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Thermal properties of hydrated cement pastes studied by the photoacoustic technique

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Abstract. Photoacoustic (PA) technique has been applied to measure the effective thermal diffusivity (α_{eff}) of hydrating cement pastes with a varying water to -cement ratio (w/c) and for variable duration (d) of hydration. Four samples with w/c = 0.3, 0.4, 0.5 and o.6 were prepared. The frequency variation of the PA signal for each sample was recorded at the begining (0 d), as well as one week and one month of hydration. The effective thermal effusivity (e_{eff}) was obtained by measuring the variation of the signal with modulation frequency and the corresponding values of the effective thermal conductivity (k_{eff}) were calculated. The results for k_{eff} show a decrease at higher w/c (0.6), no change for other samples has been observed. The thickness of the duplex film of $Ca(OH)_2$ and C-S-H formed on the surface of the samples of w/c = 0.5 were determined using the effective layer model in the 0 d and after one month of hydration; a remarkable increase was observed in the last case.

1. Introduction

Cement is one of the most common building materials used in the construction industry. As the cement hydrates and the concrete cures, significant changes in the volume fraction within the three dimensional microstructure and the spatial arrangement of solid constituents, liquids, and gases (air voids and empty capillary pores) are taking place. Hence, the thermophysical properties (such as heat capacity, thermal conductivity) of the cement paste, and thermal diffusivity vary with hydration [1-4]. Hadley et al [5], observed that, a duplex film of calcium hydroxide {$Ca(OH)_2$ } and calcium silicate hydrate (C-S-H) gel is formed on the surface of the specimen . In this work, the PA technique was applied to determine the effective thermal diffusivity (α_{eff}) and effective thermal effusivity (e_{eff}) of hydrating cement pastes of different (w/c) after increasing period of hydration (d). The corresponding values of the effective thermal conductivity k (= $e\sqrt{\alpha}$) were calculated for each hydration stage. Furthermore the measured thermal effusivity (e) values of the bulk material (paste alone) and e_{eff} were exploited to determine the thickness of the duplex film during the course of hydration using the effective layer model.

2. Experiment

The cement pastes were prepared by mixing at the room temperature, water and cement for several minute. Four samples (w/c = 0.3, 0.4, 0.5 and 0.6) have been prepared. Immediately after mixing, cement pastes were carefully inserted between the two cleaned glass photographic microscopy

slides[6]. The glass substrate was then separated carefully from the cement pastes, and a thin layer of thickness L cement pastes was mounted inside the Princton Applied Research (PAR)Photoacoustic cell. The conventional PA setup consisting of 1W Ar^+ ion laser (λ = 488 nm) chopper and PAR-PA cell, was used to measure the thermal diffusivity and thermal effusivity for hydrated cement pastes with different w/c. Measurements were taken at initial (fresh) state (0 d), as well as one weak and one month of hydration period.

3. Results and discussion

3.1. The out come of thermal properties measurements showing the variation of the PA signal amplitude with the chopping frequency for sample of w/c= 0.3, at 0 d and after one month of hydration is shown in Fig 1a and 1b. The characteristic frequency f_c at the point of crossover [7], was used to determine the thermal diffusivity (α). The relevant relationship reads $\alpha = f_c L^2$ m^2/s with L being the sample's thickness.

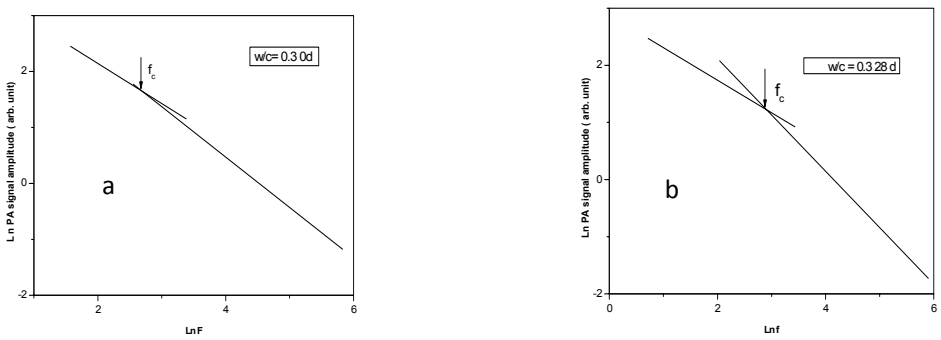

Figure 1. Variation of Ln PA amplitude with Ln of the modulation frequency for w/c = 0.3 at 0 d (a) and after one month (b).

The calculated values of thermal diffusivity α_{eff} for all the samples are given in Table 1. The effective thermal effusivity (e_{eff}) is also determined for the same samples using the PA technique where (for optically opaque thermally thick sample) the PA signal amplitude q is given by [8].

$$q = \frac{A}{e_{eff}} \frac{1}{f} \qquad (1)$$

where A is a constant The later can be eliminated by normalizing the signal measured from a specific sample to the signal obtained from the reference sample with a well known effusivity. The e_{eff} values are given in Table 1. The corresponding values of the effective thermal conductivity k_{eff} (= $e_{eff}\sqrt{\alpha_{eff}}$) are also displayed in table 1

Table 1. The calculated values of thermal parameters α_{eff}, e_{eff} and k_{eff}, for hydrated cement samples with different w/c, following varying number of hydration days.

w/c	α_{eff} x 10^{-7} m^2/s			e_{eff} (W $S^{1/2}m^{-2}$ k^{-1}) ± 7			k_{eff} (W/mK) ± 0.12		
	Zero day	One week	One month	Zero day	One week	One month	Zero day	One week	One month
0.3	4.8	5.5	5.6	1270	1415	1469	0.88	1.05	1.1
0.4	4.78	5.5	5.59	1258	1348	1444	0.87	1	1.08
0.5	4.7	5.4	5.6	1240	1347	1430	0.85	0.99	1.07
0.6	4.22	4.87	5.1	1062	1117	1190	0.69	0.78	0.85

It can be seen that, the variation of the α_{eff}, e_{eff}, and k_{eff} for the first three samples with different w/c ratios are within the experimental error, however an observable decrease was observed for w/c (0.6).

The values of thermal diffusivity α_{eff} for all the samples are larger than the value for water (1.4 x 10^{-7} m^2/s) [3], and smaller than the value of cement powder (9.8 x 10^{-7} m^2/s). The results for α_{eff} are within the range of reported literature values, which are often around 4x 10^{-7} m^2/s [9]. The k_{eff} results for the first three samples are in reasonable agreement with the data of Bentz [3], that reports k= 1W/(mK) for w/c (0.3, and0.4). It is known that pores are usually the result of water -in excess- to that required for the hydration, therefore, it is expected that as the w/c increases, the pore width gets larger (porosity), resulting in lower thermal conductivity [10]. Our results, indicate that k_{eff} of hydrated cement pastes does not change unless w/c = 0.6 which would be normally not expected. However they are in agreement with the published data for the variation of pore width for different w/c values[11]. It is found that the width of pore exhibits a slight increase (20 nm – 30 nm) for lower (0.3, 0.4) w/c values of, but increase to around 100 nm when w/c exceeds 0.5. Furthermore, it is also observed that for a given w/c range the values of k_{eff} are lower than that for cement powder (1.55 W/(m K)) and larger than thermal conductivity of the water (0.6 W/(m K))[3]. Likewise, the increase of k_{eff} value for hydrated cement samples in the period between 0 d and one week of the hydration shows that the thermal conductivity of hydrated cement is sensitive to moisture content and the relative humidity.

3.2. Thickness of duplex film

A duplex film of calcium hydroxide {Ca $(OH)_2$ } and calcium silicate hydrate (C-S-H) gel was formed on the surface of the specimen as an intact cover, hiding the detail of the paste[5]. The thickness of the duplex film of w/c = 0.5 during the period extending from 0 d and one month of hydration was determined using the effective layer model [12]. The measured PA signal of the composite sample S_{eff} (paste + film) was carried out at different frequencies and normalized to a signal S from the bulk sample (paste without film) using α_{eff} and e_{eff} as known parameters. In this model the normalized signal S_n is given by:

$$S_n = \frac{S_{eff}}{S} = \frac{e}{e_{eff}} \frac{1 + R \exp\left(-2\sigma_{eff}\ell\right)}{1 - R \exp\left(-2\sigma_{eff}\ell\right)} \qquad (2)$$

Where σ_{eff} and R defined as $\sigma_{eff} = (i\omega/2\alpha_{eff})^{1/2}$ and $R = (e_{eff} - e)/(e_{eff} + e)$, where e is the thermal effusivity of bulk sample. The amplitude (q) of the signal of the last equation is given by:

$$q = \frac{e}{e_{eff}} \frac{\left[1 + R^2\exp\left(-4a_{eff}\ell\right) + 2R\exp\left(-2a_{eff}\ell\right)\cos\left(2a_{eff}\ell\right)\right]^{1/2}}{\left[1 + R^2\exp\left(-4a_{eff}\ell\right) - R\exp\left(-2a_{eff}\ell\right)\cos\left(2a_{eff}\ell\right)\right]^{1/2}} \qquad (3)$$

where $a_{eff} = (\omega/2\alpha_{eff})^{1/2}$ is the real part of the thermal diffusion coefficient of the composite sample. The thickness ℓ is then appropriately guessed as best fitting parameters to the experimental data. The bulk sample was obtained by carefully removing successive layers of the specimen. Recently S. Abdallah et al [13], measured the thickness of porous layers for silicon samples using the effective layer model. This provides an evidence for the validity of this model for the measurements of thickness of the duplex film. The dependence of the amplitude of the PA signal at 488 nm on the modulation frequency was measured for each sample. The amplitude of the PA signals from the composite sample normalized to a PA signal obtained from the bulk sample (amplitude ratio) are shown in Fig 2(a and b) for the indicated duration of hydration. The satisfactory agreement between the experiment and calculations could be achieved by proper choice of fitting parameters ℓ. The results show that ℓ increased from 18 μm to 30 μm as the time of hydration increase from 0 d to one month.

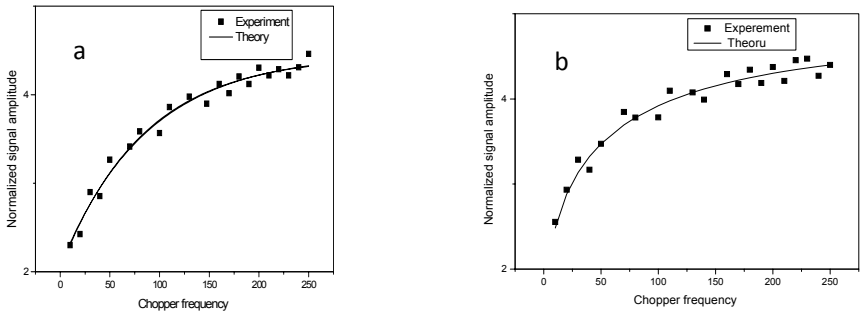

Figure 2. Normalized PA signal amplitude as a function of the chopper frequency for 0d (a) and one month (b)

The low value for initial thickness (0d of hydration) of duplex film at which results in the large change described above is attributed to a number of hydrated cement grains clinging to the duplex film on the glass substrate when separated. In addition, cement paste at 28 d hydrated further and was more cohesively bound. Likewise, during the separation, the hydrated cement grains were pulled away to the paste side rather than the glass substrate side.

4. Conclusion

The non destructive PA technique was used to determine the thermophysical parameters (α_{eff} ,e_{eff} ,k_{eff}) of hydrated cement pastes of different w/c and after varying hydration period. The decrease of k_{eff} at higher w/c (0.6) is attributed to the large increase in the pore width. Finally, the PA also proved capable of thickness measurements of a duplex film formed on the surface of cement paste.

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