

## Microstructures and mechanical properties of portland cement at an early age when subjected to microwave accelerated-curing

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This paper presents an investigation of microstructural development and mechanical properties of cement pastes when subjected to microwave energy. The microstructures of hydration products of cement pastes were examined by SEM/EDX and XRD. Compressive strengths of the cured samples were also measured. The results obtained show that the temperature increases monotonically during the microwave curing process. Significantly, the rate of temperature rise in the paste with a lower water-to-cement ratio was quite high. Calcium silicate hydrate ( $\text{Ca}_3\text{SiO}_5$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and xenotile ( $\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$ ) were identified by XRD in the cured samples. When cured at elevated temperatures, pastes develop strength quite rapidly. At an age of 8 hours after microwave curing at 100 °C, 0.25-w/c paste attained a strength of 25.1 MPa (240% higher than the lime-saturated water-cured paste); at 24 hours curing the strength was 68.3 MPa, and at 7 and 28 days the strength values were 74.9 and 75.2 MPa, respectively.

**Key words:** Microwave, Microstructure, Mechanical strength, Portland cement pastes.

### Introduction

Hydraulic Portland cement-based material is widely used in many ways in the construction industry. However, it takes longer than other cements to develop sufficient standard strength and elasticity. Many techniques have been designed and developed over time to accelerate the curing process, such as use of high early-strength Portland cement or Type III and adding an accelerating agent. One curing method involves thermal acceleration using both high temperature at atmospheric pressure and high pressure (autoclave curing). Unfortunately, the thermally-cured methods have drawbacks both in the early-age and long-term phases. For example, the combination of a high temperature and high atmospheric pressure produces lower long-term strength, which is associated with a serious durability problem. Although, this has been well-recognized, its mechanism has yet to be wholly understood. The reason might be in an increased micro-cracking and also the occurrence of delayed Ettringite formation as noted in a study by Verbeck and Helmuth [1]-specifically, that the rapid acceleration of the hydration reaction leads to the anhydrous cement grains becoming encapsulated by a product layer of low porosity that retards further hydration.

Furthermore, it is well known that any given hydration product constitute an insulating (dielectric) material that can transfer heat at a low rate and in a non-uniform way as a consequence of its poor properties. Therefore, by moving the heat source from the outside surface of the heated cement-based materials to the internal structure through the interaction between a microwave (electromagnetic) field and the heated cement-based materials, a violent interaction between the e/m fields and the cement-water system results in volumetric heat generation as shown by the main relationship in Eq. (1).

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

where  $Q$  is the microwave energy ( $\text{W/m}^3$ ) absorbed,  $\sigma$  is the effective conductivity (S/m),  $f$  is the frequency (Hz),  $\epsilon_0$  is the permittivity of free space (F/m) ( $8.85142 \times 10^{-12}$  F/m),  $\epsilon_r'$  is the relative dielectric constant (dimensionless),  $\tan \delta$  is the loss tangent coefficient (dimensionless), and  $E$  is the electric field intensity (V/m).

This concept will be used in one of the accelerated curing methods explored in the current study. Nevertheless, it should be noted that Portland cement in conjunction with water produces a reaction to complex multi-component systems and repletion coupled temperature and composition-sensitive hydration product; therefore, it is necessary to investigate the microstructural characterization of Portland cement-based materials as subjected to high-elevated temperature curing using microwave radiation energy in order to

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develop this method.

Important among the previous work involving accelerated curing is Dongxu and Xuequan's [2] application of microwave power to dewater concrete. The optimum curing conditions were found to be 45 minutes at 60 °C, which decreased the final water-to-cement ratio of concrete to about 0.38. With the help of feedback control temperature, Leung and Pheeraphan [3] and Rattanadecho *et al.* [4] illustrated that the optimization process for microwave curing concrete depended on the power level and power duration, which they determined to be 400 watt and 45 minutes, respectively for constant power.

The purpose of this study is to determine the dielectric properties of pastes during a 24-hours first-hydration period at 2.45 GHz, and to investigate the microstructural characteristics of hydration products in cement-based materials when subjected to microwave energy at a constant power level (power at 400 watt for 45 minutes), and compare that with the lime-saturated water curing method.

## Experimental Procedure

### Starting materials

The chemical composition as weight percent of the Portland cement Type I was 20.30 SiO<sub>2</sub>, 5.67 Al<sub>2</sub>O<sub>3</sub>, 60.43 CaO, 6.23 Fe<sub>2</sub>O<sub>3</sub>, 3.14 MgO, 0.90 K<sub>2</sub>O, 0.36 Na<sub>2</sub>O, 2.80 SO<sub>3</sub>. The Portland cement Type I had an loss on ignition (LOI) of 2.80%, specific gravity of 3.12, and surface area (Brunauer-Emmett-Teller (BET) method) of 0.85 m<sup>2</sup>/g. Deionized water was used to mix with Portland cement to make pastes.

### Mixing and molding

The pastes used were proportioned at w/c ratios of 0.25, 0.38 and 0.45. After mixing and molding, they were cured at room temperature by wrapping with polyethylene until the delay time (time after mixing until introducing microwave energy with a multi-mode cavity) for 30 minutes. The

appropriate amounts of starting materials were weighed out to the nearest hundredth of a gram on a Mettler PL 1200 balance. A Hobart mixer was used to mix the solids and liquids according to ASTM C 109 [5]. Cylindrical samples of dimensions  $\phi$  69.0 mm  $\times$  4.0 mm were cast. The samples were cured using saturated lime water at 25 °C, and microwave energy in a multimode cavity.

### Microwave curing setup

This microwave heating system used in this study is shown in Fig. 1, that included an industrial microwave generator model S56F manufactured by Cober Electronics, Inc., Stanford Conn., USA. This model can generate microwave energy at  $2.45 \pm 0.05$  GHz and a maximum power of 6.0 kW into a multimode applicator. This microwave apparatus does not provide real-time monitoring of temperature changes during microwave curing; therefore, the temperature of the sample was measured at the start and end of the curing process. In order to measure the temperature of the sample subjected to microwave energy, the positions of measurement were determined. The temperature of the top surface and the bottom surface was measured 5 times for each; likewise, the sample was immediately fractured and the inside temperature was also measured 5 times.

### Testing procedures

In order to measure the dielectric properties, it was necessary to use a vector network analyzer (VNA). The HP 8510 network analyzer [6] was selected, as it can measure the magnitude and phase characteristics of linear networks such as filters, amplifiers, attenuators, and antenna.

A scanning electron microscope (SEM), specifically an International Scientific Instruments ISI-130 electron microscope, was used to determine the microstructure and morphology of the samples.

The crystalline phase identification of the various samples was performed on a Scintag X-ray Diffractometer. This

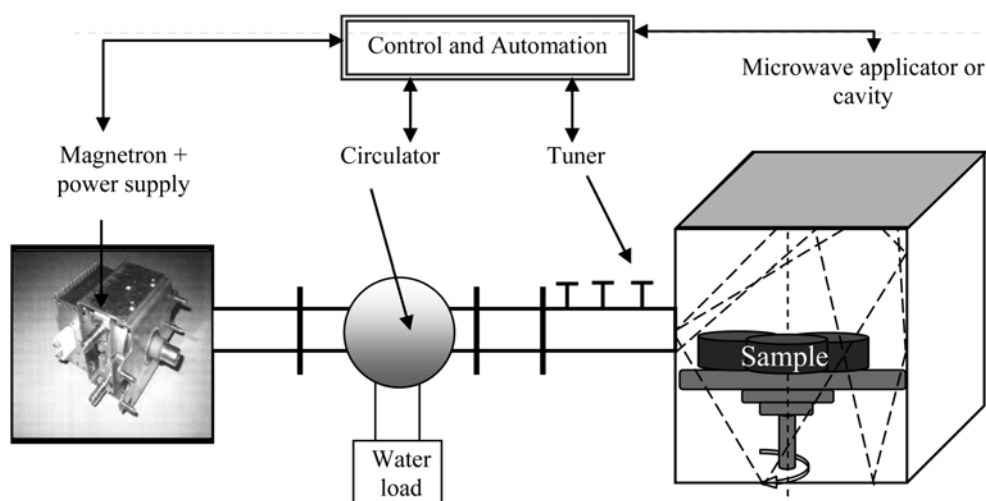


Fig. 1. Configuration of the microwave curing package.

diffractometer is equipped with a copper target X-ray source, monochromator, and Tl-drifted NaI scintillation detector. Dried-powder samples were packed into a cavity of a zero-background quartz slide and placed on a goniometry. Most of the subsequent scans were taken from 25 to 45° 2 $\theta$  at a rate of 2° 2 $\theta$  per minute.

The compressive strengths of the cement pastes were tested using a compressive strength apparatus in accordance with the ASTM C 39 [7] at 8 and 24 hours, and 3 and 28 days.

## Results and Discussion

### Dielectric properties

All measured waveforms were obtained in the time domain and a frequency range from 1.7-2.6 GHz (S-band). They were then converted into the dielectric properties (dielectric constant,  $\epsilon'$  and loss factor,  $\epsilon''$ ). The effect of the water-to-cement ratio (w/c) on its properties was studied and also discussed in this section. Factors influencing the dielectric properties of a material were summarized by Venkatesh and Raghevan [8]. The presence of water is recognized as the primary and dominant factor surrounding the increase of  $\epsilon'$  in paste [9, 10].

Fig. 2 shows the evolution of dielectric properties and the simultaneous temperature rise of cement pastes. It can be observed that the dielectric properties at the initial stage are relatively higher in comparison with the later stage; they also increase with an increase in the water content (higher w/c) of the cement pastes. This is due to the fact that immediately after contact has been made between water and cement, they start to react and then  $\text{Ca}^{2+}$ ,  $\text{OH}^-$

and  $\text{SO}_4^{2-}$  ions dissolve into the system. In addition, during the dormant period, the dielectric properties change very little because the chemical composition of the aqueous phase remains nearly constant [11]. Similarly, the relative dielectric properties also appear to be affected by the temperature rise. The lower temperature (higher w/c) leads to enhance these properties. This is due to a reduction in the water-to-cement-ratio that accelerates hydration and results in a higher temperature. This is particularly so in the accelerated period of the pastes at which it has the highest rise in temperature corresponding to the decreasing relative dielectric properties.

### Temperature rise

The temperature profile and microwave power of 376 watt with a specific application time of 45 minutes of the pastes is shown in Fig. 3. It should be noted that the power was studied and reported to be 412 watt for 45 minutes in Leung and Pheeraphan [3] for the best case with constant power. However, with a limitation of the microwave equipment used, it could only be adjusted manually in steps of microwave power level such as 200, 400, 600, 800,..., 6000 watt, therefore the optimal microwave levels with the aforementioned research should be set at 400 watt. In addition, after calibrating the microwave power, this power level was adjusted at 376 watt.

Temperature profiles obtained from averaging the five monitored data at the top surface (Fig. 3(a)), bottom surface (Fig. 3(b)) and at the middle (Fig. 3(c)). The temperature is found to increase monotonically among the positions of measurement during the microwave curing process and reaches a maximum of 105 °C at the bottom surface of the

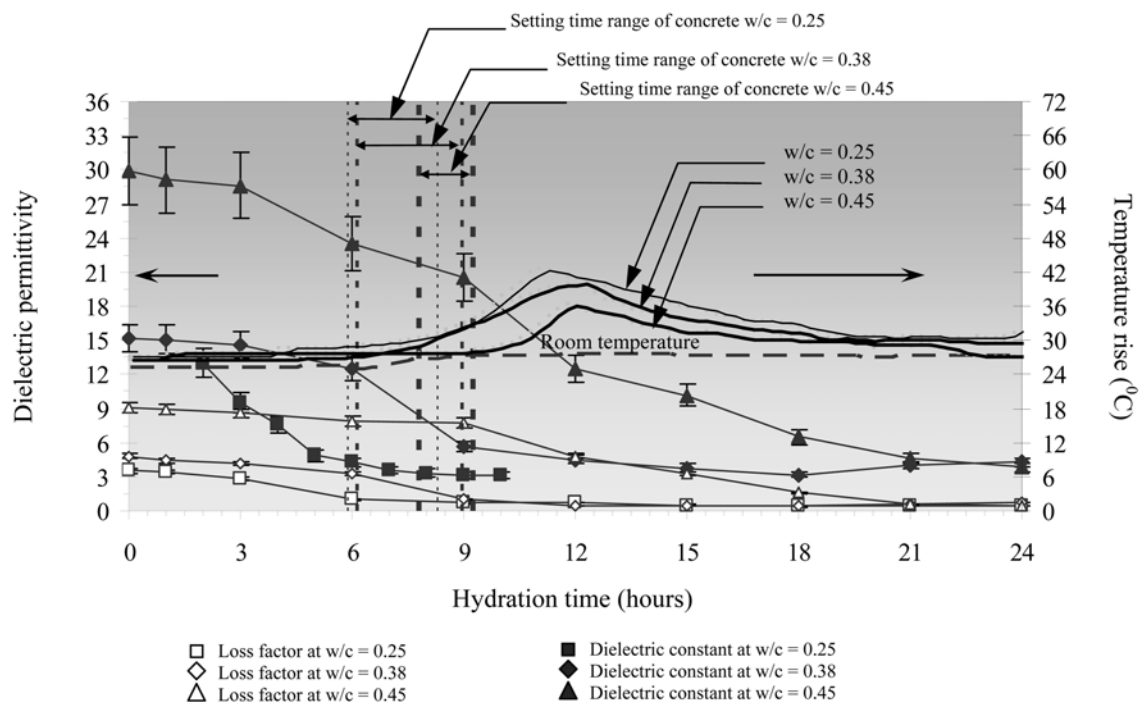
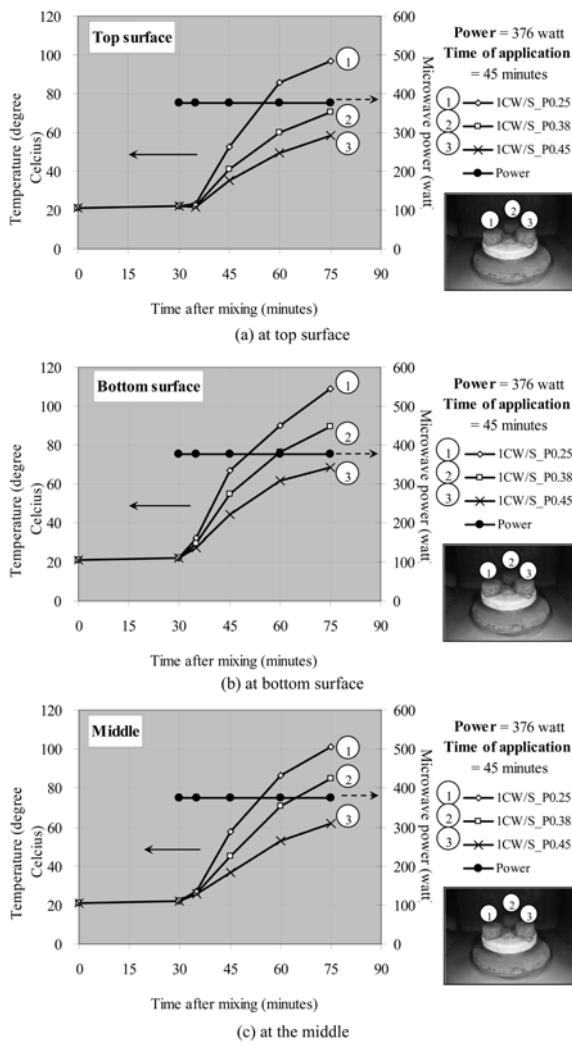


Fig. 2. Dielectric properties of concretes with different water-to-cement ratios.



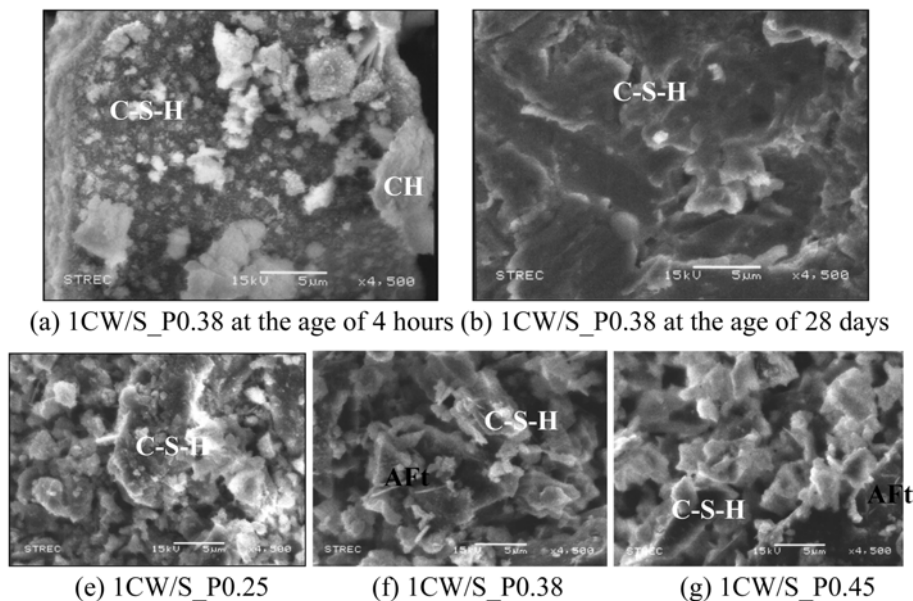
**Fig. 3.** Temperature and power history during microwave exposure of various cement pastes with different water-to-cement ratios.

cured cement paste. Significantly, the paste at a lower water-to-cement ratio experiences a high temperature rise, or 1CW/S\_P0.25 (1 stands for the Type I Portland cement, CW/S stands for the water-to-cement ratio, P stands for the paste, and 0.25 stands for the value by mass of CW/S) > 1CW/S\_P0.38 (0.38 stands for the value by mass of CW/S) > 1CW/S\_P0.45 (0.45 stands for the value by mass of CW/S). This is because of two inclusive effects; (i) heat liberation from the hydration reaction is increased with a low content of water in the system, and (ii) heat from interaction between the microwave energy and internal water leads to superposition of them. In other words, the additional heat from the microwave energy can change the kinetics of hydration in accordance with Arrhenius's law.

When comparing the temperatures obtained at three positions, the bottom of the cured specimen has the highest temperature levels than those of other positions. This may be due to the fact that during the temperature rise, the water at the top side of the specimen may evaporate, so the temperature drops gradually, while at the bottom the evaporation of water is difficult. As a result the heat accumulates on the bottom providing a temperature increase with a higher rate than the positions.

### Morphology

Typical micrographs of the 1CW/S\_P0.38 paste at the age of 4 hours after mixing, 28 days after curing in lime-saturated deionized water, and subjected to microwave energy are shown in Fig. 4. It is clearly seen from Fig. 4(a) and (b) that the samples consist of hydrated phases and pores, as well as cores of  $\text{Ca}(\text{OH})_2$  dendrite crystals or other crystals (marked CH), calcium silicate hydrate (C-S-H), and a granular structure. Furthermore, some ettringite (Aft) is found in the case of specimens cured by microwave energy. It can be shown that in the early stages of the reaction



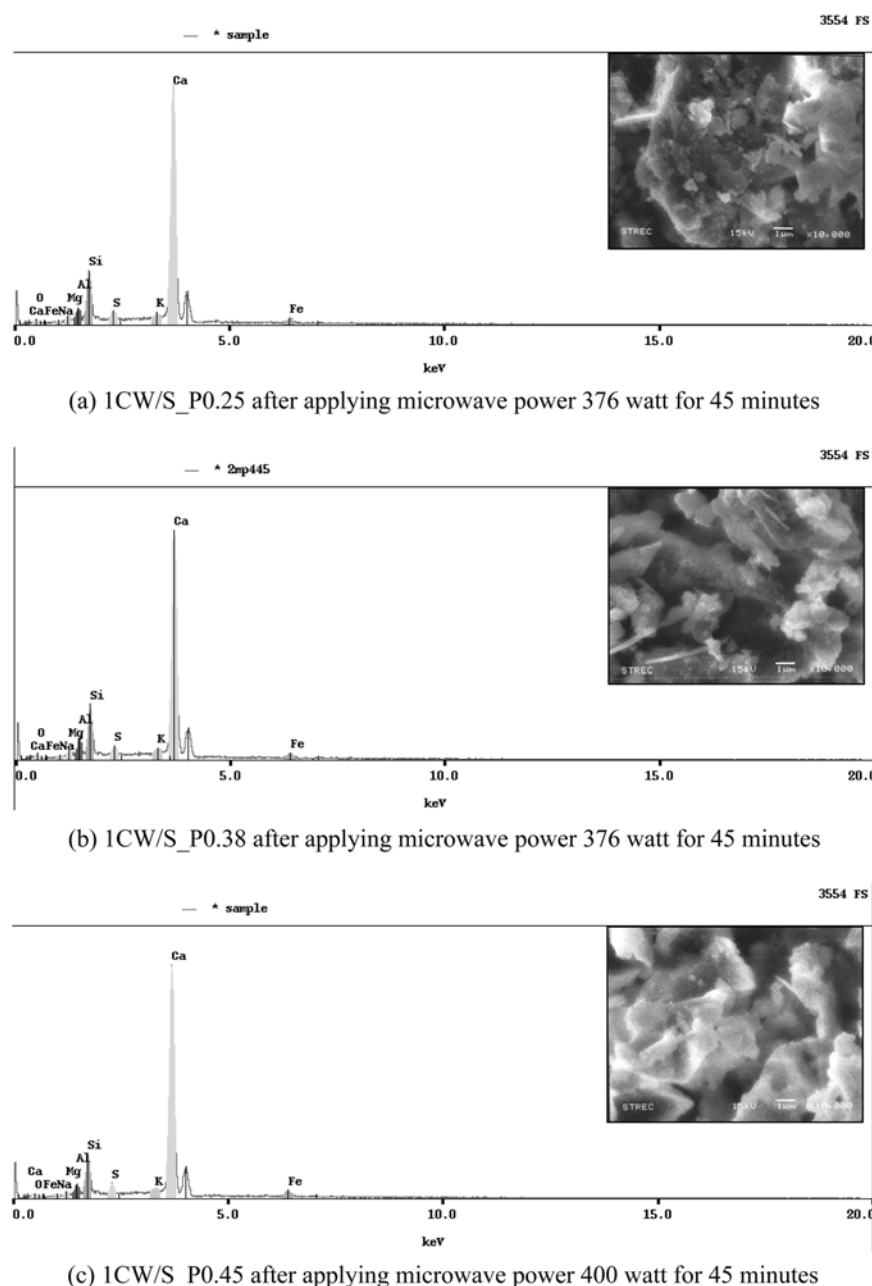
**Fig. 4.** Micrographs of various cement pastes at 4 hours subjected to normal curing (lime-saturated deionized water) and microwave energy for 45 minutes.

of the 27 °C sample, very small (about 1  $\mu$ m) irregularly-shaped ettringite particles were formed; but at the same curing time, needle-like ettringite had already formed in the 60 °C samples [11].

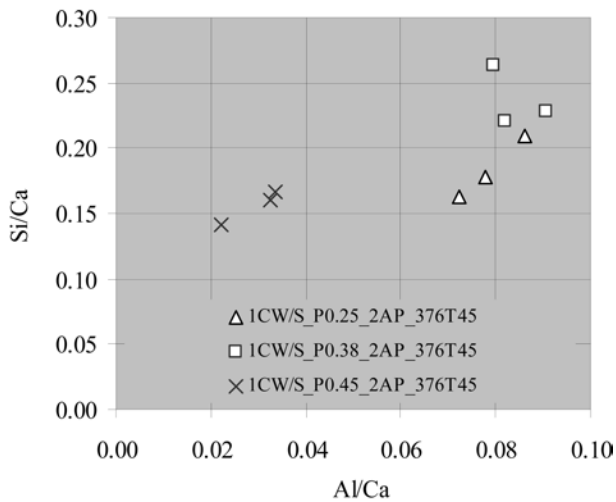
The composition of the calcium silicate hydrate (C-S-H) gel and other products formed in hydrated Portland cement systems has been studied in terms of their Ca/Si and Al/Ca ratios by several researchers [12-14]. The results reported vary due to the individual characteristics of the cements hydrated and the conditions of hydration, as well as the experimental technique used for the characterization. Calculated Ca/Si ratios also can be obtained from the measured CH concentration and the degree of hydration

of the calcium silicates. Cement hydration products are commonly classified as two products. The former are those hydration products formed within the original cement grain boundaries, and the latter are those products formed in the space initially occupied by water. Such definitions are used in this study. In the products, the main cement hydration product is a C-S-H gel, which is principally responsible for the properties of the hydrated cement.

Spectra of various cement pastes with different water-to-cement ratios at 4 hours subjected to normal curing (lime-saturated deionized water) and microwave energy are shown in Fig. 5. However, the results in the form of atomic (molar) ratios of several elements with respect to calcium, from



**Fig. 5.** Spectra of various cement pastes with different water-to-cement ratios at 4 hours subjected to normal curing (lime-saturated deionized water) and microwave energy.



**Fig. 6.** Atomic ratio of Si/Ca versus Al/Ca of the pastes of 1CW/S\_P0.25, 1CW/S\_P0.38 and 1CW/S\_P0.45 after applying microwave energy power 376 watt for 45 minutes.

the EDS analysis composition are also represented Fig. 6. This shows plots of the Al/Ca ratio versus the Si/Ca ratio for the pastes hydrated at a microwave power of 376 watt for 45 minutes. The (X) corresponds to the 0.25-w/c paste analyses, which, at 100 °C (at the middle) gathers around a Si/Ca ratio and Al/Ca ratio of 0.033 and 0.167, respectively. As the hydration temperature decreases from 100° to 62 °C, the Ca/Si ratio changes from 0.022 to 0.228, and the Si/Ca ratio from 0.141 to 0.263.

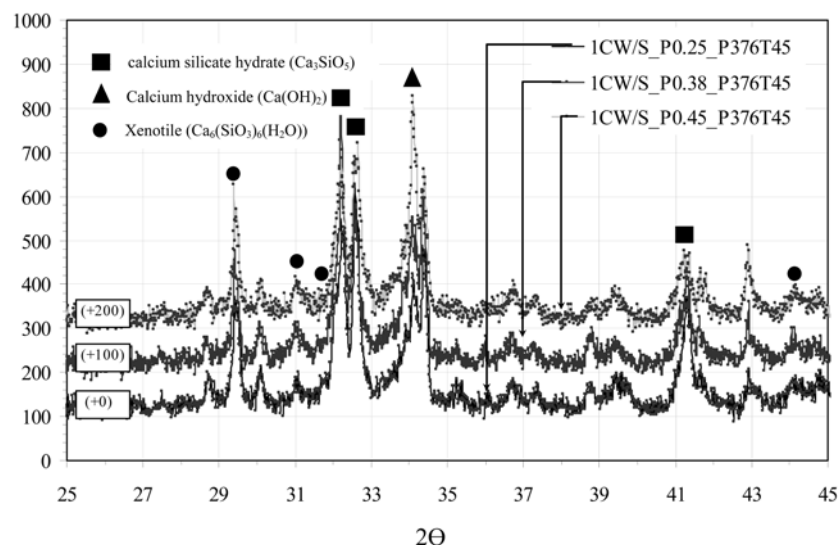
From the SEM–EDS results it was observed, although the measured Ca/Si ratios of the pastes were similar in magnitude, which they consistently decreased when the temperature was decreased from 100° to 62 °C. In this study, the same SEM equipment was always used and an effort was made to perform all the analyses under essentially the

same experimental conditions. Hence, the trends are believed to be reliable, even if the absolute values are not. Some results in the literature agree with this observed trend, but some others differ. Sorption of sulfate ions by C-S-H gel, as discussed below, may require extra calcium ions for a charge balance, hence providing a mechanism for a decrease in this ratio. The observed decrease in the Ca/Si ratio was, however, small and similar in magnitude to the standard deviation of the results. In an independent investigation, the difference between the Ca/Si ratios, this ratio and its variation with curing temperature may vary with the extent of the solid solution of foreign ions incorporated in the C-S-H gel and the amount of other phases, notably CH, intermixed in the gel phase. It seems prudent to conclude overall that, until analyses can be obtained with lower errors, the Ca/Si ratio does not vary in a systematic way with an increase in the curing temperature. It also has been observed that, for the cement pastes cured at the highest temperature, more sulfur and less aluminum are retained in the pastes. It is not possible to determine from SEM images whether the sulfur present in the IP is in the form of a finely inter-mixed AFm or AFt phase or in some other form.

#### Phase identification

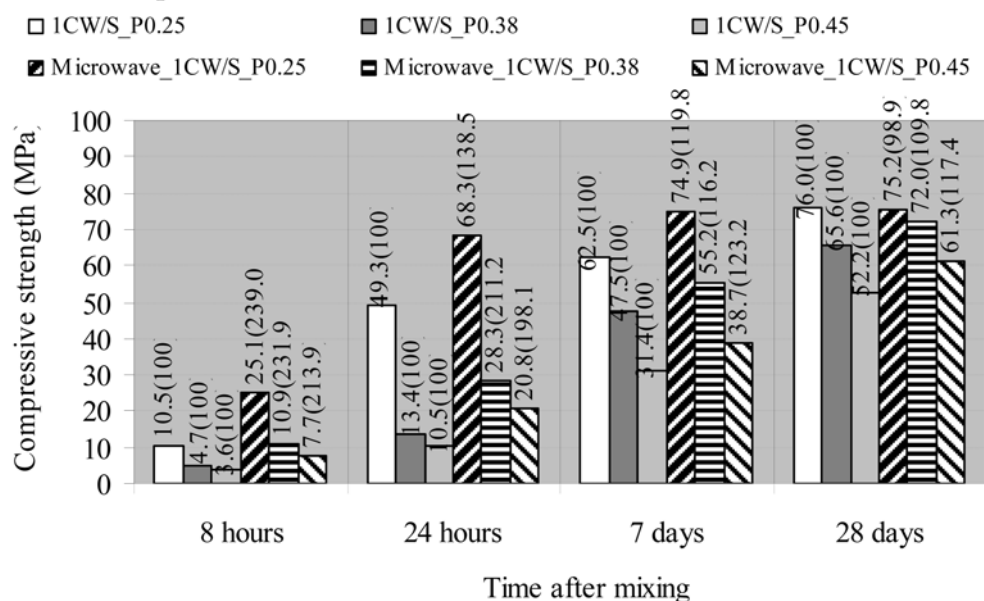
X-ray diffractometry was used to determine the degree of crystallinity of the hydrated cement products and the existence of crystalline coexisting phases. Fig. 7 shows X-ray patterns of the hydrated products in the pastes of 1CW/S\_P0.38 after applying a microwave power of 376 watt for 45 minutes. The phases identified include calcium silicate hydrate ( $\text{Ca}_3\text{SiO}_5$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), residual lime ( $\text{CaO}$ ) and Xenotile ( $\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$ ).

Regarding the effect of water-to-cement ratio on the phase characteristics of 1CW/S\_P0.25, 1CW/S\_P0.38 and 1CW/S\_P0.45 after applying microwave power of 376 watt for 45 minutes as shown in Fig. 7, it is found that the calcium



**Fig. 7.** X-ray diffraction of the pastes of 1CW/S\_P0.25, 1CW/S\_P0.38 and 1CW/S\_P0.45 after applying microwave power of 376 watt for 45 minutes.

### Microwave power 376 watt for 45 minutes



**Fig. 8.** Compressive strengths of the pastes of 1CW/S\_P0.25, 1CW/S\_P0.38 and 1CW/S\_P0.45 after applying microwave power 376 watt for 45 minutes compared to normal curing.

silicate hydrate ( $\text{Ca}_3\text{SiO}_5$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) phases are similar.

### Compressive strength

Compressive strengths of the pastes of 1CW/S\_P0.25, 1CW/S\_P0.38 and 1CW/S\_P0.45 after applying microwave power of 376 watt for 45 minutes compared to normal curing are shown in Fig. 8. It was found that when cured at elevated temperatures, pastes develop strength quite rapidly. At an age of 8 hours after microwave curing at  $100^\circ\text{C}$  (at the middle) the 1CW/S\_P0.25 paste attained a strength of 25.1 MPa (239 % higher than the normally-cured paste); at 24 hours curing the strength was 68.3 MPa, and at 7 and 28 days the strengths were 74.9 and 75.2 MPa, respectively. For the elevated temperature curing with the 1CW/S\_P0.38 and 1CW/S\_P0.45 pastes, the strength obtained at 8 hours was 10.9 MPa, exceeding the strength of the paste cured without microwave energy. However, at 24 hours and later ages the strength of the pastes cured at elevated temperature was 23 to 46% lower than that of the paste cured at room temperature. This is due to a decrease of the water-to-cement ratio less than about 0.40 [2, 15]. According to Hewlett [15], when water-to-cement ratio should equal 0.40, all the water molecules exist as a gel and combined water in the C-S-H structure; that is, there is no capillary water in the case of full hydration taking place. However, some capillary pores should be preserved as a path, through which water molecules can come in and react with cement grains near the pores. Meanwhile, these pores could serve as a space for gel expansion. The existence of a few capillary pores might be favorable for the structure and strength of the hardened cement paste. The above statement is consistent with our

experimental results; that is if the w/c ratio is less than 0.40, it is difficult for the full hydration of cement and unfavorable for the strength of concrete.

### Conclusions

The dielectric properties of cement pastes are mainly affected by the initial water-to-cement ratio; it also increases with an increase in the water content (higher w/c) of the pastes. The change in the dielectric properties is relatively high and remains constant during the dormant period; after that it decreases rapidly when the hydration reaction resumes, and it continues to decrease during the acceleratory period.

Temperature is found to increase monotonically during the microwave curing process. Significantly, the paste with a lower water-to-cement ratio gives a high temperature rise.

The phases which include calcium silicate hydrate ( $\text{Ca}_3\text{SiO}_5$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and xenotile ( $\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$ ) were identified.

Cured at elevated temperatures, pastes develop strength quite rapidly. At the age of 8 hours after microwave curing at  $100^\circ\text{C}$  (at the middle) the 0.25-w/c paste attained a strength of 25.1 MPa (239% higher than the normally-cured paste); at 24 hours curing the strength is 68.3 MPa, and 7 and 28 days the strengths were 74.9 and 75.2 MPa, respectively.

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