Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Investigation of Concrete - Clay Interaction with Regards to Thaumasite Form of Sulfate Attack

Farhat Abubaker, Cyril Lynsdale, John Cripps

Department of civil and Structural Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK
Cip09fa@sheffield.ac.uk, c.lynsdale@sheffield.ac.uk, j.c.cripps@sheffield.ac.uk

ABSTRACT

The influence of clay composition on the severity of attack due to thaumasite sulfate attack (TSA) on concrete made with CEM I and CEM I blended with 10% Limestone Filler (LF) was investigated. Concrete specimens were exposed to weathered Lower Lias Clay (LLC), for which the water soluble sulphate corresponded to the BRE sulfate class of DS-2, for 12 months at 5 and 20 °C. A parallel study was carried out in which specimens of the same concretes were placed in sulfate solutions equivalent to DS-2 and DS-4 at the same temperatures. It was found that concrete exposed to clay with sulfate design class DS-2 deteriorated at a faster rate than corresponding specimens in DS-2 solution and at a similar or greater rate to those exposed to the DS-4 sulfate solution. This suggests that the aggressively of clay and resulting concrete deterioration could exceed what might be observed in concrete exposed to equivalent standard test solutions.

Keywords: Degradation, Sulfate attack, Thaumasite, Lower Lias Clay, Pyrite

1. INTRODUCTION

Sulfate attack due to ettringite is well known but another type of sulfate attack has been identified, which has been found as a product of deterioration of cement, mortars and concrete. Hobbs (2003) quoted Erlin and Stark (1965) who reported that as early as 1965 thaumasite formation was observed in sewer pipes and concrete pavements in the USA. However, in the UK the thaumasite form of sulfate attack began receiving urgent attention in March 1998 when severe damage was discovered in concrete substructures of various M5 motorway bridges in Gloucestershire (Slater et al. 2003). Subsequently Clarke (2002) reported that buried concrete structures on the M4 in Gloucestershire, Somerset, and Wiltshire were affected and further cases had occurred in Country Durham in NE England. According to Crammond (2003) and Tsivilis and Skaropoulous (2007) thaumasite has also been identified in various other locations worldwide, including Canada, South Africa, Germany, Norway and Slovenia. Slater et al. (2003) explains that in the cases of the M5 motorway, the backfill surrounding buried concrete in the damaged bridges was reworked lower Lias Clay. Czerewko and Cripps (2006) explain that explain that this mudstone formation contains pyrite, and in the weathered horizons high levels of sulfate would be present. Disturbance to the clay and its subsequent use as backfill during construction, provided access to oxygen and water which resulted in the breakdown of pyrite and a subsequent series of chemical reactions, briefly represented by Equations 1 and 2:

$$4F_eS_2 + 14H_2O + 15O_2 \rightarrow 4F_e(OH)_3 + 8H_2SO_4 \quad (1)$$

$$H_2SO_4 + C_aCO_3 + H_2O \rightarrow C_aSO_4.2H_2O + CO_22 \quad (2)$$

As shown in Equation 1, the oxidation of pyrite (FeS_2) results in the formation of iron hydroxide minerals, sulfate and acid. The latter in equation 2, reacts with calcium carbonate ($CaCO_3$) which is present in the clay as fossil fragments and grains and results in the formation of gypsum $CaSO_4.2H_2O$). The weathered clay therefore contains the water soluble sulfate. At the time of investigation of the bridges in 1998, the amount of pyrite had decreased by 50-75% which resulted in an increase in the level of water soluble sulfate, essentially, raising the clay's effective BRE sulfate design classification (BRE, 2005) from DS-1 and DS-2 at the time of construction to DS-3 during the service life of the bridges (Slater et al. 2003, Floyd and Wimpenny 2003. Floyd et al. 2003). Thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) incorporates carbonate (CO_3), sulfate (SO_4)and silicate in the form $Si(OH)_6$, associated with the calcium cation, Ca in its structure. The sulfate might be derived from sulfate associated with different cations such as magnesium, calcium or sodium, dissolved in ground water and, carbonate ions can be either from an internal source when carbonate aggregate or limestone are used or from an external source due to acid attack on carbonate or clay mineral or it can be from atmospheric carbon dioxide. In addition, the silicate becomes available due to the decomposition of calcium silicate hydrate(C-S-H) (Collete et al. 2004, Zhou et al. 2006). An extensive search of the literature revealed very few studies into the interaction between buried concrete and pyrite rich clays. This is in spite of the widespread occurrence of such clays, as noted by Czerewko and Cripps (2006), and the huge number of buried concrete structures. It would appear that only one field investigation has yet been carried out to assess the performance buried concrete, which is reported by Crammond et al. (2003). The recommendations contained in BRE SD1 (2005) and similar standards, are based upon laboratory studies involving the immersion of concrete specimens in test sulfate solutions which might be magnesium sulfate or sodium sulfate or a combination of both. This paper appears to be the first to describe TSA deterioration in buried concrete in simulated field conditions. It focuses on the preliminary results of wider investigation into thaumasite formation and performance of concrete exposed to Lower Lias Clay.

2. EXPERMINTAL WORK

2.1 Cementitious Binders and Concrete Mixes

Concrete mixes were prepared using CEM I and CEM I blended with 10% limestone filler. Siliceous aggregate was used for both coarse and fine fractions. In addition, an high water to cement ratio of 0.6 was used in order to accelerate the attack process.

2.2 Specimens Preparation and Exposure

In order to simulate field exposure conditions for foundations cast in shutters and then backfilled with clay, 70 mm cubes were cast and demoulded after 24h, cured in water at 20℃ for 7 days followed by 21days in air at room temperature. After curing, the cubes were either buried in clay or immersed in the sulfate solutions listed in Table 1 in small containers placed in water tanks maintained at 5 and 20℃. The solutions were renewed every 3 months for the duration of the tests. Partially weathered Lower Lias Clay was obtained from the A46 Newark to Widmerpool Highway improvement scheme from a site near Cotgrave in Nottinghamshire. Table 2 gives the main cations and anions present in the clay and data about the sulfur present.

Table 1. Test Solution Compositions

Test Solution	Solution Compositions (mg/l)	
	SO_4^{2-}	Mg^{2+}
BRE DS-2	2000	500
BRE DS-4	6000	1520

Table 2. Chemical Composition of Clay

Average Water Soluble Compositions (mg/l)						Avg. Carbonate (% CaCO3)
SO_4^{2-}	Na^{+}	K^{-}	Cl^{-}	Ca^{+}	Mg^{2+}	
1366	31.68	26.26	18.27	510.63	101.6	21.3

The BRE design class for the clay is DS-2 as shown in Table 3, where the amount of pyrite is calculated from the difference between the total sulfur and acid soluble sulfur and it was assumed that all acid soluble sulfur is in the form of gypsum.

Table 3. Sulfur analysis and Design Sulfate Class of Clay

Acid Soluble Sulfate(%SO4)	Water Soluble Sulfate (mg/l)	Total Sulfur %S	Pyrite % S	BRE Design Sulfate Class
0.31	1366	1.04	0.93	DS-2

2.3 Observations and Testing of Specimens

The specimens were removed from the clay and sulfate solutions for visual observation and photography after12 months of exposure. Visual changes, including any colour changes damage or lose of materials, were recorded. In addition, deteriorated material was sampled and analysed using X-ray diffraction (XRD) and infra-red spectroscopy (IR) techniques in order to identify the phases present. Where deterioration products were absent, a part of the outer layer was removed and analysed. Samples were prepared for XRD and IR test by grinding them using an agate mortar and pestle to pass 63μm.

3. RESULTS AND DISCUSSION

3.1 Visual Observations

Figures 1 and 2 respectively show the appearance of the CEM I and CEM I/10%LF cubes after 12 months immersion in solutions or contact with Lower Lias Clay in different conditions. In Figure1, deterioration of the sample exposed to Lower Lias Clay in which the surface was disintegrated can be observed. The white material formed underneath the surface of concrete was easily scratched to a depth about 2mm in the 5℃ cube, which suggests that attack took place under the outer layer of carbonated concrete, while the extent of deterioration at 20℃ was restricted to the top edge of the cube. In addition, the specimens placed in DS-4 sulfate solution showed signs of deterioration at the corners at 5℃, while at 20^{0}Cwhite material had precipitated on to the surface. However, no signs of deterioration were recorded in cubes exposed to DS-2 sulfate solution at either temperature.

T,℃	**Exposure Condition**		
	DS-2	**DS-4**	**LLC**
5			
20			

Figure 1 .Visual appearance of CEM I concrete exposed to LLC and sulfate solutions.

In the case of CEM I blended with 10% limestone filler in Figure 2, the degree of deterioration was greater than that in CEM I concrete at both temperatures. It can be seen that the cubes buried in lower Lias Clay suffered severe deterioration at both 5 and 20°C, with spalling of the top surface and edges accompanied by conversion to white mushy material at 5^{o}C, whereas at 20℃ damage occurred to the top edges and part of the sides of the cube. As shown, the degree of deterioration of concrete exposed to LLC at low temperature was almost similar or greater than that in DS-4 solution. However, no signs of deterioration were observed in cubes immersed in DS-2 sulfate solution at 5 and 20℃.

T,℃	**Exposure Condition**		
	DS-2	**DS-4**	**LLC**
5			
20			

Figure 2 .Visual appearance of CEM I/10% LF concrete exposed to LLC and sulfate solutions

In addition, cubes placed in DS-4 solutions at high temperature showed the largest deposit of white material that covered the surfaces as well as infilling cracks at the bottom corners of cubes, as shown in Figure 2.

An overall comparison of Figures 1 and 2 revealed that the severity of deterioration of different concrete types exposed to various conditions was as follows LLC > DS-4 >> DS-2 and the degree was less for temperature of 20℃ in all cases. It was surprising that severe deterioration was observed in both concretes exposed to LLC at 20℃ as this corresponds to equivalent to BRE DS-2 water soluble sulfate. The observations provide further confirmation of the vulnerability of buried concrete to TSA.

3.2 X-Ray Diffraction (XRD)

The XRD patterns for the CEM I sample exposed to DS-2 sulfate solution can be compared with that for DS-4 and LLC at 5 and 20 °C in Figure 3, and a summary of XRD data is shown in table 4. At 5℃ thaumasite was observed in samples exposed to LLC and DS-4. Gypsum was identified in specimens immersed in sulfate solution, being greater in DS-4 solution than in DS-2 but it was absent in the LLC exposed samples.

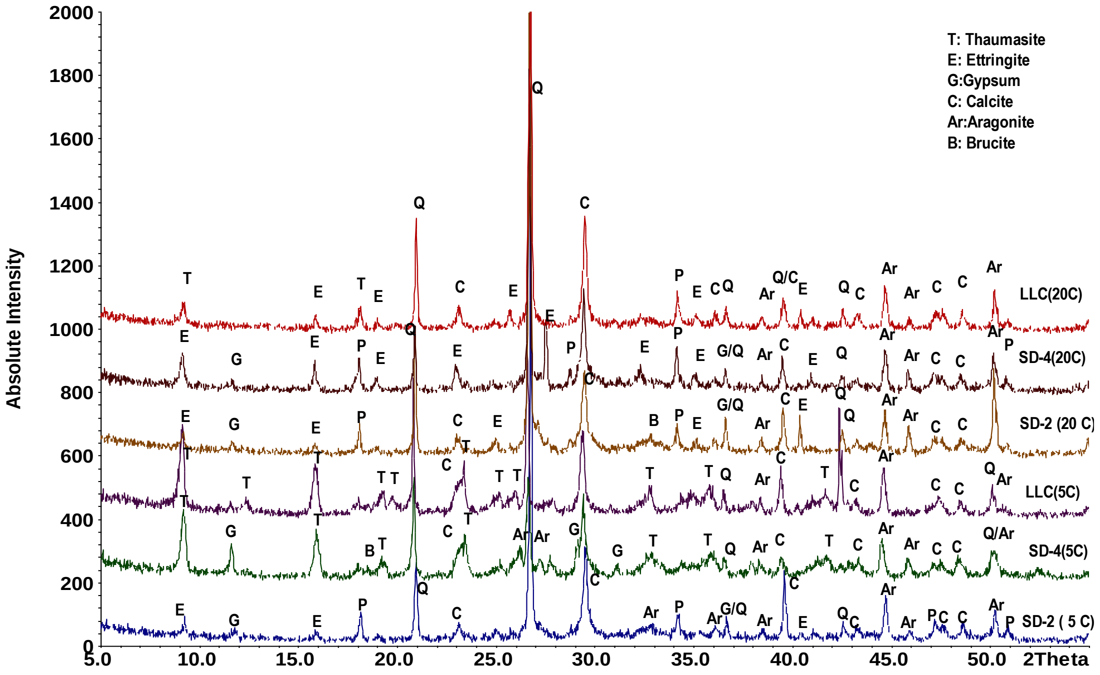

Figure 3. Comparison of XRD results of CEM I concrete type at 5 and 20℃

Calcite and aragonite were also detected in all exposure conditions. However, portlandite and ettringite were notably absent in samples exposed to LLC and DS-4 solution. At 20℃ thaumasite was oobserved only in concrete samples in contact LLC, while ettringite was the dominant product observed in samples exposed to DS-2 and DS-4 sulfate solutions. In addition, carbonate minerals such as calcite and aragonite were observed in all exposure conditions. However, gypsum was absent in samples placed in LLC but it was detected in samples exposed to sulfate solutions where the intensity was lower at 20^{o}C than at 5℃.

In the XRD pattern of for CEMI with 10 % limestone filler, thaumasite was the dominant phase that was observed in concrete buried in LLC and DS-4 solution followed by calcite and aragonite, while ettringite was absent in case of LLC at both temperatures as shown in Figure 4. A strong gypsum peak was found in samples immersed in DS-4 sulfate solution while it was detected in small traces in DS-2 sulfate solution at 5 and 20℃. However, no traces of gypsum were observed in samples placed in LLC. Ettringite was the dominant deterioration product detected in samples in DS-2 sulfate solution followed by calcite and aragonite. In addition, portlandite was observed as a moderately sized peak in DS-2 solution which had visually remained undamaged, while it was absent in deteriorated concrete cubes exposed to DS-4 and LLC.

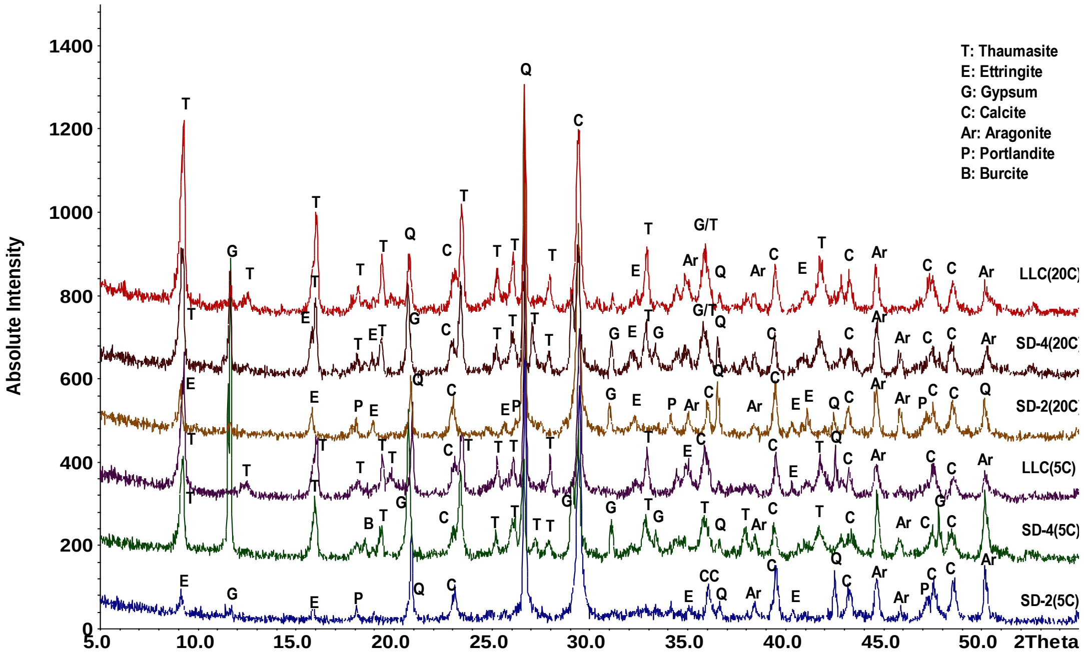

Figure 4. Comparison of XRD results of CEM I/ 10% LF concrete type at 5 and 20℃

Table 4. Relative intensity of identified phases by XRD

Binders	Conditions	Temperature℃											
		5						20					
		T	E	G	C	A	CH	T	E	G	C	A	CH
CEM I	DS-2		x	x	xxx	xx	xx		xx	x	xxx	xx	xx
	DS-4	xxx	x	xx	xxx	xx			xx	x	xx	xx	xx
	LLC	xxx			xxx	xx		xx	x		xxx	xx	xx
CEMI/10% LF	DS-2		x	x	xxx	xx	x		xx	x	xxx	xx	xx
	DS-4	xxx		xxx	xxx	xx		xx	xx	xx	xxx	xx	
	LLC	xxx			xxx	xx		xxx	x		xxx	xx	

The XRD analyses for the deteriorated material for both concretes stored in LLC at 5 and 20 ℃ revealed that the degradation was due to TSA. The overall comparison of XRD patterns showed that the presence of portlandite with small traces of gypsum in both CEM I and CEM I/10%LF concrete exposed to DS-2 solution at 5 and 20℃, indicates that less portlandite was engaged with gypsum in order to facilitate thaumasite formation, while more portlandite reacted with $CO_3$to form calcite. On the other hand, more sulfate contributed to gypsum and thaumasite formation in the DS-4 solution, especially at low temperature in which a strong gypsum peak was observed. The higher solubility of gypsum at high temperature might be the reason for the presence of small gypsum peak to the 20°C samples compared to those at 5°C (Torres 2004). In case of exposure to LLC, the absence of gypsum and ettringite in the XRD patterns emphasises the fact that more sulfate was engaged in the formation of thaumasite rather than gypsum and ettringite, while the absence of portlandite indicated that all Ca $(OH)_2$ reacted with dissolved carbonate that diffused into the concretes from the clay pore solution to form carbonate phases such as calcite and aragonite. The later is metastable form of calcium carbonate and it has higher solubility than calcite. It is formed when sufficient quantities of carbonate ions are available in the solution to permit the transformation of calcite into aragonite which was observed in investigation by Torres (2004), Torres et al. (2003) and Hartshorn et al. (2002).

3.2 IR Results

IR technique was used mainly to confirm the formation of thaumasite as it is sometimes difficult to distinguish it from ettringite using XRD. The results are shown in Figures 5 and 6 in which a peak characteristic of SiO_6 group indicative of thaumasite is present at around 500, 670 and 740 cm^{-1} in both CEM I and CEM I / 10 %LF samples exposed LLC and DS-4 solution at 5 and 20°C. These peaks were absent in specimens exposed to DS-2 solutions. The peak assigned to AlO_6 at 850 cm^{-1} which is indicative of the presence of ettringite was also found in both concrete type exposed to DS-2 and DS-4 solutions at both temperatures, while it was usually absent in concretes exposed to LLC, apart from the CEMI concretes at 20°C which displayed a small peak. Looking at the SO_4 group, peaks indicative of gypsum, at 600 cm^{-1} was present in concretes exposed to both DS-2 and DS-4solutons, but was lower for DS-2 and for DS-4 at 20°C. In addition, a sulfate bearing phase which may be related to ettringite and thaumasite was observed as a peak around 1100 cm^{-1} in all exposure conditions and both temperatures.

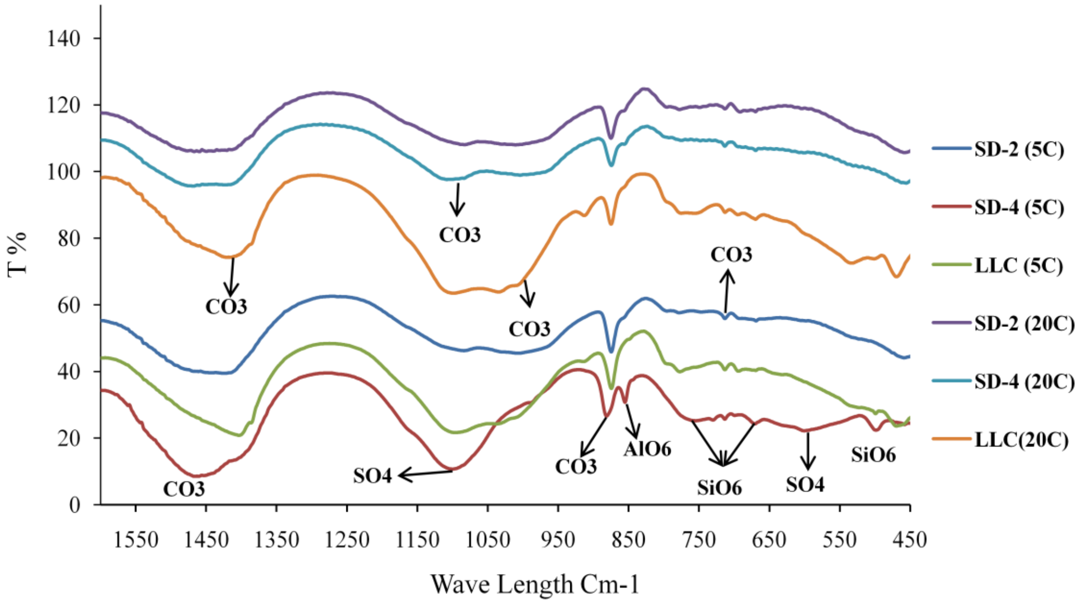

Figure 5. IR analysis of CEMI concrete at 5 and 20°C

A strong thaumasite peak was present in the deteriorated concrete, suggested that more sulfate was involved in the reaction of thaumasite while in DS-2 solution at both temperatures, sulfate was involved in gypsum and ettringite formation. Peaks characteristic of a CO_3 carbonate mineral was also detected in all concretes exposed to different conditions. Peaks related to calcite were observed at 875 and 712 and 1425 cm^{-1} while the CO3, which is part of the structure of thaumasite was observed as a peak around 1385Cm^{-1}. Moreover, peaks related to aragonite were observed at around 700 and 1485cm-1 and at 1085 cm^{-1} in concretes exposed to DS-2 solution. The results of IR confirm the XRD analyses from which it was concluded that thaumasite formed in concretes placed in LLC at 5 and 20℃. The results suggest that the clay of given class cause more deterioration due to thaumasite formation and TSA than implied by the classification based on BRE SD-1 (2005).

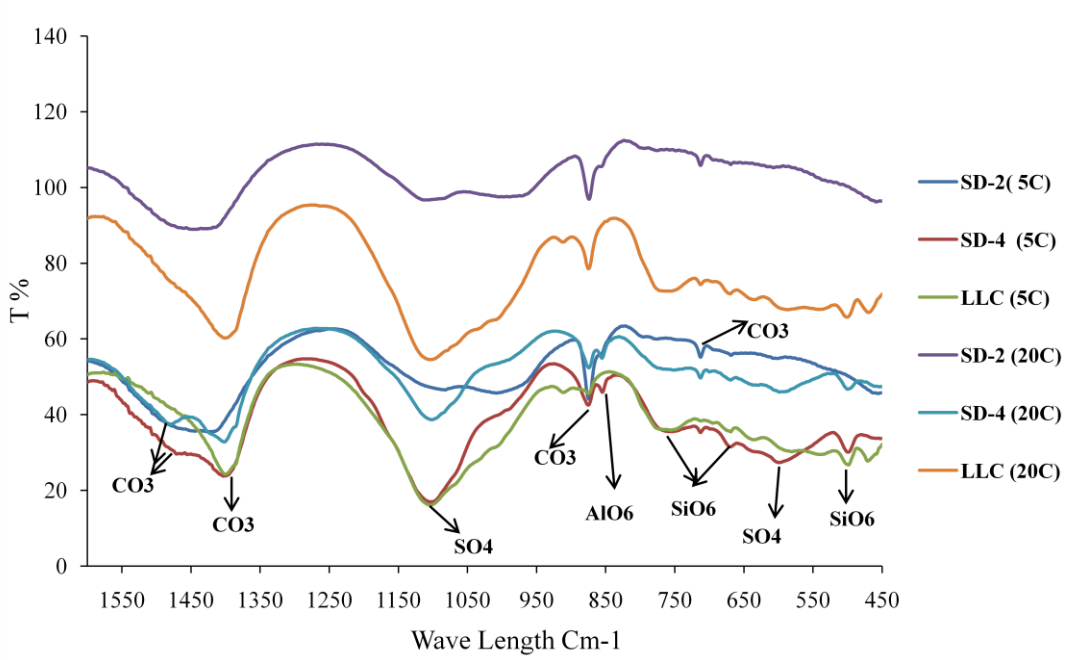

Figure 6. IR analysis of CEMI/10%LF concrete at 5 and 20℃

4. OVERALL DISCUSSION

Understanding the mechanism by which concrete is more vulnerable to TSA when it is in contact with clay rather than the equivalent solution is not clear. Hobbs and Taylor (2002) suggested that in case of the foundations of bridges of the M5 motorway, sulfuric acid, produced in Equation 1 was the primary cause of deterioration. However, a laboratory investigation by Hill et al. (2003) suggested that acid conditions do not promote thaumasite formation but it might enhance the thaumasite formation in the presence of elevated sulfate concentration derived from gypsum during acid attack.

In the case of the weathered Lower Lias Clay used in this investigation, the continued oxidation of pyrite and buffered reaction result in generation of aggressive soluble sulfate and acidity as explained in Equations 1 and 2. This results in clay pore solution of pH 7-8. In turn this would affect the degree of solubility for calcite and gypsum, being high at pH of about 7-7.5 (Collete et al. 2004) and result in increased availability of carbonate and sulfate ions. In addition, under acidic conditions, the sulfuric acid may react with clay minerals and liberate exchangeable cations such as K, Na and Mg as reported by Czerewko and Cripps (2006). Increasing the level of magnesium sulfate is considered to increase aggressivity compared with other types of sulfate solution (Hartshorn et al. 2002, Torres et al. 2003). Therefore, it is possible that the mechanisms leading to the formation of thaumasite are different for the two types of sulfate bearing media (i.e. solution and clay). In exposure to clay, due to the low pH environment the CSH is probably destabilised. This together with the availability of sulfate, carbonate and magnesium species in the clay as discussed above, increases the propensity for the formation of thaumasite in exposure to LLC over that in an equivalent DS class solution. In exposure to sulfate solution, in contrast, the initial reactions result in the formation of gypsum and ettringite and only later further interactions result in the engagement of the CSH culminating in thaumasite. In this investigation it was found that deterioration rate of concrete exposed to the clay of design class DS-2 was equivalent to or greater than the aggressively of a DS-4 solution.

5. CONCLUSIONS

This paper presents the preliminary results of an on-going extensive study in to the interaction between clays of different types in contact with several cementitious binders and test solutions. Based on these initial results, the following conclusions can be made:

- The degree of deterioration decreased in the following sequence: LLC >DS-4 >> DS-2 at both temperatures 5 and 20℃.
- Although Lower Lias Clay has water soluble sulfate corresponding to the BRE sulfate class DS-2, it was found that concrete exposed to LLC with sulfate design class DS-2 deteriorated at a faster rate than corresponding specimens in DS-2 solution and at a similar or greater rate to those exposed to the DS-4 sulfate solution at 5℃. This suggests that the aggressivity of clay and resulting concrete deterioration could exceed what might be observed in concrete exposed to equivalent standard test solutions.
- It would appear that clay composition plays an important role in thaumasite formation and severity of thaumasite sulfate attack. The attack may be enhanced by chemical reactions that occur during pyrite oxidation processes, which are absent in standard test solutions. The process will be affected by the physical properties of clay as well as the mineralogy and chemistry.
- The difference in the deterioration product of concrete exposed in sulfate solutions and aggressive clay suggest that there are two different mechanisms for the attack.
- Temperature can be considered to be a secondary factor for thaumasite formation in concrete exposed to Lower Lias Clay. Thaumasite was formed in CEMI and CEMI /10%LF at 5 and 20 ℃ unlike concrete exposed to DS-4 solutions in which thaumasite formed only in CEMI/10%LF concrete at 5℃.

6. ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Ministry of Higher Education of Libya for the financial support to this project.

7. REFERENCES

Building Research Establishment. (2005). *BRE Special Digest 1: Concrete in aggressive ground*. 3rd Edition, BRE. June 2005.

Clark, L.A. (2002) *Thaumasite Expert Group Report: Review after Three Years Experience*. BRE Technical report, Building Research Establishment. Watford, UK, March 2002.

Collete, G., Crammond, J.N., Swamy, R.N. and Sharp, J. (2004) 'The role of carbon dioxide in the formation of thaumasite'. *Cement and Concrete Research*, 34: 1599–1612.

Crammond, J.N. Collete, G.W. and Longworth, T.I. (2003) 'Thaumasite field trial at Shipston on Stour: three-year preliminary assessment of buried concretes'. *Cement and Concrete Composites*, 25(8): 1035–1043

Crammond, J.N. (2003) 'The thaumasite form of sulfate attack in the UK'. *Cement and Concrete Composites*, 25: 809–818.

Czerewko, M.A. and Cripps, J.C. (2006) 'Sulfate and sulphide minerals in the UK and their implications for the built environment'. *Proceeding of the 9th Conference of the IAEG*, Paper number 121: 1-12

Erlin, B. and Stark, DC. (1965) 'Identification and occurrence of thaumasite in concrete. Symposium on the effects of aggressive fluids in concrete'. *Highway Research Record* No 11: 108–113.

Floyd, M. and Czerewko, M.A., Cripps, J.C. and Spears, D.A. (2003) 'Pyrite oxidation in Lower Lias Clay at concrete highway structures affected by thaumasite, Gloucestershire, UK'. *Cement and Concrete Composites*, 25(8):1015-1024.

Floyd, M. and Wimpenny, D.E. (2003) 'Procedures for assessing thaumasite sulfate attack and adjacent ground conditions at buried concrete structures'. *Cement and Concrete Composites*, 25(8): 1077-1088.

Hartshorn, S.A., Sharp J.H. and Swamy, R.N. (2002) 'The thaumasite form of sulfate attack in Portland-limestone cement mortars stored in magnesium sulfate solutions', *Cement and Concrete Composites*, 24: 351–359.

Hill, Byars, E.A. , Sharp, J.H., Lynsdale, C.J., Cripps, J.C. and Zhou, Q. (2003) 'An experimental study of combined acid and sulfate attack of concrete', *Cement & Concrete Composites*. 25(8): 997–1003.

Hobbs, D.W. and Taylor, M.G. (2000) 'Nature of thaumasite sulfate attack mechanism in field concrete', *Cement and Concrete Research*, 30: 529– 533.

Hobbs, D.W. (2003) 'Thaumasite sulfate attack in field and laboratory concrete: implications for specifications'. *Cement and Concrete Composites*, 25(8): 921-929.

Slater, D., Floyd, M. and Wimpenny, D.E. (2003) 'A summary of the Highways Agency thaumasite investigation in Gloucestershire: the scope of work and main findings'. *Cement & Concrete Composites* 25 (2003): 1067–1076.

Torres, S.M., Sharp, J.H., Swamy, R.N., Lynsdale, C.J. and Huntley, S.A. (2003) 'Long term durability in Portland-limestone cement mortars stored in magnesium sulfate solution', *Cement and Concrete Composites*, 25: 947– 954.

Torres, S.M. (2004) *The influence of chloride on thaumasite form of sulphate attack in mortar containing calcium carbonate*, PhD Thesis, Faculty of Engineering. The University of Sheffield, UK, 2004.

Tsivilis-Sortiriadis, K. and Skaropoulous, A. (2007) 'Thaumasite form of sulfate attack (TSA) in limestone cement pastes'. *Journal of European Ceramic Society*, 27 (2-3): 1711-1714.

Zhou, Q., Hill, J., Byares, E.W., Lynsdale, C.J. and Sharp, J.H. (2006) 'The role of pH in thaumasite sulfate attack'. *Cement and Concrete Research*, 36: 160 – 170.