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Comparison of the microstructure and compressive strength of Type 1 Portland cement paste between accelerated curing methods by microwave energy and autoclaving, and a saturated-lime deionized water curing method

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The microstructure and compressive strength of a 0.38 water-to-cement mass ratio (w/c) cement paste when subjected to accelerated-curing by microwave energy and autoclave curing were compared with a normal curing method by soaking in saturated-lime deionized water at 25 °C. The morphology, atom ratio of Si/Ca versus Al/Ca, phase composition by XRD, and compressive strength were measured in this study. The results indicate the presence of needle-like ettringite (Aft) in pastes that had been cured using the autoclave method. However, the saturated-lime deionized water cured paste showed lath-like or plate-like shapes and did not appear to produce ettringite (Aft). In addition, the microwave-cured paste indicated some evidence of ettringite. The range of Si/Ca and Al/Ca ratios of the autoclave-cured paste were 0.039 – 0.052, and 0.207 – 0.234, respectively, while in the microwave-cured paste the ratio shifted to 0.079 – 0.091. The compressive strength of the autoclave-cured cement paste showed an increase in strength at an early age, while the strength decreased after 7 days of hydration.

Key words: Autoclave curing, Cement paste, Compressive strength, Microwave accelerated curing, Microstructure.

Introduction

Curing is the process by which hydraulic-cement-based materials develop strength hardening over time [1]. And, this process ensures that the degree of hydration is sufficient to reduce porosity enough that the desired properties of a concrete can be achieved. There are various curing methods to accelerate the development of strength in concrete during the early-age phase. However, these methods often cause drawbacks in their properties. For example, a lack of water in the water-curing process causes concrete to shrink which leads to tensile stresses within the concrete. As a result, surface cracking may occur, especially if the stresses develop before the concrete achieves adequate tensile strength. Over heating in the autoclave curing method reduces the concrete's final strength. Selecting an appropriate curing method and process helps to control the temperature during hydration. Curing by an admixture may encounter long-term durability problems [2-8].

As described above, thermal-curing methods affect concrete's properties adversely – both at an early age and long term. Considering this, a crucial question arises: Can microwave heating be applied in the concrete industry for curing? Theoretically, it is possible. This is because concrete-making materials, like hydraulic Portland cement, aggregates, water, and admixtures have a good dielectric behavior; they can absorb microwave energy very effectively. Water, in particular, has a higher relative dielectric constant (ε_r') and loss tangent ($tan\delta$) than the other components in cementitious material. As a result, when the electric component ($\vec{E}$) of the microwave electromagnetic field, interacts with concrete's constituents, energy is quite dramatically transferred and converted into heat. This mechanism causes the bonds to vibrate, and the energy is, therefore, dissipated as heat and transferred within the concrete to be processed, providing an elevated temperature and effecting accelerated hydration reactions. Consequently, free water molecules in the capillary pores of the concrete are quickly removed from the internal concrete structure before setting, which means that plastic shrinkage takes place, and leads to the collapse of the capillary pores with the simultaneous densification of the microstructure.

This study focuses on establishing how well microwave curing performs, some other curing methods and their related properties have also been considered for a comparative analysis. In this section, a normal curing method that uses lime-saturated deionized water at 25 °C defines the optimal performance by current established standards. While an autoclave curing with a temperature rate increase of 75 °C per hour and a maximum temperature of 150 °C was also used for the purposes of comparison.

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Experimental

Specimen preparation

The chemical composition in weight percent of the Type 1 Portland cement was 20.30 SiO_2, 5.67 Al_2O_3, 60.43 CaO, 6.23 Fe_2O_3, 3.14 MgO, 0.90 K_2O, 0.36 Na_2O, 2.80 SO_3. The Portland cement had a loss on ignition (LOI) of 2.80%, a specific gravity of 3.12, and a surface area (BET method) of 0.85 m^2/g. Deionized water was used to mix with Portland cement to make pastes. The pastes used were proportioned at a w/c ratio of 0.38 by weight. After mixing and molding, they were cured at room temperature by wrapping with polyethylene plastic until a delay time (time after mixing until introducing microwave energy with a multi-mode cavity) for 30 minutes. A Hobart mixer was used to mix the solids and liquids according to ASTM C109 [9]. Cylinderical samples of dimensions of ϕ 69.0 mm $\times$ 4.0 mm were cast.

Curing methods

Normal curing

The paste samples were cured until the testing time by saturated-lime deionized water at 25 °C.

Microwave curing

The microwave heating system used in this study is shown in Fig. 1, which includes an industrial microwave generator model S56F manufactured by Cober Electrics, 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.

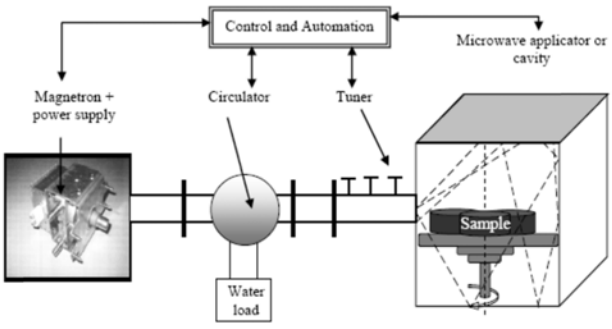


Fig. 1. Configuration of the microwave curing package.

Autoclave curing setup and procedures

Samples were cured in an autoclave chamber at a maximum temperature of 150 °C with a heating rate of 75 °C per hour. As shown in Fig. 2, this apparatus includes a heat pump, a Chromalox precision heat and control electric boiler (model CHPES-036AOF10-203), a pump circuit consisting of a motor of 560 Watt, and a chamber. A micro-computer with a feedback temperature control program was used to control the heat inlet of and, therefore, the temperature within the chamber. Under autoclave curing, specimens were introduced into the cavity after having been mixed for 30 minutes under conditions whereby the initial temperature of 75 °C increased until reaching a maximum temperature of 150 °C.

Testing procedures

A scanning electron microscope (SEM) associated with an energy dispersive X-ray spectroscope, 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 differactometer is equipped with a copper target X-ray source, a monochromator, and a 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° 2θ at a rate of 2° 2θ per minute.

The compressive strengths of the cement pastes were tested using a compressive strength apparatus in accordance with the ASTM C39 [10] at 8 and 24 hours, and 3 and 28 days.

Results and Discussion

Morphology

The morphology of the cement paste at 28 days when subjected to autoclave curing is shown in Fig. 3(c).

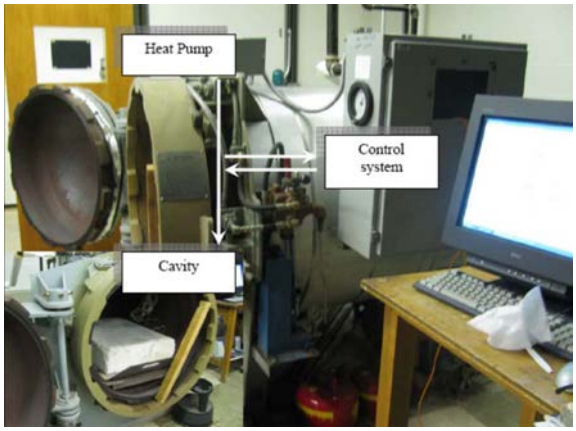
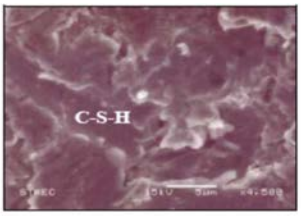
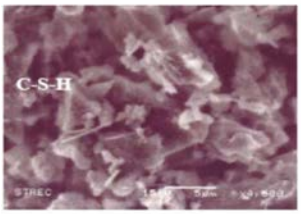


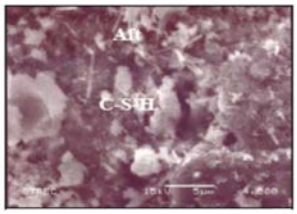
Fig. 2. Configuration of the autoclave apparatus.



(a) Paste subjected to saturated-lime deionized water curing at 28 days

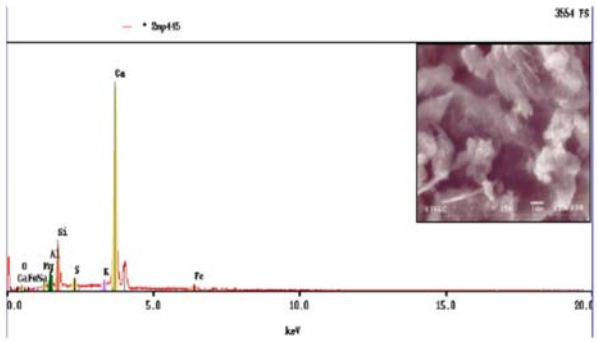


(b) Paste after applying microwave energy power 390 watt for 45 minutes

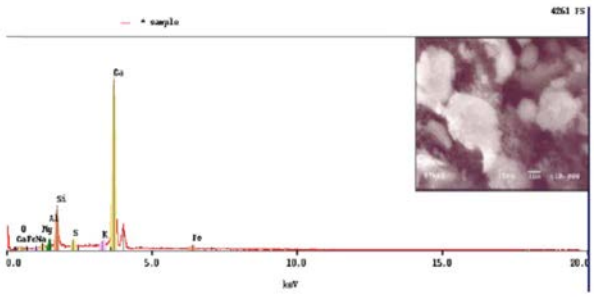


(c) Paste subjected to autoclave curing at 28 days

Fig. 3. Micrographs of the cement pastes subjected to : (a) water curing, (b) microwave curing, and (c) autoclave curing.



(a) Paste after applying microwave power of 390 Watts for 45 minutes



(b) Paste subjected to autoclave curing at 28 days

Fig. 4. Spectra of cement pastes subjected to various curing methods.

This shows the presence of needle-like ettringite (Aft) in the specimens that had been cured using the autoclave method because it had already formed at a temperature of 60 °C [11]. However, the morphology of the saturated-lime deionized water-cured paste (Fig. 3(a)) showed lath-like or plate-like shapes and did not appear to produce ettringite (Aft). In addition, the microwave-cured paste showed some evidence of

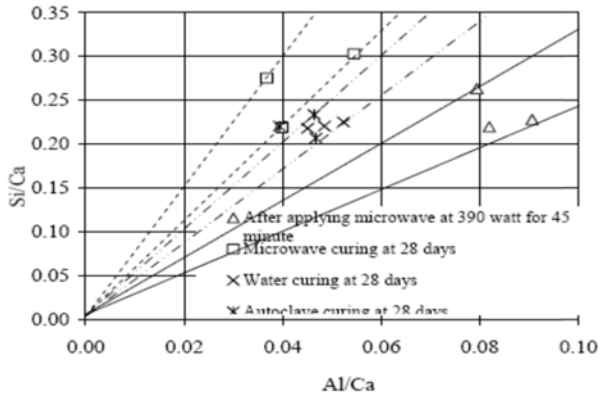


Fig. 5. Atom ratio of Si/Ca versus Al/Ca of the cement pastes at the age of 28 days subjected to microwave and autoclave curing compared to saturated-lime deionized water curing.

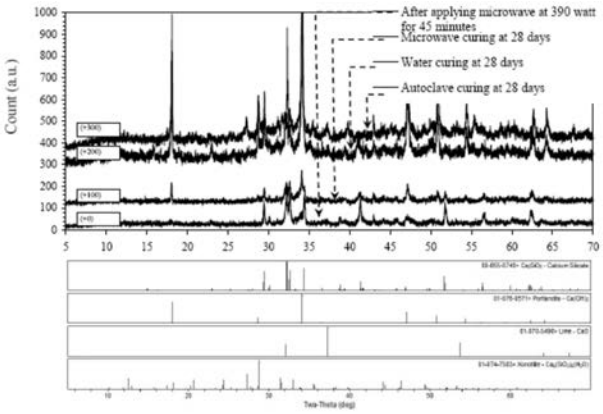


Fig. 6. X-ray diffraction of the cement pastes at the age of 28 days subjected to microwave and autoclave curing compared to saturated-lime deionized water curing.

ettringite (Fig. 3(b)).

From the plot of the atom ratio of Si/Ca versus Al/Ca of the cement paste at an age of 28 days subjected to microwave and autoclave curing compared to saturated-lime deionized water curing as shown in Figs. 4-5, the values of the Si/Ca and Al/Ca ratios subjected to autoclaving showed more clustering than does the paste under saturated-lime deionized water curing. The range of Si/Ca and Al/Ca ratios of the autoclave-curing paste are 0.039 – 0.052, and 0.207 – 0.234, respectively. For the microwave-cured paste, the ratios have a similar character, but the Al/Ca ratio shifts to 0.079 – 0.091.

Phase identification

The X-ray diffraction technique was used to examine the phase composition of the cement pastes at the age of 28 days when subjected to microwave and autoclave curing as compared to saturated-lime deionized water curing. The XRD patterns (Fig. 6) showed a composition of calcium silicate hydrate (Ca_3SiO_5), calcium hydroxide ($Ca(OH)_2$), residual lime (CaO), and Xeno-

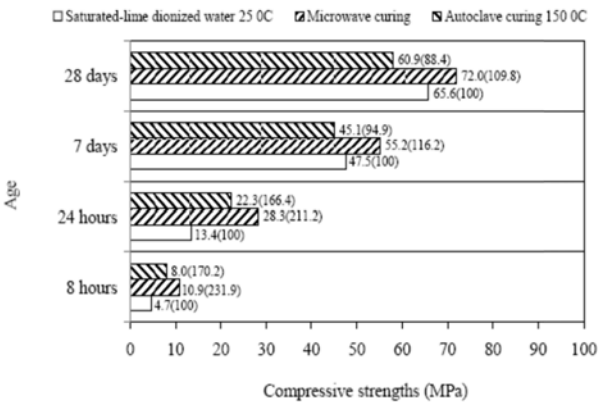


Fig. 7. Compressive strengths of the cement pastes at the age of 28 days subjected to microwave and autoclave curing compared to saturated-lime deionized water curing.

tile ($Ca_6(SiO_3)_6(H_2O)$). However, by examining the peaks at 18° and 34.5° of the calcium hydroxide phase, the intensity of the autoclave-cured cement paste indicated that this phase crystallized at a rapid rate. This was different from the case of microwave curing, under which conditions these phases appear crystalline with an uncertain and complicated shape that makes their elements difficult to identify.

Compressive strength development

The strength development becomes continuously affected through both the early- and late-age stages. Two main factors that are used to determine the strength are the rate at which hydration generates heat and the water content. Curing with microwaves can accelerate hydration, but it also promotes disorder in the C–S–H structure. Moreover, by microwave heating the C–S–H can eventually affect thermal cracking in the C–S–H structure, which could have an effect on long-term strength. However, as this study focused on monitoring the first 28 days, evaluating this aspect was beyond its scope. The compressive strength of the autoclave-cured cement paste showed an increase in strength at an early age, while the strength decreased after 7 days of hydration because of the high curing temperature of 150 °C as shown in Fig 7.

Conclusions

The normally-cured paste (saturated-lime deionized water) showed somewhat lath-like or plate-like shapes and did not appear to produce ettringite (Aft), whilst the microwave-cured and autoclave-cured pastes showed the presence of needle-like ettringite (Aft).

The range of Si/Ca and Al/Ca ratios of the autoclave-cured paste was 0.039 – 0.052, and 0.207 – 0.234, respectively. For the microwave-cured paste, the ratios have a similar character, but the Al/Ca ratio shifts to 0.079 – 0.091.

The cement paste specimens at the age of 28 days when subjected to microwave and autoclave curing and saturated-lime deionized water curing, showed a phase composition of calcium silicate hydrate (Ca_3SiO_5), calcium hydroxide ($Ca(OH)_2$), residual lime (CaO), and Xenotile ($Ca_6(SiO_3)_6(H_2O)$).

The compressive strength of the autoclave-cured cement paste showed an increase in strength at an early age, while the strength decreased after 7 days of hydration.

Acknowledgements

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