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Importance of understanding the development and significance of sulphates in the London Clay

L'importance de comprendre le développement et la signification des sulfates dans l'Argile de Londres.

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ABSTRACT: Although the differences in the engineering properties of the brown and grey London Clay are generally appreciated, less is known about the chemical changes in the unsaturated/seasonally aerated (mottled) zone. With pyrite and calcite present, calcium sulphates accumulate at this horizon.

The paper describes the formation of pyrite, its various forms and the significance of its oxidation in the mottled zone. It comments on the acid soluble sulphate results measured at 0.2 m vertical intervals which show a pronounced SO_4 peak at the brown/grey junction. However, two chemical profiles only 35 m apart illustrate a pronounced variability in chemistry. The mobilization of sulphates associated with the heat of hydration is discussed and the engineering implications of this, the sulphate-rich zones and the associated low pH are considered with particular reference to the significance for any concrete/steel emplaced at this depth.

RÉSUMÉ : Bien que les différences dans les propriétés techniques de l'argile marron et gris de Londres soient généralement appréciées, moins est connu au sujet des changements chimiques dans la zone non saturée/aérée saisonnièrement (tachetée). Quand la pyrite et la calcite sont présentes, les sulfates de calcium s'accumulent à cet horizon.

Le papier décrit la formation de pyrite, ses diverses formes et l'importance de son oxydation dans la zone tachetée. Il commente les résultats de sulfates solubles acides mesurés à intervalles verticaux de 0,2 m qui montrent une crête prononcée de SO_4 à la jonction du marron/gris. Cependant, deux profils chimiques séparés de seulement 35m montrent une variabilité chimique importante. La mobilisation des sulfates associées à la chaleur d'hydratation est discutée et on considère ses implications techniques, ainsi que ceux des zones riches en sulfate et le niveau faible de pH y associé. Une référence particulière est faite à la signification pour tout béton ou acier mis en place à cette profondeur.

KEYWORDS: sulphate, pyrite, London Clay, gypsum, sulphate attack.

1 INTRODUCTION

The London Clay Formation (LCF) is a Tertiary marine deposit up to 150 m in thickness. The sequence is predominately composed of silty clays with thin silt bands and is typically sand-rich towards the base. Selenite, the euhedral form of gypsum (calcium sulphate) is particularly common in the upper weathered zones, whilst pyrite, present as nodules, replacement of organic matter and framboids, is abundant in the unweathered Clay. During deposition, the climate was warm and rivers draining the adjacent land mass would have carried a high proportion of organic matter. The organic content would vary laterally and may have changed with time during deposition. As a result of variations in sea bed terrain and sea level, the deposits often accumulated in anoxic conditions.

2 SULPHIDES IN THE LONDON CLAY

Many dark grey/black sediments have high organic contents, the organic matter decaying the burial process. Oxygen is consumed by bacteria such that the sulphates are reduced to sulphides. When ferric iron is present in these oxygen-depleted environments, it too is reduced and reacts with the H_2S produced by the sulphate-reducing bacteria, ultimately to form pyrite (iron sulphide) (Figure 1).

Pyrite is typically found in well-bedded fine grained sediments which are dark in colour due to the high organic (carbonaceous) content. Whilst a pyrite content of some 2-4% is present throughout the grey LCF, it is often abundant in the silt/sand-rich horizons near the base and where similar horizons occur elsewhere.

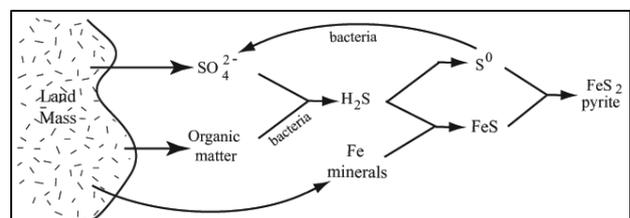


Figure 1. Sedimentary pyrite formation (after Berner, 1984).

Four major forms of pyrite are present in the LCF:

- Large crystals with varying habits (cubic, octahedral etc)
- Groups of microcrystals which have clustered together to form framboids up to 10-15 μm in diameter (eg Figure 2)
- Irregular, often greenish-coloured pyrite nodules
- Replacement of organic matter

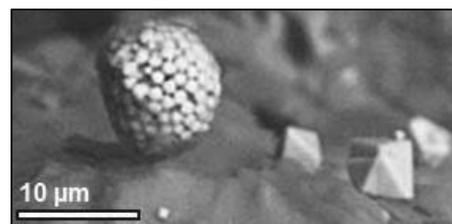


Figure 2. Pyrite framboid and octahedra in the LCF.

3 SULPHATES IN THE LONDON CLAY

As the LCF is a randomly fissured, jointed material, its secondary permeability is such that during past climates or de-watering phases, the weathering extended to considerably

greater depths than would be anticipated in the present climate. Commonly the brown LCF extends to some 6-8 m depth and in rare cases, as recorded by Chandler (2000), to 15 m. Between the saturated (grey) and aerated/oxidized (brown) material there is a mottled grey/brown zone. In the upper brown LCF much of the pyrite has decomposed. In the mottled zone the pyrite experienced a wetting/drying environment such that the iron sulphides were oxidized to produce sulphuric acid and ferrous sulphate (Eq. 1).



Although in stronger, more calcareous materials the ferrous sulphate may produce a significant initial expansion, in the weaker LCF this is less apparent. However, the formation of sulphuric not only changes the pH of the soil but reacts with calcium carbonate to produce calcium sulphate (Eq. 2). Detailed chemical reactions are given in Hawkins and Pinches (1987) and Hawkins (2013).



Gypsum can grow within the Clay in various forms including:

- Euhedral, monoclinic prisms, often known as selenite
- Stellate (star shaped) or “rosette”-like, crystals (Figure 3)
- Void infill, with irregular shapes
- Apparently amorphous “sucrose” crystals

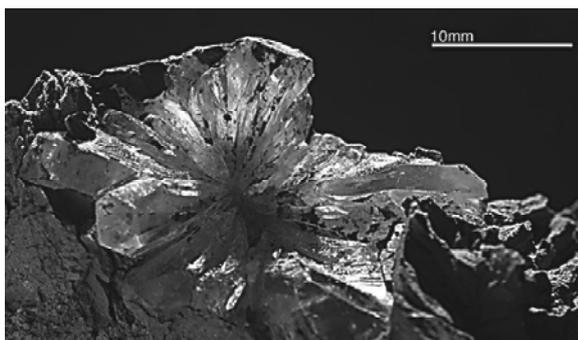


Figure 3. Stellate gypsum from the LCF at Camberwell (6-7 m depth).

The stellate form is typical of crystals which have developed over relatively long periods of time. As such crystals are common between 6 and 7 m depth, it is clear the pressure of crystallisation must have exceeded 100 kPa.

Gypsum is often associated with sandy horizons in the LCF (Bessey and Lea, 1953). The porous and relatively permeable nature of these bands will encourage water movement in wet periods and facilitate the ingress of oxygen during dry periods. As a consequence, oxidation takes place in the adjacent Clay and gypsum may be precipitated from the sulphate-rich solutes.

The development of gypsum on exposed clays can occur in a matter of weeks. Grey LCF borehole arisings from a site investigation in Camberwell left open to weathering showed fine (< 2 mm) white crystals after only four weeks while in an oven at 105 °C they formed within 1-2 days. Microscopic examination confirmed that the crystals were gypsum.

4 CHEMICAL TESTING

Although from a geotechnical point of view the sub-division between the grey Clay and the brown Clay is useful, rarely is there an explanation highlighting the importance of the chemistry of the mottled zone, which frequently contains enriched acid soluble sulphate with a corresponding lower pH.

Hawkins (2013) reports results obtained from the Camberwell site investigation in February 2012. Two boreholes only 35 m apart were tested for total sulphur (TS), acid soluble

sulphate (AS) and water soluble sulphate (WS). Table 1 also shows the calculated total potential sulphate (TPS), oxidisable sulphides as sulphate (OS) and equivalent pyrite according to the Canadian Standard CTQ-M200 (Comité Technique, 2001).

Table 1. Sulphur chemistry for Camberwell boreholes, February 2012.

Borehole 1						
Depth (m)	AS (% SO ₄)	WS (mg/l SO ₄)	TS (% S)	TPS (% SO ₄)	OS (% SO ₄)	Eqv. Pyr. (%)
2.6	0.02	118	0.01	0.03	0.01	0.01
3.6	0.02	10	0.01	0.03	0.01	0.02
4.4	0.33	116	0.11	0.33	0.00	0.20
5.5	0.91	10	0.38	1.14	0.23	0.71
6.4	0.21	906	0.21	0.63	0.42	0.34
7.6	0.25	10	0.54	1.62	1.37	1.01
8.5	0.28	685	0.48	1.44	1.16	0.85
10.6	0.24	501	0.50	1.50	1.26	0.90
12.5	0.26	505	0.56	1.68	1.42	1.02
14.6	0.24	621	1.53	4.59	4.35	2.82
16.6	0.23	405	0.67	2.01	1.78	1.23
17.4	0.17	366	0.57	1.71	1.54	1.04

Borehole 2						
Depth (m)	AS (% SO ₄)	WS (mg/l SO ₄)	TS (% S)	TPS (% SO ₄)	OS (% SO ₄)	Eqv. Pyr. (%)
3.1	0.05	110	0.05	0.15	0.10	0.09
4.1	4.94	10	2.40	7.20	2.26	4.49
5.1	1.12	1850	0.38	1.14	0.02	0.60
6.0	0.62	1410	0.15	0.45	-0.17	0.19
7.1	0.73	1550	0.70	2.10	1.37	1.21
8.0	0.28	715	0.61	1.83	1.55	1.10
9.1	0.31	1050	0.63	1.89	1.58	1.11
10.1	0.31	898	0.63	1.89	1.58	1.12
12.0	0.28	970	0.44	1.32	1.04	0.76
14.0	0.34	10	1.88	5.64	5.30	3.51
16.0	0.23	10	1.19	3.57	3.34	2.22
18.0	0.20	10	0.52	1.56	1.36	0.97
18.9	0.14	10	0.45	1.35	1.21	0.84

At the Camberwell site, the brown-grey junction is at approximately 6-7 m depth while the groundwater level is at 1-2 m depth. To a depth of around 3 m the LCF is depleted of sulphates due to leaching, while a number of elevated values were recorded from between 4 and 8 m. Below 8 m the AS content is relatively uniform at 0.25-0.3 % SO₄. The TS in both boreholes attains a high value of between 1.5 to 2 % S at around 14 m depth, approaching the base of the LCF. The sulphur at these depths is likely to be related to pyrite nodules. With the exception of 4 m depth in BH 2, the equivalent pyrite is highest towards the base of the boreholes. Several pyrite nodules from this depth were noted in nearby borehole cores. Despite being only 35 m apart, there are stark differences between the two boreholes. For example, at 4 m depth, the AS is 0.3 % and the TS almost 0.1 % in BH 1 compared with an AS of almost 5 % and a TS of 2.4 % in BH 2.

The high SO₄ values at 4 m depth in BH 2 are probably due to the presence of coarse gypsum in the sample. As the sample mass used in these tests is less than 5 g, it is quite possible for a crushed gypsum crystal to occupy a large proportion of the sample and hence contribute to anomalously high sulphur and sulphate test results. This may in part be related to the presence of two mature trees within < 3 m of BH 2 (Hawkins 2013).

As a consequence of this significant variation, in September 2012 a new set of samples was taken at 0.2 m intervals close to the original BH 2. The sulphate and pH of these samples was determined (Figure 4).

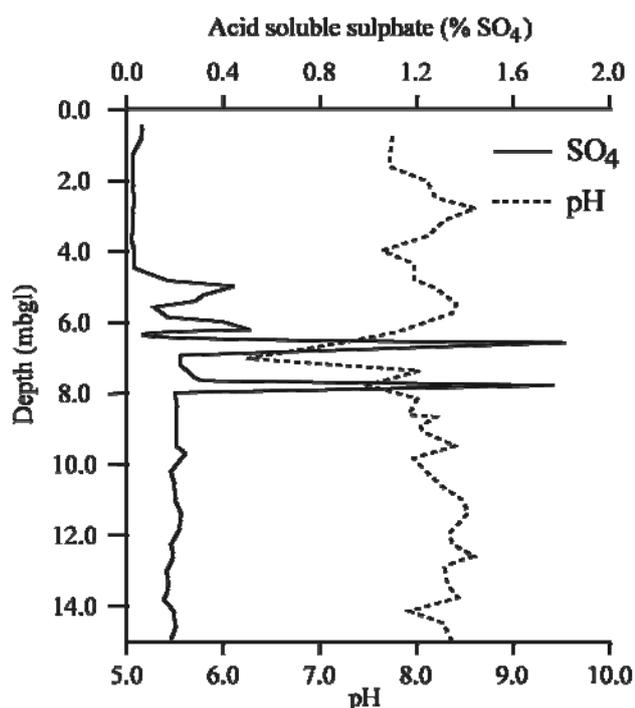


Figure 4. Sulphate and pH profile for the additional borehole at Camberwell.

The results shown in Figure 4 can be summarised as follows:

- To 4.5 m depth the clay is almost devoid of any sulphate, below which there is a 2 m zone of minor sulphate peaks
- A zone of sulphate enrichment is present at c. 6.5-8 m with a maximum of 1.8 % SO_4 . This is over 2.5 times higher than the peak in the original BH 2. This highlights the need for an appreciation of the potential variation in sulphate profiles, in this case from boreholes only 5 m apart
- Below 8 m the AS is relatively constant at c. 0.2 % SO_4

5 ENGINEERING IMPLICATIONS

The significance of sulphates in the LCF has been appreciated for many years such that in the 1930s the Institution of Civil Engineers set up a research sub-committee to examine this, although it was interrupted by the war years (Bessey and Lea, 1953). During their investigations, Bessey and Lea undertook total sulphur and water soluble sulphate analyses, which until the early 2000s was the common procedure. The determination of acid soluble sulphate is now favoured, taking into consideration the potential for acidic ground conditions to develop. In addition, sulphate values were originally presented as % SO_3 whereas % SO_4 is now used.

A well-known case study of concrete attack due to sulphate-bearing ground is that of the St Helier Hospital in Surrey. The 750-bed hospital at Carshalton was constructed in 1938 and by 1959 it was found that some of the concrete foundations placed in the brown LCF had seriously deteriorated. The remedial work in the early 1960s involved supporting the hospital on piles (Legget and Karrow, 1983).

5.1 Seasonal variation in sulphate concentration

Bessey and Lea noted the marked difference in sulphate values taken in dry and wet conditions. For instance, following a very dry summer/autumn, when measured in December the sulphate values in two boreholes at Benfleet were as high as 0.30 % SO_4 . However, following the wet winter, by March they had dropped to 0.042-0.070 % SO_4 . Whilst the seasonal influence on the shrink-swell of the LCF is well known, the effect on ground

sulphates is not appreciated by many geotechnical engineers. Bessey and Lea also report sulphate contents taken from six boreholes between three different depths where the average acid soluble sulphate varied between 0.024-3.38 % SO_4 (Table 2).

Table 2. Difference in AS values given by Bessey & Lea (1953) with averages of all six samples and of the highest two, which BRE (2005) recommend should be taken as the characteristic value.

Depth (m)	Range, SO_4 (%)	Avg. six samples, SO_4 (%)	BRE avg. top two, SO_4 (%)
0.3-0.9	0.024-0.372	0.1	0.22
0.9-1.83	0.036-0.516	0.23	0.44
1.83-2.74	0.444-3.38	0.78	1.99

Table 2 highlights the significance of appropriate sampling. Although this has been in the literature for nearly 60 years, too frequently samples are taken without due consideration of the variation in sulphur/sulphate concentration with depth. Field sampling should always take into account the depth at which it is proposed to place concrete or steel in dark weathered clays.

Although Bessey & Lea draw attention to the fact that gypsum is often present in the sandier horizons, this is also true with calcareous/limestone bands which may become aerated in dry periods, resulting in oxidation of the adjacent pyritic mudrocks/clay.

5.2 Harrow on the Hill

Raison (1992) indicated the boundary of the LCF/Woolwich and Reading Beds Formation (Lambeth Group) was at 35.5 m AOD at Harrow. The relatively low liquid limit (c. 50 %) and a moisture content below the plastic limit at the base of the LCF are consistent with the presence of a silty-sandy horizon – the Basement Beds. Although Raison shows the groundwater level obtained during the investigation period to be at 50 m AOD (15 m deep) attention is not drawn to the difficulty of obtaining a realistically quick piezometric response in clay-rich soils. Detailed logging of continuous U_{100} samples from a supplementary borehole at Harrow on the Hill indicated the brown LCF to some 7 m has selenite crystals up to 10 mm long below which is a 1 m mottled horizon in which selenite crystals of around 6 mm length are present. Chemical analyses of the borehole samples gave the results in Figure 5.

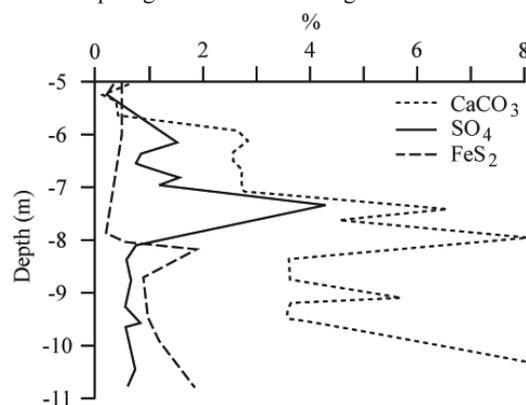


Figure 5. Borehole chemistry at Harrow on the Hill.

The results can be summarised as follows:

- To a depth of 7.5 m the pyrite content is relatively low (0.2 - 0.5 %). Below 8 m the pyrite content is > 0.75 % with a peak of 1.8 % at 8.5 m depth
- The calcite content is low to a depth of 6 m – frequently < 0.5 %. Although it rises to 2.5 % between 6 and 7 m, the main rise to 5-8 % is below 7 m

- c) The acid soluble sulphate content is relatively low ($< 0.5\%$) to a depth of 5 m, rises between 5.25 and 7 m and has a significant peak of 4.2% SO_4 at 7.25 m, below which it is in the order of 0.6% SO_4

During the construction of an underground car park the opportunity was taken to collect samples at 10 mm intervals between two 600 mm CFA piles, 320 mm apart (Figure 6).

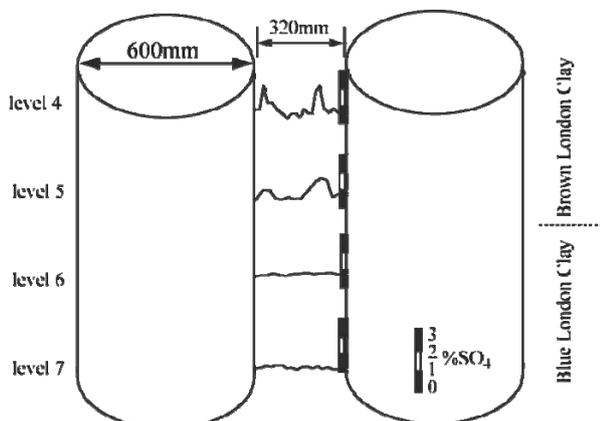


Figure 6. SO_4 content with distance from concrete piles in the LCF. Note variation in the brown Clay.

As noted by Hawkins and Higgins (1997), the sulphate level in the brown LCF was generally in the order of 0.5% SO_4 but between the 4th and 5th floors rose to 2% , approximately 30 mm from each of the piles. In the underlying saturated grey LCF (6th and 7th floors) where the pyrite and calcite had not chemically reacted, raised SO_4 values were not present. It is considered that when the sulphates are mobilized as a consequence of the heat of hydration, the sulphate-rich solutions move into the zone of shear which commonly occurs in the *in situ* ground adjacent to material affected by the auger torque.

A laboratory experiment was undertaken by Hawkins and Higgins to determine the influence of temperature when the LCF was heated in a moist environment at $30\text{ }^\circ\text{C}$ for four, six and eight weeks, the acid soluble sulphate rose from 0.22 to 1.32% . This six-fold rise emphasises the effect of the heat of hydration on the ground chemistry close to CFA piles, and hence the care required when assessing the concrete aggressivity class if concrete piles are to be installed in ground containing or likely to develop sulphates.

To assess the outward migration of heat from the hydrating concrete, Hawkins and Higgins undertook an experiment by placing a copper pipe in an augered hole in the LCF. Three thermometers were installed at 7.5, 15 and 30 mm from the pipe. When water at $65\text{ }^\circ\text{C}$ was placed in the copper pipe the temperature of the Clay rose by a maximum of $8\text{ }^\circ\text{C}$ in six minutes at 7.5 mm; by $5\text{ }^\circ\text{C}$ in six minutes at 15 mm and by $4\text{ }^\circ\text{C}$ in 35 minutes at 30 mm (Figure 7).

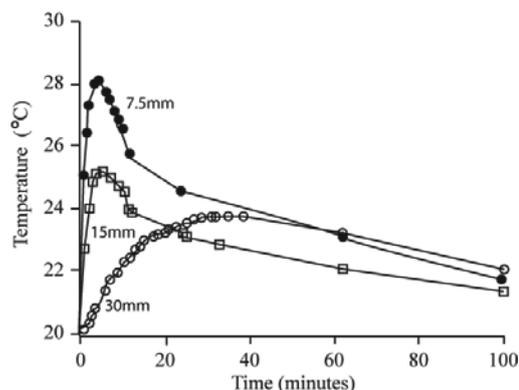


Figure 7. Variation in ground temperature with time at given distances from a heated pipe in the LCF.

6 CONCLUSIONS

- Sulphur is present in the LCF predominantly as pyrite and gypsum. The distribution and abundance of these forms can be highly variable
- Planning of site investigation works should appreciate the spatial variation (lateral and vertical) in ground sulphur, as well as the type and location of sub-surface structures
- Appropriate laboratory testing would include a full suite of chemical testing including AS, WSS and TS
- The determination of detailed sulphate and pH profiles is advocated
- The heat of hydration of concrete may result in a concentration of sulphates and appropriate measures should be taken to protect concrete from sulphate attack

7 ACKNOWLEDGEMENTS

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