The Effect of Wetting and Drying Cycles on Thaumasite Formation in Cement Mortars

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ABSTRACT

As part of a study into the controls on the deterioration of concrete due to sulfate attack, mortars (50 *mm* cubes and $40 \times 40 \times 160$ *mm* prisms) made with Portland cement CEMI, and 90% CEMI + 10% limestone blend were exposed to BRE DS4 sulfate solution based on magnesium sulfate $MgSO_4.7H_2O$ under wetting and drying cycles for 12 months at 5°C. The effect of these cycles on thaumasite formation was studied and compared with samples immersed continuously in the same solutions. Visual observations, mass and length changes were used to assess the mortar deterioration, along with X-ray diffraction and infra-red spectroscopy that were used to determine the mineralogy of deterioration products. It was found that at the 5°C, wetting and drying cycles significantly delayed thaumasite formation compared with control specimens.

Keywords. Thaumasite, sulfate attack, wetting/drying, carbonation

INTRODUCTION:

(Hong and Hooton 1999) explain that wetting and drying cycles are implicated in creating an aggressive environment for mortars and concretes due to the movement of sulfate ions and enhanced concentrations in concrete pores. The same study also showed an increase in chloride penetration into the samples. Of the various studies into the performance of different binders, (Yigiter et al. 2007) compared concrete samples made from Portland cement with others containing Portland cement blended with slag. Under cyclic wetting and drying conditions with exposure to sea water they found that both compressive and tensile strength decreased for PC but not for slag cement. In a study by (Sahmaran et al. 2007) to study the sulfate resistance of plain and blended cements exposed to wetting-drying cooling-heating environments, it was concluded that in PC the rate of deterioration was increased for samples subjected to wetting drying cycles compared to those continuously in sulfate solutions, it was also found that sulfate resisting PC performed better than PC but high sulfate resistance was not guaranteed. Further findings were that blended cements containing class F fly ash and natural pozzolana were also highly affected by a cyclic exposure regime. In a study by (Wang et al. 2006) severe damage, confirmed by strength and mass losses, was found in concrete samples exposed to $CaCl_2$ solution under wetting-drying

and freeze-thaw conditions. In research into delayed ettringite formation involving heat-cured mortars stored in water, (Escadeillas et al. 2007) concluded that wetting-drying cycles are not necessary for the occurrence of DEF but their contribution may be limited to slightly accelerating the reaction. (Ganjian and Pouya 2005) claimed different deterioration mechanisms make silica fume and ground granulated blast furnace slag (GGBS) concrete more vulnerable to magnesium sulfate bearing seawater, particularly within the tidal zone under wetting and drying cycles. (Novak and Colville 1989) suggested that rapid failure by mechanisms such as sodium sulfate crystallisation can be caused by localised extraordinarily high sulphate concentrations that result from wetting-drying cycles. According to (Plowman and Cabrera 1996) in the UK it is generally observed that the intertidal, splash, and spray zones represent the most aggressive sea water exposure zones to concrete.

However, in spite of an extensive literature search, there are no previous studies of the impact of wetting-drying cycles on concrete exposed to conditions in which deterioration due to thaumasite formation liable to occur.

This paper describes preliminary results of an on-going research into the performance of plain and blended cements under cyclic wetting and drying conditions with sulfate exposure conducive to thaumasite formation.

EXPERIMENTAL WORK

For the purpose of this study, a series of 50 *mm* cement mortar cubes and prisms (40×40×160 *mm*) were produced using Portland Cement (CEMI-52.5N) according to BS EN 197-1:2011 and blended cement in which 10% of the PC was replaced with limestone filler. The chemical analyses for these materials are shown in Table 1. The mortars were prepared with water to binder ratio of 0.65, a binder: sand ratio of 1:2.50 and a cement content of 380 kg/m^3. Once cast, the specimens were kept in the laboratory at about 20°C for 24 hours; after which they were de-moulded and placed in water at 20°C for 6 days, then removed from the water and air cured at 20±2°C for 21 days. This regime was used to simulate field conditions (Tsivilis et al. 2003), (Torres 2004). After this initial curing regime, the samples were exposed to deionised water (control) and magnesium sulfate test solution at 5°C. Magnesium sulfate (MgSO$_4$.10H$_2$O) was dissolved in deionised water to make sulfate solution based on BRE DS4. The concentration of the sulfate ions in the solution was 6 gm/l of SO$_4^{-2}$.

Table 1. Chemical (A) and mineralogical (B) composition (weight %) of Cement, LF (10%)

A	SiO$_2$	CaO	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	K$_2$O	MgO	LOI	SO$_3$	Total
CEM I	19.85	64.61	4.67	2.74	0.23	0.449	1.09	3.015	2.52	99.17
Limestone	0.63	55.2	0.28	0.15	< 0.003	0.054	0.47	42.89	< 0.002	99.67

B. Component	C$_3$S	C$_2$S	C$_3$A	C$_4$AF
CEM I	68.28	5.4	7.74	8.34

Two types of long-term curing were employed: (A) continuous immersion in solutions and (B) wetting and drying cycles, where samples successively immersed in solution for 10 days

followed by drying for 20 days (1 month cycle). The samples were visually monitored at the end of each cycle in order to assess the degree and pattern of attack and to record any changes in surface appearance. The mass and length were also periodically recorded. The deterioration products were analysed using X-ray diffraction (XRD) and infra-red (IR) spectroscopy. XRD facilitates the identification of most mineral phases in these materials; however, it is sometimes difficult to distinguish between ettringite and thaumasite by this method. Infra-red spectroscopy enables the octahedral coordination of silica (SiO_6) seen in thaumasite to be recognised, separately from octahedral aluminates ($Al(OH)_6$) which are present in ettringite (Zhou et al. 2006).

Samples of the deterioration products were carefully collected from the surface of mortars, and then gently ground using an agate pestle and mortar to pass *63µm*. The powders were then backfilled into aluminium holders to minimize any preferred orientation. XRD analysis of these powders was carried out on a Phillips PW1830 XRD diffractometer using CuKa radiation, 40 kV and 30 µA. The analyses were run between 5° and 55° 2θ at speed of 2°/min and step size of 0.02. Samples for IR spectroscopy were made from the same powders where a mixture of 2 *mg* of the sample and 198 *mg* of KBr was used to make 16 *mm* discs. A Perkin–Elmer FT-IR 2000 spectrometer was use to collect the IR spectra with a resolution of ± 4 cm^{-1}.

RESULTS AND DISCUSSION

Visual Assessment

Fig 1 shows the appearance of the samples after exposure to solutions for 12 months. The first signs of deterioration were observed after around 84 days, when the continuously immersed LF samples started to show some cracking around the corners and along the edges. These cracks soon expanded and became filled with white soft materials. CEMI samples started to deteriorate after about 100 days of exposure.
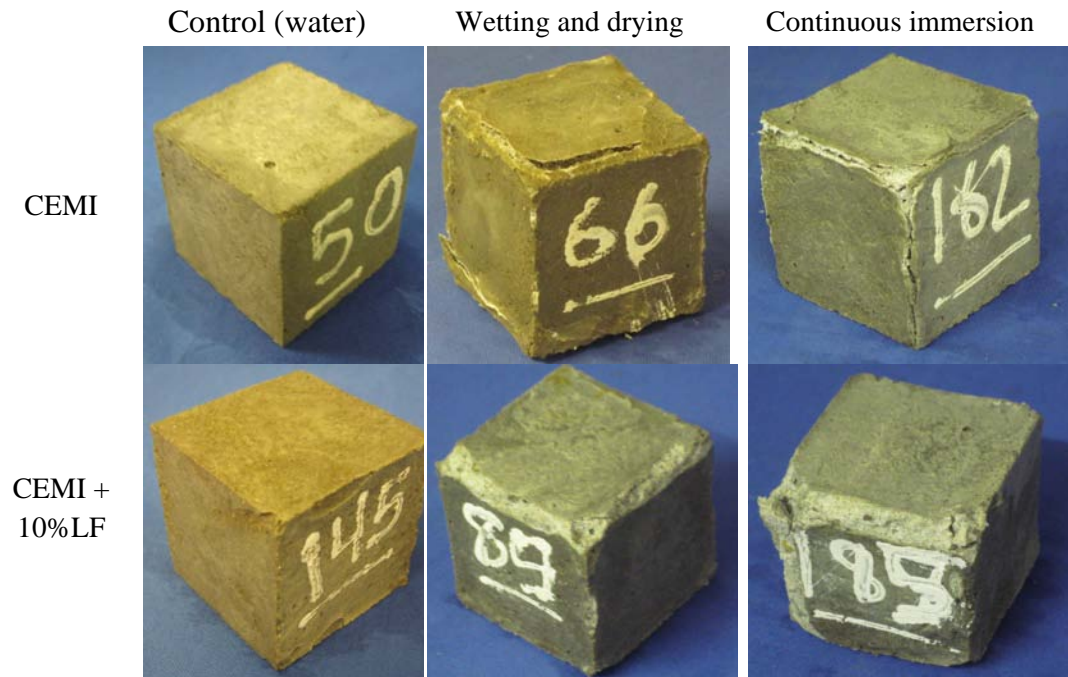

Figure 1. Mortar cubes under continuous immersion in DS4 sulfate solution at 5 °C.

The samples that were subjected to wetting and drying showed no signs of deterioration until 250 days, where, again the LF samples started to show the same signs of attack as described for continuous immersion. In fact all deteriorated samples showed the same mode of deterioration regardless of the binder types and the exposure solution.

It is worth mentioning here that the outer layer of the specimens did not exhibit attack and remained intact where the deterioration was going on beneath it as shown in Fig 2.
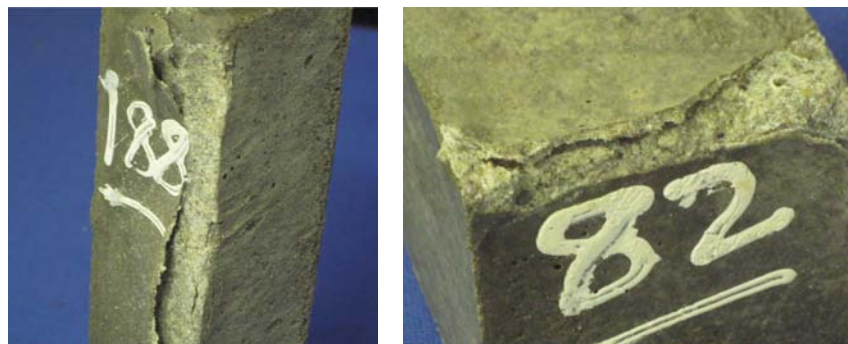
Figure 2. The outer layer of specimens is un-attacked with the deterioration is progressing underneath it.

According to visual observations, after 12 months of testing the rate of attack for the samples subjected to wetting and drying was slower than that seen in the continually immersed samples.

Length and Mass Changes

The length and mass changes are presented in Figs. 3 to 6. As Figures 3 and 4 show the wetting and drying cycles cause a very obvious change in length in the limestone cement samples compared to CEMI samples. However, there was no significant change in over-all length due to the formation of thaumasite for all binders and all solutions despite the clear mass loss, which may indicate that measuring length change in not a useful tool to assess the deterioration caused by thaumasite formation.
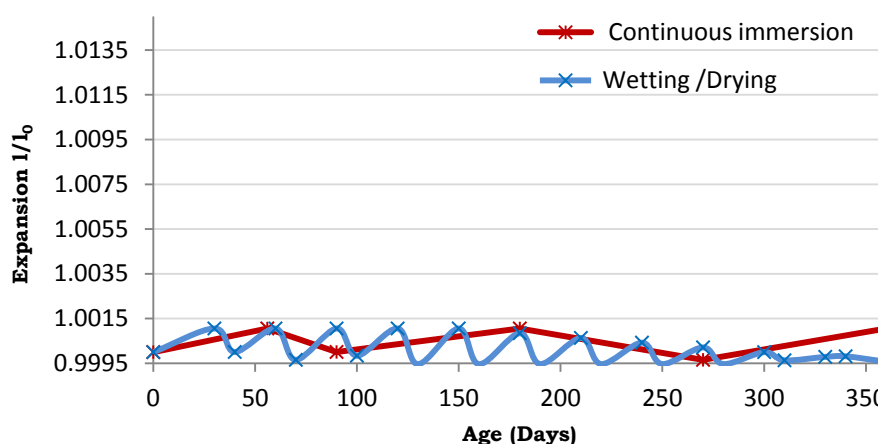

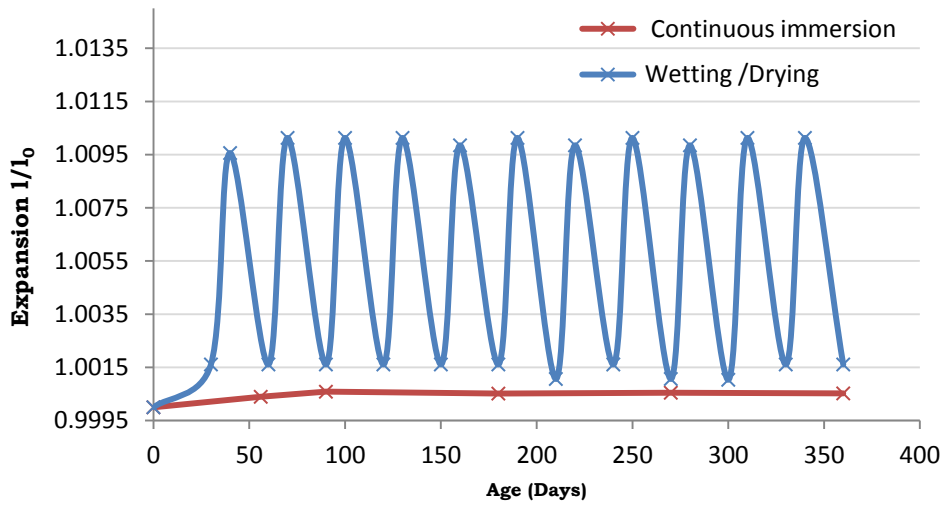**Fig 3. Length change in CEMI samples in DS4 solution**.

Fig 4. Length change in CEMI+ 10% LF samples in DS4

The relevant mass changes are shown in Figures 5 and 6. It can be observed that in both sets of samples the mass increased during the first 200 days due to the uptake of solutions. It seems that weight gain continued until the samples started to show signs of deterioration, when the opening of the cracks allowed more solutions to enter and caused expansion and finally loss of material by spalling. The scenario in the wetting and drying samples was slightly different, where both samples lost weight in the first 200 days the and by the time where cracks started to appear the samples started to gain weight, following a similar tend to those in conditions of continuous immersion.

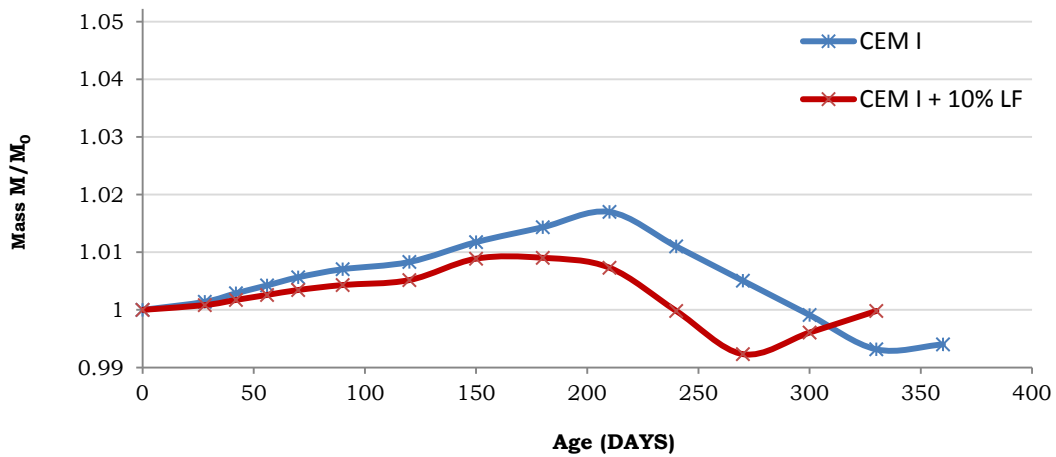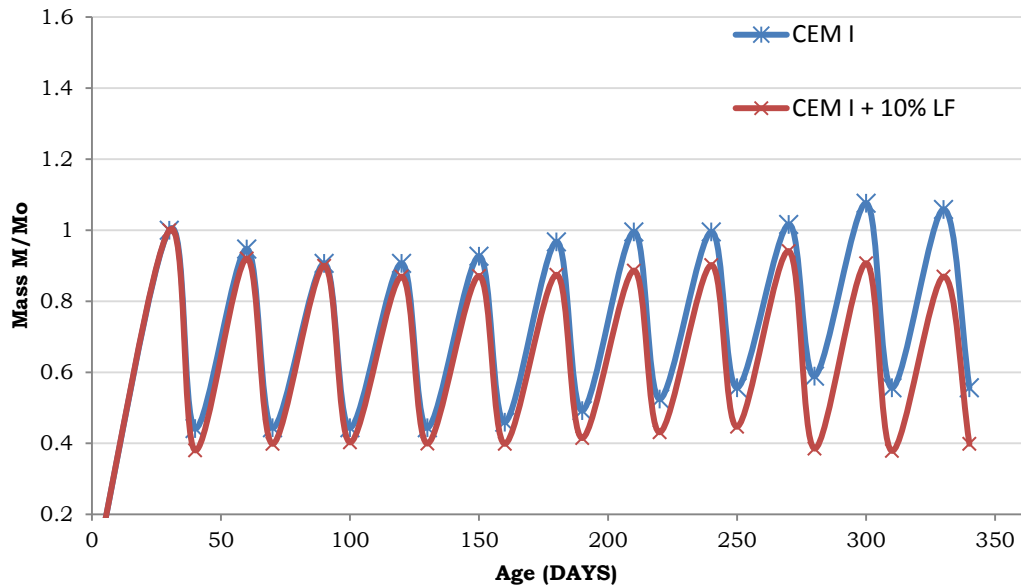Figure 5. Change in mass for binders in continuous immersion

Figure 6. Change in mass for binders in wetting and drying exposure

X-Ray Diffraction

The XRD traces for the deterioration products are shown in Figures 7 and 8. As these indicate, the mineralogical compositions of all are quite similar and include thaumasite, calcite, and quartz as the main peaks. Higher intensity thaumasite peaks were found in the continuously immersed samples and intensities of calcite peaks were stronger in the samples containing limestone filler, as would be expected. Indeed the calcite peaks were more intense in the wetting and drying samples than those of continuous immersion possibly resulting from the carbonation reaction.
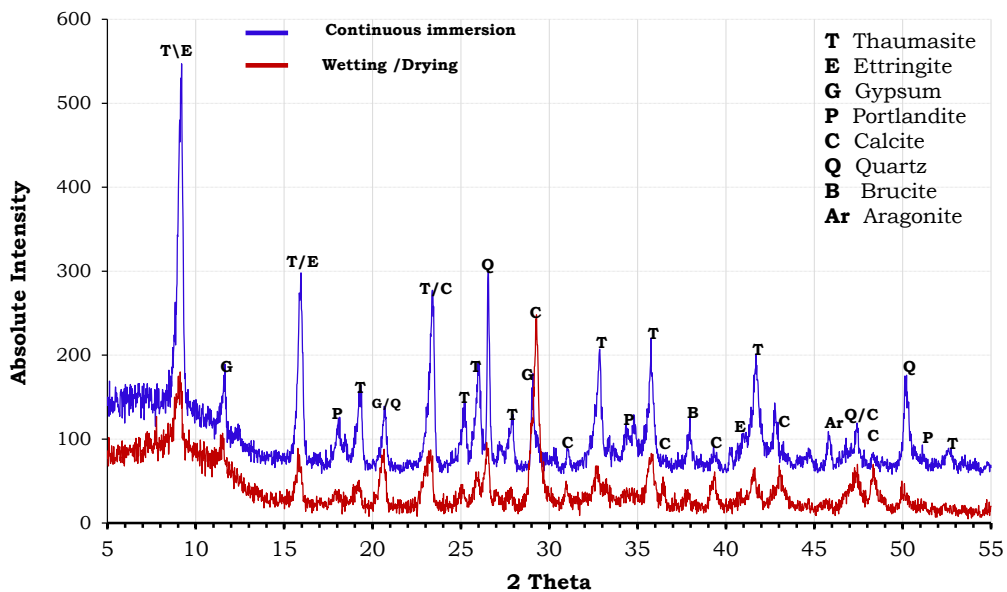

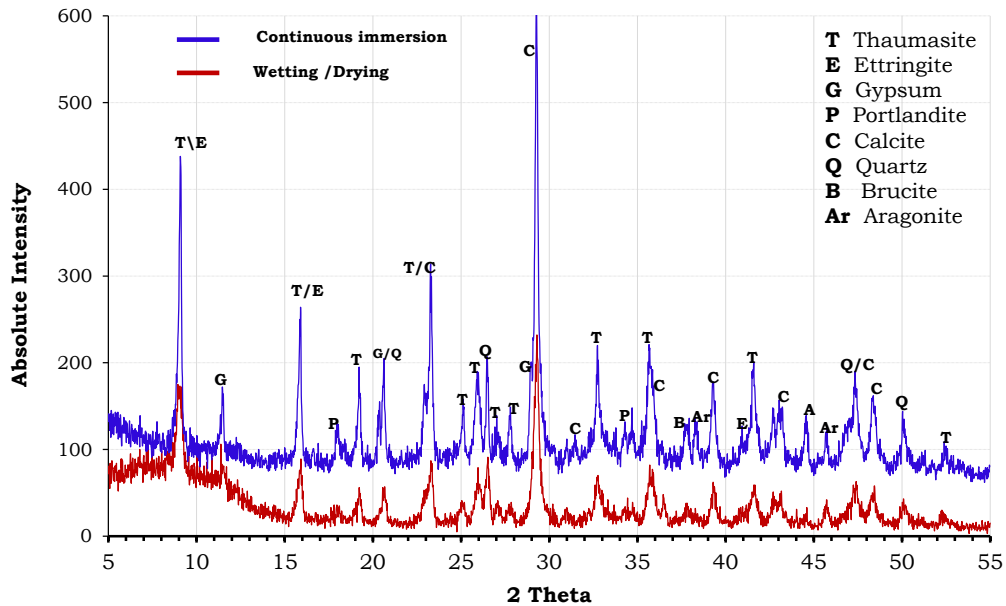Fig 7. XRD patterns for samples of CEMI in DS4 solution

Fig 8. XRD patterns for samples of CEMI+ 10%LF in DS4 solution

Gypsum peaks were greater for the continuous immersion samples indicating a higher damage rate. However, the relatively weak portlandite peaks, especially in the wetting and drying samples may indicate the consumption of portlandite in the formation of other products such as calcite rather than thaumasite. Thaumasite-ettringite solid solution peaks can also be observed. The calcite peaks in the wetting and drying samples are higher than those for continuous immersion, which is probably the result of the carbonation of the outer layer.

Infrared Spectroscopy (IR)

Figures 9 and 10 show the IR spectra for both binders, where strong peaks at around $500cm^{-1}$ related to octahedral silicates in addition to CO_3 and SO_4 indicate that thaumasite is present. The presence of SO_4, which might be indicative of gypsum, is also indicated at higher intensities for continuously immersed samples. The presence of peaks at around 850 cm^{-1} assigned to AlO_6, indicates ettringite, where the coexistence of these peaks might be an indication of a thaumasite-ettringite solid solutions (Barnett et al. 2002, Torres et al. 2004). A strong calcite peak occurs at 712 cm^{-1} for samples subjected to wetting and drying cycles, which is possibly due to the carbonation of the outer layer
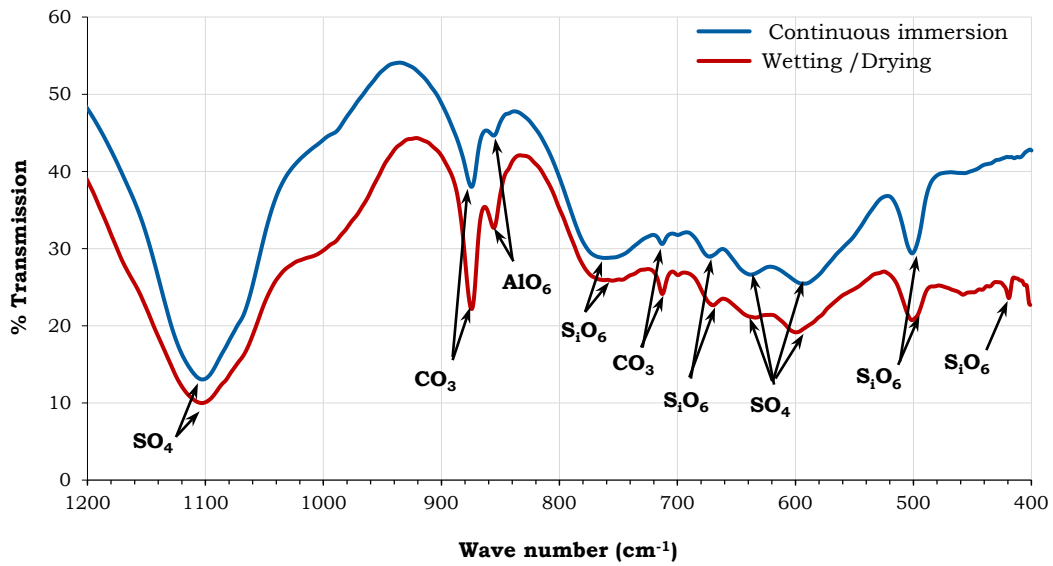
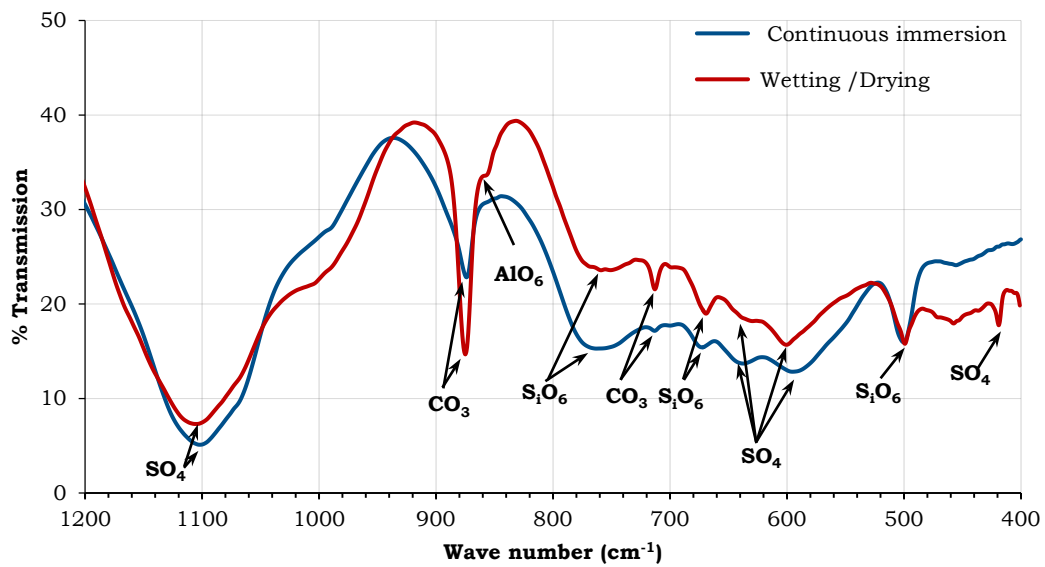Fig 9. IR spectra for CEMI samples in DS4 solution

Fig 10. IR spectra for CEMI +10% LF in DS4 solution

CONCLUSIONS

The following main conclusions can be drawn:

- Wetting and drying cycles have a delaying effect on deterioration caused by thaumasite formation.
- In this study the time needed for thaumasite to form in wetting and drying samples is about 3 times that needed for continuously immersed samples. This corresponds directly with wetting period of the wetting and drying cycle being 1/3 of the continuous immersion (i.e. in

both cases the time needed for thaumasite to form is around three months in the solutions used.

- A gradual increase in mass in both exposure conditions occurred during immersion in solutions. This continued until spalling led to a reduction in mass of the samples. However the onset of mass loss was earlier and the magnitude was higher in the continuous immersion regime.
- No significant changes in over-all length of specimens due to formation of thaumasite were observed, however the variation in length due to changes in moisture content were much greater for the binder containing limestone.
- Carbonation may have an impact on the rate of deterioration. This may be due to a physical effect, resulting from calcite being deposited in pores thereby reducing permeability and restricting sulfate ingression, and chemically by consuming portlandite which is the main reactant for thaumasite formation.

ACKNOWLEDMENT

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