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MICROWAVE CLINKERING OF ORDINARY AND COLORED PORTLAND CEMENTS

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ABSTRACT

Regular and colored cement clinkers were prepared by microwave processing at 2.45 GHz. Microwave enhancement in clinker reaction was observed. The preliminary results show that microwave processing can lower the clinkering temperature by about 100°C compared to the samples processed in a fast-heating electric furnace.

Introduction

Microwave heating of ceramics goes back to the post WW II era when old radar equipment was used for drying large whiteware. Early work on the use of microwave sintering was concentrated on dark ceramics, especially magnetic materials as discussed in the review by Sutton. (1) Extraordinarily rapid heating and high temperatures were reported by Haas et al. (2) in urania gels. The first report on the same effects, including thermal runaway, in white ceramics (specially Al_2O_3 and silica) was reported by Roy, Komarneni, and Yang.(3) Subsequent to this, starting in about 1990 a wide range of symposia have brought together an enormous variety of papers on the practice and theory of microwave sintering of white ceramics. These are reported in several proceedings volumes starting in 1988.(4) So far the value of microwave sintering of white ceramics in these papers has principally been demonstrated in speed (by one to two orders of magnitude) and to a lesser extent in microstructure control and in total energy consumption (e.g., for Al_2O_3 by Cheng et al. (5)). Yet no major innovation has demonstrated the use of microwave heating. While transparent Lucalox has been known for decades, only our own work on (hydr)oxyapatite (6) has led to transparent ceramics by microwave sintering.

Microwave processing of various ceramic materials has been reported. Microwave heating is a process of microwave-material interaction. The heating efficiency mainly depends on the dielectric properties of the materials to be heated. The first attempt of microwave processing of clinker was reported by Quemeneur et al.(7) Their experiment was done at 2.45 GHz in a grooved resonant applicator and the results showed that dielectric losses of the different constituents, at 1450°C, are sufficient to maintain the heating of the material and ensure the clinkering. The properties of the clinker thus prepared were close to those of an industrial cement. In the current study, we prepared regular clinker with a commercial Type I cement raw meal, and white and colored clinkers with laboratory chemical agents.

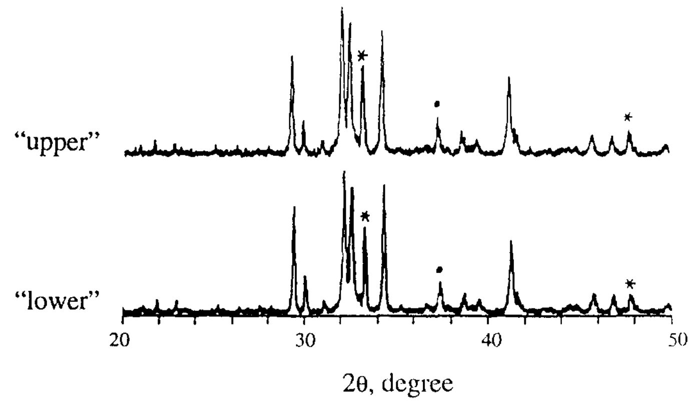

FIG. 1.
XRD patterns of two white cement samples used for temperature calibration. The microwave processing was carried out at 1400°C for 30 min. The marked peaks are (*) C_3A and (•) CaO. The unmarked peaks belong to C_3S with a small amount of β-C_2S.

Experimental

1. Starting Materials. For regular Portland cement, a black raw meal for Type I cement (Keystone Cement Company, PA) was used for clinkering. The chemical composition of this material, on an ignited wt.% basis, was CaO = 64.89, SiO_2 = 20.39, Al_2O_3 = 6.63, Fe_2O_3 = 2.6, MgO = 3.41, Na_2O = 0.46, K_2O = 0.82, P_2O_5 = 0.35, TiO_2 = 0.32, and MnO = 0.12. To obtain white cement, iron oxide should be avoided. The raw mixture was prepared with calcium carbonate ($CaCO_3$), Ludox silica sol, and boehmite (AlOOH). The phase composition of the product was designed as (wt.%) Ca_3SiO_5 (C_3S) = 70%, Ca_2SiO_4 (C_2S) = 15%, and $Ca_3Al_2O_6$ (C_3A) = 15%. Correspondingly, the weight ratio of the chemical composition was $CaCO_3/SiO_2$/AlOOH = 65.37/30.91/3.72. A small amount of CaF_2 (0.3 wt.%) was added to the mixture as a flux. The raw mixture was compacted at 35 MPa to circular pellets of 1.27 cm in diameter and about 0.5 cm in thickness.

Colored cements are usually obtained by adding appropriate pigmenting materials into white cement. Alternatively, one may directly add certain agents to the raw meal and produce colored clinkers. As a trial to obtain colored clinkers, a small amount (<1%) of either cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$, J.T. Baker Chemical Co., Phillipsburg, NJ] or chromium (III) 2,4-pentanedionate [$Cr(C_5H_7O_2)_3$, Alfa Products, Danvers, MA] was added to the raw mixture for coloring. It was expected that by firing the samples in a reducing atmosphere, cobalt oxide (CoO) would lead to a light blue, while chromium oxide would give a green color to the clinker.

2. Sintering Setup. Microwave sintering was conducted in a 900 W, 2.45 GHz multimode microwave cavity with a turntable to rotate a sintering packet in which the sample was loaded. The configuration of the sintering package in the cavity is illustrated elsewhere (8). The temperature of the specimen in the microwave field was monitored with an S type thermocouple. The alumina-sheathed thermocouple was shielded with platinum foil and properly grounded to the metallic wall of the microwave cavity. In this way, microwave interference to the thermal electromotive force of the thermocouple was completely prevented.

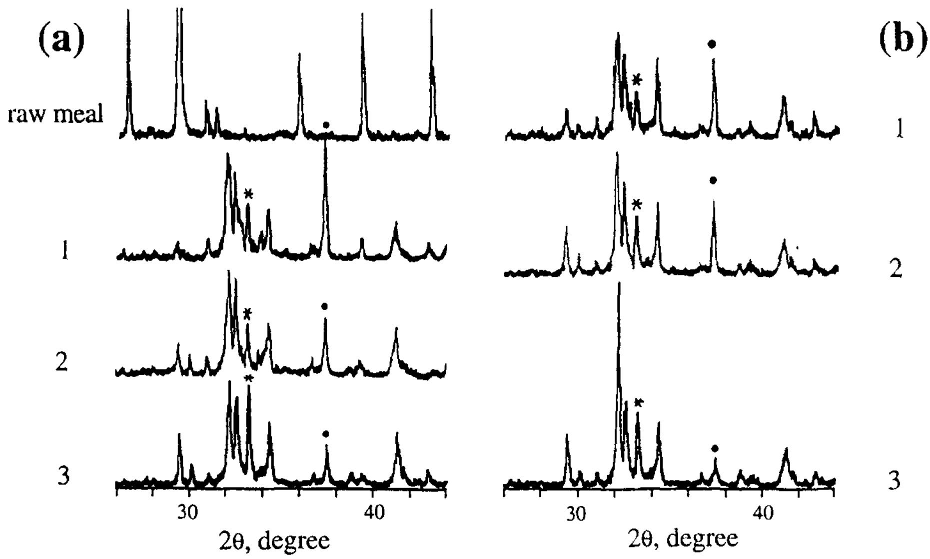

FIG. 2.
XRD patterns of Portland cement clinkers prepared by (a) conventional and (b) microwave processing at (1) 1300°C, (2) 1350°C, and (3) 1400°C, for 10 min. The marked peaks are (*) C_3A and (●) CaO. The unmarked peaks of the clinkers belong to C_3S with a small amount of β-C_2S. The raw meal shows patterns of calcite and quartz.

A specially designed fast-heating electric furnace, with $MoSi_2$ as heating elements, was used for conventional firing for comparison. The temperature of the sample in the conventional process was also measured with an S type thermocouple with the tip in contact with the bottom of the sample holder--a platinum crucible. The furnace can achieve similar heating rates as in the microwave heating. The sample can be heated to 1500°C within about 15 min.

3. Processing. Single-pellet sintering was adopted. The same heating schedules were used in both conventional and microwave processing. The samples of commercial raw meal were fired for 10 min. at 1300, 1350, and 1400°C, respectively. A trial firing of the white cement clinker at 1300°C led to powdering of the clinker during cooling, because of the formation of γ-C_2S, so that the white cement samples were fired at higher temperatures, i.e., 1400, 1450, and 1500°C, respectively. The processing time at firing temperatures was fixed at 10 min. To check the influence of processing time on clinkering reaction, firing at 1400°C for 20 and 30 min. was carried out as well. The samples containing the coloring additives were microwave sintered at 1400°C for 30 min.

In order to compare microwave effects with those in conventional processing, accurate temperature measurement is critical. In the current microwave processing, the thermocouple tip was 2-3 mm above the sample. During processing the sample was rotating horizontally about its vertical axis, while the thermocouple was static. To make sure that there was no significant difference between temperature readings of the thermocouple and the temperature of the sample, the temperature measurement was calibrated. A circular pellet of 6.35 mm diameter for white cement clinker was directly fixed to the thermocouple tip (shielded by

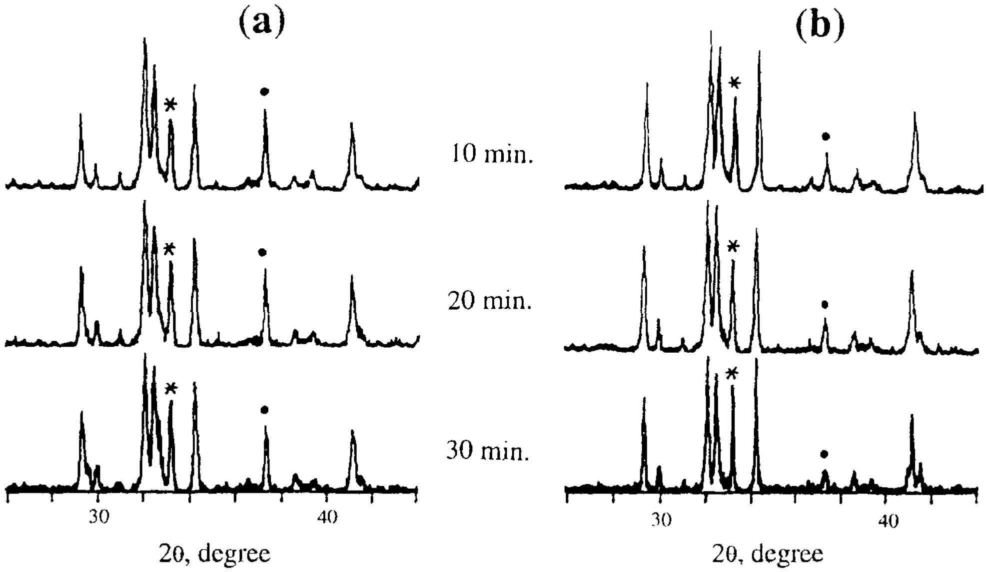

FIG. 3.
XRD patterns of white cement clinkers fired at 1400°C for 10, 20, and 30 min. by (a) conventional and (b) microwave processing. The marked peaks are (*) C_3A and (●) CaO. The unmarked peaks belong to C_3S with a small amount of β-C_2S.

platinum foil) and a 12.75 mm diameter sample was placed in the regular sample place below. The two samples were simultaneously subjected to microwave heating at 1400°C for 30 min. After processing, x-ray diffraction (XRD) analysis was conducted on both the "upper" and "lower" samples to determine if there was any significant difference in phase composition, and, therefore, in temperature between the two. To check if there were any significant temperature gradients in the compacted samples during the conventional heating-up cycle, which, if significant, would result in a lower clinkering reaction extent in the center, a powder sample of white raw mixture was fired at 1400°C for 10 min. and the XRD of the fired sample was compared with that of the pellet fired under the same conditions.

4. Characterization. Phase compositions of all the microwave and conventionally processed samples were analyzed by XRD on a Scintag diffractometer (Scintag, Sunnyvale, CA) at 3° 2θ per min., using Cu K_α radiation. Since clinkering is basically a process in which CaO is combined with SiO_2, Al_2O_3, and, in ordinary Portland cement, Fe_2O_3, to form a series of clinker minerals, the amount of the unreacted CaO, or so-called "free lime", in the clinker can be used as an indicator of the degree of completion of the clinkering reaction. The relative XRD intensity of CaO at $d = 2.4059$Å ($2\theta \approx 37.4°$) was used for comparison between samples.

Results and Discussion

1. Temperature Calibration in Microwave Processing. The two white samples used for temperature calibration remained white after processing at 1400°C for 30 min. Their XRD

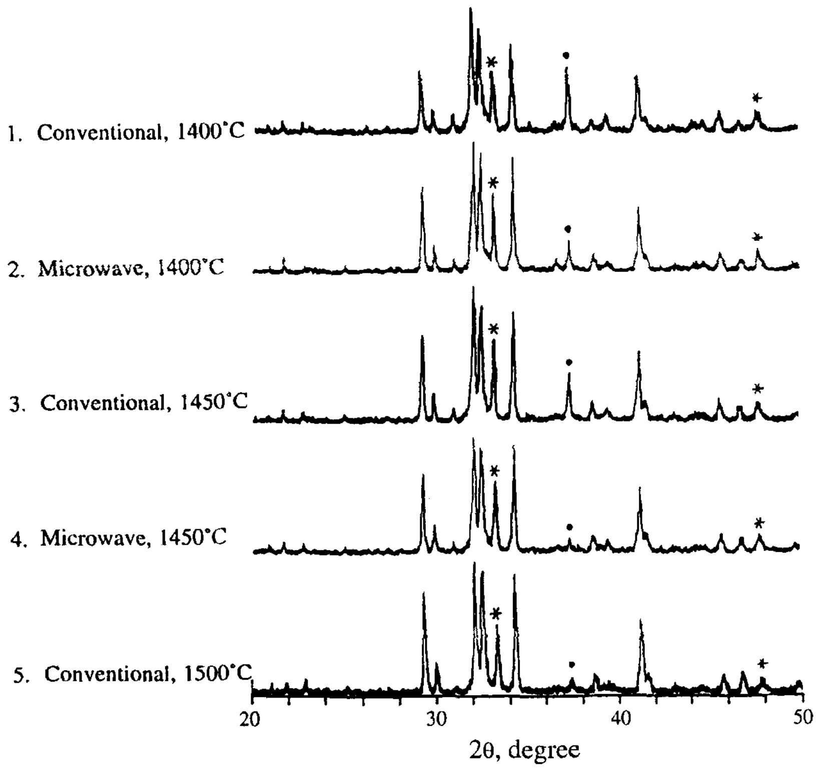

FIG. 4.
Comparison of the XRD patterns of white cement clinker samples fired at various temperatures for 10 min. The marked peaks are (*) C_3A and (•) CaO. The unmarked peaks belong to C_3S with a small amount of β-C_2S.

patterns are shown in Fig. 1. It is seen that both samples contained C_3S, β-C_2S, C_3A and free lime, and the relative intensities of these phases in the two samples are the same. This indicates that during microwave processing there was no significant temperature difference between the two samples. Thus the temperature readings during the microwave processing were accurate. The powder and compacted samples conventionally fired at 1400°C for 10 min. showed the same phase composition, although much more free lime than the microwave samples. This indicates that the temperature gradients in the compacted samples in the conventional heating-up cycle were not as significant.

2. Portland Cement Clinker. The clinker samples processed at 1300°C both by microwave and by conventional methods were light brown, while those processed at higher temperatures were dark gray. The XRD patterns of the samples are shown in Fig. 2. The main phases in these clinkers are C_3S, β-C_2S, C_3A and free lime. In the clinkers fired at 1300°C for 10 min., the content of lime in both microwave and conventional samples was large, but the microwave processed one obviously contained less. In the samples fired at 1350°C for 10 min., there was not much difference in the lime content, but the microwave sample showed lower β-C_2S intensity at 31° 2θ than the conventional one. The clinkers fired at 1400°C contained much less

free lime. The most significant characteristic of the microwave processed sample is that a very strong diffraction peak of C_3S at about 32° 2θ. This indicates that preferential growth of C_3S crystals took place in the microwave field.

3. Colored Cement Clinkers. The white cement clinkers prepared by both microwave and conventional processing remained white, with C_3S and C_3A as the major phases, and β-C_2S as the minor. Free lime existed in all samples in various amounts depending on the processing conditions.

Figure 3 shows the XRD patterns of the samples processed at 1400°C for 10, 20, and 30 min., respectively. Although all samples contained some free lime, the content was obviously less in the microwave processed samples than in the corresponding conventional sample. On the other hand, extending firing time from 10 min. to 30 min. at 1400°C did not reduce the amount of free lime very much, especially in the case of conventional process.

The XRD patterns of the white cement clinkers processed at various temperatures are compared in Fig. 4. On the one hand, as processing temperature increased, the content of free lime decreased, but increasing temperature from 1400 to 1450°C resulted in a more significant decrease in free lime content in the microwave samples than in the conventional ones. On the other hand, the samples microwave processed at both 1400 and 1450°C contained less free lime than the conventional samples processed at the corresponding temperatures. In fact, the sample microwave processed at 1400°C (Fig. 4-2) showed less free lime than that conventionally processed at 1450°C (Fig. 4-3), close to that conventionally fired at 1500°C (Fig. 4-5); the sample microwave processed at 1450°C (Fig. 4-4) showed a similar amount of free lime to that of the conventional sample at 1500°C (Fig. 4-5). From the above, it is seen that microwave processing did enhance the clinkering reaction for the white cement, lowering the reaction temperature by about 100°C.

The trial experiments showed that after microwave processing, the sample with cobalt oxide turned dark blue and the those containing chromium oxide were green, as expected. The surface of the setter pellet (alumina) in contact with the cobalt oxide containing sample turned light blue, indicating that the atmosphere during the sintering was reducing (otherwise it would be orange-red), or oxygen-insufficient, since the oxygen was mostly displaced by the CO_2 released in the decomposition of $CaCO_3$ during the processing in the relatively closed sintering package.

4. Discussion. The above results indicate that ordinary Portland cement and white or colored cement could be clinkered by microwave processing. A microwave enhancing effect did exist in the clinkering process. The commercial raw meal for Portland cement has a more complex composition than the raw mixture for white cement. The additional components or impurities certainly lowered the temperature at which liquid phase first appeared, thus the clinker of Portland cement could be processed at lower temperatures than white cement. Since iron oxide is a good microwave absorber, the existence of Fe_2O_3 in the commercial raw meals for Portland cement may explain, at least partially, the microwave enhancing effect on its clinkering.

In the case of white cement clinker, the existence of amorphous silica must have contributed much to the microwave absorption of the samples. Our previous study (8) suggested that the lowered viscosity of amorphous silica and, therefore, the enhanced ion diffusion during microwave radiation are the main mechanisms of microwave enhancement in the reaction of the materials containing amorphous silica. These mechanisms should hold in the case of the white cement clinker since the raw mixture contained amorphous silica (Ludox).

Conclusions

Clinkers for ordinary Portland cement and white as well as colored cements were prepared by microwave processing. The results show that microwave processing enhanced the clinkering reaction to certain extent on both ordinary and white cements. The microwave enhancement was manifested by the lowered clinkering temperatures. The iron oxide in the ordinary cement raw meal and amorphous silica in the white cement samples are believed to be responsible for the microwave enhancing effects.

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