Cement and Concrete Research 40 (2010) 1688–1696

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Response of alkali activated fly ash mortars to microwave curing

Jeevaka Somaratna, Deepak Ravikumar, Narayanan Neithalath *

Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY 13699, United States

ARTICLE INFO

Article history:
Received 6 July 2010
Accepted 13 August 2010

Keywords:
Microwave processing (A)
Alkali activation
Fly ash (D)
Compressive strength (C)
Microstructure (B)

ABSTRACT

Volumetric heating provided by microwave curing results in faster property development as compared to conventional heat curing that relies on heat conduction from the skin to the core. This paper discusses the compressive strength and microstructure development of microwave cured NaOH activated fly ash mortars, and relates them to the microwave energy absorption by the material which is a function of its dielectric properties. Microwave curing parameters are chosen so as to eliminate the effects of thermal runaway. Strengths that are comparable to or greater than those of mortars heat cured for 48 h at 75 °C are obtained in less than 120 min of microwave curing. The rate of energy absorption by the mortars is found to be relatively constant for a considerable fraction of the microwave curing duration, attributable to the compensation for the drop in dielectric loss factor as a result of moisture loss by the increase in internal electric field. Compressive strength is shown to be related to the microwave energy absorbed by the specimens, especially during the time when free water is present in the system.

1. Introduction

Alkali activation of aluminosilicate materials as binder systems for concretes are being extensively studied because of the several advantages they offer in terms of enhanced material properties as well as sustainability [1–4]. Fly ash or ground granulated blast furnace slag are the aluminosilicate materials commonly used because of the presence of soluble silica and alumina species in these materials that undergo dissolution, polymerization with the alkali, condensation on particle surfaces, and solidification that is responsible for the strength and stability of these binders. The influence of the source material and activator chemistry on the reaction mechanisms, reaction product and pore solution composition, and the microstructure of such systems have received considerable attention [5–12]. Activation of aluminosilicates with alkaline solutions generally requires the supply of external energy as heat for the formation of alkali aluminosilicates, especially when the activating solution does not contain soluble silica. A wide range of temperatures ranging from 40 °C to 90 °C have been reported in order to produce alkali activated binders with appreciable mechanical properties [5,6,11]. The influence of thermal curing conditions on the reaction mechanisms, carbonation of reaction products, and mechanical and microstructure development of alkali activated fly ash binders has been extensively reported [13–15].

Conventional heat curing techniques deliver thermal energy to the surface of the material by radiant or convective heating, which is transferred to the bulk through conduction. This creates thermal gradients in the material and thus non-uniform heating that might result in less than desirable properties. An alternative is microwave curing, where microwave energy is delivered directly to the material through the interactions at the molecular level with the electromagnetic field. Microwaves penetrate the material and provide energy, resulting in volumetric heating. The electromagnetic energy is converted to thermal energy which in turn is used to enhance the reaction kinetics and accelerate the strength gain. Hence microwave curing relies on energy conversion rather than heat transfer [16,17]. Since the energy transfer does not rely on diffusion of heat from the surfaces, rapid and uniform heating is possible [18]. A few studies on microwave curing of concretes have been reported, mostly dealing with the strength development of concretes under microwave curing [19–22]. Microwave assisted zeolite synthesis has also been studied [23–25], with the conclusion that the activation time was drastically reduced when compared to conventional hydrothermal synthesis. This paper attempts to provide information on the response of alkali activated fly ash mortars to microwave curing. In the quest for sustainable binders for concretes, it is essential to consider the energy implications of concrete production, and hence it is believed that an understanding of the mechanisms and efficiency of microwave curing of such binders would be greatly beneficial. Microwave energy absorption and its rates in activated fly ash mortars, and the influence of dielectric properties are also provided.

1.1. Material properties of significance when subjected to an electromagnetic field

The interaction of the electromagnetic field with the material structure results in energy transfer, and the mechanisms are

* Corresponding author. Tel.: +1 315 268 1261; fax: +1 315 268 7985.
E-mail address: nneithal@clarkson.edu (N. Neithalath).

0008-8846/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2010.08.010

described in detail elsewhere [18,26–28]. Microwave-material interactions result in translational motions of the free or bound charges and the rotation of dipoles. The inertial, elastic, and frictional forces that resist these motions causes volumetric heating of the material. The effect of the electromagnetic field on the material is primarily dependent on the complex dielectric permittivity (ε) of the material, given as:

$$\varepsilon = \varepsilon' - i\varepsilon'' \tag{1}$$

where ε′ is the dielectric constant, and ε″ is the dielectric loss factor. ε′ describes the ease with which a material is polarized by the electric field, and ε″ measures the efficiency with which the electromagnetic radiation is converted to heat. The ratio of dielectric loss factor to the dielectric constant is the loss tangent (tan δ). This parameter depends on the frequency of the microwave radiation and the temperature. The effectiveness of heating a material using microwave energy depends on the amount and rate of energy absorption by the material. The rate of energy absorption, expressed as the power per unit volume (P) is one of the important parameters for microwave processing of materials, and is given as:

$$P = \omega\varepsilon_0\varepsilon''|E_{\text{int}}|^2 = \omega\varepsilon_0\varepsilon' \tan\delta|E_{\text{int}}|^2 \tag{2}$$

where ω is the angular frequency, ε_0 is the permittivity of free space (8.854×10^{-12} F/m), and E_{int} is the intensity of the internal electric field. As can be observed from Eq. (2), the dielectric properties (ε′ and ε″) exert a significant influence on the absorbed power, and thus the volumetric heating in the material. A significant portion of the absorbed power is converted to heat within the material as [28]:

$$\frac{\Delta T}{\Delta t} = \frac{P}{\rho C_p} = \frac{\omega\varepsilon_0\varepsilon''|E_{\text{int}}|^2}{\rho C_p} \tag{3}$$

where T is the temperature, t is the time, ρ is the density and C_p is the heat capacity. The dielectric parameters also influence the depth to which microwaves penetrate into the material, defined as either the depth at which the incident power is reduced by half [28], or the depth at which the power density drops to e^{-1} of the surface value [19,29]. The latter definition is used in this paper.

2. Experimental program

2.1. Materials, mixtures, and specimen preparation

The alkali activated mortars used for this study were prepared using a Class F fly ash that conforms to ASTM C 618 as the binding material. The chemical composition of fly ash is as follows: SiO_2 — 50.2%, Al_2O_3 — 28.7%, Fe_2O_3 — 5.72%, CaO — 5.86%, MgO — 1.74%, Na_2O_e — 0.96%, SO_3 — 0.51%, and LOI — 2.80%. Fly ash is rich in the aluminosilicate phases, which can undergo dissolution–polymerization–condensation reactions in the presence of alkalis to form the binding gel. Analytic reagent grade sodium hydroxide was used to prepare the alkaline activating solutions having concentrations of 4 M, 6 M, 8 M, and 10 M. River sand (d_{50} of 0.6 mm) was used as the fine aggregate. The mortar mixtures were proportioned to contain a paste volume of approximately 50%. Activating solution-to-binding material ratio of 0.40 was used for all the mixtures. Fly ash and the fine aggregates were mixed thoroughly in a laboratory mortar mixer. Requisite amount of the alkaline activator solution of the chosen concentration was gradually added while mixing until the components were homogenized. The mortar was filled in cubical acrylic molds of 50 mm size, and compacted using a table vibrator. The specimens were cured for 12 ± 1 h in the molds at 23 ± 2 °C, demolded, and then subjected to either the microwave curing or heat curing regime. Heat curing was carried out in a laboratory oven at 75 °C for either 24 or 48 h after the initial 12 h at ambient conditions, based on a previous study [5].

2.2. Determination of microwave curing parameters

As stated earlier, microwave curing was started only after 12 h of ambient curing, primarily due to difficulties in subjecting the mold material to microwave radiations for extended periods of time. The average incident microwave power of the oven used was tunable from 0 to 1200 W, at increments of 10%, and the microwave frequency used was 2.45 GHz (this is the most commonly used frequency). Three 50 mm cubical specimens corresponding to a particular mixture were kept in the microwave cavity (37.5 cm × 37.5 cm × 25 cm) for curing. A few initial experiments carried out at higher incident power levels such as 1200 W and 600 W led to severe cracking and deterioration of the specimens within a few minutes. At higher incident powers, in a dielectrically inhomogeneous material, the electromagnetic waves encounter a variety of boundary conditions, resulting in extreme local variations in the electric field intensity. As shown in Eq. (2), absorbed power is proportional to the square of the electric field intensity, and hence local variations in the field results in local temperature fluctuations within the material. It is possible that the temperature of a local area increases rapidly under non-uniform fields, resulting in "thermal runaway" [16], leading to very high internal stresses and material fracture. With rapid increase in temperature, ε″ also rises rapidly, consequently increasing the absorbed power also.

An example of temperature development in 8 M NaOH activated mortar cubes subjected to 240 W, 360 W, and 600 W of average incident power are shown in Fig. 1. Temperatures were measured using an infrared thermal scanner with its emissivity set to 0.95, which is the optimum to read concrete temperatures as suggested in standard emissivity charts (0.94–0.96 for cement and concrete). With increasing incident power, the specimen temperature is seen to increase. At an average incident power level of 600 W, the specimens fractured between 5 and 10 min of microwave curing while at 360 W, the fracture occurred after 60 min and before 120 min. No specimen cracking was observed when the specimens were subjected to a power level of 240 W. Hence an average incident power level of 240 W (corresponding to 20% of the maximum rated power) was used for the remaining experiments. A maximum microwave curing duration of 120 min was chosen because the compressive strengths of the specimens did not increase significantly beyond this curing duration, and random surface cracking began to be observed after this time.

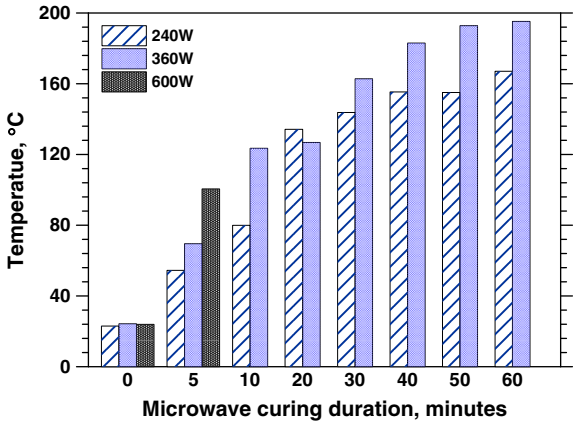

Fig. 1. Temperature development as a function of microwave curing time and incident power for 8 M NaOH activated mortars. Specimens disintegrated between 5 and 10 min at 600 W power and between 60 and 120 min at 360 W power.

2.3. Test methods for strength, microstructure, and dielectric properties

The compressive strength of the mortar cubes were determined as per ASTM C 109 after they were taken out of the microwave and returned to ambient conditions by storing in a desiccator for a few hours. To understand the morphology of the reaction products formed as a result of exposure to microwave energy, scanning electron microscopy (SEM) was used on activated paste specimens. The paste specimens were prepared and cured in a manner similar to those of the mortar specimens. X-ray diffraction (XRD) was used to determine the phase composition of the reaction products. The XRD patterns of selected paste samples were recorded using a Bruker DX-8 diffractometer. Cu-Kα radiation (λ = 1.504 Å) was used and the tests were carried out in the 2θ range of 5–40°, with a step size of 0.02° and step time of 2 s.

The dielectric parameters of the material significantly influence its response to electromagnetic radiation. The very high frequency (in the GHz range) response of concretes are typically difficult to measure, but can be accomplished using network analyzers. However, in this study electrical impedance spectroscopy was used to determine the dielectric parameters of the system in the frequency range of 1 Hz to 10 MHz. A Solartron 1260™ impedance-gain phase analyzer was used to determine the impedance response at different microwave curing durations. The specimen was kept in between two stainless steel plate electrodes (in a parallel plate configuration) with a layer of moist porous foam in between the sample and the electrode for better electrical contact. The frequency dependent impedance, Z(ω), is represented in a Nyquist plot as:

$$Z(\omega) = Z'(\omega) - iZ''(\omega) \tag{4}$$

where Z′(ω) is the resistive (real) and Z″(ω) is the reactive (imaginary) component of the impedance. The complex impedance, Z(ω), of a lossy dielectric material placed between two parallel plates can be related to its complex dielectric permittivity, ε(ω), as:

$$Z(\omega) = \left[\frac{i\omega\varepsilon_0\varepsilon(\omega)(A_e)}{l}\right]^{-1} \tag{5}$$

where A_e and l are the area of cross section and the distance between the electrodes respectively. The complex dielectric permittivity, ε(ω), can be resolved into its real and imaginary components, i.e., the dielectric constant and the dielectric loss factor, using Eq. (1).

2.4. Methodology to calculate the microwave energy absorption by the specimens

Microwave curing relies on the absorption of microwave energy by the specimens and its conversion to heat so as to activate the chemical processes. The entire incident energy (product of incident power and time) is not utilized in heating the specimen because of the losses occurring in the process. Therefore it is imperative to quantify the amount of energy that is absorbed by the mortar specimens so that it can be related to the development of material properties. Based on Eq. (2), the rate of energy absorption can be determined from the dielectric properties of the material and the intensity of the internal electric field. However, accurate measurements of these parameters are difficult and they are also dependent on several other factors. Hence this paper uses an experimental approach reported in [30] where the specimens were microwaved along with a known quantity of water for a short time. The energy absorbed by the water in this time interval along with a quantification of the microwave losses is used to determine the energy absorbed by the specimens as explained below.

Three 50 mm sized cubes of 8 M NaOH activated mortars were placed in the microwave cavity after 12 h of casting and microwaved at an average incident power of 240 W for durations of 30, 45, 60, 75, 90, and 120 min. At the end of the respective curing durations, 100 g of water in a microwave transparent container was introduced into the cavity and the entire system (water and the three mortar cubes) was subjected to microwave radiation for another 2 min. In this period, the total energy supplied by the microwave generator into the cavity (E_{Total}) can be expressed as:

$$E_{Total} = E_{abs-specimen} + E_{abs-water} + E_{loss} \tag{6}$$

where $E_{abs-specimen}$ is the energy absorbed by all the three cubes together, $E_{abs-water}$ is the energy absorbed by the water, and E_{loss} is the energy loss that incorporates all the losses including the energy absorbed in the cavity, and the energy lost in the transmission process from the generator to the cavity. Since the total loss is a fraction of the energy generated,

$$E_{loss} = kE_{Total}. \tag{7}$$

The constant k is termed the microwave loss factor. If the microwave cavity contains only 100 g of water ($E_{abs-specimen} = 0$), which is microwaved at the chosen power for 2 min, the energy absorbed by water can be expressed as:

$$E_{abs-water} = m_{water}c_{water}(\Delta T) \tag{8}$$

where m_{water} is the mass of water, c_{water} is the specific heat capacity of water (4.18 kJ/kg °C), and ΔT is the temperature increase of the water when subjected to microwave radiation for 2 min. Using the calculated value of $E_{abs-water}$ in Eq. (6), the microwave loss factor k can be determined. The loss factor can be assumed to be a constant irrespective of the curing duration. From the known values of k and $E_{abs-water}$ during the 2 min of microwave curing of the system that contains water in the container along with the specimens after the respective curing duration of the specimens alone, $E_{abs-specimen}$ (of the three cubes together) at different microwave curing times can be determined.

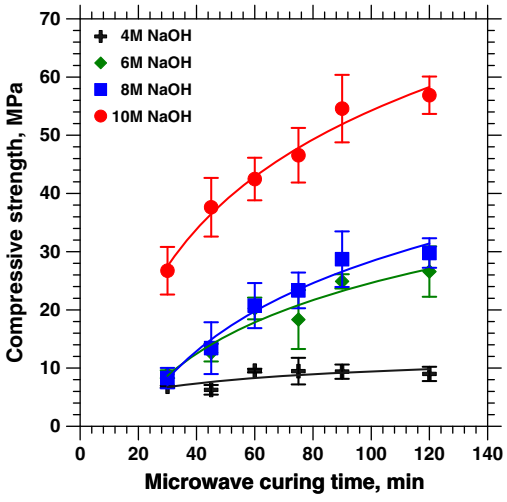

Fig. 2. Compressive strength as a function of microwave curing time for fly ash mortars activated using NaOH solutions of varying concentrations. The specimens were cured at an average incident power of 240 W. Error bars indicate one standard deviation from the mean compressive strength of three companion specimens.

3. Results, analysis, and discussions

3.1. Compressive strengths of microwave cured activated fly ash mortars: Influence of activator concentration and curing duration

Fig. 2 shows the compressive strengths as a function of microwave curing duration for fly ash mortars activated using NaOH solutions of different molar concentrations and cured using microwave radiation. In general, an increase in microwave curing duration increases the compressive strengths. Microwave curing provides volumetric heating to the specimen, which enhances the reaction kinetics. The formation of sodium aluminosilicate gel, which is the product of alkali activation of fly ash, results in strength development. A longer microwave curing duration facilitates the formation of increased amounts of the reaction product, and consequently strength enhancement. The evidence is presented in Fig. 3 where the micrographs of 8 M NaOH activated fly ash pastes at 30, 75, and 120 min of microwave curing are shown. Dissolution of fly ash particles by the activating agent, and some amount of reaction gel formation can be observed after 30 min of microwave curing, shown in Fig. 3(a). The reaction product formation increases with curing duration, as can be observed in Fig. 3(b) and (c). After 120 min of microwave curing, most of the fly ash particles are engulfed by the reaction gel as seen in Fig. 3(c).

Fig. 2 also provides indications of the influence of the activator concentration on the compressive strengths of microwave cured activated fly ash mortars. The compressive strengths are observed to be higher for the mortars activated using a higher concentration of the activator, irrespective of the curing duration. This is in line with the observations on strength development of heat cured Class F fly ash activated concretes [5]. For the mortars activated using lower concentrations of NaOH, there is no appreciable strength difference between mixtures activated using different NaOH concentrations at early periods of microwave curing (at 30 min), but there is strength enhancement with increasing activator concentration after that time. At short microwave curing durations and lower activator concentrations, the dissolution of fly ash particles and their poly-condensation to form a significant amount of aluminosilicate gel would not have happened due to the lack of activation energy. Increased dissolution rates under higher activator concentrations might have resulted in the formation of somewhat higher amounts of aluminosilicate gel even at shorter curing durations, and thereby higher strengths for such mixtures.

It is also seen from Fig. 2 that there is no appreciable strength increase with microwave curing for the mortars activated using a lower concentration of NaOH (4 M). The lower alkalinity of the activator is likely not very effective in solubilizing the silica and alumina species from fly ash and hence lower amounts of reaction

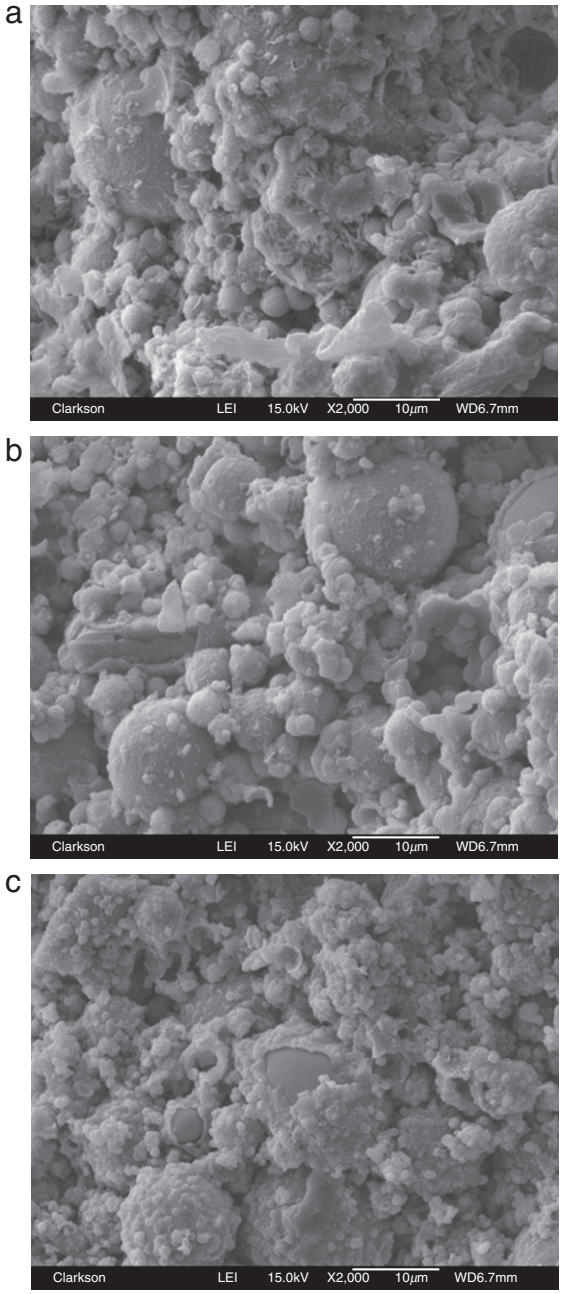

Fig. 3. Microstructure of 8 M NaOH activated fly ash pastes microwave cured for: (a) 30 min, (b) 75 min, and (c) 120 min. The scale bars correspond to 10 μm.

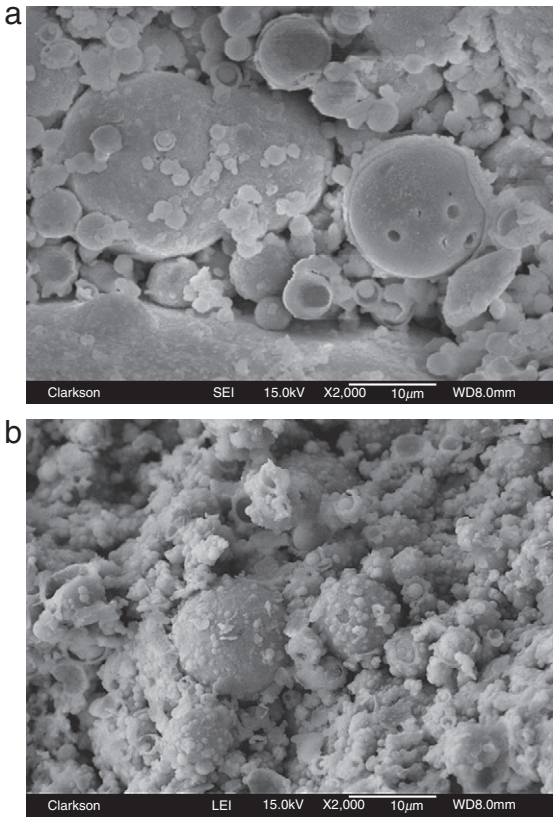

Fig. 4. Microstructure of: (a) 4 M NaOH activated, and (b) 10 M NaOH activated fly ash pastes, microwave cured for 120 min. The scale bars correspond to 10 μm.

products are formed. Fig. 4(a) and (b) provides a comparison of the microstructures of fly ash pastes activated using 4 M and 10 M NaOH respectively, microwave cured for 120 min. The influence of activator concentration on the amount of reaction products formed is evident from these figures. X-ray diffraction (XRD) patterns for unreacted fly ash, and 4 M and 10 M NaOH activated fly ash pastes after 120 min of microwave curing are shown in Fig. 5. No indication of the formation of new crystalline reaction products are observed for the 4 M NaOH activated fly ash paste whereas in the paste activated with 10 M NaOH, crystalline peaks of hydroxy sodalite are observed. In both cases of activation, the presence of quartz and mullite phases from fly ash in the XRD spectra points to the low reactivity of these phases in alkaline conditions. Quartz and mullite have dielectric loss factors (ε'') of 0.01 and 0.0001 respectively, rendering the microwave frequencies inefficient in heating them [31].

3.2. Comparison of the strengths of microwave cured and heat cured activated mortars

Fig. 6 shows the compressive strengths of 4 M, 6 M, 8 M and 10 M NaOH activated fly ash mortars that were heat cured for 48 h at 75 °C or microwave cured for 120 min at an average incident power of 240 W. In general, microwave curing at 240 W incident power for 120 min provides compressive strengths that are comparable to or higher than those for the mortars heat cured at 75 °C for 48 h. For the 4 M NaOH activated mortars, heat curing is found to result in slightly higher compressive strengths. This could be attributed to the longer duration of heat curing (48 h) that contributes to the better dissolution of the Al and Si species and gel formation in the case of lower activator concentration mortars. The better compressive strengths of microwave cured activated mortars can be attributed to two plausible reasons. First, microwave curing provides volumetric heating to the specimen that results in a uniform microstructure. Using the expression for penetration depth of microwave radiation given in [29], and approximate values of ε' and ε'' for concretes (taken as 5.69 and 0.62 respectively, which falls in the range of these values for concrete [32]), the penetration depth is obtained as 0.15 m, which is larger than the specimen size, confirming that volumetric heating takes place under microwave curing conditions. For heat cured specimens, the specimen surface (skin) is heated first and, and heat transfer takes place from the skin to the core owing to the temperature differential. This could potentially lead to non-uniform microstructures and stresses due to thermal gradients, and thus reduced strength as compared to the microwave cured specimens. However issues with thermal runway or increased microcracking

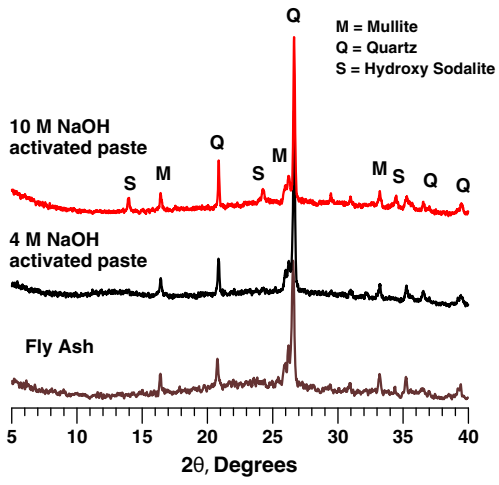

Fig. 5. XRD patterns of fly ash, and 4 M and 10 M NaOH activated fly ash pastes after 120 min of microwave curing.

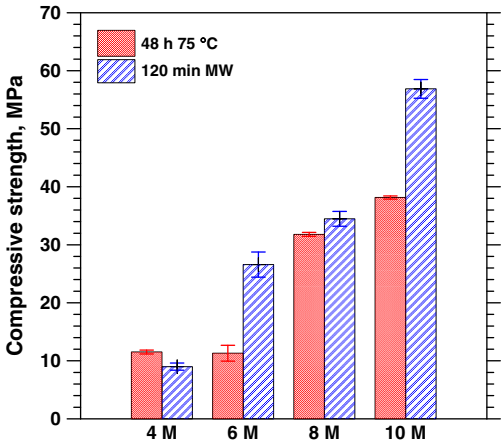

Fig. 6. Comparison of compressive strengths of heat cured (75 °C for 48 h) and microwave cured activated mortars. Error bars indicate one standard deviation from the mean compressive strength of three companion specimens.

when non-optimal microwave curing parameters such as incident power and duration are chosen need to be considered.

The second reason for the increased compressive strengths of microwave cured mortars can be attributed to the non-thermal "microwave effects". On exposure to microwave radiation, enhancements in the rates of activated processes in solids involving material transport have been reported [18,31], which are generally considered to be microwave effects because a reduction in activation energy is required. These effects are reported not to require the conversion of microwave energy into thermal energy. Though a universally agreed scientific basis for microwave effects is not available, a model based on thermodynamic stability of pores in a matrix of grains can be used to provide a reasonable explanation. The dielectric inhomogeneity of the material results in very high electric field enhancements at the solid phase-pore and particle–particle interfaces [33]. The local field enhancements improve the material flux in the convex surfaces of the pores [33] and results in non-isotropic pore closure [34], thus influencing the local driving force for densification of the microstructure. It needs to be stated that the presence or absence of microwave effects is intensely debated, with the critics pointing out that it is due to temperature gradients.

3.3. Temperature development during microwave curing and the rate of mass loss

3.3.1. Temperature development as a function of microwave curing time

The temperatures of the surface and the core of the microwave cured fly ash mortars activated using 8 M NaOH are shown in Fig. 7(a) as functions of microwave curing duration. The surface temperatures of the cubes were recorded using an infrared thermal scanner soon after the power to the cavity was shut down. The specimens were immediately taken out of the cavity and split using an impact device along the grooves on the surface, and the internal temperatures at various depths from the surface were recorded. It can be noticed from Fig. 7(a) that the surface temperatures are higher than the core temperatures until about 30 min of microwaving. Afterwards, the core temperatures are seen to be higher. The difference between the surface and core temperatures at different curing durations are not very high, indicating that the microwave input energy results in relatively uniform heating of the 50 mm size cubical specimens. It can also be seen from this figure that during the first 20 min of microwave curing, the temperature rises at a faster rate. During this time the energy absorbed by the specimen is utilized to increase the temperature of the pore solution to the level of or above its boiling point. The increased temperature enhances the reaction kinetics thus forming more reaction products, filling the voids previously occupied

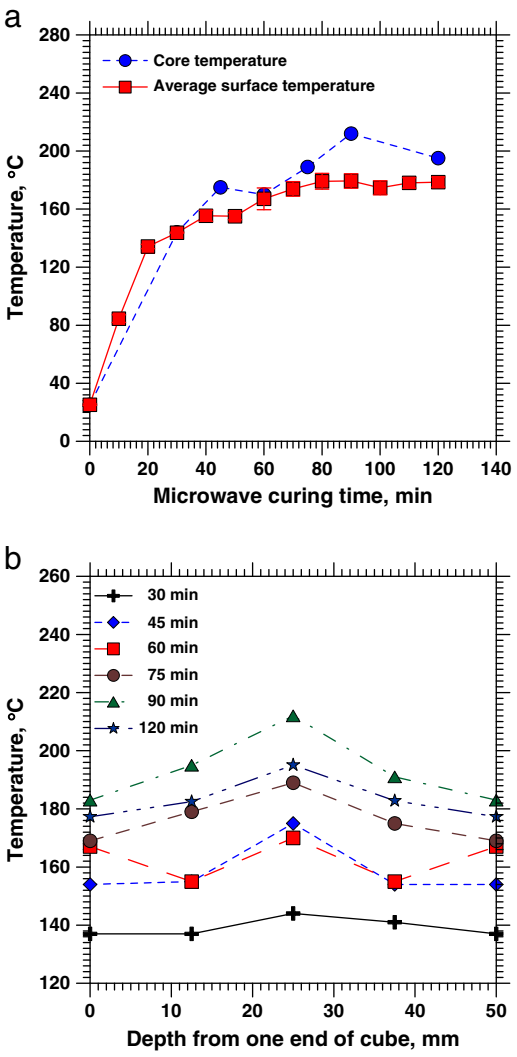

Fig. 7. (a) Variation of surface and core temperature with microwave curing duration, and (b) temperature distribution along the depth of the cube.

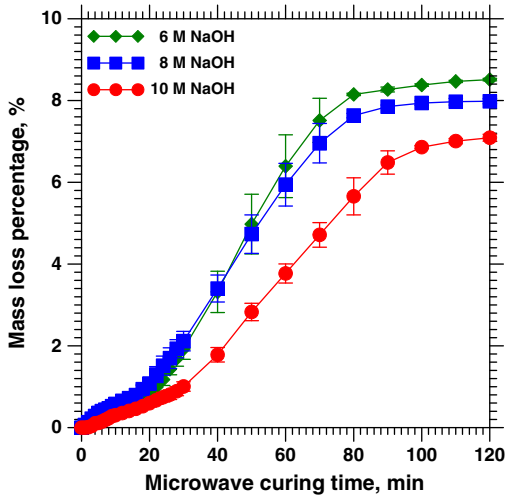

Fig. 8. Mass loss of the specimens as a function of activator concentration and microwave curing duration. Error bars indicate one standard deviation from the mean values for three companion specimens.

by the pore solution, and consequently enhancing the strength with microwave curing duration as observed in Fig. 2. The reaction product contains reduced amounts of moisture, and the available moisture is mostly bound. The frictional forces that generate heat are lower in the absence of free or loosely bound water, leading to temperature rises that are not very significant after this time.

Fig. 7(b) shows the temperature profile along the specimen depth at different microwave curing durations. Relatively uniform temperature across the specimen depth is observed in this case also. The temperature difference between the core and the surface of the specimens is found to increase with microwave curing duration. This is because, as the specimen temperatures increase with increasing curing duration, the temperature differential between the specimen and the microwave cavity increases. This introduces convective and radiative heat loss from the specimen surface to the cavity. Since the heat loss is proportional to the temperature differential, there is increased heat loss from the specimen surface with increasing microwave curing duration, resulting in an increased measured temperature of the core.

3.3.2. Mass loss during microwave curing and its impact on strength

The volumetric heating of the pore solution subjected to microwave fields induces moisture loss from the specimens. Fig. 8 shows the percentage mass loss of the specimens during microwave curing, expressed as the ratio of the difference between the mass of the cubes before and after microwave curing for a particular duration to the mass after microwave curing. As can be observed in this figure, there is a relatively lower rate of mass loss from the specimens during the initial 20 min or so of microwave curing. This is because the water loss is low at temperatures less than 100 °C. Fig. 7(a) has shown that the specimen temperature is rising during this time, because of the absorption of microwave energy. During the time interval between 20 and 90 min of microwave curing, the specimen temperature is much higher than 100 °C, and the evaporation of water (or pore solution) occurs at a higher rate which results in a higher mass loss rate, as shown by the steeper portion of the curve. Since water loss is occurring during this time, the temperature of the specimens does not increase significantly, as can be seen in Fig. 7(a). After about 75 to 90 min of microwave curing, most of the free water as well as the loosely bound water in the specimens are lost irrespective of the activator concentration. Therefore the mass loss remains relatively constant after 90 min of microwave curing. The microwave energy supplied is not very effective in heating a dry solid, with the consequence that the energy transfer rates are very low, and therefore negligible improvement in strength gain between 90 and 120 min is observed, as shown in Fig. 2.

For the most part of the microwave curing regime, it can be seen in Fig. 8 that the mass loss at various curing durations for the 10 M NaOH activated mortars are lower than those for the 8 M and 6 M NaOH activated mortars. This could be attributed to the increased reaction product formation and the consequent development of a more compact microstructure in mortars activated using highly alkaline activator, which hinders moisture transport. Also, the boiling point of the pore solution increases with ionic strength (5 to 15 °C boiling point rise when the NaOH concentration increases from 4 M to 10 M [35]), and hence moisture is less readily removed from mortars activated with a higher concentration of the activator. For the mortars activated using solutions of higher alkalinity, pore volume creation because of loss of moisture (Fig. 8) is more than compensated for by the faster reaction rates and increased gel formation, resulting in better strength enhancement with curing duration. However, this is not the case for mortars activated using solutions of lower NaOH concentrations, where the increased reaction product formation with microwave curing time is negated by the increase in pore volume fraction because of moisture loss, as can be seen from the strength results of 4 M NaOH activated mortars.

3.3.3. Implications of increased temperature and rapid moisture loss

The measured surface temperature of the specimens increases from about 120 °C after 20 min to more than 160 °C after 60 min of microwave curing as shown in the previous section. Such high temperatures could be attributed in part to the small specimen size used in this study (50 mm cubes). The theoretical maximum specimen size of 150 mm, which will still ensure volumetric heating for the conditions used in this study, might result in reduced specimen temperatures. The moisture loss from the mortar cubes are accelerated by the increased temperatures, even though these high temperatures enhance the reaction product formation (Fig. 3) thus resulting in better strength gain (Fig. 2). The high specimen temperatures and the pronounced rate of moisture loss might contribute to microcracking in the specimens, which is likely to result in strength reduction (even though evidences of microcracking were not observed in the micrographs in this study). Hence it is important to adequately understand and quantify the influence of temperature attained by the specimens in the microwave cavity (which depends on power supplied (see Eq. (3)) and the specimen size), and the associated moisture loss on the kinetics of activation, reaction product formation, and potential microcracking that will influence the resultant microstructure and hence the mechanical and transport properties. In addition, microwave (non-thermal) effects might also influence microstructure and property development. The optimization of specimen sizes based on the power supplied by the microwave, curing method (permitting drying as done in this work, or restricting drying by sealing the specimens), and curing duration are expected to be important aspects that would need further consideration, but beyond the scope of this paper.

3.4. Quantification of energy absorption by the mortars in the microwave

The efficiency of microwave curing depends on the amount and rate of microwave energy absorbed by the specimens. The average energy absorption rate (or the power absorbed) for a single 50 mm cube of 8 M NaOH activated fly ash mortar is shown in Fig. 9 as a function of the microwave curing duration. The energy absorbed by the specimens is primarily due to the dielectric heating of the pore solution. It can be noticed from Fig. 9 that the energy absorption rate remains relatively constant until about 75 min of microwave curing, and then drops significantly. Similar trends are reported for the power absorbed by humidified cement powder [36]. The mass loss as a function of microwave curing duration for this mortar mixture is also plotted in Fig. 9 to establish the fact that the reduction in power absorbed by the specimen begins when no further mass loss occurs. In other words, energy absorption rate drops to about half when most of the free water in the system is removed.

3.4.1. Energy absorption rate (power) and dielectric parameters

The absorbed power is dependent on the dielectric loss factor and the internal electric field intensity (Eq. (2)). The relatively constant energy absorption rate during the initial 75 min or so shown in Fig. 9 even when the temperature has gone up can be explained by considering the variation of both these parameters. Reduction in moisture content reduces the dielectric loss factor (ε''). Since the ε'' values at 2.45 GHz frequency were not obtained in this study, the ratio of ε'' at various microwave curing durations to ε'' just before the start of microwave curing ($\varepsilon''_t/\varepsilon''_{t=0}$) corresponding to a frequency of 10 MHz is shown as a function of the microwave curing duration in Fig. 10. The normalized loss factors can reasonably be assumed to be frequency independent within a few decades of frequency. It can be seen that the normalized ε'' values decreases for the initial 75 min and then remains relatively constant, indicating the influence of moisture content on the measured dielectric loss factor. A similar trend, but less pronounced in magnitude, is also noticed for the normalized loss tangent at 10 MHz frequency, showing that ε'' drops at a much rapid rate than ε' with increasing microwave curing time (and decreasing moisture content).

If the power absorbed has to remain relatively constant, a reduction in dielectric loss factor with microwave curing time necessitates an increase in the internal electric field intensity during this time. The internal electric field is controlled by the dielectric constant (ε') and is a fraction of the external electric field, depending on the depolarization factor (N). The depolarization factor has to be considered because the surface charges produce a depolarization field opposing the applied electric field [27]. The external electric field can be considered to be fairly uniform if the cavity size is larger than the wavelength of microwaves. The ratio of internal to external electric fields is given as [27]:

$$\frac{E_{int}}{E_{ext}} = 1 - \frac{N(\varepsilon' - 1)}{1 + N(\varepsilon' - 1)}. \quad (9)$$

Using a value of 1 for the depolarization factor (corresponding to a thin slab normal to the applied field), electric field ratios were calculated and plotted as a function of microwave curing duration in Fig. 10. The dielectric constant values at 10 MHz were used in this case also. If the external electric field is considered not to be time dependent, it can be seen that E_{int} increases until about 75 min of microwave curing and then starts to decrease. The increase in E_{int} is

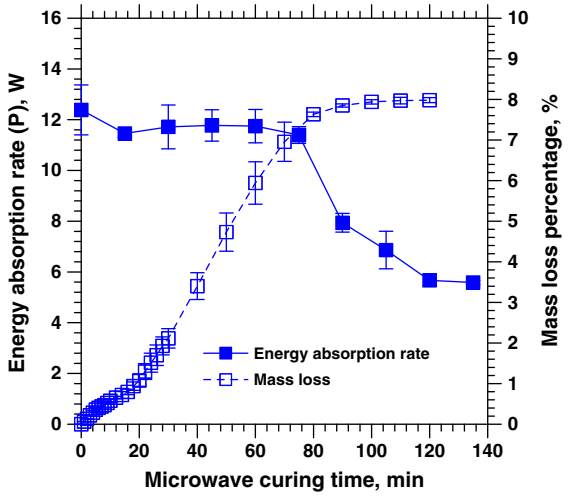

Fig. 9. Energy absorption rate and percentage of mass loss of 8 M NaOH activated mortars. Error bars indicate one standard deviation from the mean values for three companion specimens.

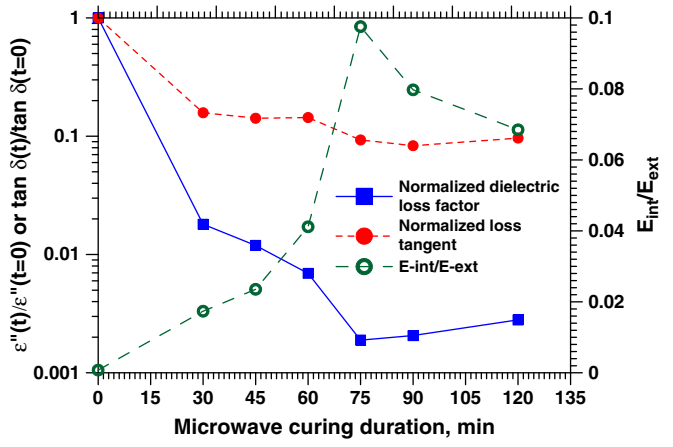

Fig. 10. Variation of normalized dielectric loss factor and dielectric loss tangent, and the ratio of internal to external electric field intensity as a function of microwave curing duration.

possibly a non-thermal microwave effect (the reasons for which were explained in an earlier section) because the temperatures are not found to change much between, say 30 and 75 min of microwave curing, and the temperature gradients are also low as seen in Fig. 7(b). The absorbed energy remains relatively constant until 75 min because the reduction in ε'' is compensated by an increase in E_{int}. The reduction in absorbed power after this time even when ε'' stays relatively constant can be attributed to the drop in the internal electric field. It has been reported that the microwave effect diminishes at lower values of dielectric loss factors [37], resulting in a reduction in E_{int} as can be observed in Fig. 10. All these processes can be related to the presence or absence of free water in the system that creates dissimilarities in the dielectric parameters between the pore and solid phases. Microwave curing under sealed conditions (where moisture loss from the specimen is prevented) would then be expected to lead to very different electric field ratios and dielectric parameters, and thus a different material behavior would ensue.

3.4.2. Cumulative energy absorbed and compressive strength

The cumulative energy absorbed by the specimens is obtained by integrating the power absorbed–time curve which was shown in Fig. 9. The relationship between compressive strength and the cumulative energy absorbed by a single 50 mm cubical specimen of 8 M NaOH activated fly ash mortar at several microwaving durations is shown in Fig. 11. In general, the compressive strength increases with an increase in absorbed energy as expected. It is observed that beyond an absorbed energy of about 60 kJ, there is no appreciable increase in compressive strength. The time at which this amount of energy is absorbed is related to the microwave curing duration at which: (i) mass loss plateaus, (ii) dielectric loss factor stops decreasing, and (iii) the internal electric field stops increasing. All of these processes can be related to the free water content in the system and the rate at which microwave energy provides volumetric heating so as to heat the water and enhance the reaction kinetics.

The absorbed energy depends on the specimen size, its mass and moisture content, in addition to the dielectric parameters of the material. Within the parameters of this study, it is seen that the energy required to achieve an average compressive strength of 30 MPa for a 50 mm cube of 8 M NaOH activated fly ash mortar is approximately equal to the energy required to raise the temperature of 1 kg of water by about 15 °C. Activation using higher alkali concentrations would bring down the microwave energy required to achieve the same compressive strength. Optimization of the material parameters (water content, activator concentration, and additives that absorb microwave energy), specimen characteristics (size and shape, and sealed or unsealed), and microwave curing parameters (power level and time) can thus be accomplished using the strength-to-energy ratio maximization as one of the key targets. In addition, considerations must also be given to the influence of increased activator concentration on aspects such as efflorescence and carbonation, as well as health and safety issues and cost.

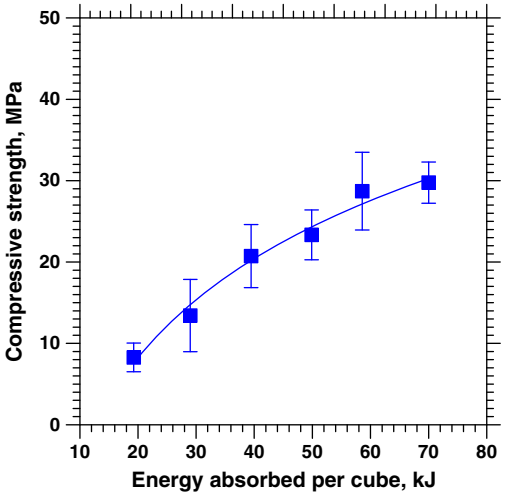

Fig. 11. Relationship between cumulative energy absorbed and compressive strength for 8 M NaOH activated mortars. Error bars indicate one standard deviation from the mean values for three companion specimens.

4. Conclusions

The focus of this study was mainly on the compressive strength and microstructure development of alkali activated fly ash mortars under microwave curing, and their relationship to the dielectric characteristics and internal electric field in the material. The following conclusions, pertaining to the range of parameters considered, are drawn from this study.

i) The compressive strengths of NaOH activated fly ash mortars were found to increase with microwave curing duration and activator concentration. It was found that 120 min of microwave curing at the chosen power levels resulted in compressive strengths that were similar to or higher than those of mortars heat cured at 75 °C for 48 h. Volumetric heating and the absence of thermal gradients that results in a uniform microstructure, as well as potentially some non-thermal microwave effects that facilitates microstructure densification can be attributed to better strengths under microwave curing conditions.

ii) A more compact microstructure that hinders moisture movement, and the higher ionic strength of the pore solution in mortars activated with a higher concentration of NaOH resulted in reduced moisture loss from these specimens. Lack of strength gain after about 90 min of microwave curing was attributed to the loss of free water by this time, and the fact that microwave energy is not very efficient in heating a dry solid with a low loss factor.

iii) The energy absorption rate by the mortar specimens in the microwave cavity stayed relatively constant until the time when free water was available in the system. It was shown that a reduction in dielectric loss factor (because of the loss of water) was compensated by an increase in internal electric field intensity (possibly attributed to microwave effects), thereby resulting in constant energy absorption rates. The loss of free water stabilizes the loss factor, but the electric field intensity drops because the microwave effects cease to exist at lower values of loss factor, causing the energy absorption rate also to drop. The compressive strength was found to be well related to the total energy absorbed by the specimens, especially in the time period when free water was available in the system.

References

[1] M. Sofi, J.S.J. van Deventer, P.A. Mendis, G.C. Lukey, Engineering properties of inorganic polymer concretes (IPCs), Cement and Concrete Research 37 (2007) 251–257.
[2] T. Bakharev, Geopolymeric materials prepared using Class F fly ash and elevated temperature cueing, Cement and Concrete Research 35 (2005) 1224–1232.
[3] H. Xu, J.S.J. van Deventer, The geopolymerization of alumino-silicate minerals, International Journal of Mineral Processing 59 (2000) 247–266.
[4] P. Duxson, J.L. Provis, G.C. Lukey, S.W. Mallicoat, W.M. Kriven, J.S.J. van Deventer, Understanding the relationship between geopolymer composition, microstructure and mechanical properties, Journal of Colloids and surfaces A: Physiochem. Eng. Aspects 269 (2005) 47–58.
[5] D. Ravikumar, S. Peethamparan, N. Neithalath, Structure and strength of NaOH activated concretes containing fly ash or GGBFS as the sole binder, Cement and Concrete Composites 32 (2010) 399–410.
[6] D. Panias, I.P. Giannopoulou, T. Perraki, Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymer, Journal of Colloids and Surfaces A: Physicochemical Engineering Aspects 301 (2007) 246–254.

[7] M. Criado, A. Fernández-Jiménez, A. de la Torre, M.A.G. Aranda, A. Palomo, An XRD study of the effect of SiO_2/Na_2O ratio on the alkali activation of fly ash, Cement and Concrete Research 37 (2007) 671–679.
[8] I. Teoreanu, A. Volceanov, S. Stoleriu, Non portland cements and derived materials, Cement and Concrete Composites 27 (2005) 650–660.
[9] J.G.S. van Jaarsveld, J.S.J. van Deventer, G. Lukey, The characterization of source materials in fly ash-based geopolymers, Materials Letters 57 (2003) 1272–1280.
[10] F. Puertas, A. Fernandez-Jimenez, M.T. Blanco-Varela, Pore solution in alkali-activated slag cement pastes. Relation to the composition and structure of calcium silicate hydrate, Cement and Concrete Research 34 (2004) 139–148.
[11] J.E. Oh, P.J.M. Monteiro, S.S. Jun, S. Choi, S.M. Clark, The evolution of strength and crystalline phases for alkali-activated ground blast furnace slag and fly ash based geopolymers, Cement and Concrete Research 40 (2010) 189–196.
[12] E. Alvarez-Ayuso, X. Querol, F. Plana, A. Alastuey, N. Moreno, M. Izquierdo, O. Font, T. Moreno, S. Diez, E. Vazquez, M. Barra, Environmental, physical and structural characterization of geopolymer matrixes synthesized from coal (co-)combustion fly ashes, Journal of Hazardous Materials 154 (2008) 175–183.
[13] M. Criado, A. Palomo, A. Ferna´ndez-Jime´nez, Alkali activation of fly ashes. Part 1: effect of curing conditions on the carbonation of the reaction products, Fuel 84 (2005) 2048–2054.
[14] G. Kovalchuk, A. Ferna´ndez-Jime´nez, A. Palomo, Alkali activated fly ash: effect of thermal curing conditions on mechanical and microstructural development — Part II, Fuel 86 (2007) 315–322.
[15] M. Criado, A. Palomo, A. Ferna´ndez-Jime´nez, Alkali activation of fly ash. Part III: effect of curing conditions on reaction and its graphical description, Fuel 89 (2010) 3185–3192.
[16] S. Das, A.K. Mukhopadhyay, S. Datta, D. Basu, Prospects of microwave processing: an overview, Bulletin of Material Science 32 (2009) 1–13.
[17] D.K. Agrawal, Microwave processing of ceramics, Current Opinion in Solid State and Materials Science 3 (1998) 480–485.
[18] E.T. Thostenson, T.-W. Chou, Microwave processing: fundamental and applications, Composites: Part A 30 (1999) 1055–1071.
[19] P. Rattanadecho, N. Suwannapum, B. Chatveera, D. Atong, N. Makul, Development of compressive strength of cement paste under accelerated curing by a continuous microwave thermal processor, Materials Science and Engineering A 472 (2008) 299–307.
[20] T. Pheeraphan, L. Cayliani, M.I. Dumangas Jr., P. Nimityongskul, Prediction of later-age compressive strength of normal concrete based on the accelerated strength of concrete cured with microwave energy, Cement and Concrete Research 32 (2002) 521–527.
[21] C.K.Y. Leung, T. Pheeraphan, Determination of optimal process for microwave curing of concrete, Cement and Concrete Research 27 (1997) 463–472.
[22] D. Sohn, D.L. Johnson, Microwave curing effects on the 28-day strength of cementitious materials, Cement and Concrete Research 29 (1999) 241–247.
[23] X. Querol, A. Alastuey, A. Lopez-Soler, F. Plana, A fast method for recycling fly ash: microwave-assisted zeolite synthesis, Environmental Science and Technology 31 (1997) 2527–2533.
[24] O.G. Somani, A.L. Choudhari, B.S. Rao, S.P. Mirajkar, Enhancement of crystallization rate by microwave radiation: synthesis of ZSM-5, Materials Chemistry and Physics 82 (2003) 538–545.
[25] X. Xu, Y. Bao, C. Song, W. Yang, J. Liu, L. Lin, Microwave-assisted hydrothermal synthesis of hydroxy-sodalite zeolite membrane, Microporous and Mesoporous Materials 75 (2004) 173–181.
[26] G.M.B. Parkes, P.A. Barnes, G. Bond, E.L. Charsley, Qualitative and quantitative aspects of microwave thermal analysis, Thermochimica Acta 356 (2000) 85–96.
[27] NMAB 473, Microwave Processing of Materials, National Academy Press, Washington DC, 1994, p. 150.
[28] D.E. Clark, D.C. Folz, J.K. West, Processing materials with microwave energy, Materials Science and Engineering A 287 (2000) 153–158.
[29] W. Cha-um, P. Rattanadecho, W. Pakdee, Experimental analysis of microwave heating of dielectric materials using a rectangular wave guide (MODE: TE_{10}) (Case study: water layer and saturated porous medium), Experimental Thermal and Fluid Science 33 (2009) 472–481.
[30] S.J. Ma, X.W. Zhou, X.J. Su, W. Mo, J.L. Yang, P. Liu, A new practical method to determine the microwave energy absorption ability of materials, Minerals Engineering 22 (2009) 1154–1159.
[31] D.E. Clark, D.C. Folz, What is microwave processing, in: D.E. Clark, D.C. Folz, C.E. Folgar, M.M. Mahmoud (Eds.), Microwave Solutions for Ceramic Engineers, The American Ceramics Society, Inc., Westerville, OH, 2005, pp. 1–26.
[32] O. Buyukozturk, T.-Y. Yu, J.A. Ortega, A methodology for determining complex permittivity of construction materials based on transmission-only coherent, wide-bandwidth free-space measurements, Cement and Concrete Composites 28 (2006) 349–359.
[33] M. Willert-Porada, A microstructural approach to the origin of microwave effects in sintering of ceramics and composites, in: D.E. Clark, W.H. Sutton, D.A. Lewis (Eds.), Microwaves: Theory and Applications in Materials Processing IV, Proceedings of the First World Congress on Microwave Processing, The American Ceramic Society, Orlando, 1997, pp. 153–163.
[34] G. Link, S. Miksch, S. Takayama, M. Thumm, Direct experimental demonstration of non-thermal microwave effects during sintering of ceramics, Proceedings of the 33rd IEEE International conference on Plasma Science, Traverse City, MI, June 2006, 10.1109/PLASMA, 2006, p. 1707227.
[35] M. Bialik, P. Sedin, H. Theliander, Boiling point rise in sodium salt solutions, Industrial Engineering and Chemical Research 47 (2008) 1283–1287.
[36] M.A. Abdelghani-Idrissi, Experimental investigations of occupied volume effect on the microwave heating and drying kinetics of cement powder in a mono-mode cavity, Applied Thermal Engineering 21 (2001) 955–965.
[37] J. Binner, D. Price, J. Wang, B. Vaidyanathan, M. Reading, Evidence for non-thermal microwave effects using hybrid conventional/microwave heating, Proceedings of the 10th International Conference on Microwave and High Frequency Heating, Modena, Italy, 2005, p. 4.