

Influence of microwave-accelerated curing procedures on the microstructure and strength characteristics of Type I-Portland cement pastes

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Microwave energy at a frequency of 2.45 GHz with a multi-mode applicator was used to accelerate the early-age hydration reaction in type I-Portland cement pastes. The influence of curing procedures on the microstructural evolution of Portland cement paste with a water-to-cement mass ratio (w/c) of 0.38 was investigated. By varying the sequential application processes, the phases and microstructural characteristics were assessed using a scanning electron microscope (SEM) associated with energy dispersive X-ray spectroscopy (EDS), and weight changes by thermogravimetric analysis (TGA). Furthermore, the efficiency of the curing procedures was evaluated by comparing the compressive strength with pastes that were cured by soaking in lime-saturated deionized water. From the test results it can be concluded that curing procedures strongly influence the temperature rise inside the microwave-cured pastes, and also the development of microstructures and compressive strength.

Key words: Microwave, Curing procedures, Microstructures, Strength, Portland cement pastes.

Introduction

Hydraulic Portland cement-based materials are widely used in construction work throughout the world. It requires much effort to develop the microstructure, strength, and durability properties of a cement in order to satisfy the standards of strength and elasticity. Many techniques and methods have been developed to archive these standards such as the use of high-early strength Portland cement [1], adding an accelerating agent [2], using a thermal accelerating method i.e. both high temperature at atmospheric pressure and high pressure (autoclave curing) [3-5]. However, thermally cured methods do not produce the desired properties at both an early-age and long term stages. For example, high temperature at atmospheric pressure gives lower long-term strength and is associated with a serious durability problem, the exact cause of which is not wholly understood yet [6-8]. One explanation is that an increase in micro-cracking and delayed ettringite formation (DEF) as mentioned in a paper by Verbeck and Helmuth [9] are responsible for this. Also the rapid acceleration in the hydration reaction led to the encapsulation of anhydrous cement grains by a product layer of low porosity, which retarded further hydration. Furthermore, it is well known that hydration products insulate (dielectric) materials that can transfer heat at a low rate and non-uniformly, resulting in poor properties. Therefore, if the heating mechanism is

changed from the outside surface of the cement-based material (conventional heating) to volumetric heating using the interaction between microwaves (electromagnetic) and the cement-based materials, it will accelerate the curing of the cement [10-11]. However, because Portland cement-water inherently reacts to a complex multi-component system of hydration products, therefore, an investigation of microstructural evolution of Portland cement-based materials when subjected to high temperature curing using microwave radiation energy is necessary. In this study, the influences of curing procedures on microstructural evolution of Portland cement paste with a water-to-cement mass ratio (w/c) of 0.38 were investigated experimentally. A previous study involving accelerated curing of Leung and Pheeraphan [12] is important. They illustrated that the optimization process for microwave curing of concrete depended on power level and power duration, which they determined to be 400 W and 45 minutes, respectively.

Experiments

The chemical composition as weight percent of the Type I Portland cement used in this study was 20.30 SiO₂, 5.67 Al₂O₃, 60.43 CaO, 6.23 Fe₂O₃, 3.14 MgO, 0.90 K₂O, 0.36 Na₂O, 2.80 SO₃. This had loss on ignition (LOI) of 2.80%, specific gravity of 3.12, and surface area (BET method) of 0.85 m²/g. Deionized water was used to mix with Portland cement to make cement paste samples.

The pastes used were proportioned at a w/c ratio of 0.38. After mixing and molding, they were cured at room temperature by wrapping with polyethylene plastic sheets until a delay time (time after mixing until introducing

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microwave energy) of 30 minutes. The appropriate amounts of starting materials were weighed out on a Mettler P1 1200 balance. A Hobart mixer was used to mix the solids and liquids according to ASTM C 109 [13]. Samples were cast as ϕ 69.0 mm $\times$ 40.0 mm cylinders. The samples were cured by using saturated lime water at 25 °C and microwave energy using a multimode cavity.

The microwave processing system used in this study is shown in Fig. 1, that includes an industrial microwave generator model S56F manufactured by Cober Electronics, Inc., Stanford Conn., USA. This model can generate microwave energy at 2.45 ± 0.05 GHz and a maximum power of 6.0 kW in a multimode cavity. Since this microwave apparatus does not provide real-time monitoring of temperature changes during curing, 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 the sample for measurements are shown in Fig. 2. The sample was fractured such that temperature within it was also measured 5 times.

In addition, according to IEC publication 60705 (Household Microwave Ovens: A Method for Measuring Performance) [14] recommends a principle and method for determining microwave power output as the following: the measurement is taken by using a water load in a glass container. Initially below ambient temperature, the water temperature is raised to approximately ambient temperature by heating in the microwave oven. This procedure ensures that the heat losses and the heat capacity of the glass container have a minimum temperature disturbance effect on the measured heat output of the microwave. In addition, the test uses a cylindrical container that is made of borosilicate glass and has a maximum thickness of 30.0 mm and an external diameter of approximately 190.0 mm.

Sequential microwave curing procedures in regard to seven cases:

- (a) At a power of 390 W for 30 minutes and a power 180 W for 15 minutes ((390(30)180(15)).

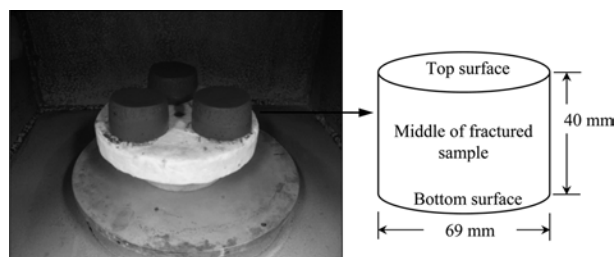


Fig. 2. The positions of the sample for temperature measurements.

- (b) At a power of 180 W for 15 minutes, a power of 390 W for 15 minutes, and a power of 180 W for 15 minutes ((180(15)390(15)180(15)).
- (c) At a power of 180 W for 15 minutes, a power of 390 W for 15 minutes, and a power of 811 W for 15 minutes ((180(15)390(15)811(15)).
- (d) At a power of 390 W for 15 minutes, a power of 811 W for 15 minutes, and a power of 180 W for 15 minutes ((390(15)811(15)180(15)).
- (e) At a power of 390 W for 15 minutes, a power of 811 W for 15 minutes, and a power of 390 W for 15 minutes ((390(15)811(15)390(15)).
- (f) At a power of 180 W for 15 minutes, a power of 811 W for 15 minutes, and a power of 180 W for 15 minutes ((180(15)811(15)180(15)).
- (g) At a power of 811 W for 15 minutes, a power of 390 W for 15 minutes, and a power of 180 W for 15 minutes ((811(15)390(15)180(15)).

A scanning electron microscope (SEM), 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 diffractometer was equipped with a copper target X-ray source, monochromator, and a Tl-drifted NaI scintillation detector. Dried-powder samples were packed into the

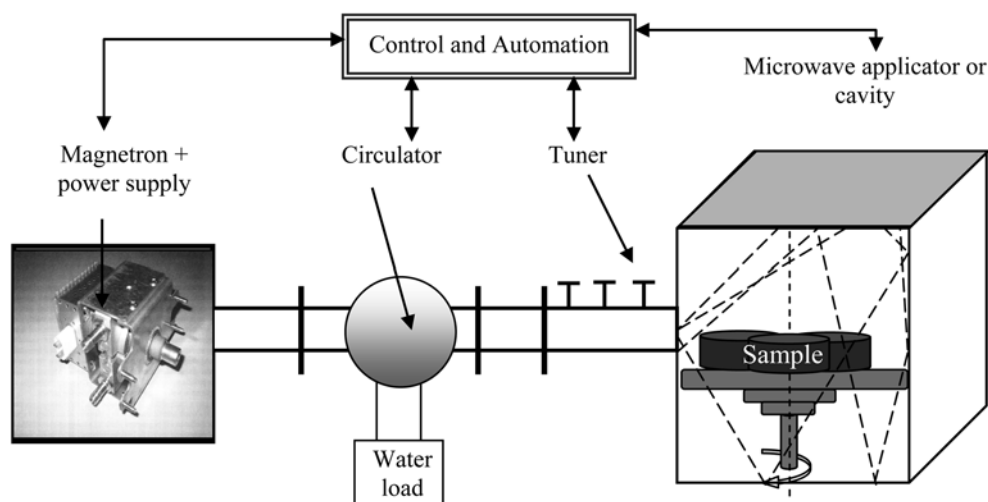


Fig. 1. Schematic diagram of the microwave curing system.

cavity of a zero-background quartz slide and placed on a goniometry. Most of the subsequent scans were taken from 25 to 45° 2 θ at a rate of 2° per minute. The compressive strengths of the cement pastes were tested using a compressive strength apparatus in accordance with the ASTM C39 [15] at 8 and 24 hours, and 7 and 28 days.

Results and Discussion

Temperature and power histories

Fig. 3 illustrates the temperatures and power histories inside the samples as measured during the application of microwave energy. The cement paste used in this study has a water-to-solid mass ratio (w/s) of 0.38. The delay time

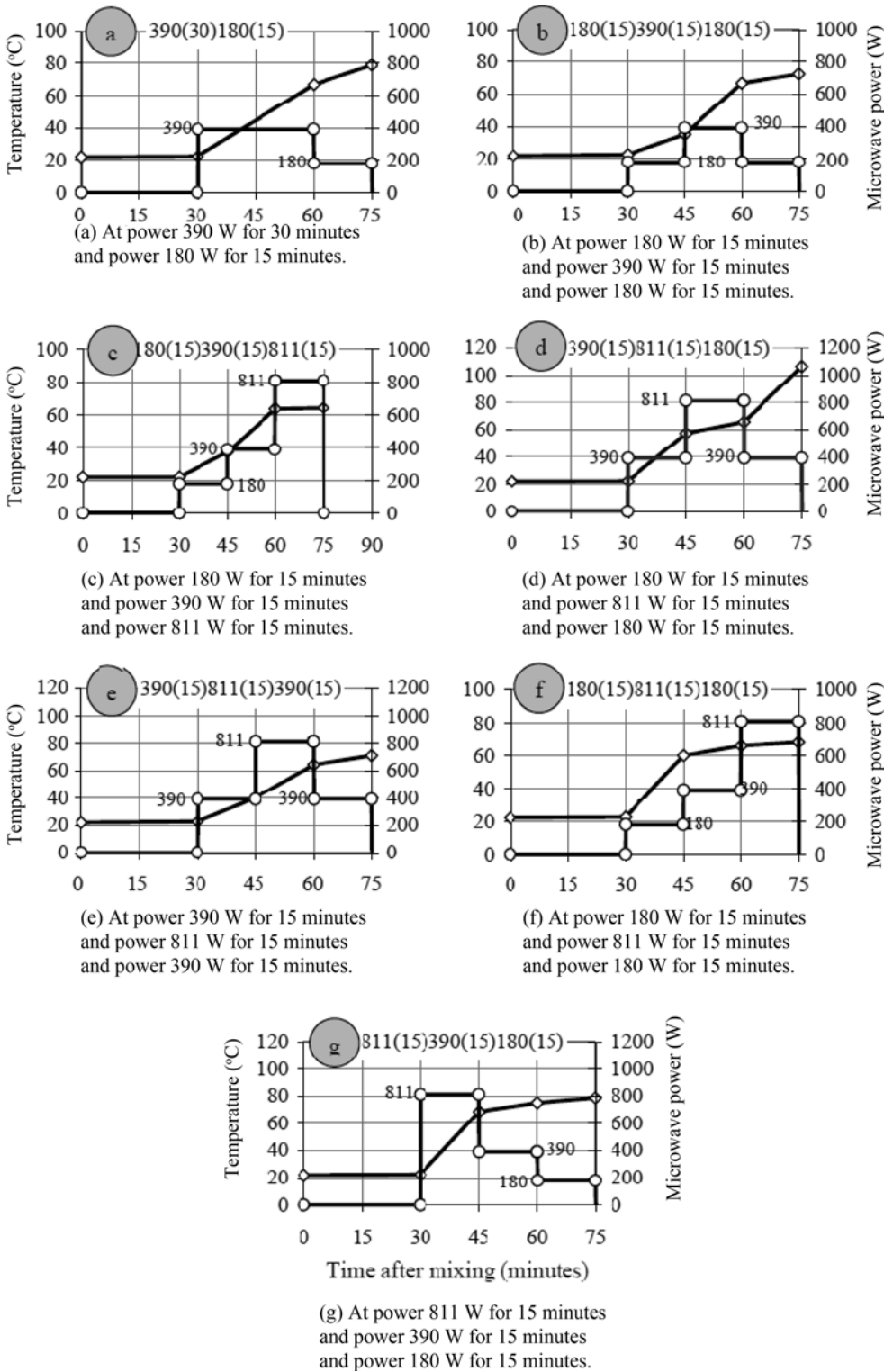


Fig. 3. Temperature and power history inside the sample during applying microwave energy.

before applying microwave energy was kept constant at 30 minutes after the water molecules and cement grains had made contact. The results, temperatures, and power histories are as the follows:

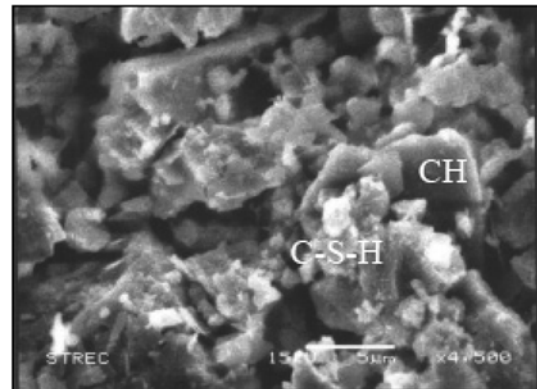
- (a) The temperature increases linearly corresponding to the first application of microwave energy at 30 min and the final temperature of up to 67 °C. Consecutively, the rate at which the temperature rise decreases is gradual and the final temperature is 79 °C.
- (b) The temperature rise increases with three different rates, with the second period having the highest rate. The last period has a lower rate of temperature rise than the first one. This is due to the change of free water into fixed water in the C-S-H structure. The final temperature is 73 °C.
- (c) The rate of temperature rise has the highest value in the second period of microwave curing. The application of microwave to the sample during the last period does not cause the temperature to increase. The final temperature is 64 °C.
- (d) The temperature rise increases at a high rate during the first period, and then the rate decreases despite an increase of microwave power to 811 W. In the last period, the rate at which the temperature rises again increases. This may be due to the evaporation of water, which again induces heat in the hydration product. The final temperature is 106 °C.
- (e) A microwave power of 811 W in the second consecutive period increases the temperature rise at a lower rate, and then decreases gradually in the last period. The final temperature is 71 °C.
- (f) An increase in the applied microwave power during the first period causes a significant increase in the rate at which the temperature rises; however, in the second period, the rate at which the temperature rises decreases. During the last period, a lower rate of temperature rise occurs even though a higher level of microwave energy is applied. The final temperature is 71 °C.
- (g) The temperature rise increases rapidly when the highest microwave power (811 W) is applied. In the second period, it increases at a lower rate than during the first period. In the last period, the rate at which the temperature rises is much lower than during the second period. The final temperature is 79 °C.

From all the above cases, it can be concluded that an increase in the rate of temperature rise relates to the length of time of applying microwave energy; that is, if the highest microwave power level (811 W) were applied in the first period, it could accelerate the hydration reaction and the temperature would rise rapidly. However, when the lowest microwave power level (180 W) is applied to the sample, it can also cause the temperature to rise at an accelerated rate, although the acceleration is lower than that shown at the higher temperatures. Furthermore, as water evaporates, this also affects the rate at which the temperature rises because a material's free water content absorbs considerable

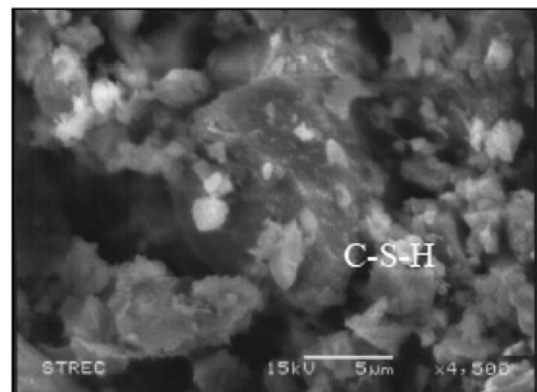
microwave energy and converts it to heat [10]; in addition, the subsequent high temperature induces further evaporation of the material's free water content. As a result, the lower free water content contributes to a low rate of temperature increase [16-17].

SEM

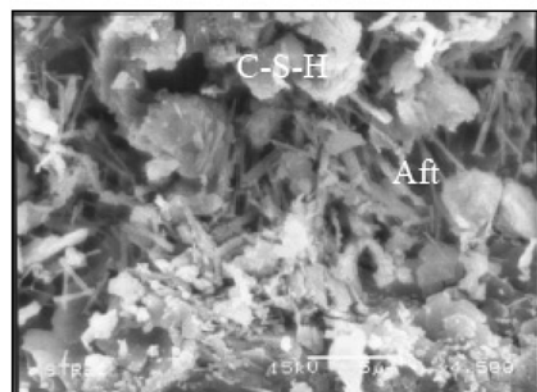
Fig. 4 shows the typical micrographs of the paste under the following conditions: at a power of 180 W for 15 minutes, a power of 390 W for 15 minutes, and a power



(a) 180(15)390(15)811(15)



(b) 390(15)811(15)390(15)



(c) 180(15)390(15)180(15)

Fig. 4. Micrographs of pastes with different procedures.

of 811 W for 15 minutes, at the age of 4 hours after mixing of cement and water, at a power of 390 W for 15 minutes, a power of 811 W for 15 minutes, and a power of 390 W for 15 minutes, and at a power of 180 W for 15 minutes, a power of 390 W for 15 minutes, and a power of 180 W for 15 minutes. Figs. 4(a) and 4(b) clearly show 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), C-S-H, and a granular structure. Furthermore, some ettringite (Aft) is found in the samples cured by microwave energy, as shown in Fig. 4(c).

SEM-EDS

From the SEM-EDS results, as shown in Fig. 5, it was observed that, although the measured Ca/Si ratios of the pastes are similar in magnitude, the Ca/Si ratios cover the

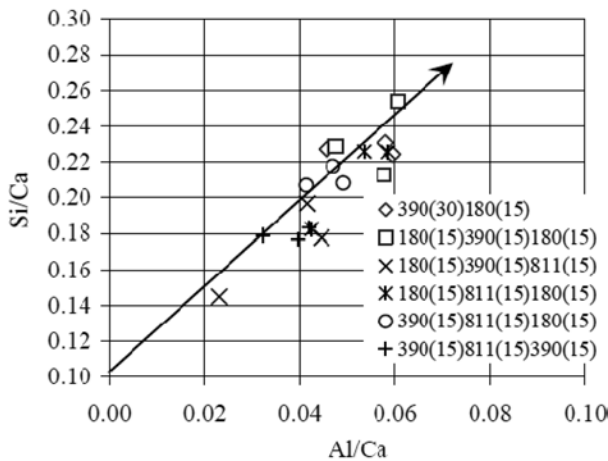


Fig. 5. Atom ratio of Si/Ca versus Al/Ca of the paste of 1CW/S_P0.38 with different power levels and application times of microwave energy.

range of 0.145 to 0.254, while the Al/Si ratios lie from 0.023 to 0.061. It appears that the application of microwave at a power of 180 W for 15 minutes, a power of 390 W for 15 minutes, and a power of 811 W for 15 minutes can cause the distribution of both Ca/Si and Al/Si ratios.

Compressive strength

Fig. 6 shows the compressive strengths of the microwave-cured paste and the normal paste at the higher levels of microwave power. The strength development shows a relationship with the amount of microwave energy applied. In detail, applying a high level of microwave energy during the first period can produce C-S-H in an irregular shape [18]. In addition, the remaining free water is needed to effect continuous hydration of the cement particles. If the microwave-cured paste has a low water content due to its loss through evaporation, the strength is reduced automatically.

TGA

Fig. 7 shows the $\text{Ca}(\text{OH})_2$ content of the paste subjected to microwave energy at (a) 811 W for 15 minutes, 390 W for 15 minutes, and 180 W for 15 minutes ((811(15)390(15)180(15))); (b) 390 W for 15 minutes, 811 W for 15 minutes, and 390 W for 15 minutes ((390(15)811(15)390(15))); and (c) 180 W for 15 minutes, 390 W for 15 minutes, and 811 W for 15 minutes ((180(15)390(15)811(15))). The $\text{Ca}(\text{OH})_2$ contents of the three cases are 0.77% (w/w), 0.55% (w/w), and 0.80% (w/w), respectively, which show a correspondingly increasing content of the C-S-H. It can be concluded, in accordance with the previous studies [19], that applying microwaves at 390 W during the first period constitutes an effective method of curing using microwave energy.

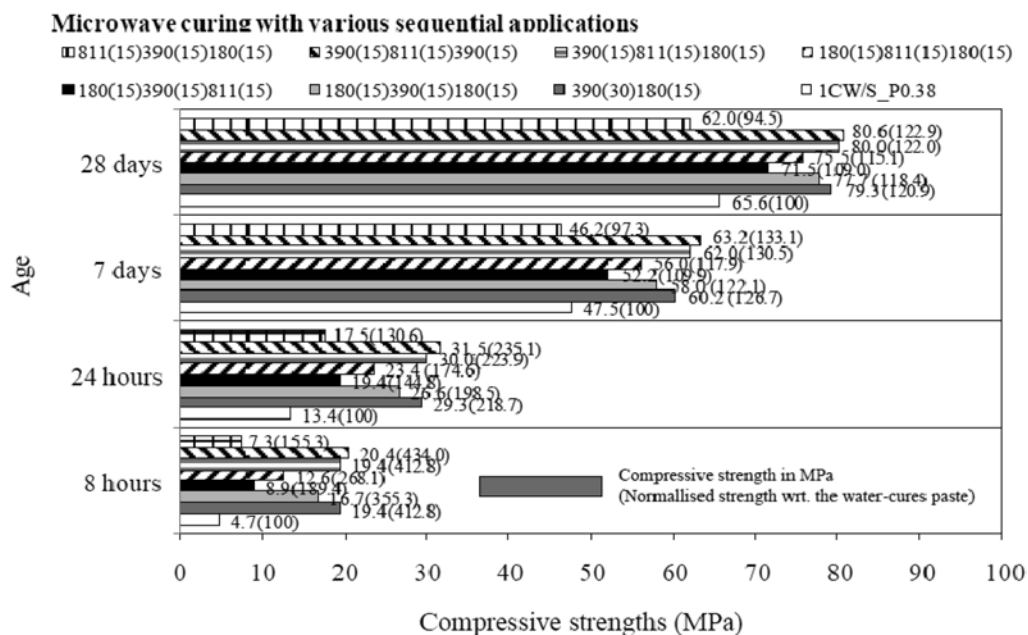


Fig. 6. Compressive strengths of the paste with different sequential processes.

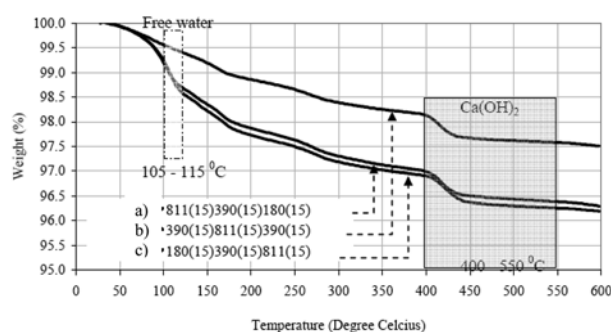


Fig. 7. Thermogravimetric analysis (TG) results by comparison among different sequential processes.

Conclusions

The study took into account microwave energy's ability to accelerate hydration reactions and increases in temperature within the microwave-cured sample, as well as the effects of sequential processes. The temperature increase corresponds to microwave power applied during the curing process. Typical micrographs of the microwave-cured paste showed that the samples consisted of hydrated phases and pores, as well as cores of $\text{Ca}(\text{OH})_2$ dendrite crystals or other crystals (marked CH), C-S-H, and a granular structure. Furthermore, some ettringite (Aft) was found in the samples cured by microwave energy. From the SEM-EDS results, it was observed that although the measured Ca/Si ratios of the pastes were similar in magnitude, they consistently decreased when the temperature decreased. For the compressive strengths, the microwave-cured pastes developed strength quite rapidly in accord with the maintenance of the level of microwave power and time of application.

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