Cement & Concrete Composites 25 (2003) 1015–1024

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Pyrite oxidation in Lower Lias Clay at concrete highway structures affected by thaumasite, Gloucestershire, UK

M. Floyd [a,*], M.A. Czerewko [b], J.C. Cripps [b], D.A. Spears [c]

[a] *Halcrow Group Ltd., Burderop Park, Swindon SN4 0QD, UK*
[b] *Department of Civil and Structural Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK*
[c] *Earth and Environmental Sciences, University of Sheffield, Dainton Building, Brookhill, Sheffield S3 7HF, UK*

Abstract

The process of pyrite oxidation with the resulting formation of sulfates in disturbed pyrite-rich mudstone is recognised in the UK as a potential engineering hazard. This paper describes and quantifies the extent of pyrite oxidation in Lower Lias Clay in Gloucestershire using a large data set collected in 1998 and 1999 during the investigation of twenty-eight, approximately 30-year old highway structures affected by the thaumasite form of sulfate attack. Most of the structures have concrete spread footings founded on undisturbed and relatively unweathered Lower Lias Clay, and are surrounded by backfill of reworked Lower Lias Clay. Chemical, X-ray diffraction and X-ray fluorescence analyses are used to determine the composition of the soils. Differences are identified in the sulfides, sulfates and total sulfur concentrations between unweathered and weathered Lower Lias Clay and the backfill. The work is supported by pyrite oxidation trials in the laboratory on clay samples stored in bags and sealed tubes. The results indicate that pyrite oxidation, sulfate formation and leaching have occurred as the Lower Lias Clay weathers in situ and also during and following disturbance and reworking for highway construction. The amount and rate of pyrite oxidation are estimated, and comparison is made with the concentration of sulfate in the surrounding groundwater, and the extent of thaumasite sulfate attack measured at adjacent structures.

Keywords: Thaumasite; Pyrite; Sulfate; Lower Lias Clay; Gloucestershire

1. Introduction

In March 1998 the thaumasite form of sulfate attack (TSA) was identified in the reinforced concrete foundations of a road bridge on the M5 Motorway in Gloucestershire, UK. The Highways Agency appointed Halcrow to assess the extent and implications of the problem in their structures in the county. A summary of the investigation and its principal findings is provided by Slater et al. [1]. By February 1999, when site works had been completed, a total of twenty-eight structures had been investigated, and TSA was found and measured at nineteen of them. The source of the sulfates for the TSA was considered to be the surrounding ground, consisting of pyritic Lower Lias Clay, which also constitutes the backfill to the structures, combined with and transported by groundwater within these soils. Therefore at most structures the ground was investigated by trial pits and boreholes. The foundations were exposed and detailed and extensive sampling and testing of the soil, groundwater and concrete were carried out. In addition, two reference boreholes were sunk in ground unaffected by construction activity at a location off set from the motorway, to enable the weathering profile of undisturbed Lower Lias Clay to be investigated. Specific procedures are described by Floyd and Wimpenny [2]. A study was also undertaken by Sheffield University to assist in the assessment of pyrite oxidation, employing procedures recently proposed by the Highways Agency for the assessment of the suitability of materials as structural backfills [3,4].

2. Geological setting and soil description

2.1. Location

The investigation was centred around Junction 11a of the M5 motorway to the east of Gloucester and extended over an approximately 40 km NE–SW stretch

---

[*] Corresponding author. Tel.: +44-1793-812479; fax: +44-1793-812089.

E-mail address: floydm@halcrow.com (M. Floyd).

0958-9465/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0958-9465(03)00125-2

of the M5 Motorway between Junctions 9 and 14 (16 structures investigated), and a 14 km E–W stretch of the A40 trunk road (10 structures investigated, plus two on adjacent trunk roads). All the structures are identified by a unique number assigned by the Highways Agency (e.g. M5_70.50).

2.2. Regional geology

In England the outcrop of the Lower Jurassic Lias Group occupies a broad tract extending from Dorset through the Midlands to North Yorkshire. It is particularly well exposed along coastal sections in SW England and Yorkshire but inland, due to its low durability, it forms a landscape of low relief with occasional exposure along scarp slopes capped by more durable limestones. The Lias sediments were deposited in three principal marine basins, the Cleveland, Midlands-Severn and Wessex Basins, separated by shallow shelf seas or islands. The M5 motorway corridor follows the NNE-SSW outcrop of the Lias Group of the Midlands-Severn Basin that forms the Vale of Gloucester and Vale of Berkeley at an elevation of 20–60 m above OD between the River Severn floodplain to the west and the Cotswold limestone escarpment to the east. Here there is a complete stratigraphic succession of dark blue grey to black massive and fissile mudstones with marls, argillaceous limestone beds and carbonate nodular horizons. Shaw [5] confirms that the mudstones and shales often contain pyrite as framboidal clusters, nodules, vein infills and also replacing fossil remains.

The stratigraphy of the Lias Group has recently been updated [6]. Twenty of the investigated structures are founded on the Charmouth Mudstone Formation (formerly Lower Lias Clay), whilst in the north of the study area, six structures are founded on the underlying Blue Lias Formation (formerly Blue Lias member of the Lower Lias Clay). Two structures are founded on piles driven through Recent estuarine alluvium of the River Severn, and at the locations of many of the structures, in particular concrete stream culverts, there is a thin veneer of drift deposits consisting of river alluvium above the Lias Group. The geological memoir for the area [7] describes the Lower Lias Clay as consisting mainly of grey silty mudstone, and the Blue Lias member to comprise interbedded mudstone and argillaceous limestone. The limestone beds are reported to be on average 0.1 m thick, alternating with mudstone beds of around 0.6 m in thickness. For the purpose of the study, unless specific differentiation is required, the Lias deposits are all termed 'Lower Lias Clay'.

2.3. Weathering of Lower Lias Clay

The Lower Lias Clay is recognised as possessing a distinctive weathering profile. At Blockley, NE Gloucestershire, six zones (I–VI) of weathering are identified based on a colour change, destruction of original fabric and change in fissure spacing [8]. The moisture content and liquidity values are reported to increase with weathering [9]. For the purpose of the study, it was sufficient to differentiate 'weathered' from 'unweathered' material on the basis of colour, structure and strength. The two groups are denoted as LL_w and LL_f, respectively (see Table 1). The main descriptive features of these materials are as follows.

Unweathered Lower Lias Clay (*LL_f equivalent to zones I and II*)	*Weathered Lower Lias Clay* (*LL_w equivalent to zones III–VI*)
Very stiff to stiff, dark blue grey, friable, sub-horizontal thinly laminated to thinly bedded, silty clay with occasional horizons of laminated weak mudstone. Contains some calcareous shell debris and pyrite crystals. Occasional orange brown staining along discontinuities. With occasional thin beds of limestone	Soft to firm becoming stiff with depth, light olive grey mottled light olive brown, silty clay. Contains occasional selenite crystals

At the two reference boreholes the weathered zone was between 2.5 and 3.5 m thick whereas along the motorway route it was observed as usually less than 1 m thick. The pre-construction ground investigation [10] reported a weathered zone generally less than 2 m thickness. In many places, the unweathered Lower Lias Clay was directly overlain by made ground of backfill and embankment fill, where weathered Lower Lias Clay had been removed during construction.

Table 1
Definitions of abbreviations used for the main soil types

Class	Definition
LL_f	Unweathered Lower Lias Clay
LL_w	Weathered Lower Lias Clay
MG_ll	Made Ground of Lower Lias Clay
MG_m1	Made Ground of >75% Lower Lias Clay and <25% alluvium
MG_m2	Made Ground of 25–75% Lower Lias Clay and 25–75% alluvium
MG_m3	Made Ground of <25% Lower Lias Clay and >25% alluvium

2.4. Placement of backfill

Most of the structures are constructed on pad foundations formed in temporary excavations with concrete cast directly onto unweathered Lower Lias Clay. The backfill around the structures is composed primarily of reworked Lower Lias Clay, with some original clods remaining intact as lithorelicts up to approximately 200 mm diameter. The fill is heterogeneous, including both weathered and unweathered Lower Lias Clay and occasional inclusions of organic materials and carbonate gravel derived from superficial deposits (mainly alluvium) and construction materials.

The outer surfaces of the clods and the remoulded clay between lithorelicts were observed to be discoloured olive brown. This suggests that a similar weathering process has occurred in the backfill material within the last 30 years as has developed over tens of thousands of years in the undisturbed clay. For the purpose of analysis, the cohesive fill is classified into several soil types based on the proportion of Lower Lias Clay to alluvium as shown in Table 1.

3. Process of pyrite oxidation

Pyrite is an authigenic constituent of most ancient marine sediments and in dark coloured marine clays and mudrocks such as the Lower Lias Clay it can account for up to 5% of the sample mass. Pyrite readily oxidises when exposed to atmospheric conditions or oxygenated groundwater. Aqueous, acidic, sulfate-rich solutions are produced. Reactions of these with calcite produces sulfate minerals, the most common of which is gypsum. The proportion of pyrite or sulfate found in the Lower Lias Clay is a function of:

- The original geological strata (the depositional and diagenetic conditions—a reducing environment and organic matter are required to form pyrite).
- The weathering history of the strata (exposure to atmospheric conditions).
- The groundwater flow patterns, including the possible leaching of sulfates from the top metre or so of the soil by rainwater percolation and the accumulation of sulfates towards the base of the tree root zone.

A review of pyrite oxidation in disturbed ground is discussed in numerous reports and papers [3,11–13]. Reid et al. [3] report the process of pyrite oxidation, which is summarised in Table 2 together with the ensuing reactions that are responsible for various forms of concrete degradation. In the presence of oxygen or air and water the ferrous iron in pyrite is oxidised to ferric iron and the sulfur to sulfate. These products are dissolved in water and become mobile. Protons are generated

Table 2
Simplified equations showing the natural weathering reactions of pyrite and the formation of various reaction products

	Saturated conditions	
1	$\underset{\text{Pyrite}}{2FeS_{2(s)}} + 2H_2O + 7O_2 \rightarrow \underset{\text{Ferrous iron}}{2Fe^{2+}} + 4SO_4^{2-} + 4H^+_{(aq)}$	Initial oxidation of pyrite proceeds by purely chemical means, producing ferrous iron
	$\underset{\text{Ferrous iron}}{4Fe^{2+}} + 4H^+_{(aq)} + O_2 \rightarrow \underset{\text{Ferric iron}}{4Fe^{3+}} + 2H_2O$	Ferrous iron is oxidised to ferric iron by bacterial mediation
	$\underset{\text{Pyrite}}{FeS_2} + \underset{\text{Ferric iron}}{14Fe^{3+}} + 8H_2O \rightarrow \underset{\text{Ferrous iron}}{15Fe^{2+}} + 2SO_4^{2-} + 16H^+_{(aq)}$	Ferric iron is a strong oxidising agent, acts as an electron acceptor in further oxidation of pyrite
1-b	$4Fe^{2+} + 10H_2O + O_2 \rightarrow \underset{\text{Ochre}}{4Fe(OH)_{3(S)}} + 8H^+_{(aq)}$	If conditions of pH $\geqslant 4$, i.e. flushing of the system and atmospheric exposure, results in hydrolysis and precipitation of orange ochre
	Humid conditions	
2	$\underset{\text{Pyrite}}{2FeS_{2(s)}} + 7O_2 + x \cdot H_2O \rightarrow \underset{\text{Ferrous sulfate salt}}{2FeSO_4 \cdot nH_2O_{(s)}} + \underset{\text{Sulfuric acid}}{H_2SO_{4(l)}}$ $(x \geqslant 2$, when $x = 2$, $n = 0)$	Ferrous sulfate salts seen as efflorescent deposits, such as yellow, blue–green melantorite ($FeSO_4 \cdot 7H_2O$)
3	$\underset{\text{Sulfuricacid}}{H_2SO_{4(l)}} + \underset{\text{Calcite}}{CaCO_{3(s)}} + H_2O_{(l)} \rightarrow CO_{2(g)} + \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_20_{(s)}}$	Calcite and limestones react with sulfuric acid forming gypsum
4	$\underset{\text{Cement}}{Ca(OH)_2} + \underset{\text{Ground-water}}{SO^{2+}_{4(aq)}} + 2H_2O \leftrightarrow \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O_{(s)}} + 2OH^-_{(aq)}$ $\underset{\text{Cement}}{Ca_3Al_2O_6} + \underset{\text{Gypsum}}{3CaSO_4 \cdot 2H_2O} + \underset{\text{Water}}{30H_2O} \rightarrow \underset{\text{Ettringite}}{[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O}$	Ettringite formation requires a source of sulfate, mobile groundwater, calcium hydroxide and hydrated calcium aluminate from the cement matrix. The reaction initially produces gypsum due to calcium hydroxide and sulfate ion interaction. Ettringite is unstable in acidic conditions
5	$\underset{\text{Cement}}{CaSiO_3 \cdot 3H_2O} + \underset{\text{Cement}}{2Ca(OH)_2} + \underset{\text{Ground–water}}{SO_4^{2-}} + \underset{\text{Limestone}}{HCO_3^-} + 8H_2O + 3H^+_{(aq)}$ $\rightarrow \underset{\text{Thaumasite}}{Ca_3[Si(OH)_6](CO_3)(SO_4) \cdot 12H_2O}$	Thaumasite formation requires a source of sulfate, groundwater, hydrated calcium silicate and carbonate phases present in concrete and a low temperature of <15 °C. Thaumasite is unstable in acidic conditions
6	$\underset{\text{Ferrous sulfate}}{12FeSO_4} + \underset{\text{Illite}}{4(KAl_2Si_3O_8(OH)_2)} + 48H_2O + 4O_2$ $\rightarrow \underset{\text{Jarosite}}{4(KFe_3(SO_4)_2(OH)_6)} + 8Al(OH)_3 + 12Si(OH)_4 + \underset{\text{Sulfuric acid}}{4H_2SO_4}$	In clay-rich deposits under acidic conditions generated during pyrite weathering the oxidation products react with illite forming jarosite

in the reaction producing highly acidic and corrosive conditions. The sulfuric acid reacts with any calcite present in the clay producing calcium sulfate that crystallises as gypsum. In some clay-rich deposits where the quantity of available carbonate minerals is insufficient to neutralise the acidity, the ferrous sulfate may react with illite forming jarosite. Several authors have reported the relatively rapid process of pyrite oxidation in initially unweathered mudstone that has been disturbed by construction activity [11].

4. Methods of assessment

Soil samples were stored under refrigerated conditions in airtight jars or sealed plastic core liner. Selected samples were split and tested for a combination of (i) physical parameters (geotechnical classification tests), (ii) wet chemistry, and (iii) bulk geochemistry using X-ray fluorescence analysis (XRF) combined with mineralogical determination by X-ray diffraction (XRD). Wet chemical testing was specified as either 'full suite' comprising all major cations and anions, or 'basic suite' comprising only those parameters required for classification to the UK guidelines on aggressive ground conditions [11,14]. XRD investigation involved analysis of both whole rock and clay sized (<2 μm) fractions. The approximate number of chemical and mineralogical tests that were undertaken is shown in Table 3. All test methods were NAMAS accredited and used a combination of British Standards and in-house procedures. Duplicate testing, comparability checks and spurious data filtering were carried out to ensure data consistency.

5. Results

5.1. Chemical and mineralogical composition

The major mineralogical composition determined by XRD analysis and the sulfur speciation evaluated by wet chemistry are shown for the main soil types in Table 4. The sulfur species are reported as percentage sulfur (%S) to allow direct comparison between tests. This includes a value for 'indirect sulfide' determined as the difference between total sulfur and acid-soluble sulfate and is assumed to comprise the amount of pyrite in the ground. This procedure tends to overestimate the pyrite content as non-acid-soluble sulfur species other than the sulfide pyrite, including organic sulfur compounds and inert sulfates such as barites, may constitute a proportion of the derived value.

The only mineral forms of sulfur detected by XRD analysis were pyrite, (mainly in unweathered Lower Lias Clay and traces in the backfill) and gypsum (mainly in weathered Lower Lias Clay and backfill). A correlation was determined in the backfill between water-soluble sulfate and water-soluble magnesium (Fig. 1). The results suggest that liberated sulfate ions remain in solution as the highly soluble magnesium sulfate and also react with calcium, to form calcium sulfate precipitating as gypsum. The study has identified that the Lower Lias Clay has a high calcite content, and therefore sufficient calcium carbonate was likely to be present during pyrite oxidation to neutralise the sulfuric acid being generated. As Table 5 shows, the Lower Lias Clay in the project area was found to contain more calcite with less pyrite and clay minerals than Lower Lias Clay compositions previously reported.

5.2. Chemical and mineralogical changes due to weathering

The fill is mainly weathered and it is not clear what effects post-placement weathering may have had on the mineralogy because the amount of pyrite that was originally present in the fill at the time of construction is not known. One possible way of determining the extent of weathering in the fill material is to compare the bulk composition with that of unweathered Lower Lias Clay.

Table 4 illustrates the difference in composition between unweathered, weathered Lower Lias Clay and backfill. The results for the sulfur species are expressed graphically in Fig. 2, illustrating the changes that have occurred in the formation of weathered Lower Lias Clay, and during the approximately 30-year post-construction period. If it is assumed that the backfill is mainly derived from the surrounding predominantly unweathered Lower Lias Clay the differences observed can be considered to be mainly due to reworking and change of environment affecting clay during the last 30 years. Although there is some weathered material in the fill and some chemical changes may have occurred to the clay if it was stockpiled prior to placement, the effects on

Table 3
Approximate numbers of test suites undertaken on the main soil types

	LL_f	LL_w	MG_ll	MG_m1	MG_m2	MG_m3
Physical tests	47	8	74	108	39	17
Basic wet chemistry	62	10	112	175	55	14
Full suite wet chemistry	23	7	72	89	28	10
XRD and XRF	22	4	41	56	22	5

Table 4

A summary of the mineralogical composition (by XRD) and sulfur species (by wet chemistry) for the main soil types

	All Lower Lias Clay	All Made Ground	Difference (LL–MG)	Unweathered Lower Lias	Weathered Lower Lias	Difference (LL_f–LL_w)	MG_ll	MG_m1	MG_m2	MG_m3
Water-soluble sulfate (%S)	0.06 ± 0.04	0.1 ± 0.07	−0.04 (−67)	0.06 ± 0.04	0.07 ± 0.06	−0.01 (−17)	0.1 ± 0.07	0.1 ± 0.06	0.08 ± 0.07	0.1 ± 0.06
Acid -oluble sulfate (%S)	0.23 ± 0.55	0.17 ± 0.15	0.06 (26)	0.16 ± 0.36	0.68 ± 1.08	−0.52 (−325)	0.19 ± 0.17	0.14 ± 0.13	0.14 ± 0.14	0.13 ± 0.07
Total sulfur (%S)	1.15 ± 0.58	0.75 ± 0.49	0.4 (35)	1.21 ± 0.53	0.77 ± 0.79	0.44 (36)	0.87 ± 0.57	0.79 ± 0.44	0.52 ± 0.42	0.36 ± 0.25
Indirect sulfide (%S)	0.92	0.59	0.33 (36)	1.05	0.09	0.96 (91)	0.68	0.65	0.38	0.23
Quartz (%) SiO_2	8.6 ± 2.94	12 ± 4.4	−3.63 (−42)	9.43 ± 2.02	8.6 ± 0.36	0.83 (9)	13 ± 3.9	12 ± 3.69	12 ± 6.43	9.7 ± 4.4
Calcite (%) $CaCO_3$	24 ± 14	24 ± 15	0.28 (1)	24 ± 14	24 ± 8.17	−0.22 (−1)	19 ± 12	24 ± 13	29 ± 19	50 ± 15
Gypsum (%) $CaSO_4 \cdot 2H_2O$	1.7 ± 4.42	0.64 ± 0.75	1.06 (62)	0.58 ± 0.35	7.88 ± 8.74	−7.30 (−1264)	0.86 ± 1.22	0.52 ± 0.24	0.5 ± 0.19	0.5 ± 0
Dolomite (%) $CaMg(CO_3)_2$	12 ± 2.68	10 ± 3.51	1.61 (14)	12 ± 2.68	13 ± 2.11	−1.13 (−10)	9.85 ± 1.21	11 ± 2.49	9.28 ± 3	15 ± 13
Pyrite (%) FeS_2	1.46 ± 0.93	0.76 ± 0.49	0.70 (48)	1.64 ± 0.88	0.53 ± 0.32	1.12 (68)	0.79 ± 0.55	0.86 ± 0.5	0.55 ± 0.27	0.5 ± 0.4
Combined clay minerals (%)	46 ± 14	45 ± 12	1.10 (2)	47 ± 15	43 ± 7.6	4.26 (9)	49 ± 11	46 ± 10	42 ± 14	21 ± 13

Notes: 1. Data presented as mean values with one standard deviation.
2. Indirect sulfide is calculated as total sulfur minus acid-soluble sulfate.
3. Percentage difference is shown in brackets.

the data are considered to be relatively minor. The results indicate that:

- With the exception of gypsum content and acid-soluble sulfate concentration, there is a similar relationship between the natural weathering of Lower Lias Clay and the changes that occurred during and after the Lower Lias Clay was placed as backfill.
- Only eight samples of weathered Lower Lias Clay were tested and revealed great variation in the gypsum and acid-soluble sulfate contents. This is due to the distribution of gypsum, which forms discrete clusters of selenite crystals.
- Mean pyrite content decreases by approximately 0.59% S (68%) and indirect sulfide decreases by about 0.96% S (91%) between unweathered and weathered Lower Lias Clay. Between all Lower Lias Clay samples and backfill samples, mean pyrite decreases by approximately 0.37% S (48%) and indirect sulfide by about 0.33% S (36%). The decrease is attributed to the oxidation of the pyrite.
- Because the clay contents are similar in both the unweathered Lower Lias Clay and backfill sample sets, it is reasonable to conclude that, in the backfill, the pyrite content was originally similar to that of unweathered Lower Lias Clay, close to 1.64% (0.87% S). If this was the case then there has been 0.47% S pyrite released, only some of which has been retained as gypsum.
- Leaching has occurred in the weathered Lower Lias Clay, with an average 0.44% S (36%) decrease in total sulfur recorded. However, the loss of pyrite is much greater than the loss of total sulfur because gypsum is being formed.
- The change in indirect sulfide in the backfill of 0.33% S (36%) is almost the same as the change in total sulfur of 0.40% S (35%). Unlike weathered Lower Lias Clay, there is no significant increase in acid-soluble sulfate or gypsum. This suggests that pyrite, once oxidised, is being lost from the backfill system, although a slight increase in water-soluble sulfate was recorded. Sulfate is being generated by pyrite oxidation and is probably being leached relatively rapidly by percolating drainage and ground water in the relatively permeable backfill. Some of this sulfur may be involved in the formation of thaumasite in the adjacent concrete, and some is likely to have been lost from the system if the backfill was stockpiled and leached prior to placement.

5.3. Assessment of pyrite 'loss' at each structure

Twenty-eight structures were investigated for TSA. At those sites where sufficient soil sampling and testing was completed, the chemical and mineralogical data have been reviewed in an attempt to determine the

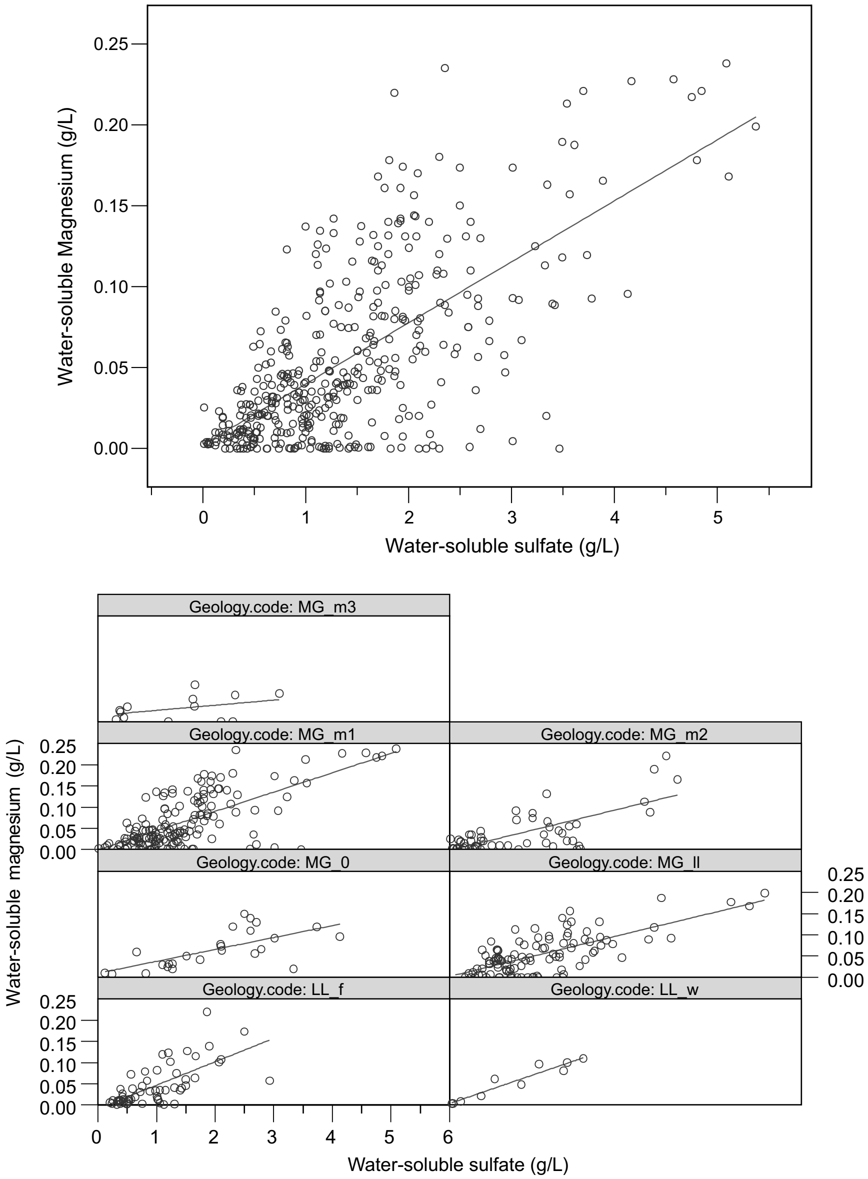

Fig. 1. Plots of water-soluble magnesium vs. water-soluble sulfate for each soil type.

amount of pyrite that may have been lost through weathering associated with the placement of backfill and subsequent construction work. The pyrite content is determined using the indirect sulfide value (total sulfur minus acid-soluble sulfate). Sufficient data for such a calculation were available for twelve sites. A comparison is made between a locally determined value for the pyrite content of the unweathered Lower Lias Clay and the pyrite content of the adjacent backfill. However, due to the inherent variability of the pyrite content in the unweathered Lower Lias Clay, at most sites there are insufficient data to determine a reliable value. Therefore a 'global' figure of 1.05% S is used that combines all the results from unweathered Lower Lias Clay as reported in Table 4. The estimated percentage of pyrite oxidised at the twelve structures is shown in Fig. 3. Pyrite losses vary between 9% and 90% (52% average value). Differences in the amount of pyrite oxidation are likely to relate to:

- The variability of pyrite content measured in a heterogeneous backfill with adjacent structures of the same design showing differences between one-another of about 30%.
- Stratigraphic differences between sites where the pyrite content is higher in the north of the area (in and close to the Blue Lias Formation) than in the south of the area.
- Differences in the method and duration of stockpiling the fill material prior to placement and in the placing of the fill (for example the degree of reworking during placement).

Table 5
A comparison of Lower Lias Clay mineralogy with published data

Data source	Quartz (%)	Calcite (%)	Feldspar (%)	Pyrite (%)	Siderite (%)	Clay minerals (%)
Previously published data						
Chandler [9]	16–26	4–6	<1	5–10	1–6	53–69
Smith [16]	13–15	3	<1	3–5	nd	70–80
Coulthard and Bell [17]	9	3–10		5–10	nd	70–90
* = weathered samples	(2–11)*	(<1)*		(<5)*		(78–91)*
Campbell [18]	8–31	<1–30	~5	7–10	nd	52–77
Thaumasite expert group report [11]				5–8		
Range and average (in brackets) for the main soil types from thaumasite investigation						
Unweathered Lower Lias Clay (LL_f)	6–15 (9)	1–53 (24)	3–7 (4)	<1–4 (2)	nd	22–71 (47)
Weathered Lower Lias Clay (LL_w)	8–9 (9)	14–37 (25)	3–4 (4)	<0.1–1 (0.5)	nd	33–49 (43)
Made Ground (MG_ll, MG_m1, MG_m2, MG_m3 combined)	1–38 (11)	1–80 (24)	1–19 (6)	<0.1–2.3 (0.75) (many at detection limit)	nd	7–69 (45)

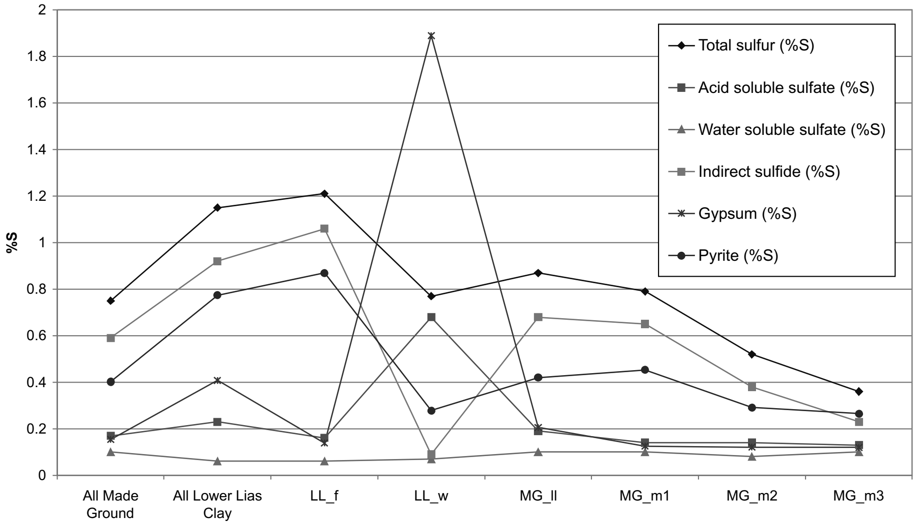

Fig. 2. Variation in mean sulfur species (as %S) for each soil type.

- Differences in the environmental conditions within the fill (particularly the degree of oxygenation and groundwater movement) after placement.

5.4. Pyrite loss compared with groundwater sulfate concentration and degree of TSA in adjacent structures

The loss of pyrite from the backfill may lead to an increased groundwater sulfate. In general, there is an increase in the BRE [15] groundwater sulfate classification of one class between groundwater in undisturbed Lower Lias Clay and groundwater in adjacent backfill [19]. The percentage of pyrite loss determined at each structure has been plotted against the mean sulfate concentration of the groundwater in the backfill at the structure, and against the BRE SD1 classification. No significant trends were apparent. Likewise, pyrite loss was plotted against mean dissolved oxygen (winter and summer readings) and mean redox potential (winter and summer readings) of the groundwater in the backfill. Again, no trends or correlation were apparent.

At each structure the amount of thaumasite has been semi-quantitatively assessed to provide a relative degree of attack (‘Attack Grade’) from 1 to 4 for each structure [2]. The amount of pyrite loss in the backfill has been compared against the Attack Grade at the adjacent structure but no relationship could be determined.

5.5. Laboratory oxidation results

Deterioration of reduced sulfur species such as pyrite is known to occur during sample storage [4,20]. This can affect the test results for both chemical and geotechnical investigations, changing the materials’ properties and

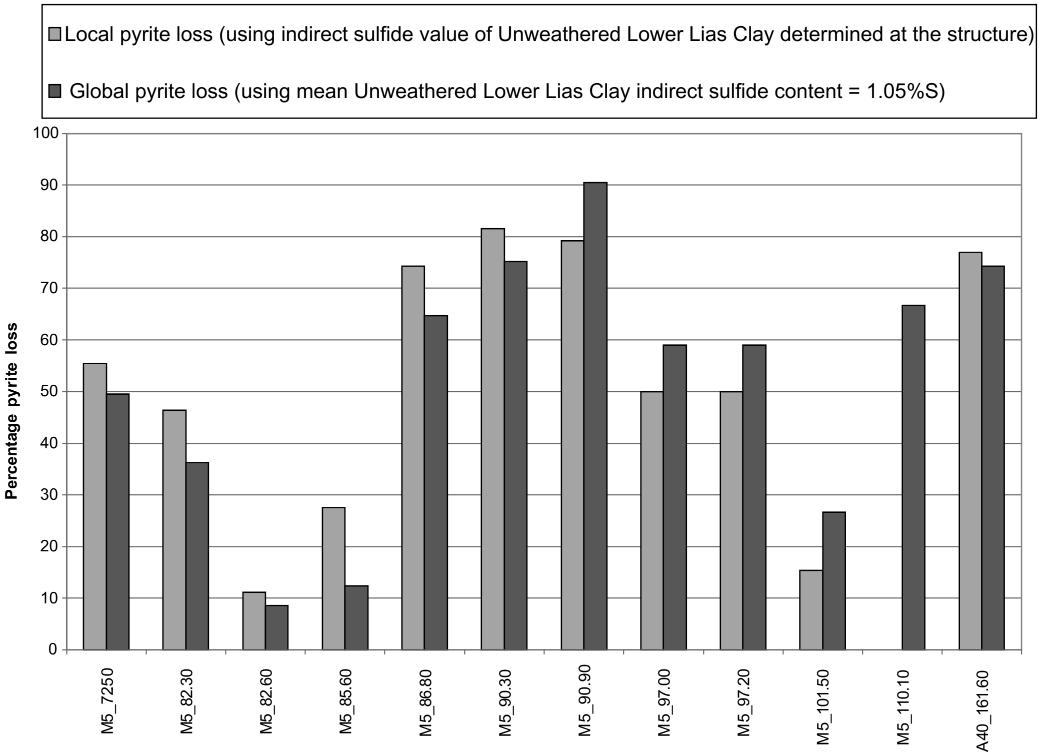

Fig. 3. Estimated pyrite loss in backfill at each structure.

preventing an accurate long-term assessment to be made of the materials' potential impact on engineering projects. Site and laboratory investigations need to consider whether there is potential for chemical change in samples, particularly those that may affect the assessment of sulfate related problems. In this context it is important to determine the actual sulfur speciation of the material at the time of sampling. Uncontrolled storage conditions can have an unknown effect on the chemical and mineralogical character of the material.

A laboratory investigation into the effects of storage of Lower Lias Clay core samples was carried out to monitor the nature, amount and factors affecting changes in the sulfur species present. The aim was to simulate various commonly used sample storage methods in situations lacking environmental control. Six fresh Lower Lias Clay samples, consisting of unweathered, weathered and fill material were stored for 9 months under carefully monitored laboratory storage conditions as both carefully sealed core liner samples and as bagged samples. In addition, core samples that had been chemically characterised at the time of sampling and then stored in a covered core store for up to 8 months were also investigated to determine what changes had occurred during storage. Details of the storage experiment, testing procedures and test results are presented in Czerewko et al. [4]. Sub-samples taken during the experiment were subject to analysed to determine water-soluble sulfate, acid-soluble sulfate, pyrite, total sulfur and carbonate.

Due to the heterogeneous nature of the Lower Lias Clay, the results show some scatter, but clear trends can be discerned in the results, summarised in Table 6. Overall the results show greater losses of pyrite in bagged samples when compared to the more carefully sealed core liner stored samples. Losses of carbonate measured in the samples were accompanied by the increases in acid-soluble sulfate content shown in Table 6, demon-

Table 6
Chemical changes due to storage of clay samples

Type of storage	Fresh Lower Lias Clay		Weathered clay		Fill	
	Percentage change (range)		Percentage change (range)		Percentage change	
	Pyrite	Acid sol sulfate	Pyrite	Acid sol sulfate	Pyrite	Acid sol sulfate
Core liner	−(10–32)	+(4–54)	−(0–17)	+(2–61)	−48	+82
Bag	−(43–56)	+(21–46)	−(22–33)	+(0–61)	−85	+84

Note: − signifies a percentage loss; + signifies a percentage gain.

strating the formation of gypsum from the products of pyrite oxidation. The three site-stored core samples tested also showed severe change during the 8 months storage period with drastic decreases of between 43% and 87% in pyritic-sulfur content measured and increases in acid-soluble sulfate content of between 11% and 89% [4].

6. Conclusions

Data from a large area of the Lower Lias Clay outcrop in Gloucestershire show that the pyrite content of unweathered Lower Lias Clay has decreased by approximately 70–90% (0.59–0.97% S) in the naturally weathered, undisturbed clay strata. The process also entails an approximately 36% (0.44% S) loss of total sulfur from the clay, presumably as a result of leaching. The remainder of liberated sulfur is likely to react with calcite to form gypsum, but due to the localised concentration of selenite crystals, establishing a typical concentration of gypsum was not practical without completing significantly more sampling and testing of weathered Lower Lias Clay.

A similar change in mineralogy due to accelerated pyrite oxidation was observed when comparing 30-year old backfill with adjacent unweathered Lower Lias Clay. A change in colour and breakdown of structure has also occurred in the backfill. At twelve highway structures, pyrite loss varied between 9% and 90%, but was typically 50–60%. The liberated sulfur appears to have formed magnesium sulfate and calcium sulfate dissolved in pore water and groundwater, with only a small proportion precipitating as selenite (gypsum) crystals. Groundwater in the backfill is often one BRE sulfate class higher than the groundwater in the adjacent undisturbed Lower Lias Clay. However, no relationship was observed between the relative amount of pyrite oxidation and the sulfate concentration of the groundwater or the degree of TSA on adjacent structures. A loss of pyrite of approximately 50% means that at these structures, there remains the potential for the remaining 50% of pyrite to oxidise in the future, where conditions are suitable, producing additional sulfates that may continue the process of TSA. The remaining pyrite is likely to be present in the centre of clods of unweathered material and therefore the rate of oxidation could be expected to be slowing.

Results from the sample storage investigations show that over a 9-month period, well sealed core material of unweathered Lower Lias Clay stored in controlled conditions, lost between 10% and 32% pyritic-sulfur and gained between 4% and 54% acid-soluble sulfate. Bagged samples showed even greater losses of pyritic sulfur. Site stored core showed losses of between 43% and 87% pyritic sulfur and a gain of between 11% and 89% acid-soluble sulfur during 8 months storage. These results show similar volumetric losses in pyrite as those in the fill material surrounding the concrete structures and confirm that pyrite oxidation is sufficiently rapid for significant oxidation to have potentially occurred during the motorway construction period. Once the Lias Clay had been backfilled, further oxidation will be dependent on the environmental conditions in the fill. A secondary permeability created by voids between clods of clay, and a percolating, oxygenated highway drainage water or fluctuating groundwater level would promote oxidation. Should the in situ conditions be changed to expose the remaining pyrite to air and oxygenated water, for example due to excavation, the rate of pyrite oxidation is likely to once again become accelerated.

Acknowledgement

The authors gratefully acknowledge the support of the Highways Agency.

References

[1] Slater D, Floyd M, Wimpenny DE. A summary of the Highways Agency thaumasite investigation in Gloucestershire: the scope of work and major findings. In: First International Conference on Thaumasite in Cementitious Materials, BRE, June 2002 (paper No. 1101).

[2] Floyd M, Wimpenny DE. Procedures for assessing thaumasite sulfate attack and adjacent ground conditions at buried concrete structures. In: First International Conference on Thaumasite in Cementitious Materials, BRE, June 2002 (paper No. 1102).

[3] Reid JM, Czerewko MA, Cripps JC. Sulfate specification for structural backfills. Report 447, TRL Limited, Crowthorne, 2001.

[4] Czerewko MA, Cripps JC, Reid JM, Duffell CG. An investigation into the effects of storage conditions on the sulfur speciation in geological material. Quart. J. Eng. Geol. Hydrogeol. 2003; in press.

[5] Shaw HF. Mineralogy of the Lower Lias Clay and the influence of soils and groundwater chemistry on thaumasite formation. Thaumasite Investigation Project, Halcrow Group Ltd., 1998, unpublished report.

[6] Cox BM, Sumbler MG, Ivimey-Cook HG. A formational framework for the Lower Jurassic of England and Wales (onshore area). British Geological Survey Research Report, RR/99/01, 1999.

[7] Worssam BC, Ellison RA, Moorlock BSP. Geology of the country around Tewkesbury. Memoir of the British Geological Survey. Sheet 216 (England and Wales), 1989.

[8] Coulthard JM, Bell FG. The engineering geology of the Lower Lias Clay at Blockley, Gloucestershire, UK. Geotech Geol Eng 1993;11:185–201.

[9] Chandler RJ. Lias clay: weathering processes and their effect on shear strength. Geotechnique 1972;3:403–31.

[10] Soil Mechanics Ltd. The final soil survey for the Birmingham—exeter motorway (M5) Ross Spur Junction to Eastington, vol. 1–5, 1965.

[11] Thaumasite Expert Group. The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction. DETR, 1999.

[12] Pye K, Miller JA. Chemical and biochemical weathering of pyritic mudrocks in a shale embankment. Quart J Eng Geol 1990;23:365–81.

[13] Cripps JC, Edwards RL. Some geotechnical problems associated with pyrite bearing rocks. In: Hawkins AB, editor. Proceedings of International Conference on the Implications of Ground Chemistry/Microbiology for Construction. Rotterdam: Balkema; 1997. p. 77–87.

[14] Building Research Establishment. Sulfate and acid resistance of concrete in the ground, BRE Digest, vol. 363, CRC, 1996.

[15] Building Research Establishment. Concrete in aggressive ground. Part 1: assessing the aggressive chemical environment. BRE Special Digest, vol. 1, 2001.

[16] Smith TJ. Consolidation and other geotechnical properties of shales with respect to age and composition. PhD thesis. University of Durham, 1978.

[17] Coulthard JM, Bell FG. The influence of weathering on the engineering behaviour of Lower Lias Clay. In: Cripps JC et al., editors. The Engineering Geology of Weak Rock. Amsterdam: Balkema; 1993. p. 183–92.

[18] Campbell I. Mineralogical and diagenetic controls on the durability of overconsolidated clays. PhD thesis. University of Sheffield, 1993.

[19] Floyd M. An assessment of UK classifications of aggressive ground conditions by comparison with the relative degree of thaumasite sulfate attack found at concrete structures in Gloucestershire. In: First International Conference on Thaumasite in Cementitious Materials, ABS 020, BRE, June 2002 (paper No. 1100).

[20] Hawkins AB, Pinches GM. Timing and correct chemical testing of soils/weak rocks. Engineering Geology Special Publication, No. 2. London: Geological Society; 1996. p. 272–7.