating C_3S amorphous structure. Its morphological observation by scanning electron microscopy is shown in Fig. 11.

The XRD patterns of No. 3 series of samples (containing Fe_2O_3) are shown in Fig. 12. The CaO content in these samples was higher than that with Al_2O_3 addition except for the 2.0% Fe_2O_3 addition.

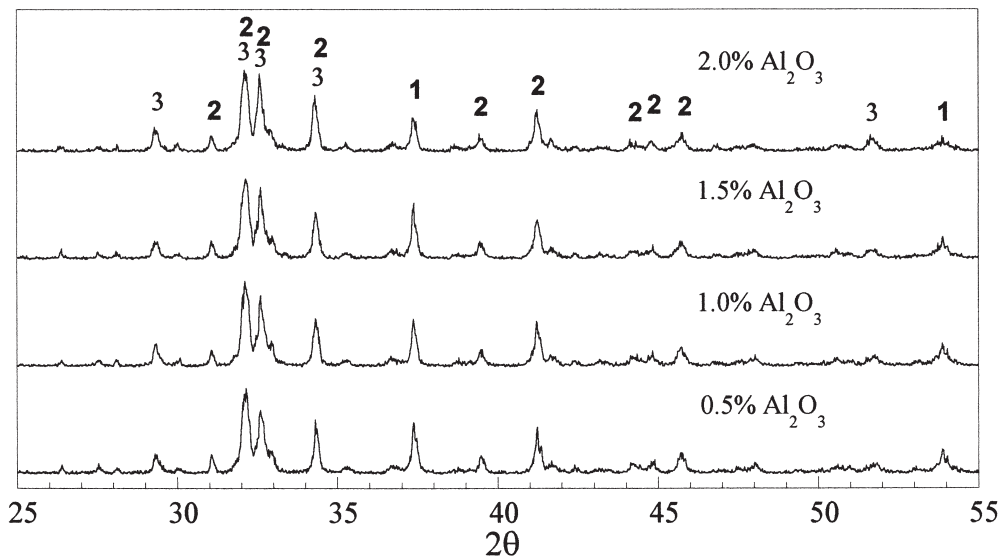


Fig. 8. Microwave, 1300°C. (3) C_3S , (2) β - C_2S , (1) CaO .

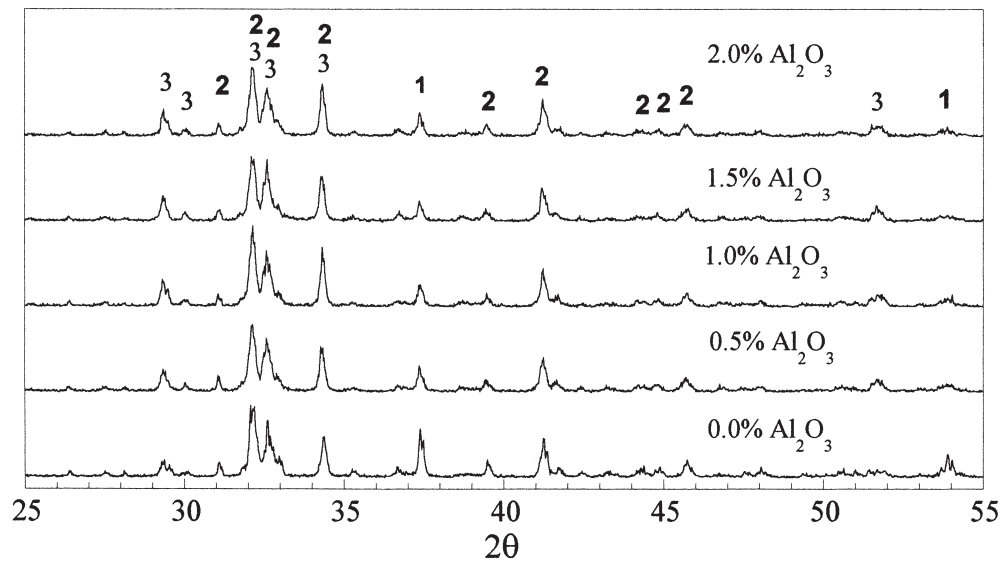


Fig. 9. Microwave, 1350°C. (3) C_3S , (2) β - C_2S , (1) CaO .

3.4. Calorimetry

A Thermochemical SEC calorimeter (model SEC c12-45-2E, with a refrigerated bath and circulator) was used for calorimetry experiments. All samples for calorimetry were passed through a No. 325 sieve and used a water/cement ratio = 1.00. The hydration temperature was 25°C.

Fig. 13 shows hydration heat evolution of C_3S conventionally and microwave sintered at 1400°C or higher. It is obvious that microwave-sintered C_3S showed a shorter induction period in early hydration while maintaining the same total heat evolution. This demonstrated that microwave-prepared C_3S containing Al_2O_3 had higher hydraulic reactivity. On the other hand, microwave-prepared C_3S containing Fe_2O_3 showed a rather long induction period and

less heat evolution during early hydration, as shown in Fig. 14, indicating the restriction of early hydration by the Fe_2O_3 additive.

4. Discussion

From conventional sintering results it has been shown that heating rate played a very important role in solid-state C_3S formation. With a low heating rate (8°C/min, which is common in many laboratories throughout the world) C_3S is difficult to form in solid-state reaction. As the heating rate is increased, raw mix components' decomposition or phase transformation overlapped with product formation, which may be called "thermal activation": the newly formed, im-

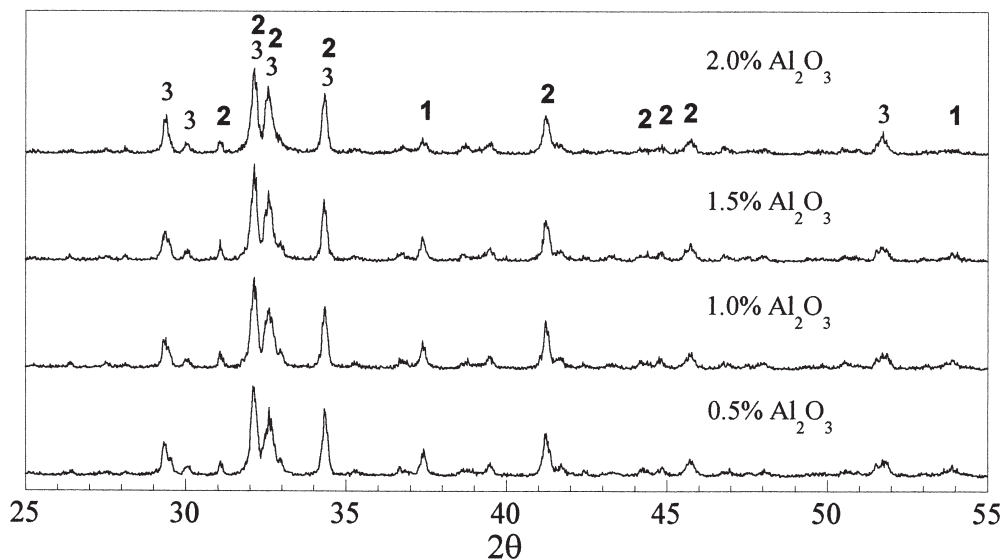


Fig. 10. Microwave, 1400°C. (3) C_3S , (2) β - C_2S , (1) CaO .

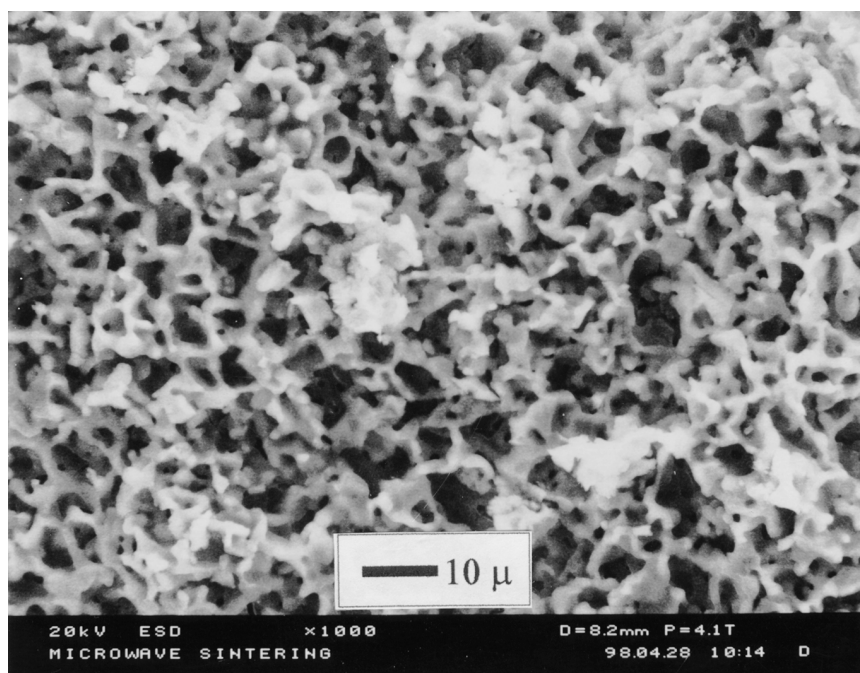


Fig. 11. Microwave, 1400°C. $\text{Al}_2\text{O}_3 = 2.0\%$.

perfect structure reactants take part in reaction quickly, leading to easy occurrence of solid-state reaction.

It is clear that the microwave generates rapid sintering. Besides this, a microwave processing has still other advantages, which greatly facilitate C_3S formation in solid-state reaction. The following are some of the features.

4.1. Volumetric (bulk) heating

Microwave can penetrate into the sample and heat is generated throughout the whole sample. Therefore microwave sintering is less dependent on heat transfer than is conven-

tional sintering. The sample can be sintered more uniformly in a microwave field.

4.2. Selective heating

Microwave heating efficiency is closely related with the relative dielectric constant (ϵ_r') and loss tangent ($\tan \delta$) of the sample. The absorbed power can be expressed in the following Eq. (1) or Eq. (2) [7]:

$$P = 2\pi f \epsilon_0 \epsilon_r' \tan \delta |E|^2 \quad (1)$$

$$P \propto \epsilon_r' \tan \delta \quad (2)$$

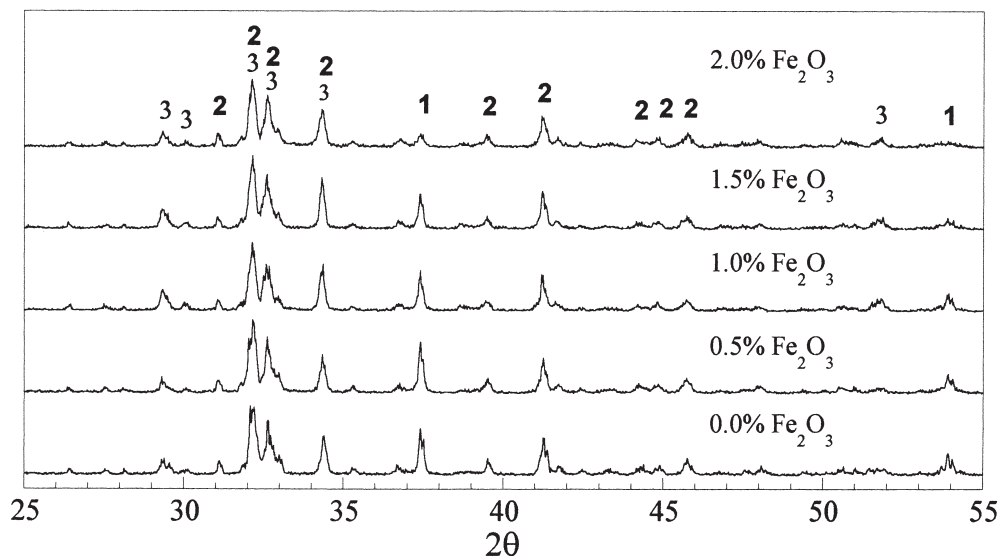


Fig. 12. Microwave, 1350°C. (3) C_3S , (2) $\beta\text{-C}_2\text{S}$, (1) CaO .

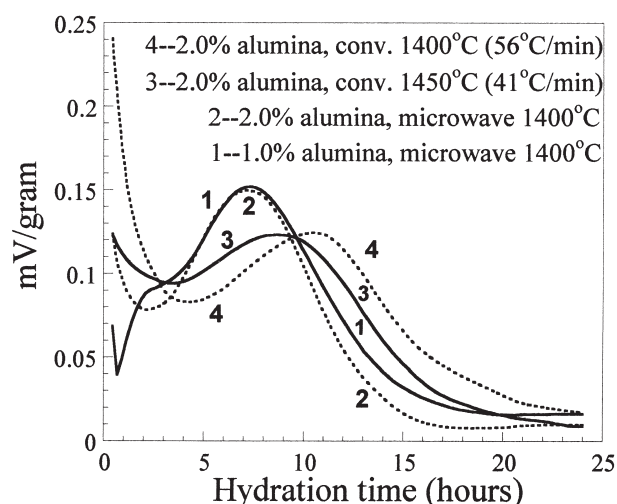


Fig. 13. Hydration heat evolution of samples sintered at 1400 and 1450°C.

Components with greater ϵ_r' and/or $\tan \delta$ will absorb more microwave energy. As the temperature rises, ϵ_r' and $\tan \delta$ can also become greater, eventually resulting in a phenomenon known as “thermal runaway.”

In cement raw mix system crystalline SiO_2 (quartz) is the most thermally inert component. It has been reported that SiO_2 was less microwave-energy receptive at lower temperature [5] and the $\tan \delta$ of SiO_2 increased greatly as the temperature rises above 1100°C [7]. It has also been reported that SiO_2 gels heat and melt quickly during microwave sintering [8].

4.3. Electric field effect

In solid-state reaction one of the most important factors affecting reaction rate is ion diffusion. In conventional sintering ion diffusion is less important due to the lack of a liquid phase. Microwaves are a high-frequency electric field with which ions interact, leading to the increase of ion diffusion and improving solid-state reaction.

In addition, as it has been shown, microwave-prepared C_3S with Al_2O_3 addition had a shorter induction period during early hydration, that is, the acceleration period of C_3S hydration occurred earlier than the conventionally sintered ones. It was reported that Al_2O_3 additions in C_3S led to higher hydraulic reactivity [9]. Therefore, the possible implication is that in a microwave field Al_2O_3 is more active and more of the Al_2O_3 is included in the C_3S structure, producing a more active alite as a sintered product.

5. Conclusion

1. Heating rate in conventional sintering had a very important role in solid-state formation of C_3S . With low heating rates C_3S was difficult to form even at 1400°C due to the absence of a liquid phase.
2. Microwave-sintered C_3S containing Al_2O_3 had been formed at temperatures as low as 1300°C, and was the major component by 1350°C. Advantages of micro-

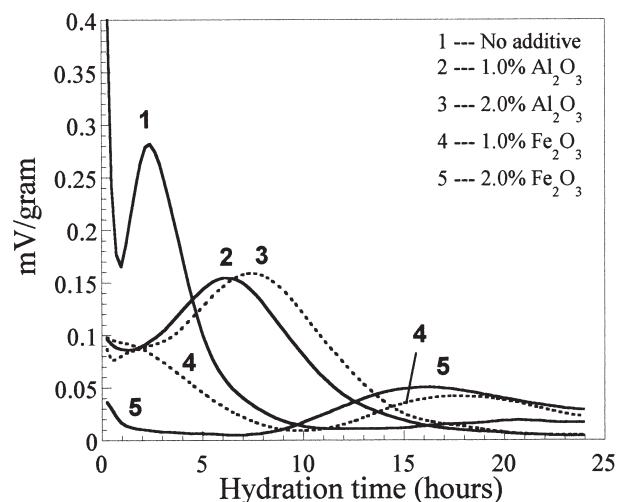


Fig. 14. Hydration heat evolution of samples microwave sintered at 1350°C.

wave sintering promoted much of the C_3S formation via solid-state reaction.

3. Microwave-prepared C_3S containing Al_2O_3 showed a shorter induction period during early hydration, which may be due to the incorporation of Al_2O_3 into the C_3S structure.
4. The effect of Fe_2O_3 on C_3S formation was not as favorable as expected; C_3S containing Fe_2O_3 had longer induction periods and lower heat evolution during early hydration.

Acknowledgments

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