

Microwave heating on cement-pozzolan pastes: Dielectric permittivity, physical properties and numerical heat transfer characteristics

Natt Makul*

Faculty of Industrial Technology, Phranakorn Rajabhat University,
9 Changwattana Road, Bangkok Bangkok, 10220, Thailand

Abstract

Cement-pozzolan pastes at a very early stage subjected to microwave heating were investigated. Microwave at an operating frequency of 2.45 GHz associated with a multi-mode cavity was used. The pastes containing pulverized fuel ash (PFA) or silica fume (SF) were proportioned with a 0.22-water/solid mass ratio (w/s). Test results showed that the temperature increased continuously during microwave heating. Some small fibers appear in the paste but none appear in the microwave-heated PFA-cement paste. For the SF-cement paste the SF particles under microwave heating had dispersed. The pastes can be consumed more $\text{Ca}(\text{OH})_2$ in the pozzolan reaction to produce more C-S-H. The calculated temperature rise of the paste containing PFA without loss of moisture and steady heat transfer conduction consistently agreed with the proposed mathematical model.

Keywords: Microwave heating, Cement-pozzolan pastes, Dielectric, Heat transfer

1. Introduction

Up to the present time, pozzolan has been used for many years for construction applications. It is used as a substitute material in Portland cement for enhancing various properties of cement and concrete. The popular pozzolan materials include pulverized fuel ash (PFA) and silica fume (SF). For examples, pulverized fuel ash (PFA) offers to improve concrete workability, lowers water requirement, reduces heat of hydration, reduces the permeability and adsorption of concrete, and is economical [1,2]. The silica fume (SF) improves the properties of fresh and hardened concrete such as strength and density, etc. [3]. However, these materials require selective processing for enhancing their performance, such as heating (heating) condition at early age of hydration reaction. Thermal acceleration method is taken into consideration. However, though thermally cured methods evince drawbacks both in the early-age and long-term phases. For example, it induces micro-cracking and delayed ettringite formation [4]. Therefore, by changing the heating mechanism as in microwave heating in which the heating occurs from inside the sample when an interaction between the microwave field and the cement-water system results in volumetric heating [5]. This concept will be used in one of the accelerated heating methods [7-10] or enhancement of the reaction of Portland cement paste explored in the current study. In addition since these fields have been grown gradually, as there has not been much research over the last years. Therefore, this work is to extend microwave heating knowledge. A theoretical heat transfer model, the temperature rise within the paste at an early stage after mixing for 30 minutes when subjecting microwave energy is also proposed.

2. Experimental program

2.1 Materials

Hydraulic Portland cement Type 1 (OPC), pulverized fuel ash (PFA) and silica fume (SF) were used throughout this study. Their chemical compositions and physical properties are listed in Table 1. The ASTM C618 [11] classifies the PFA as a low calcium (Type F)

and metakaolin. Silica fume was also used as a high-pozzolan material in accordance with the ASTM C1240 [12]. Deionized water with a pH 7.5 and a high range water reducing admixture as well known as superplasticizer, conformed to the ASTM C494 [13] were also used.

Table 1 Chemical composition (% by mass) and physical properties of the materials used.

Element	OPC	SF	PFA
SiO_2	16.37	96.00	47.80
Al_2O_3	3.85	0.10	22.70
Fe_2O_3	3.48	0.10	21.90
MgO	0.64	0.13	0.92
CaO	68.48	0.12	2.18
Na_2O	0.06	0.10	0.32
K_2O	0.52	0.45	2.15
SO_3	4.00	0.02	0.37
Physical properties			
Loss on Ignition	1.70	2.57	1.44
Specific Gravity	3.12	2.90	2.45
Specific Surface			
Area (m^2/g)	0.85	18.02	0.70

2.2 Sample preparation

The pastes were proportioned at a water-solid mass ratio of 0.22 as shown in Table 2. Herein, the superplasticizer was used as a recommended dosage rate of 1% of total solid content. After mixing and molding, they were cured at room temperature by wrapping with polyethylene plastic until the delay time (time after mixing until introducing microwave energy with a multi-mode cavity) of 30 minutes. A Hobart mixer was used to mix the solids and liquids according to ASTM C305 [14]. Cylindrical samples of the dimensions of ϕ 69.0 mm \times 40.0 mm were cast.

For conventional curing method, the paste samples were cured until testing time by saturated-lime deionized water at 25 $^{\circ}\text{C}$ to compare the characteristic of microwave-cured paste.

*Corresponding Author: E-mail: shinomomo7@hotmail.com

Table 2 Mixtures used (by weight in grams).

Mix	OPC	PFA	SF	Water
	(g)	(g)	(g)	(g)
PFA20_Super_1%	400	100	0	110
SF20_Super_1%	400	0	100	110

2.3 Microwave heating method

The microwave heating system used in this study is shown in Fig. 1 that includes an industrial microwave generator model. This model can generate microwave energy at 2.45 ± 0.05 GHz and a maximum power of 6.0 kilo-Watt into a multimode applicator. This microwave apparatus does not provide real-time monitoring of temperature changes during microwave heating; therefore, the temperature of the sample was measured at the start and end of the heating process. In order to measure the temperature of the sample subjected to microwave energy, the positions of measurement were determined. Microwave energy at a power of 390 Watt for 45 minutes application time and 30 minutes delay time after mixing the paste specimens was employed that is an optimal condition from preliminary study. The temperature of the top surface and the bottom surface was measured 5 times for each; likewise, the sample was immediately fractured and inside temperature was also measured 5 times.

2.4 Test procedures

For measuring dielectric permittivity of cementitious materials in the range of 2.45 GHz, a network analyzer with open-ended coaxial probe as shown in Fig. 2 was used. After mixing and placing into the mold, it was then wrapped by Styrofoam with 5 mm in thickness in order to protect the heat loss. Both dielectric permittivity and semi-adiabatic temperature using a data logger with thermo-couple (Type K) was simultaneously recorded every 180 and 15 minutes, respectively.

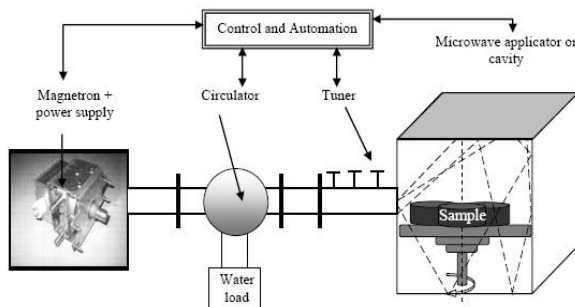


Fig. 1 Configuration of the microwave heating package.

A Scanning Electron Microscope (SEM) associated with energy dispersive X-ray spectroscopy 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 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 at a rate of $2^\circ 2\theta$ per minute.

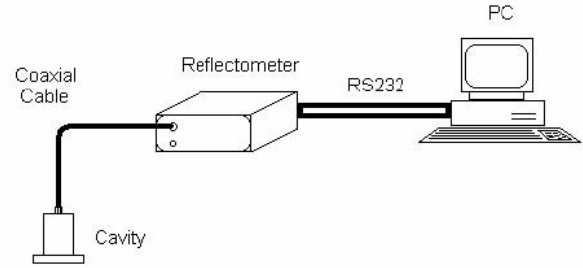


Fig. 2 Portable network analyzer.

3. Numerical analysis

3.1 Physical model

A schematic diagram of the physical model is shown in Fig. 3. The temperature of the material introduced to the incident wave is obtained by solving the conventional heat transport equation with the microwave power included as a local electromagnetic heat-generation term [15].

The materials considered were cement pastes at a w/s equal to 0.22, which consist of Portland cement Type 1, water, and air. They are, therefore, homogeneous and isotropic in terms of structure. In order to analyze the process of heat transport due to microwave heating of dielectric materials, the following assumptions were made:

- The local thermodynamic equilibrium is achieved.
- The liquid phase is not compressible $\rho_l = \text{constant}$.
- No chemical reactions within the material.
- Radiation modes are negligible.
- The effect of the natural and induced convections can be neglected.

In this task, from a macro-level point of view, the pore structure within the microwave-cured paste is assumed to be homogeneous and isotropic. Therefore, a heating model for a homogeneous and isotropic material is used in this analysis.

3.2 Governing equations

The governing equations describing the temperature rise in the paste to be processed by microwave energy are:

(1) Electromagnetic wave:

$$\nabla \times (\mu_r^{-1} \nabla \times \vec{E}) - k_0^2 \left(\epsilon_r - j \frac{\sigma}{\omega \epsilon_0} \right) \vec{E} = 0 \quad (1)$$

where μ_r is the relative permeability, \vec{E} is the electric field intensity (V/m), k_0 is the free space wave number, ϵ_r is the relative permittivity, σ is the electric conductivity (S/m), ω is the angular frequency (radians per second).

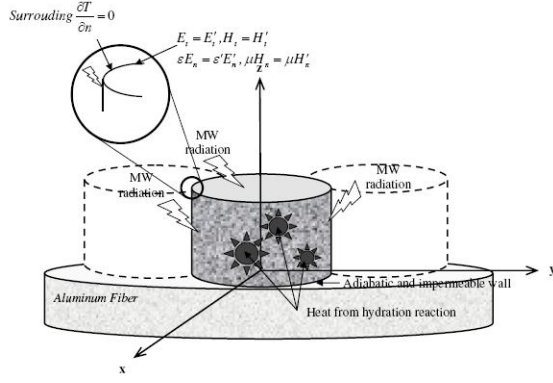


Fig. 3 Physical model.

(2) Heat transfer (conduction mode):

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = Q \quad (2)$$

where k is the thermal conductivity ($\text{W}/(\text{m}\cdot\text{K})$), T is the absolute temperature (K), Q contains heat sources other than viscous heating (W/m^3), ρ is the density (kg/m^3), and C_p is the specific heat capacity at constant pressure ($\text{J}/(\text{kg}\cdot\text{K})$).

3.3 Boundary conditions

3.3.1 Adiabatic boundary condition

Assuming that the surroundings of the paste are insulated (no heat and moisture transfer between the system and surroundings):

$$\left. \frac{\partial T}{\partial n} \right|_{\text{sample surface}} = \left. \frac{\partial T}{\partial t} \right|_{\text{sample surface}} = 0 \quad (3)$$

3.3.2 Continuity boundary condition

For the microwave heating of the cement paste, the temperature and heat flux at the interface of sample and air within the microwave cavity to be continuous:

$$T = T', \quad \lambda_{\text{eff}} \left. \frac{\partial T}{\partial n} \right|_{\text{boundary}} = \lambda'_{\text{eff}} \left. \frac{\partial T}{\partial n} \right|_{\text{boundary}} \quad (4)$$

3.3.3 Electromagnetic boundary condition

$$n \times \vec{E} = 0 \quad (5)$$

where n is the normal vector.

3.3.4 Initial conditions

The initial condition of the microwave-cured cement paste sample defined as:

$$T = T_0 = 298.15 \text{ K at } t = 0 \quad (6)$$

3.4 Numerical method

A commercial Finite Element package COMSOLTM [16] was employed. A non-uniform triangular grid was in excess of 9.12×10^4 cells, resulting in more than 5.15×10^5 degrees of freedom. The execution time on a Intel® CoreTM Quad CPU

Q8400@2.66 GHz (4 GB RAM) was 9.45×10^4 s. The tolerance has been kept to 1.0×10^{-4} for all executable variables.

3.5 Parameters used to calculate

The parameters used in this calculation are shown in the Table 3.

Table 3 Variables used for calculation.

Variables	Values	Unit
ρ (density)	1936	$\text{kg} \cdot \text{m}^{-3}$
C_p	$0.75 + 3.43 \times M_f^{\text{water}}$ $M_f^{\text{water}} = 0.22/1.22$	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
Q (heat of hydration)	316.13	$\text{W} \cdot \text{m}^{-3}$
Relative permittivity	$13.8245 - j \cdot 3.556$	

4. Results and discussion

4.1 Dielectric properties

Effects of silica fume (SF) and pulverized fuel ash (PFA) on dielectric permittivity; temperature rises and setting time of the pastes are shown in Fig. 4. The dielectric constant of the paste containing PFA through the first 24 hours hydration time is higher than that of the plain paste, whereas the paste containing SF is lower. Both reactions involving SF and PFA occur as secondary reactions [2]. This means, however, that the PFA can produce excessive water in the paste while increasing Si^{3+} and Ca^{2+} ions in the system. This results in an increasing dielectric constant of the paste. Contrary to the SF paste, the compositions with PFA can dissolve it at a high rate, its fineness induces the bounding of its water molecules and ion-richness at the surface. As a result, the dielectric constant is lower than that of the plain cement paste. For loss factor evolution, the difference of loss factor is low between the conventional paste and SF-paste and large with PFA-paste; indicating that the remaining water content both during introduction and acceleratory periods in the paste has strong effect on the dielectric loss. On the other hand, the PFA particles can retain the free water in the paste system and this may raise the loss factor of the PFA-paste very high.

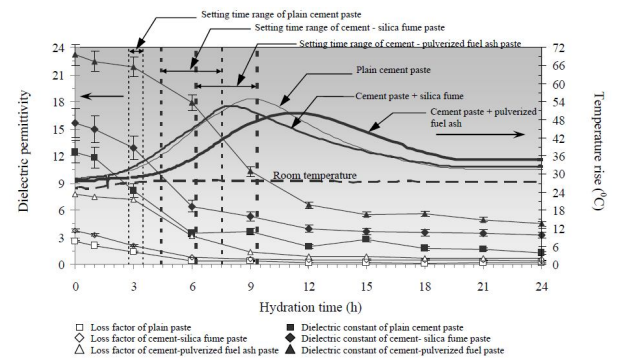


Fig. 4 Dielectric permittivity of pastes with different pozzolan materials.

4.2 Temperature and power evolution

The temperature profile of the pastes at a microwave power of 390 Watt with a specific application time of 45 minutes is shown in Fig. 5. The temperature increases monotonically among the points of measurement during the microwave-heating process and

reached a maximum temperature of 91 °C at the inside of the microwave-cured PFA-cement paste, while equal to 59.5 °C of the microwave-cured SF-cement paste. Significantly, for pastes containing pozzolan temperature rise relates to the free water that was not absorbed by the pozzolan, and the amount of heat that microwave energy generates is also decreased as well. It is well-known that the PFA particles are more rounded in shape than the SF particles, and as a result the PFA-cement paste shows the highest temperature increase among the three.

Furthermore, at early-age microwave heating, the rate at which the temperature increases is higher than the sequential temperature profile of the PFA-cement paste. This is due to the fact that microwave energy accelerates rapidly the hydration [17] and pozzolan reactions and thus affects the production of Portlandite ($\text{Ca}(\text{OH})_2$). This is subsequent to an increase in the concentration of Portlandite, which, in turn, also speeds up the pozzolanic reaction. And, it should be noted that an increase in this reaction is accompanied by an increase in heat liberation or temperature rise.

In regard to the bottom of the microwave-cured paste, it has a higher temperature level than the top side or the inside. At the top side, the temperature level was affected by the rate at which the water evaporated; that is, the temperature dropped gradually; at the bottom water evaporation took place even more slowly. While the heat accumulated on the bottom side, and thus caused the temperature to increase more quickly at the bottom than at other points of measurement.

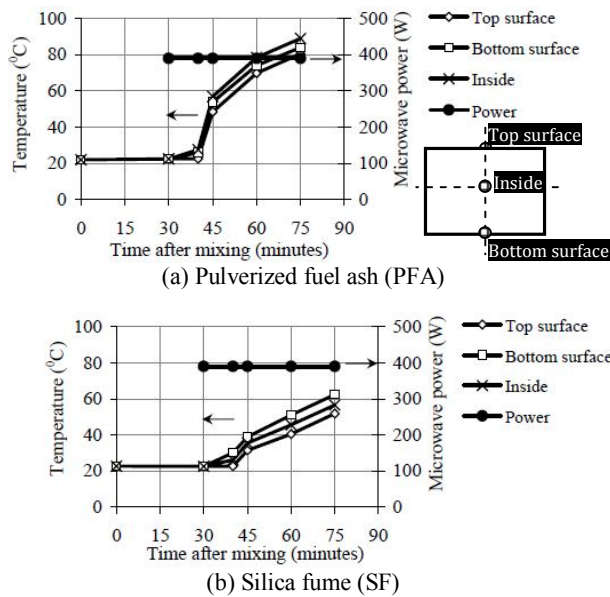


Fig. 5 Temperature and power history during applying microwave energy of various cement pastes mixed with pozzolan materials.

4.3 Morphology

The typical micrographs of PFA-cement and SF-cement pastes at the age of 4 hours after mixing and heating by wrapping with a plastic sheet; at 28 days after heating in lime-saturated deionized water; and after being subjected to microwave energy at a microwave power of 390 Watt for 45 minutes are shown in Fig. 6. The PFA-cement paste shows little difference among the microstructures at the three detecting times. Some small

fibers appear at the age of 4 hours, but none appear in the PFA-cement paste that was heated by microwave energy. On the other hand, for the SF-cement paste the SF particles under microwave heating have dispersed more than the 4-hours normal heating, while the paste at 28 days looks like a plate of C-S-H in which SF particles cannot be distinguished.

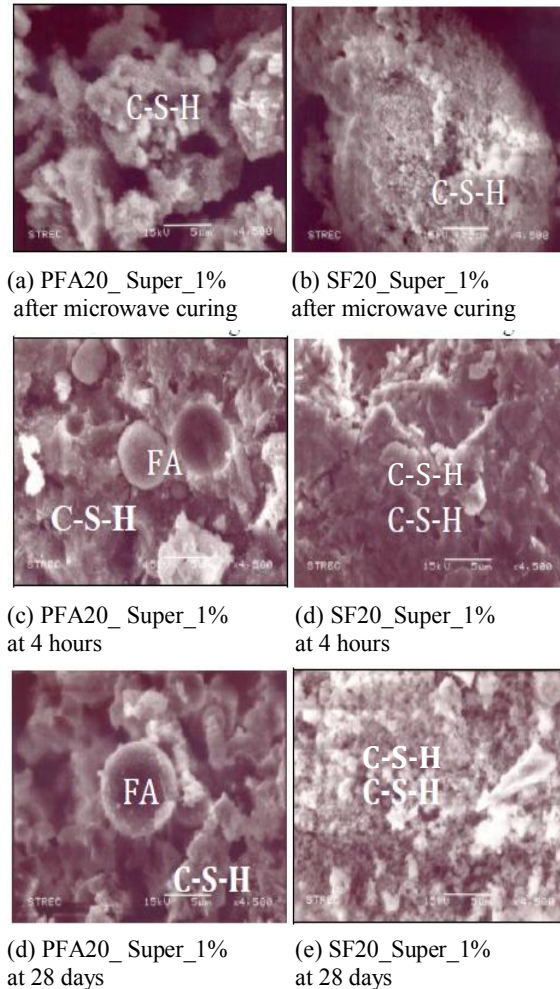


Fig. 6 Micrographs of various cement pastes mixed with pozzolan materials subjected to normal heating (lime-saturated deionized water) and microwave energy.

4.4 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 diffraction of PFA20_Super_1%, and SF20_Super_1% after MW power of 390 Watt had been applied for 45 minutes. The phases identified include calcium silicate hydrate (Ca_3SiO_5), calcium hydroxide ($\text{Ca}(\text{OH})_2$), residual lime (CaO), and Xenotile ($\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$).

As shown in Fig. 7, in regard to the effect of pozzolan material on the phase characteristics of PFA20_Super_1% and SF20_Super_1% after microwave power of 390 Watt had been applied for 45 minutes, the calcium silicate hydrate (Ca_3SiO_5) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) phases are similar.

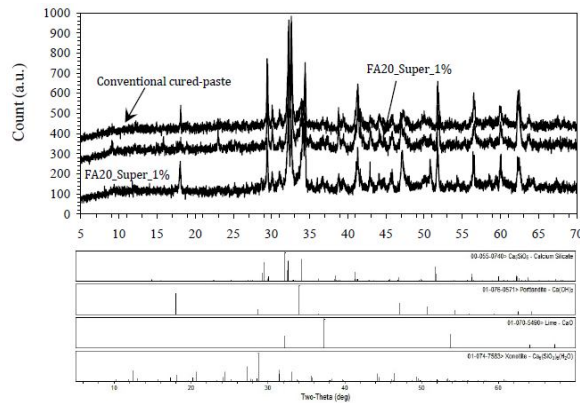


Fig. 7 X-ray diffraction of PFA20_Super_1% and SF20_Super_1% after applying microwave power 390 Watt for 45 minutes.

5. Numerical results

Based on the steady state analysis, the calculated temperature of the paste containing PFA under microwave exposure times of 45 minutes is shown in Fig. 8. It illustrates an increase of maximum temperature within the samples as the microwave exposure time increases, such that temperatures of 83.0 °C were reached at exposure times of 45 minutes, respectively. The heat generated by the microwave energy works in conjunction with the heat generated by the hydration of the cement (exothermic reaction).

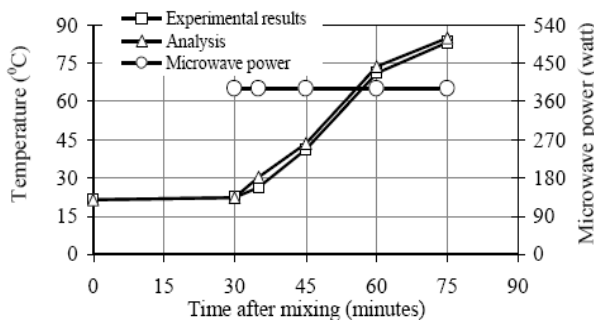


Fig. 8 Temperature within the paste containing PFA during subjecting microwave energy for 45 minutes.

6. Conclusions

Based on the study of microwave heating of pozzolan-Portland cement pastes at a very early age with a 2.45 GHz-multimode cavity at a power of 390 Watt for 45 minutes, the following conclusions are drawn:

- The temperature increases monotonically during the microwave-heating process and reached a maximum temperature of 91 °C PFA-cement paste and 59.5 °C of SF-cement paste.
- The PFA-cement exhibits little difference among the microstructures. On the other hand, for the SF-cement paste the SF particles under microwave heating have dispersed more than with the 4-hours normal heating, while the paste at 28 days looks like a plate of C-S-H.
- The phases identified of PFA-cement and SF-cement pastes included calcium silicate hydrate (Ca_3SiO_5), calcium hydroxide ($\text{Ca}(\text{OH})_2$), residual lime (CaO), and Xenotile ($\text{Ca}_6(\text{SiO}_3)_6(\text{H}_2\text{O})$).

- The pastes containing pulverized fuel ash and silica fume materials was gained compressive strength development after 24 hours and later ages and corresponded to a decreasing $\text{Ca}(\text{OH})_2$ content.

- In order to predict temperature rise during heating by microwave energy, the model explored the interaction between the microwave (electromagnetic field) and 0.22-w/s cement paste containing PFA, the heat dissipation (conduction mode) model. The results showed that the simple model associated with assumptions, and initial and boundary conditions obtains temperature rises similar to the experimental data.

7. Acknowledgment

The authors gratefully acknowledge the Thailand Research Fund (TRF) for supporting this research project.

8. References

- [1] Kim, H.K. and Lee, H.K. (2011). Use of power plant bottom ash as fine and coarse aggregates in high-strength concrete, *Construction and Building Materials*, Volume 25: Issue 2, pp. 1115-1122.
- [2] Taylor, H.F.W., (1997). *Cement Chemistry*, 2nd Edition, Great Britain: Thomas Telford Publishing.
- [3] Bhanja S. and Sengupta B. (2003). Modified water-cement ratio law for silica fume concretes, *Cement and Concrete Research*, Volume 33: Issue 3, pp.447-450.
- [4] Verbeck, G.J. and Helmuth, R.A. (1969). Structures and Physical Properties of Cement Paste, 5th Int. Congress Cement Chemistry, Tokyo, Japan, pp. 1-44.
- [5] Metaxas, A.C. (1991). Microwave heating, *Journal of Microwave Power and Electromagnetic Energy*, pp.237-247.
- [7] Dongxu, L. and Xuequan, W. (1994). A study on the application of vacuum microwave composite dewatering technique in concrete engineering, *Cement and Concrete Research*, pp.159-164.
- [8] Hutchison, R. G., Chang, J.T., Jennings, H.M., and Brodwin, M.E. (1991). Thermal acceleration of Portland cement mortars with microwave Energy, *Cement and Concrete Research*, 21, pp. 795-799.
- [9] Leung, K.Y.C., and Pheeraphan, T. (1995). Microwave heating of Portland cement concrete: Experimental Results and Feasibility for Practical Applications, *Construction and Building Materials*, 9, pp. 67-73.
- [10] Hutchison, R.G., Chang, J.T., Jennings, H.M., Brodwin, M.E. (1991). Thermal Acceleration of Portland Cement Mortars with Microwave Energy. *Cement and Concrete Research*, 21, pp. 795–799.
- [11] American Society for Testing and Materials, (2008). ASTM C618 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, *Annual Book of ASTM Standard, Section 4 Construction*, Volume 04.02 Concrete and Aggregate.
- [12] American Society for Testing and Materials, (2008). ASTM C1240 Standard Specification for Silica Fume Used in Cementitious Mixtures, *Annual Book of ASTM Standard, Section 4 Construction*, Volume 04.02 Concrete and Aggregate.
- [13] American Society for Testing and Materials, (2008). ASTM C494 Standard Specification for Chemical Admixtures for Concrete, *Annual Book of ASTM Standard, Section 4 Construction*, Volume 04.02 Concrete and Aggregate.
- [14] American Society for Testing and Materials, (2008). ASTM C305 Standard Practice for Mechanical Mixing of

Hydraulic Cement Pastes and Mortars, *Annual Book of ASTM Standard, Section 4 Construction*, Volume 04.01 Concrete, Lime and Gypsum.

[15] Metaxas, A.C., Meredith, R.J. (1998). *Industrial Microwave Heating*; Peter Peregrinus: Herts, UK, 1998.

[16] COMSOL©Multiphysics, (2010). *User's Guide*, COMSOL AB., Stockholm.

[17] Moukwa, M., Brodwin, M., Christo, S., Chang, J. , and Shah, S. P. (1991). The influence of the hydration process upon microwave properties of cements, *Cement and Concrete Research*, 21, pp. 863-872.