Engineering Implications of the Oxidation of Pyrite: An Overview, with Particular Reference to Ireland

A. Brian Hawkins

Introduction

Although the effect of sulphates on concrete had been appreciated for many years, it was not until the 1970s that problems related to sulphate-generated heave became prominent in the geotechnical/geochemical literature, largely as a result of the early work undertaken in Canada on the problems at the Rideau Health Centre which was constructed on the in situ black shales of the Ordovician Lorraine Formation.

In the UK, various problems were reported in northern England where dark colliery waste was used as fill beneath floor slabs in housing developments. Bickerdike and Allen (1972) noted that in the middle of some rooms the floor had risen by up to 75 mm. Subsequently, Nixon (1978) appreciated that the cause of the heave of house floors in the Teeside area (north east England) was similar to that which had been discussed by the Canadian researchers. In the summer of 1982 it became clear that the eastern wing at Llandough Hospital, Cardiff (Wales) was suffering significant distress. Trial pits and sampling were undertaken which confirmed that this was related to the formation of selenite crystals (gypsum) within the bedding discontinuities and fractures in the underlying black laminated mudstones (Hawkins and Pinches 1987a).

The first record of sulphate-generated heave in Ireland appears to have been in a house constructed in 1997 in the central part of the country. In 2005 it was reported that some of the floor slabs which had been laid on 0.9 m of fill had risen by up to 35 mm, causing cracks in walls, difficulty in opening doors etc. The fill was sampled in 2006 and found to contain framboidal pyrite. The remediation involved the removal of the fill and its replacement with effectively inert material (Taaffe pers com 2011).

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A. B. Hawkins, *Implications of Pyrite Oxidation for Engineering Works*,
DOI: 10.1007/978-3-319-00221-7_1,

In the last decade, major problems have occurred in numerous buildings in the Dublin area which were constructed on fill containing pyrite/pyrrhotite. This paper provides a background to the process by which the oxidation of iron sulphides can lead to distress in structures, with particular reference to the problems which have occurred in the Dublin area in the 2000s. It discusses the formation of pyrite and pyrrhotite and the chemical processes involved in their oxidation, the effects of the oxidation process, and how its by-products can lead to both heave and/or the degradation of concrete.

Examples are provided from the UK, Canada and Ireland. Attention is drawn to the significance of the different forms of iron sulphide and the nature of the various host lithologies. The factors which affect the rate/extent of oxidation are considered.

Having reviewed some of the relevant guides and Standards, the chapter draws attention to the difficulties in assessing the potential for sulphate-related damage to structures and the limitations of the documentation currently available. Some common misunderstandings in interpreting the results of both physical and chemical tests on pyritiferous material are discussed.

Although several thousand houses are known to have been affected by sulphate-generated heave in the Dublin area, to date the only method of remediation which can guarantee a permanent solution for these properties is the removal of the pyritiferous material and its replacement with inert fill. In the UK, however, where the source of the iron sulphide was the in situ ground, mini piles and suspended floor slabs have been used successfully. Various other remedial measures have been proposed by researchers, particularly in relation to aggregate/fill, but as their long term effectiveness has not yet been established, they are not discussed here.

Formation of Pyrite and Pyrrhotite

The most common form of iron sulphide is pyrite (FeS_2). This is found in both cubes/lumps and as clusters of microcrystals/seeds referred to as framboids (from the French "raspberry"). Although the existence of cubes of pyrite (fool's gold) has been appreciated for many hundreds of years, it was not until the advent of microscopy and the scanning electron microscope that framboidal pyrite could be studied in detail.

Iron sulphide also occurs as pyrrhotite ($Fe_{1-x}S$ where $x = 0 – 0.125$), a highly reactive mono-sulphide, and in the orthorhombic form of FeS_2 as marcasite (Fig. 1). In addition, it may be present with other elements: with nickel as pentlandite (Fe,Ni)S, with copper as chalcopyrite ($CuFeS_2$) and with arsenic as arsenopyrite (FeAsS). However this paper only considers pyrite and pyrrhotite, discussing their significance in producing sulphate-generated heave and the deterioration of concrete.

Iron sulphides are found in all of the major rock types—igneous, sedimentary and metamorphic. They are recorded from the Pre-Cambrian to the present day,

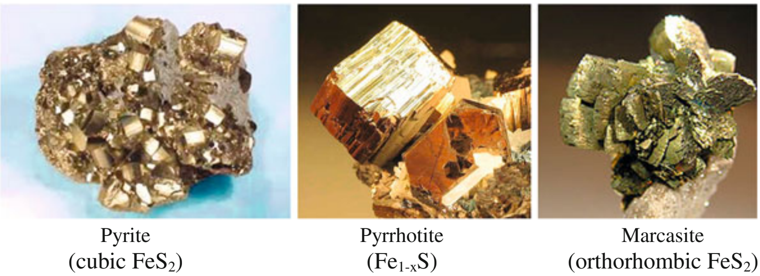


Fig. 1 Images of the main iron sulphide minerals (from Google)

where they develop in estuarine and low energy marine environments as well as some inland wet areas. Most museums have specimens of pyrite in its various crystallographic forms. When unweathered pyrite occurs in rocks it can easily be distinguished by its bright gold colour. When weathered, it may have various colours but is likely to be present where there is a pronounced brown "rusty" staining in the adjacent rock. Although commonly scattered throughout the rock mass, iron sulphides are also found in mineral veins, often with copper, nickel, or zinc (sphalerite, ZnS). They also occur in concentrations in the vicinity of faults or master joints as a consequence of hydrothermal action.

Igneous Rocks

Pyrite occurs as an accessory mineral in some igneous rocks where iron sulphides may form due to magmatic segregation. In this situation, the pyrite may be accompanied by pyrrhotite—the less ordered form of iron sulphide. At Sudbury in Canada there are important deposits of pyrrhotite accompanied by nickel-bearing pentlandite. Here the pyrrhotite ore bodies, which are genetically associated with a gabbro mass, occur as mineral veins fringing the igneous material. Duchesne and Fournier (2011) report the recent problems which have occurred at Trois-Rivières, Québec, where gabbroic rocks were used as concrete aggregate. They report that distress was noted in a housing development within three to five years after construction and that analysis indicated up to 7 % pyrite/pyrrhotite in the aggregate used in the concrete.

Metamorphic Rocks

Pyrite is ubiquitous in the UK while both pyrite and pyrrhotite have developed extensively adjacent to the granites of south west England. In the Okehampton Geological Memoir, which covers the geology over some 550 km^2, Edmonds et al. (1968) reference pyrrhotite seventeen times. They note, for instance, that

Metalliferous minerals, notably pyrrhotite, pyrite, chalcopyrite and arsenopyrite occur in relatively thin veins and as patchy disseminations in thermally metamorphosed rocks of the Carboniferous. The Memoir also records that in the limestones *pyrrhotite is a common accessory constituent and probably results from the alteration of pyrite originally contained in the rocks. Despite the metamorphism, the limestones still carry numerous carbonaceous lamellae.*

To date, the main locations where pyrrhotite has been identified in south west England are in mineral veins. Undoubtedly it is because of the economic value of the sulphides in this area that their mineralogy has been studied in detail and hence the pyrrhotite has been identified. Hawkins and St John (2013a this book) report that the main concentration of recorded pyrrhotite is near the town of Okehampton, close to the major Sticklepath wrench fault and its associated parasitic structures. These faults pass through the Dartmoor Granite and adjacent metamorphic aureole, which includes the metamudrocks and dolerites of the Bude Formation. Pyrrhotite is also found in the Exford area where it can be distinguished because of its magnetism and where it forms widespread coatings on cleavage surfaces. Edmonds et al. (1985) indicate that heating due to metamorphism or burial produces temperatures above 300 °C and suggest that as a result of these temperatures the properties of the iron sulphide in some of the vein mineralisation have been changed/re-set such that the iron sulphide has been converted to pyrrhotite. It is likely the pyrrhotite on the bedding planes and joints in the continental facies of the Devonian Brownstones in South Wales (Barclay et al. 1988) is related to hydrothermal fluids.

The Mundic problem in south west England was related to the presence of sulphides in mine waste which was used as aggregate in concrete pre-1950. Both the Mundic Report (Anon 1994) and Bromley and Pettifer (1997) note that pyrite, pyrrhotite and chalcopyrite were all found in the mine waste material used as aggregate. As a consequence, chemical reactions took place in the concrete, resulting in expansion which caused distress in many buildings, particularly north of Plymouth.

Observations indicate that in low grade metamorphic rocks, such as slates, the cleavage may be locally distorted around a pyrite cube. However, in the phyllites, schists and gneisses, where a distinct foliation is developed due to higher stresses and temperatures, the pyrite may be re-distributed within the rock mass and may have suffered temperature/stress changes.

Bérard et al. (1975) drew attention to the significance of pyrrhotite in the Montreal area where it is present in the Trenton Group shale as very fine grains and as framboids. These authors did not report its lateral or vertical consistency within the rock mass. However, from a visual estimation and calculations based on a single chemical analysis, they considered that pyrrhotite accounted for about 4.5 % of the shale.

Increasingly, attention is being drawn to the identification and significance of pyrrhotite in both metamorphic and igneous rocks. Both Duchesne and Fournier (2011), referring to gabbro, and Chinchón-Payá et al. (2012), referring to metamorphic rocks, note that pyrrhotite degrades much more rapidly than pyrite.

Sedimentary Rocks

As discussed below, pyrite is particularly common in sedimentary rocks where the nature of the sediment, the environment of deposition and the process of lithification are conducive to the formation of iron sulphides. However, in view of the significance of the environment, the amount of pyrite in a geological unit may vary considerably from place to place. In the Liassic mudrocks of the Bristol/Gloucester region, for example, in one area the abundant pyrite-replaced fossils (such as ammonites) are collected by naturalists while only a few kilometres away the very fine grains and framboids of pyrite are barely observable even under the microscope. As a consequence, it is unwarranted to assume that, even within a single geological stratum, the pyrite content will be consistent over a kilometre—let alone tens or hundreds of kilometres.

Where carbon-rich, fine-grained sedimentary rocks experience considerable overburden pressures (burial), the temperature rises significantly. Clayton et al. (1989) and Jones (1992) considered that on burial the temperature experienced by the Carboniferous rocks of the Dublin area was in the order of 280–300 °C. More recently, Goodhue and Clayton (2012) suggested the temperature in the Carboniferous offshore of Dublin rose by 115 °C/km, implying a 2–3 km burial could give thermal conditions in which the structure of pyrite may be changed to that of pyrrhotite.

There is abundant reference to the presence of pyrite in the Dublin Basin but a surprising lack of identification of pyrrhotite in the dark carbonaceous rocks which form much of these strata. Although some phases of pyrrhotite are weakly magnetic, most geologists would not recognise the slight difference in the visual appearance of pyrrhotite compared with the more ubiquitous pyrite; pyrrhotite having a more silvery/bronze colour. As a consequence, without detailed chemical analysis using energy dispersive spectroscopy (EDS) to provide an Fe/S ratio and/or X-ray diffraction (XRD), pyrrhotite could easily be mis-identified as pyrite in general laboratory examinations. Hawkins and St John (2013a) show the 24 locations in Ireland where pyrrhotite has been reported in the geological literature. In addition, as pyrrhotite has recently been identified in both bedrock and fill in the area around the airport (north of Dublin) it is likely that with a detailed examination of fresh rock the presence of pyrrhotite in other areas will be confirmed.

Mudrocks

Mudrocks are the most common sedimentary rocks, accounting for some one-third of the surface area of England. Where there is a clear dominance of one of the components, the material may be referred to as a siltstone or claystone; where the proportions are more similar and/or a clear distinction cannot be made, the sediment is referred to as a mudstone. The word “shale”, however, causes some confusion and as a consequence many workers prefer to avoid this term. Rather, they refer to these laminated argillaceous rocks, which were frequently deposited in anoxic conditions, as “fissile mudstone”. As the conditions in which laminated argillaceous rocks are deposited are similar to those conducive to the formation of pyrite, it is relevant to discuss the terminology in more detail.

Misunderstandings Over the Term “Shale”

In anoxic conditions there is little biological activity to disturb the accreting material hence the sediment accumulates in distinct layers. Such layers may be related to a natural upward fining or form when there is a sufficient time interval between the main clastic inputs for the accumulated fine sediment to become partly lithified prior to deposition of the next layer.

For more than a century the geological literature has used the word *shale* as synonymous with laminated mudstones and hence *shale* was generally understood to refer to material with bedding/layering thicknesses of less than some 20 mm (e.g. Hawkins and Pinches 1992). More recently, the new European Standard (EN 14689:2003, Annex A) has defined the term *shale* in an engineering context by specifying the bedding thickness as <6 mm; equivalent to the definition of thinly laminated materials in BS 5930:1999/2010. However, numerous geological maps, memoirs and papers referred to by engineers throughout the world have used—and continue to use—the word *shale* with its former meaning (i.e. mudrocks with distinct layers of <20 mm). Indeed, many practicing field geologists still use the term *shale* when referring to such thinly bedded mudrocks. As a consequence, there will continue to be some confusion between the geological (colloquial) use of the term and the post-2003 European use, with its associated engineering implications.

The word *shale* is often used in engineering specifications and hence the decision in EN 14689 to restrict/redefine the term causes difficulty in the interpretation of some contract documents. For instance, in Ireland the 6th edition of the Homebond Manual (2006) continued to state that hardcore should be *free from shale* although it was undoubtedly intended that the hardcore should be free from material with layer thicknesses of <20 mm, consistent with use of the word *shale* in their earlier (pre-2003) editions. However, in the 2008 edition, Homebond require hardcore to be *clean and free from matter liable to cause damage to concrete.*

Although British Highways Agency (1986 and subsequently) mention *shale*—without defining the thickness of the bedding—they mainly refer to argillaceous rock. For instance, HA74/00 (Highways Agency 2007) Table 6/1 *Acceptable Earthworks Materials: Classification and Compaction Requirements* states argillaceous rock is unacceptable in fill adjacent to structures (6 N). The word *shale* is not mentioned in Table 14 of BS 5930 *Identification of rocks for engineering purposes* (1999 and 2010) which simply refers to argillaceous rocks including siltstones and mudstones.

The Geological Survey of Ireland use *shale* as referring to *fine-grained sedimentary rock with an irregular parting.*

The Canadian Standards Association (2004), *Methods of test and standard practices for concrete,* points out (Para A1.4.1.3.2) *The naming of fine-grained sedimentary rocks is an inexact process due to inherent difficulties in determination of their texture and mineralogy and in the application of field terminology to small aggregate particles. Some latitude is, therefore, needed in identification of mudrock.* It continues with the definition *Shale: very fine-grained; laminated; wavy/undulating bedding commonly results in ovoid particles; can slake or swell, depending upon type and amount of clay minerals present.* It does not specify a bedding thickness.

Significance of Lithology/Interbedded Sequences

Within most sedimentary sequences there are changes in lithology and it is common to find interbeds of limestone and sandstone in a mudstone succession. Of particular significance in the present context are the argillaceous lamellae found in limestones or highly calcareous, brittle mudstones. The platy clay minerals in these microscopic layers may have been bent/deflected during burial, but when de-stressed they form a plane of weakness and attempt to re-shape and re-develop their adsorbed layers.

As discussed below, the engineering implications of these thin clay bands in otherwise strong, brittle rocks are of vital importance with regard to the problems of sulphate-generated heave, particularly when aggregate is sourced from an interbedded limestone/mudstone succession such as is typically present in the Carboniferous strata.

The colour of a rock is clearly related to its mineralogy. Limestones (calcium carbonate) are generally light in colour but rocks (particularly mudstones) containing organic carbon and/or pyrite are proportionally darker in colour (Fig. 2).

The abundance of pyrite in sedimentary rocks varies as a consequence of their differences in lithology, associated mainly with the nature of the inflowing sediment-rich waters (their organic, sulphate and iron contents) and whether the inflow carried a constant supply of detritus. When sediment inflow was low the accumulate would be dominantly calcareous but during the deposition of limestone bands occasional small fluvial inputs would result in thin, perhaps microscopic, argillaceous/carbonaceous horizons as seen in Fig. 3.

It is known that many of the world's dark grey/black sediments have high organic contents. Berner (1974) notes that as the organic matter decays, the oxygen is gradually used up such that the sulphur/sulphates are reduced to sulphides. Where iron is present in these oxygen-depleted environments, it too is reduced and pyrite is formed (see Fig. 4).

Berner (1982) describes the process as: *Pyrite forms during shallow burial,* via *the reaction of detrital iron minerals with* H_2S*. The* H_2S*, in turn, is produced by the*

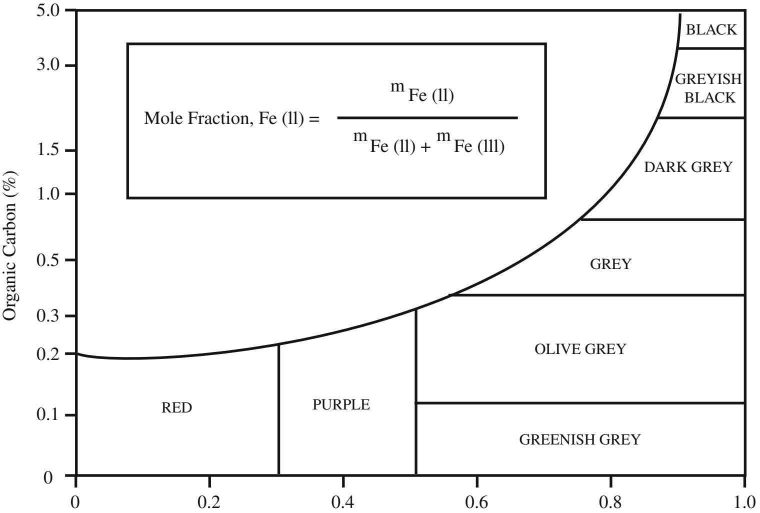


Fig. 2 The colour of mudrock as a function of the organic content and the Fe^{2+}/Fe^{3+} contents (after Potter et al. 1980)

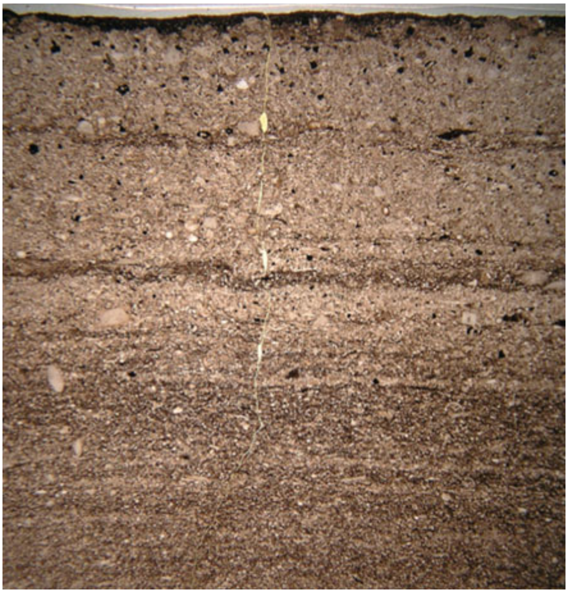


Fig. 3 Clay lamellae in calcareous mudstone/ argillaceous limestone (height of photo 25 mm)

reduction of interstitial dissolved sulphate by bacteria using sedimentary organic matter as a reducing agent and energy source. The initial production of this reaction is not, in fact, pyrite but rather a series of metastable iron monosulphides

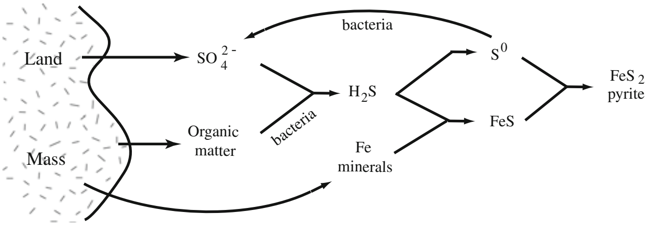


Fig. 4 Main steps in sedimentary pyrite formation (re-drawn based on Berner 1984)

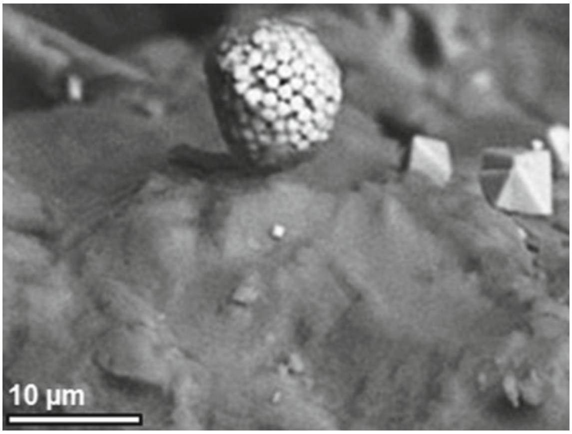
[e.g. pyrrhotite] *which during early diagenesis readily transform to pyrite under most conditions.*

The main environment in which pyrite is typically found, therefore, is a well-bedded, fine grained sediment which is dark in colour due to the organic/carbonaceous content. Such rocks occur in anoxic marine sedimentary basins, particularly towards the edges of the deposits where fluvial inflows are most significant. Wherever dark, carbonaceous rocks occur, the presence of pyrite/pyrrhotite should be anticipated.

Forms of Pyrite/Pyrrhotite

As noted above, pyrite/pyrrhotite occurs as larger crystals (lumps/cubes) and as disseminated grains of 0.5–3 μm (1,000 μm is equal to 1 mm). These grains come together, often as a magnetic sulphide known as greigite, to form framboids some 2–40 μm across (Wilkin and Barnes 1997). Figure 5 shows a typical framboid from the London Clay adjacent to octahedral pyrite.

Fig. 5 3D image of a framboid and octahedral pyrite on a fracture surface in London Clay



In the Carboniferous of Dublin, cubic pyrite commonly exists in close proximity to framboids of various sizes (Figs. 6 and 7). The formation of more complex and polyframboids is not yet fully understood. Ohfuji and Akai (2002) suggest two packing structures are common; cubic close packing or icosahedral packing; the individual microcrystals being drawn together by magnetic forces.

Ohfuji et al. (2005) discussed the forms of framboids they had identified using electron backscatter diffraction techniques. The abstract to their paper notes *The crystallographic ordering of microcrystals correlates positively with morphological ordering; the crystallographic orientations are random in morphologically disordered framboids and are almost ordered in morphologically ordered framboids…. The crystallographic orientation of microcrystals is not uniform, even in highly ordered framboids. This suggests that the self organization of microcrystals in pyrite framboids is not crystallographically controlled, for example by sequential replication of existing microcrystals, since this would result in high lattice misorientation angles between adjacent microcrystals. Presumably, the self organization process is a consequence of the aggregation of multiple equi-dimensional and equimorphic microcrystals that have nucleated in a fixed volume.*

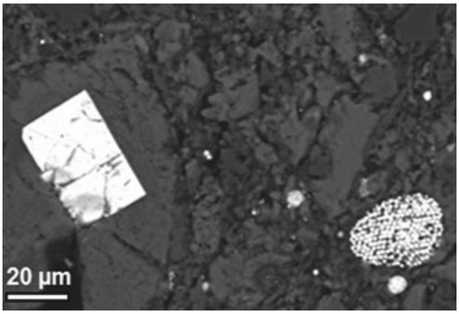


Fig. 6 Both cubic and framboidal pyrite in a calcareous mudrock sequence

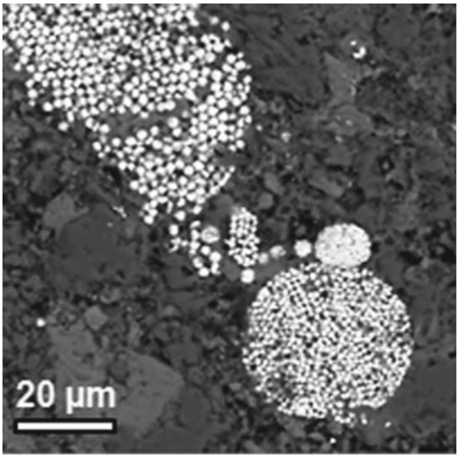


Fig. 7 Variously sized pyrite microcrystals in framboidal form

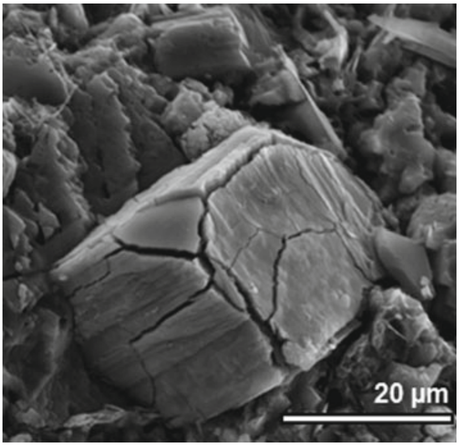


Fig. 8 Fractured lump of pyrite; note striae/corrugations on sides

We suggest that the regular arrangement of microcrystals occurs by the physical rotation (reorientation) of individual microcrystals, driven by the reduction in surface free energy between neighbours. Ohfuji et al. (2005) show excellent photographs of both ordered and disordered framboids.

Although much of the literature refers to cubes and framboids, it does not draw attention to the fact that both types of crystal may be fractured. Figures 8 and 9 show fractures in cubes of pyrite which were probably created during the quarrying process, crushing etc., Hawkins and St John (2013a) have drawn attention to the presence of cracks in some of the microcrystals which make up a framboid. Further, in their Figs. 12 and 13 they indicate that the individual seeds of a framboid may comprise even smaller microcrystals, only some 0.1–0.3 µm across.

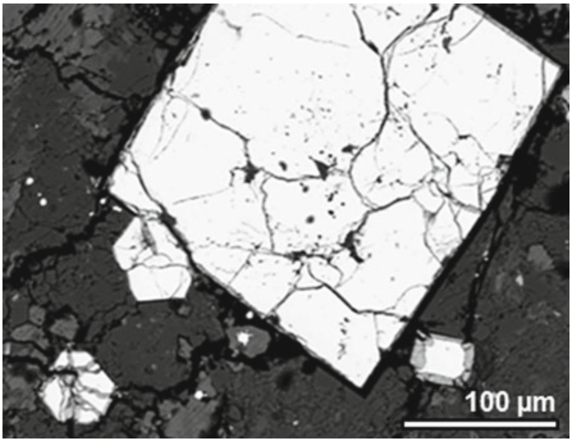


Fig. 9 Commencement of oxidation on fractures in pyrite cubes/lumps

Chemical Reactions Leading to the Formation of Pyrite

Alvarex-Iglesias and Rubio (2012) draw attention to the different chemical reactions which lead to the formation of pyrite in marine environments.

1. The oxidation of iron monosulphides by hydrogen sulphide occurs in a matter of days ($FeS + H_2S \rightarrow FeS_2 + H_2$), (Rickard et al. 1995). Rickard (1997) and Butler and Rickard (2000) suggest this process is responsible for the formation of framboids just below the redox boundary of strictly anoxic sediments where the pH is around 7.
2. The polysulphide pathway ($FeS + S_x^{2-} \rightarrow FeS_2 + S_{x-1}^{2-}$) is relatively slow and leads to the formation of isolated crystals, usually at greater depths than those where framboids are typically found, and in a low pH environment.
3. Smaller <5 µm framboids are associated with formation at the time the sediment was being deposited, such that their residence time at the oxic-anoxic boundary was limited. The >5 µm framboids are likely to be authigenic (formed in place), but not necessarily contemporaneous with the sediment accretion.

Bryant (2003) gives a succinct review and valuable explanation of the formation of pyrite in sedimentary rocks. Bryant quotes Fanning and Fanning's (1989) equation:

$$\begin{array}{ccccccccccccc} Fe_2O_3 & + & 4SO_4^{2-} & + & 8CH_2O & + & \frac{1}{2}O_2 & \rightarrow & 2FeS_2 & + & 8HCO_3 & + & 4H_2O \\ \text{Ferric iron oxide} & + & \text{Sulphate} & + & \text{Organic matter} & + & \text{Oxygen} & \rightarrow & \text{Pyrite} & + & \text{Bi-carbonate} & + & \text{Water} \end{array}$$

Factors Affecting the Oxidation of Pyrite

Sulphides are present in most saturated confined bedrocks, but as they are unoxidised significant sulphate is rarely found. When pyrite develops in its cubic form the outer surface area available for oxidation is small relative to its weight/volume, i.e. it has a low specific surface. In comparison, the individual microcrystals which make up a framboid have a much greater specific surface and as a consequence framboidal pyrite is often referred to as the reactive form.

Oxidation takes place when oxygen and moisture can move into an unsaturated rock. As seen in Fig. 10, the oxidised zones are distinctly brown in colour compared with the very dark unweathered mudstone.

In addition to the presence of oxygen and moisture, the following factors are important during the decomposition of iron sulphide.

Fig. 10 Oxidation along discontinuities in the London Clay

Surface Area Exposed to Oxygen and Moisture

Smooth-sided crystals will have a smaller specific surface than when the sides are rough. When they occur as irregular lumps (Fig. 11) and/or contain cracks (Figs. 8, 9 and 12), the surface exposed to oxidation will be larger, albeit not as great as the combined surfaces of the numerous microcrystals which make up a framboid. In view of the presence of such fractures, extreme caution should be used when referring to the larger grains of pyrite/pyrrhotite as non-reactive. Figure 11 shows a wide alteration rim forming around a pyrite lump while the individual faces of cubes frequently have corrugations which also increase the surface area available for oxidation (Fig. 8).

As noted above, a framboid is a cluster of microcrystals, i.e. "seeds" held together by a weak bonding (Fig. 5). The size of both the microcrystals (0.1–2 μm) and the framboid cluster varies significantly (Fig. 7) and influences the specific surface available for oxidation. The tightness/openness of the framboid structure will affect how easily the oxidising agents are able to penetrate into the framboid and weather the individual seeds (Figs. 13 and 14).

In some cases there are one or more fractures passing through the microcrystals (Fig. 13). In a number of SEM images it can be seen that as a consequence of these fractures the surface area may be effectively doubled. Hawkins and St John

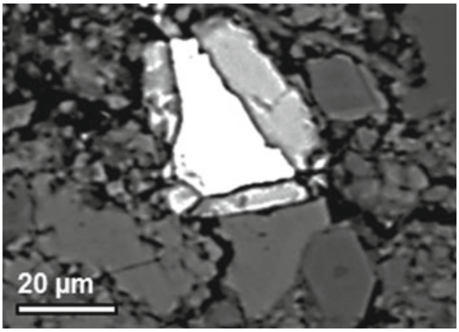


Fig. 11 Alteration on outer edges of a pyrite lump

Fig. 12 Pyrite lump oxidising along internal fractures

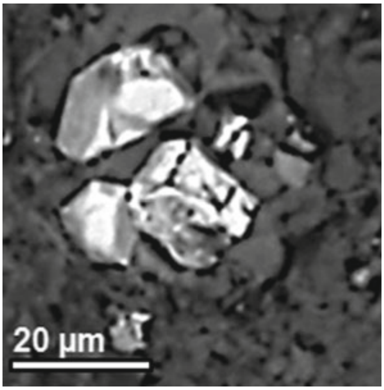


Fig. 13 Oxidizing framboid; note cracks in microcrystals and separation of the seeds in the outer part

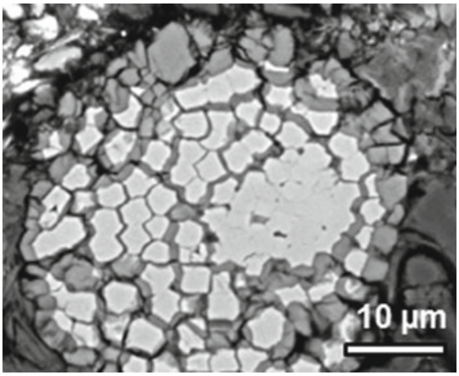
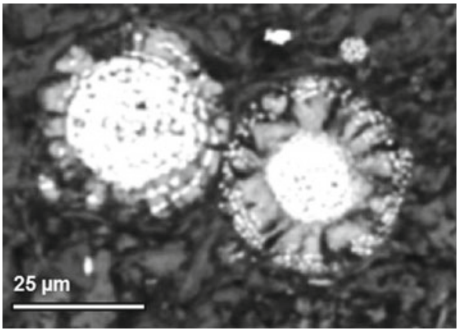


Fig. 14 Framboids showing varying degrees of oxidation and corresponding thicknesses of alteration rims; note seeds moved out as alteration rim formed



(2013a) discuss this further and point out that these cracks, which may affect almost a half of the microcrystals, are not related to quarrying/compaction processes as they have been observed in fresh cores from boreholes in the Dublin area. Cracks are also present in framboids in samples collected in the field from the

Chattanooga Shale in the USA; see for instance Fig. 1a in the paper by Ohfuji et al. (2005).

As a consequence of these fractures and the variation in the size/shape of the microcrystals, an assessment of the specific surface is not simple. In addition, within a single lithology more than one form of pyrite may be present (Figs. 5 and 6) and the cubes/lumps may also contain fractures. Although some authors have drawn attention to the variation in size of the microcrystals which cluster together to form framboids, the full engineering implications of the variation in size of both the microcrystals and the framboids themselves, and the effect of these on the rate of oxidation of pyrite and pyrrhotite have not been adequately considered.

Temperature

A rise in temperature accelerates the oxidation of pyrite, the release of H_2SO_4 and the growth of sulphates (Quigley and Vogan 1970). Working with past research students (Pinches, Wilson and Higgins), Hawkins showed that when samples of material containing pyrite were placed in moist conditions at various temperatures for a number of weeks, the rate of oxidation and the formation of sulphates increased dramatically while the pH decreased. Table 1 and Fig. 15 show the results from a sample from the Westbury Beds which had an acid soluble sulphate value of 0.64 % SO_4 at the start of the experiment. Table 2 shows a similar experiment undertaken over 12 weeks on a different sample of the Westbury Beds and Table 3 an 8 week experiment on the Lias Clay from Gloucester using a larger range of temperatures.

As seen in Table 1, even at 18.5 °C (room temperature) the acid soluble sulphate more than doubled within the 15 weeks of the experiment while Table 2 shows that when a sample from the Westbury Beds with an initial sulphate content of 1.19 % was heated at 41.5 °C for 12 weeks, the value reached nearly 3 % SO_4.

Hawkins and Wilson (1990) report an increase of some 12 % in the acid soluble sulphate content when powdered samples from the Lower Lias were kept for five months in open bags at a temperature of some 18 °C. Subsequently samples were

Table 1 Changes in acid soluble sulphate (%SO_4) when samples from the Westbury Beds were kept in moist conditions at various temperatures (after Hawkins and Pinches 1987b)

Duration (Weeks)	Temperature							
	7.5 °C		18.5 °C		29.5 °C		41.5 °C	
	SO_4	pH	SO_4	pH	SO_4	pH	SO_4	pH
1	0.71	4.1	0.72	3.5	0.76	3.6	1.24	2.7
2	0.72	3.8	0.74	3.2	1.03	2.8	1.45	2.5
4	0.90	3.8	1.06	3.3	1.30	2.8	1.62	2.6
15	0.94	3.0	1.51	2.6	1.80	2.7	2.16	2.5

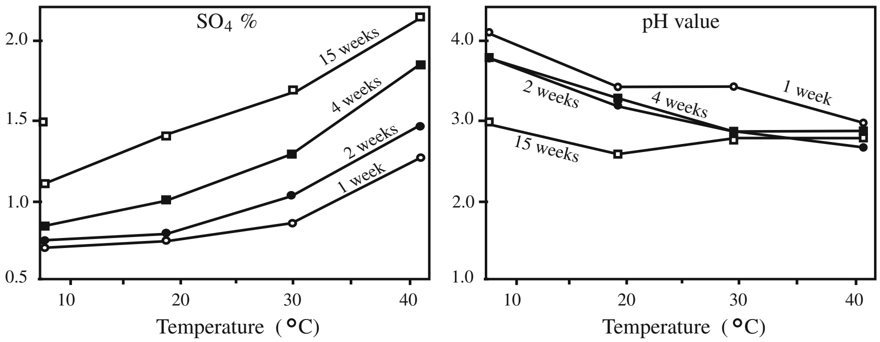


Fig. 15 Changes in acid soluble sulphate (%SO_4) and pH values at different temperatures; Westbury Beds samples from Chipping Sodbury (see Table 1)

Table 2 Changes in acid soluble sulphate (%SO_4) when samples from the Westbury Beds at Cribbs Causeway were kept in moist conditions at various temperatures

Weeks	Temperature			
	7.5 °C	18.5 °C	29.5 °C	41.5 °C
1	1.2	1.3	1.5	1.6
2	1.2	1.3	1.8	2.3
4	1.3	1.4	1.9	2.2
12	2.4	1.6	2.3	2.9

Table 3 Changes from an initial acid soluble sulphate value of 0.52 %SO_4 when samples from the Lias Clay at Gloucester were kept in moist conditions at various temperatures

Weeks	Temperature					
	5 °C	15 °C	25 °C	35 °C	45 °C	55 °C
1	0.54	0.54	0.60	0.60	0.60	0.72
3	0.54	0.60	0.66	0.78	0.84	0.90
5	0.60	0.84	0.90	1.02	1.08	1.14
8	0.60	0.90	1.02	1.20	1.32	1.44

taken from four of the major Clay horizons in the UK and heated for up to 8 weeks. The results (Table 4) support the importance of a significant calcite content in the host material for extensive gypsum formation.

In the light of their research, Hawkins and Pinches recommended that it was not advisable to use underfloor heating if pyrite was present in the bedrock or in the fill.

Mitchell (1986), appreciating the importance of recording total sulphur and acid soluble sulphate values representative of the conditions when sampled, recommended storing the material at temperatures as low as 4 °C. BRE (2005), referring to the chemical testing of concrete, states *The samples must then be stored in a*

Table 4 Changes in acid soluble sulphate (%SO_4) values when four UK Clays were heated at 30 °C in a moist environment for eight weeks

			Changes in acid soluble sulphate (% SO_4)			
Clay Formation	Pyrite %	Calcite %	Start	4 weeks	6 weeks	8 weeks
Kimmeridge Clay	3.94	4.27	0.60	0.67	0.96	0.96
Lias Clay	2.83	6.07	0.31	0.60	0.73	0.97
London Clay	4.51	6.43	0.22	0.31	0.71	1.32
Oxford Clay	3.52	20.62	0.50	0.71	0.92	1.70

cool dark place, at a temperature between 2 and 4 °C, and be tested as soon as possible, the maximum delay being three weeks,(see also Czerewko et al 2003b).

It is clearly beneficial that any post-extraction sulphate growth should not be included in the results used to determine the required aggressivity class for concrete to be placed in the ground. However, where material is retrieved from beneath ground-bearing floors slabs and the maximum present or potential sulphate content is being assessed, this recommendation is less relevant. Indeed, when considering the risk created by sulphides/sulphates in a placed pyritiferous fill, it may be more appropriate to maintain samples at temperatures which (effectively) replicate the conditions pertaining when the material was collected. For practical purposes, therefore, in the UK and Ireland such samples should be kept in sealed bags in a cool (say 10 °C) environment, away from the direct insolation of the sun. Elsewhere, where the ground temperatures are different, it may be appropriate to consider using lower/higher storage temperatures to better replicate the conditions in the upper 1.5 m.

Defects

The chemical nature of the iron sulphide affects the structure of pyrite cubes and microcrystals and any “irregularities” may be exploited during the oxidation process. Such “defects” may be related to the original chemical structure, the degree of ordering in framboids of pyrite or pyrrhotite, alteration/replacement processes and/or the presence of extraneous material. In addition, when rocks containing pyrite/pyrrhotite have been stressed during tectonic activity, the strains imposed may cause incipient weaknesses in the structure of the crystals, which would again facilitate the oxidation process, in the same way as strained quartz affects the development of concrete cancer (West 1996).

Hawkins and St John (2013a) examined an unweathered framboid from a cored borehole in north Dublin and found that some half of the microcrystals appeared to be cracked. As the microcrystals making up framboids are not generally examined in detail, the extent of tectonically-induced strain and fracturing has not been fully appreciated. If, as postulated, the stress shadows and cracks are tectonically produced, it is likely the effect will be most pronounced in the vicinity of faults and may not be consistent throughout a rock mass.

It has been suggested above that the fracturing of cubes/lumps (Figs. 8, 9 and 12) occurs during the quarrying and compaction processes, albeit they may exploit existing stress-induced weaknesses. To what extent the microcrystals making up framboids are affected by the quarrying process is not known. However, from observations of borehole samples it appears that the cracks have no particular orientation and it is considered likely that they were formed as a consequence of interaction between the microcrystals at times of tectonic stress.

Organic Content

If the rock has a significant organic carbon content, it readily absorbs moisture and hence the risk/rate of oxidation is increased (Farrimond et al. 1984). Many of the test results reported on dark grey/black rocks which contain pyrite have organic contents in the range of 2–5 %.

When 1.5 m of Westbury Beds at Chipping Sodbury, north of Bristol, were analysed by Hawkins and Pinches, the organic contents varied between 1.07 and 10.15 %. As seen in Table 5, the organic contents can vary by 8.62 % in only 0.3 m. It is of note that sample CSQ2 had sufficient organic material that it would burn with a small flickering flame.

Clearly, when dark mudrocks are accumulating, the incoming organic content may change both laterally and vertically. As this affects the sulphides formed, the effect of the organic material on future oxidation may be very significant.

Porosity/Permeability

Few rocks are entirely impermeable, but the extent to which the rock will experience water ingress affects the potential movement of oxygen and moisture, and hence the rate of oxidation. Clearly, during blasting, crushing and on-site

Table 5 Variation in particle size, Atterberg limits and chemistry in five samples from the Westbury Beds at Chipping Sodbury taken over a vertical distance of 1.5 m

Sample	Depth m	Clay %	Silt %	w_l %	w_p %	TS % S	ASS % SO_4	pH	Org Carb %
CSQ5	0.26	68	29	67	32	0.26	0.25	7.8	1.36
CSQ4	0.45	56	39	60	26	0.23	0.38	7.6	1.07
CSQ3	1.15	54	46	61	28	1.19	0.84	6.3	1.53
CSQ2	1.45	70	27	74	33	2.48	0.37	6.6	10.15
CSQ1	1.70	65	28	69	29	1.45	0.60	6.5	2.01

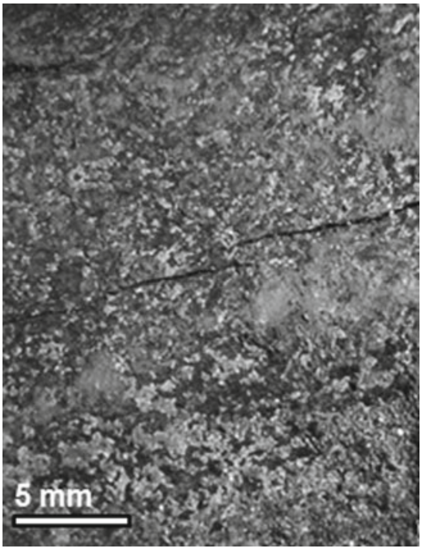


Fig. 16 Cracks developing in argillaceous limestone, Dublin

compaction, aggregate particles may develop incipient discontinuities which increase the porosity of a fragment as well as its permeability.

In addition, a rock which is de-stressed during quarrying will expand in its new, unconfined state. In mudstones, stress release fissures may develop, while in very calcareous mudstones/argillaceous limestones containing clay lamellae, the rock fragment will tend to de-laminate at the platy clay mineral horizons. Figures 16 and 17 show such de-lamination beginning in rock fragments picked up in a quarry north of Dublin.

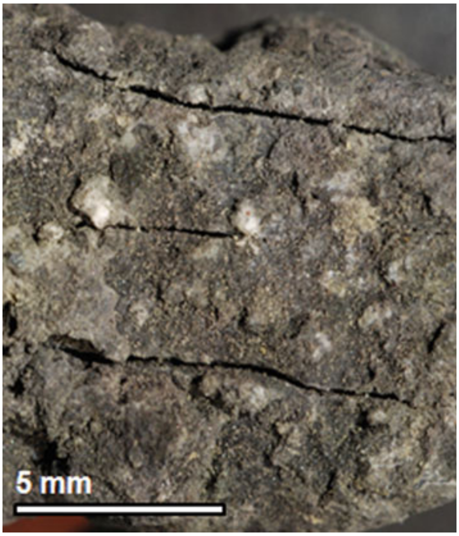


Fig. 17 Splitting of calcareous mudrock, Dublin

When pyrite is present in the aggregate used in concrete/concrete blocks, the porosity of the host material may be an important factor in the ease with which oxidising agents can reach the deleterious material. In many concrete blocks voids occupy 10–20 % of the material; a similar figure to the voids in fill compacted beneath ground-bearing floor slabs.

Discontinuities

Natural or induced discontinuities not only provide an easy pathway for oxygen and moisture to enter the rock but also facilitate the movement of oxidation products (sulphuric acid and sulphates) from the oxidising pyrite, such that the oxidation process can continue. This not only influences the rate of sulphate development but may also change the pH of the material.

Bacteria

Some species of bacteria encourage the continuation of the oxidation process, by removing the ferrous sulphate alteration rim which initially forms around the decomposing mineral, and by releasing sulphuric acid into the host material (see idealised chemical equations in Fig. 18). As noted by Vishniac (1974), these bacteria generally prefer a low pH environment and are most prolific in temperatures of 30–40 °C.

The Rate and Extent of Oxidation of Pyrite/Pyrrhotite

The rate and extent of oxidation will depend dominantly on whether one or more types of iron sulphide are present and the size and nature of the individual pyrite/pyrrhotite cubes or microcrystals. It will also depend on the degree to which the individual crystals have been affected by the factors discussed above. This is not a simple issue.

1. In addition to iron sulphide, other sulphides/sulphates may also be present in the rocks. In the Dublin Basin, for instance, sphalerite, chalcopyrite, marcasite and barytes have been recorded (McConnell and Philcox 1994; McConnell et al. 2001). Czerewko and Cripps (2006) note that *Mineral sulphates, such as barytes, and organic sulphur are both relatively stable in weathering environments, and these would not normally be expected to contribute to the sulphur present in groundwaters unless conditions are unusual.*
2. As a consequence, it is important to appreciate that the amount of sulphur/sulphate measured in a laboratory sample may include that derived from other

1. Initial oxidation of pyrite

$$\begin{array}{ccccccccc}
2FeS_2 & + & 2H_2O & + & 7O_2 & \rightarrow & 2FeSO_4 & + & 2H_2SO_4 \\
\text{pyrite} & + & \text{water} & + & \text{oxygen} & \rightarrow & \begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array} & + & \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}
\end{array}$$

2. Bacterially mediated oxidation of pyrite

In a low pH environment, where Acidophilic bacteria are most prolific:

a) Oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron by Acidithiobacillus *ferrooxidans*

$$\begin{array}{ccccccccc}
4FeSO_4 & + & O_2 & + & 2H_2SO_4 & \rightarrow & 2Fe_2(SO_4)_3 & + & 2H_2O \\
\begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array} & + & \text{oxygen} & + & \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array} & \rightarrow & \begin{array}{c}\text{ferric}\\\text{sulphate}\end{array} & + & \text{water}
\end{array}$$

b) Oxidation of pyrite

i)*Production of ferrous sulphate and sulphuric acid (water present)*

$$\begin{array}{ccccccccc}
7Fe_2(SO_4)_3 & + & FeS_2 & + & 8H_2O & \rightarrow & 15FeSO_4 & + & 8H_2SO_4 \\
\begin{array}{c}\text{ferric}\\\text{sulphate}\end{array} & + & \text{pyrite} & + & \text{water} & & \begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array} & + & \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}
\end{array}$$

ii)*Alternatively, production of ferrous sulphate and sulphur (water absent)*

$$\begin{array}{ccccccc}
Fe_2(SO_4)_3 & + & FeS_2 & \rightarrow & 3FeSO_4 & + & 2S \\
\begin{array}{c}\text{ferric}\\\text{sulphate}\end{array} & + & \text{pyrite} & \rightarrow & \begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array} & + & \begin{array}{c}\text{elemental}\\\text{sulphur}\end{array}
\end{array}$$

c) Generation of sulphuric acid

i) *Conversion of sulphur to sulphuric acid by Acidithiobacillus*

$$\begin{array}{ccccccc}
S & + & 1.5O_2 & + & H_2O & \rightarrow & H_2SO_4 \\
\begin{array}{c}\text{elemental}\\\text{sulphur}\end{array} & + & \text{oxygen} & + & \text{water} & \rightarrow & \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}
\end{array}$$

ii)*Alternatively, reaction of sulphur and ferric sulphate to generate sulphuric acid*

$$\begin{array}{ccccccccc}
2S & + & 6Fe_2(SO_4)_3 & + & 8H_2O & \rightarrow & 12FeSO_4 & + & 8H_2SO_4 \\
\begin{array}{c}\text{elemental}\\\text{sulphur}\end{array} & + & \begin{array}{c}\text{ferric}\\\text{sulphate}\end{array} & + & \text{water} & \rightarrow & \begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array} & + & \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}
\end{array}$$

3. Formation of gypsum

$$\begin{array}{ccccccccc}
H_2SO_4 & + & CaCO_3 & + & H_2O & \rightarrow & CaSO_4.2H_2O & + & CO_2 \\
\begin{array}{c}\text{sulphuric}\\\text{acid}\end{array} & + & \text{calcite} & + & \text{water} & \rightarrow & \text{gypsum} & + & \begin{array}{c}\text{carbon}\\\text{dioxide}\end{array}
\end{array}$$

Fig. 18 Idealised equations involved in the oxidation of pyrite

more stable minerals, hence this value is not of itself a reliable single indicator of the potential for ground heave/concrete attack.
It would be anticipated that the finest crystals and those with the most unstable structure would oxidise most rapidly. As a consequence, when considering the future behaviour of fill beneath ground-bearing floor slabs, it is not realistic to compare the amount and rate of oxidation which has already taken place with the possible rate of oxidation in the future, when both the form of the iron sulphide being oxidized and the chemical environment may be significantly different.

3. In calcareous rock, where the acidophilic bacteria may be less prolific and/or active, a thick ferrous sulphate alteration rim develops around the oxidising material (Fig. 19). Fasiska et al. (1974) report chemical calculations which indicate that the development of ferrous sulphate involves a volume increase of up to 350 %, but do not discuss the rate of the expansion.
4. From SEM photographs it appears that a framboid can oxidise in several ways depending initially on the tightness of the framboidal structure. Two mechanisms are postulated:

   (a) With a tight framboid structure the initial oxidation will only affect the peripheral arcs of the outer seeds; sulphuric acid being produced as well as what appears to be an almost complete rim of ferrous sulphate around the framboid. In fact this is more likely to be the amalgamation of many microscopic rims which developed on the individual seeds as they weathered. With the continuing development of the ferrous sulphate rims around each of the outer seeds, the bonding between the seeds is weakened and the outer, partially oxidised microcrystals are pushed away from the general cluster by the force of the ferrous sulphate growth. This not only facilitates oxidation of the other faces of these seeds but also allows the oxidising agents to reach further into the framboid where the process continues. This results in the formation of concentric rings of partially degraded microcrystals as the oxidation of the framboid develops and further ferrous sulphate is produced (Fig. 19). Seen in 3D, such oxidation products appear as “footballs” (Fig. 20).

   (b) With a less tightly structured, disordered framboid, the oxidising agents can move into the cluster more easily and hence the weathering of the individual microcrystals occurs in a more random fashion (Figs. 13 and 21). As a consequence, the concentric rings seen with the ordered framboid are less evident and the partially oxidised seeds appear to be randomly scattered, almost as if “floating” within the iron oxide alteration product left when the ferrous sulphate becomes depleted of sulphur (Fig. 21). If, as postulated by Hawkins and St John (2013a), at least some of the individual microcrystals are themselves framboids which have taken on an almost crystal shape, the “microseeds” within these microcrystals will in time also be attacked and break down in a similar manner. Clearly the packing, size, purity and stress state of the individual seeds, whether they contain cracks and whether the microcrystals are themselves framboids, will all affect the

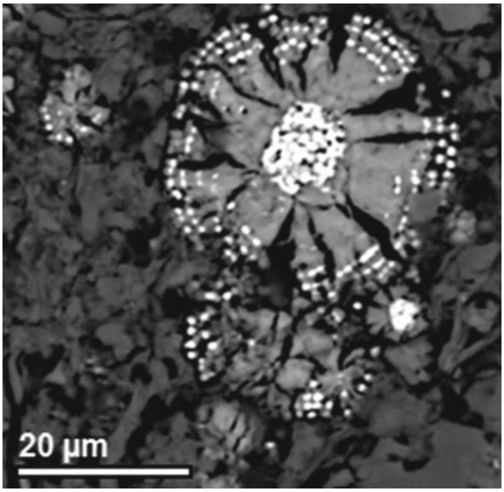


Fig. 19 Alteration rim around a framboid containing microcrystals moved outwards as the rim is formed (after Hawkins 2012)

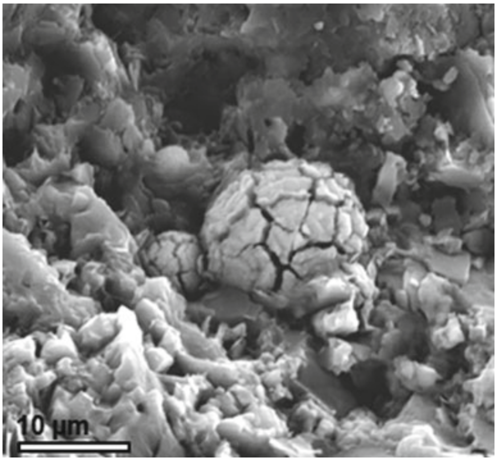


Fig. 20 3D view of alteration rim resembling a cracked sphere/football (after Hawkins 2012)

rate of the expansion caused by the development of the ferrous sulphate rim/s. They also influence the rate at which sulphuric acid is released and subsequently gypsum is formed in the second stage of sulphate-generated (pyritic) heave (Hawkins 2012).

(c) In view of the above, it is clear that the rate of sulphate-generated heave in an acidic environment, in which bacteria are more prolific, cannot be directly correlated with that which occurs in calcareous conditions.

5. In a Géotechnique discussion on Hawkins and Pinches (1987b), Loveland (1988) suggested the degree of oxidation could be assessed from the pH of the material. This is basically true for such very weakly or non-calcareous materials as the Namurian in Derbyshire where the $CaCO_3$ content may be <3 %. In

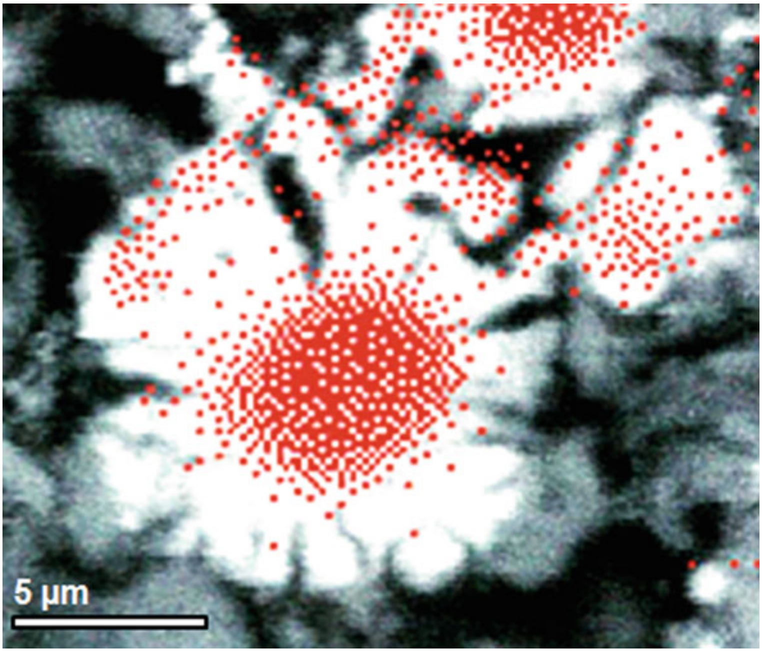


Fig. 21 X-ray map showing the oxidation product (*white*); some of the microcrystals are suspended in the alteration rim (the *red* indicating sulphur)

these conditions the calcite is quickly converted to gypsum (see below) and subsequently jarosite may be formed by a reaction between sulphuric acid and illite. As a consequence, red stained "mine waters" with a pH of <3 are released; note for example the material used in the Carsington Dam (Pye and Miller 1990; Jackson and Cripps 1997). However, oxidation and expansion also occur in the interbedded limestones and mudstones of some of the Carboniferous rocks in the UK and the Dublin Basin. Abundant gypsum crystals are present in these strata, although the $CaCO_3$ content is often >30 % and the pH is commonly 6–9.

Significance of the Development of Ferrous Sulphate in Different Lithologies

As noted above, during the initial stage of the oxidation process ferrous sulphate is formed which Fasiska et al. (1974) suggested involves a significant expansion. This is particularly important if pyrrhotite is present as it is reported to produce more sulphates than pyrite. Figure 22 shows the development of a ferrous sulphate

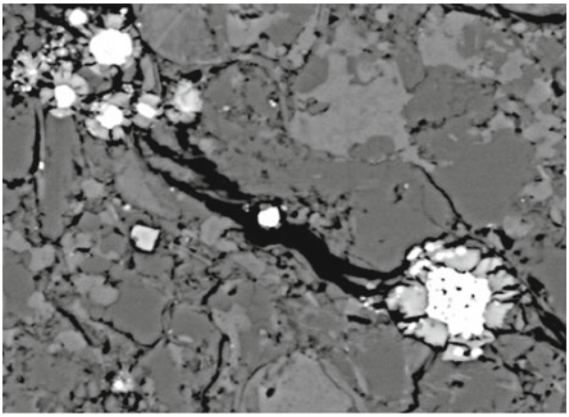


Fig. 22 Dilation of mudstone as framboids oxidise

rim around framboids and its effect on the host mudstone. In these weaker strata the pressure exerted during the development of the ferrous sulphate rim is capable of fracturing the rocks, causing an initial dilation. In brittle rocks the framboids are often aligned, hence when they oxidise the resultant expansion tends to split the rock along any weakness in the sedimentary structure (Fig. 23).

As seen in Fig. 3 clay lamellae/carbonaceous horizons are common in argillaceous limestones. When these brittle rocks are de-stressed, the presence of such lamellae cause a weakness in the rock itself such that during quarrying, crushing etc. the rock may preferentially split at these changes in lithology. Where the lamellae remain in the aggregate fragments, they will tend to dilate with time due to stress release.

Once the material begins to dilate (Figs. 16 and 17), there is a greater facility for moisture and oxygen to enter the system and move within the developing openings, such that any contained pyrite/pyrrhotite is oxidised. Similarly,

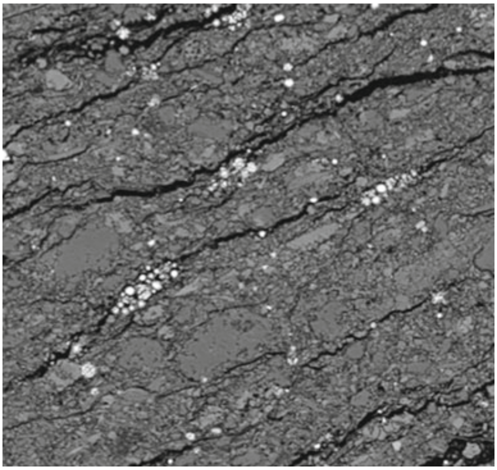


Fig. 23 Aligned framboids which on oxidation cause cracking of the mudstone

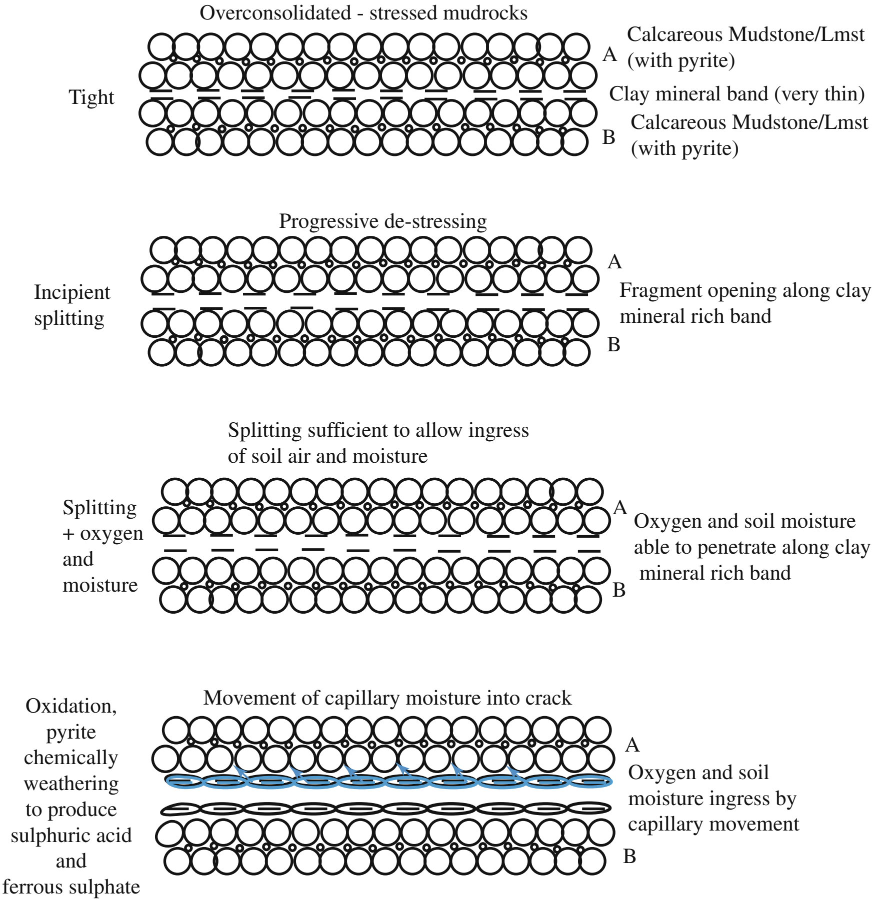


Fig. 24 Diagram to illustrate the progressive splitting of a relatively strong rock which includes very thin clay lamellae with pyrite/pyrrhotite (see Fig. 3)

fractures/weaknesses developed due to the quarrying process or on-site compaction will facilitate the movement of sulphuric acid within aggregate particles. This process of de-stressing followed by the movement of oxygen and moisture into the stronger particles is shown diagrammatically in Fig. 24.

Formation of Gypsum

Most geologists first examine gypsum (calcium sulphate) in its monoclinic crystal form—selenite (Fig. 25). These crystals commonly grow in very weak to weak mudstones, such as the London Clay and Oxford Clay, where they develop in the lower part of the unsaturated zone some 3–8 m below the ground surface. As noted

Fig. 25 Typical museum selenite crystal

by Wellman and Wilson (1965), less energy is required for an existing crystal to grow than to start a new crystal. Theoretically therefore, provided the components are present, there is no need for the growth of individual crystals to stop until the confining stress is greater than the pressure of crystallisation.

Figure 26 shows a "petal" structure formed at a depth of 6–7 m in the London Clay, recovered from a site investigation in 2012. Such petals form when crystals growing outwards from a nucleus increase in both length and thickness. At this depth the crystal would have developed in a confining pressure of some 100 kPa by pushing against the weak clays.

There are a number of published examples indicating the pressure which is exerted by the growth of gypsum within fill or rock material. Spanovich and Fewell (1969) considered that to create the heave they recorded in Pennsylvania

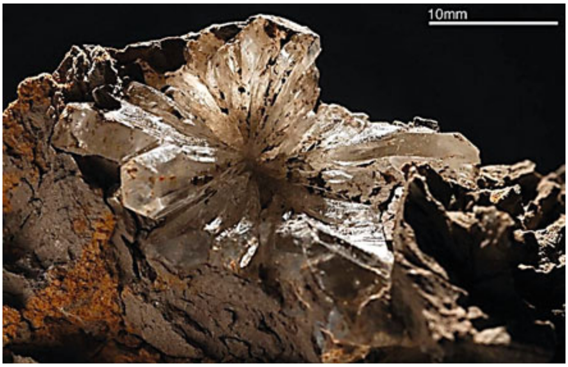


Fig. 26 Gypsum crystals from a 2012 site investigation in the London Clay (6–7 m depth)

would require a pressure of 280 kPa and quoted values of 5–600 kPa. Knill (1975) and Sherrell (1979) postulated a pressure of crystallisation of 500 kPa while Maher et al. (2011) from calculations of the stress required to fracture a concrete pipe, suggested a value as high as 600 kPa.

At the time of placement on a building site, the individual rock fragments within the fill mass will have experienced blasting, de-confinement and crushing resulting in the development of incipient fractures, some of which will have opened to form finer particles. On site the fill, which is already beginning to de-stress, is compacted in layers, resulting in further opening of the incipient fractures, particularly if they have developed associated with thin layers of platy clay minerals. Such openings allow the oxygen and moisture to move within the aggregate/aggregate fragments and progressively decompose any contained pyrite/pyrrhotite (see Fig. 24).

Commonly, the pyrite on the outer edges of the aggregate fragments is oxidised first and the sulphuric acid released during oxidation moves until it combines with any in situ calcium carbonate, which may be present as euhedral grains, shell fragments/microfossils or cement. The chemical reaction which takes place results in the formation of selenite which has a volume some twice that of the original components. In this situation the gypsum develops at the location of the $CaCO_3$ (authigenic). As the calcium carbonate is likely to be scattered throughout the rock, a number of isolated growths of gypsum begin. These may take the form of selenite crystals or fibrous gypsum.

In pyritiferous fill, gypsum develops not only within the fill mass but also within the individual particles. For the oxidising agents (moisture and oxygen) to reach the pyrite, they pass through the matrix of fine particles between the aggregate fragments. The gypsum crystals which form on the outer edges of the aggregate fragments push into the fine fraction causing densification and possibly some early expansion of the fill mass.

Although occasional euhedral crystals of gypsum are observed in the fine matrix of the fill mass, it appears that most voids remain open and continue to act as a passageway for the ingress of moisture and oxygen. As any clay minerals present in the fine fraction will attempt to re-establish their adsorbed layers, they will draw moisture into the fill mass by capillary action, either from the underlying in situ material and/or through the concrete block rising walls, and into discontinuities within the individual particles.

As seen in Fig. 27, the crystal growth typically occupies some 20 % of the discontinuity surface. As the selenite grows, the pressure of crystallisation is sufficient to prise open the rock fragments, with the individual crystals acting as props to the developing aperture. As depicted in Fig. 28, it is not the volume of gypsum which is important but the relationship between the width/height of the individual props. This controls the size of the aperture and hence the extent of the expansion.

The presence of these random columns of gypsum facilitates the continued movement not only of the oxidising agents into the dilating rock fragment but also of the released sulphuric acid and any sulphate-rich solutes. It is sometimes

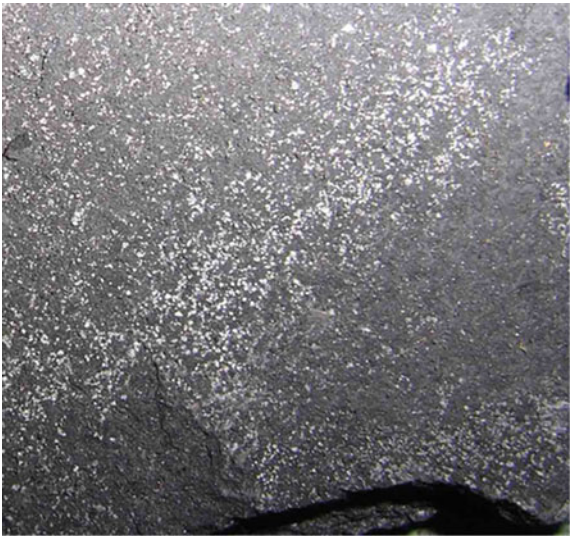


Fig. 27 Random growth of crystals exposed when lamination prised open (photo 40 mm)

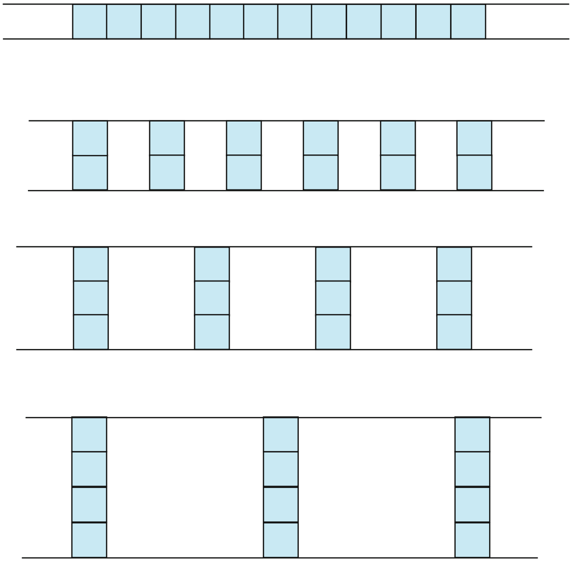


Fig. 28 Different amounts of dilation with same volume of gypsum

assumed that sulphates from these liquids will then be precipitated in areas of low stress. However, after a crystal has begun growing at the site of a calcite fragment, when the source of calcite is exhausted it can continue to develop by removing sulphate from a migrating solution.

In some cases, in order to retain the idiomorphic structure additional crystals will form attached to/intergrown with a pre-existing crystal. With the continuing input of calcium sulphate, the crystals around the outside of the original gypsum

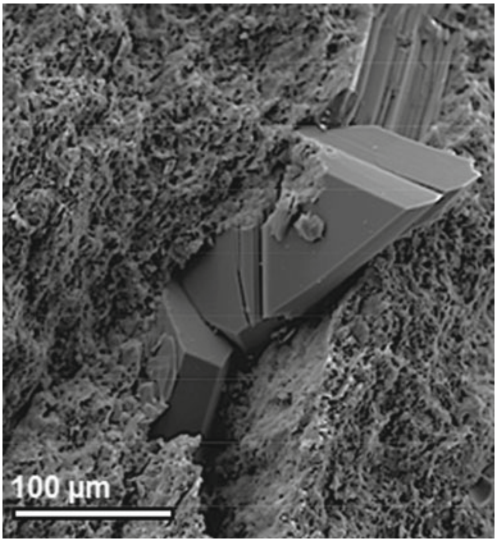


Fig. 29 Developing rosette pushing through the mudstone

crystal/cluster become progressively larger (Fig. 29). Figure 30 shows an almost perfect rosette structure from the Ballymun Youth Centre collected in 2007, within three years of the fill being placed.

It is of note that in the weaker mudstones of the Dublin area the new crystals frequently create small depressions in the rock surface. Although the early growth can take place by consolidating the adjacent mudstone (similar to the euhedral crystals growing in the London Clay) at some point further resistance to consolidation results in the new crystal dilating the fragment, creating expansion. In stronger rocks, this depression is not observed, indicating that expansion takes place almost as soon as the gypsum crystal begins to form.

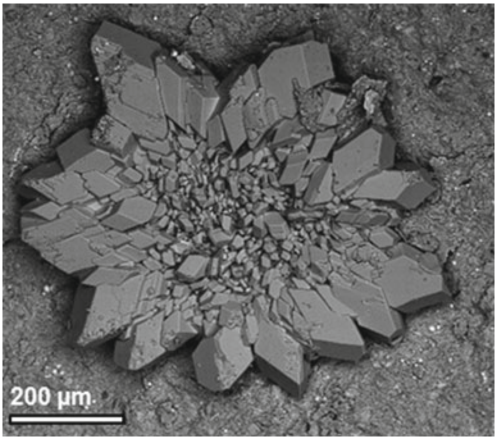


Fig. 30 Rosette exposed in the fill at Ballymun Youth Facility

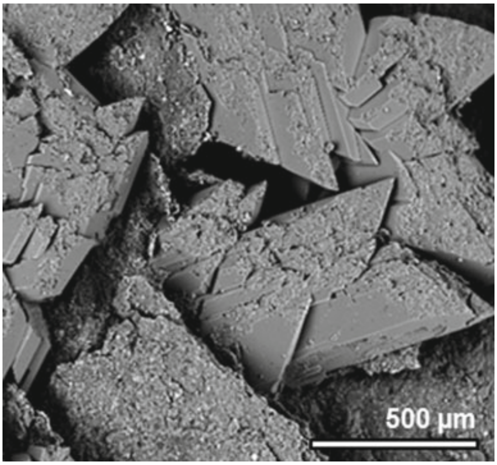


Fig. 31 Parallel-sided crystals growing in calcareous mudstone

Where the confining pressure is greater, the crystals grow outwards from the initial nucleation point with almost parallel sides (Fig. 31). Figure 32 shows individual crystals growing at four different levels within a calcareous mudstone. These rosettes may develop less than a millimetre apart and hence when seen on an oblique fracture surface they appear to have created a stepped formation, as the crystals at each level force the rock apart.

If the confining pressure is very low (e.g. on the outer edges of aggregate fragments or in cliff faces), the crystals may be needle-like, with separate crystals growing outwards from a nucleation point to form "starbursts" (Fig. 33).

A number of authors have written on the formation of fibrous gypsum, notably Taber (1918) and Shearman et al. (1972). Taber appreciated that the fibres may grow outwards from the two sides of a discontinuity such that they commonly include a median line formed of material which has broken off from the host rock

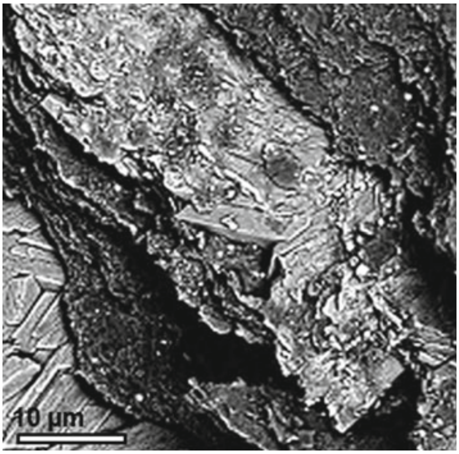
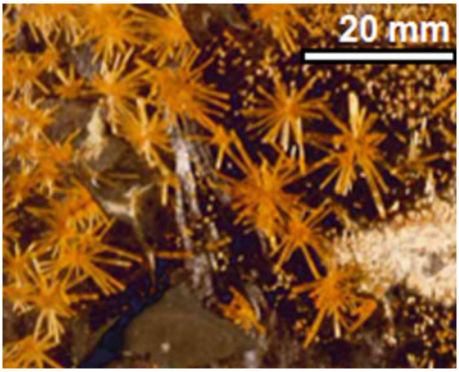


Fig. 32 Crystals growing at different levels within the calcareous mudstone (after Hawkins 2012)

Fig. 33 Starbursts of selenite from a coastal cliff, S Wales



at the early growth stage. Shearman, describing the growth of fibrous gypsum in Triassic rocks, drew attention to the fact that a "pit" is often present in the host rock where the fibrous growth began.

Figure 34 shows typical fibrous gypsum growth in a sample from Carsington Dam where the contained material forming the median line can clearly be seen. This form of gypsum is very common in low pressure situations, e.g. when borehole cores dry out. However, it has rarely been found during the removal of compacted deleterious fill from beneath houses in the Dublin area.

Although some cracks/incipient discontinuities are opened by the growth of gypsum, in other cases an existing crack may simply be infilled with calcium sulphate with no associated expansion (Fig. 35).

Hilgers et al. (2003) showed experimentally that when cracks are infilled by the precipitation of calcium sulphate from a mobile solute, the larger crystals occur in the direction of the source liquid, with the crystals becoming smaller as the solute passing through the crack is progressively depleted (Fig. 36). Eventually almost all

Fig. 34 Fibrous crystals with pronounced median line which developed when a sample of Carboniferous mudrock was kept in a humid oven at 30 °C

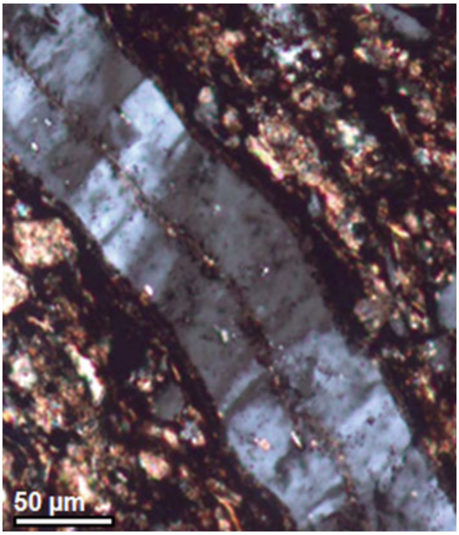


Fig. 35 Gypsum-filled vein; note median line

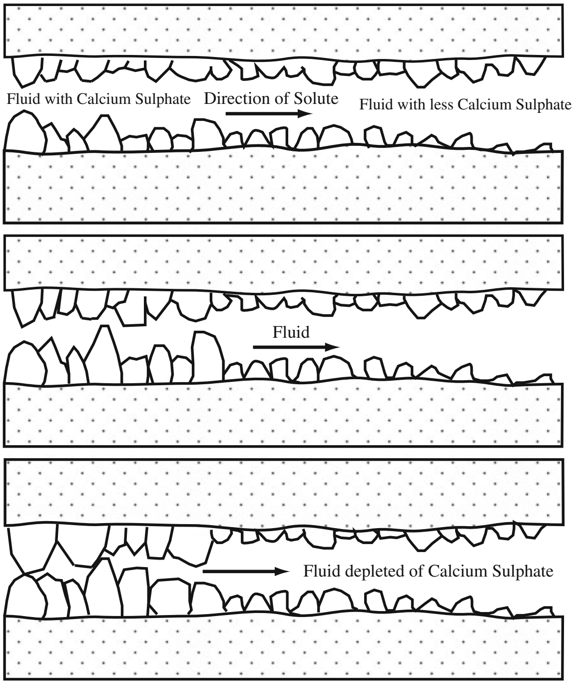


Fig. 36 Direction of solute and crystal growth (after Hilgers et al. 2003)

the crack will become filled with gypsum. However, in a voided fill the precipitated calcium sulphate tends to grow at the junction of adjacent voids, i.e. in the location of the pore throats, rather than simply infilling the voids themselves.

Fig. 37 Elongate gypsum crystals which developed after evaporation of 1 litre of water which had drained through pyritiferous fill into a borehole

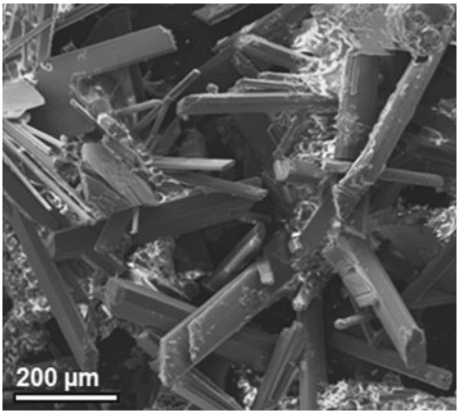


Fig. 38 Flat lying gypsum crystals which developed after evaporation of 1 litre of water which had drained through pyritiferous fill into a borehole

It is of note that when calcium sulphate-rich liquids taken from a standpipe piezometer in fill containing pyrite were evaporated, euhedral gypsum crystals were formed. Water soluble sulphate contents of 1,050 and 553 mg SO_4/l were measured on these liquids, indicating the high proportion of calcium sulphate which moves in solution in the deleterious fill. Two kinds of crystal which developed under atmospheric pressure from water obtained from shallow boreholes in the Dublin area are shown in Figs. 37 and 38. It is well known that precipitation takes place mainly in dry periods when the concentration of the liquids is greatest. As a consequence the effect on structures will be greater in warmer weather.

Review of Sulphate-Generated Heave (1950–2000)

North America

Sulphate-generated heave in the eastern United States has been appreciated since the 1950s, notably associated with the Carboniferous rocks of the Pennsylvania area. One of the earliest publications dealing with heave in carbonaceous shales was by Spanovich and Fewell (1969). They assessed the chemistry and indicated that for a 5 % pyrite content, an expansion of some 25 mm could be expected in a 300 mm layer if all the chemical reactions took place, producing a heave pressure in the order of 280 kPa. These authors noted that if a particularly hazardous horizon was identified prior to construction, the design should be modified; if it was encountered during or after construction the remedial measures possible would be limited and very expensive.

In 1970, Quigley and Vogan reported heave of up to 76 mm beneath part of the Rideau Health Centre in Ottawa. The Centre was constructed on the Ordovician black shales of the Lorraine Formation. It was noted that the heave only occurred where a mound of shales extended above the water table. Subsequent work revealed flat gypsum crystals some 0.7 mm thick were propping apart bedding laminations and coating inclined joint surfaces. Quigley and Vogan recognised that these gypsum crystals formed as a result of the chemical reaction between the calcium carbonate in the shales and the sulphuric acid released when the pyrite was exposed and oxidised. They note that Moum and Rosenqvist (1959) recommended applying a coating of asphalt or cement as soon as the shales were exposed, in order to prevent air or oxygen-bearing water reaching the pyritiferous material and initiating the oxidation process.

Quigley and Vogan (1970) identified Thiobacillus *ferrooxidans* (now known as Acidithiobacillus *ferrooxidans*) and postulated these bacteria may act as a catalyst in the oxidation process. They noted that underfloor heating created higher temperatures, which may have been a contributory factor in the heave as it encouraged activity in the oxidising bacteria. From the damage already caused to the Health Centre they calculated that the gypsum growth must have had a pressure of at least 70 kPa.

Quigley and Vogan considered that the sulphuric acid released by the oxidation of pyrite combined chemically with the calcium carbonate and the resultant calcium sulphate solution migrated through the soil to its point of precipitation. However, in a discussion of their paper Morgenstern (1970) suggested that the gypsum appeared to form “in place” causing a local volume increase which disrupted the host material.

Penner et al. (1970) described the heave in the Bell Canada Building, founded on the Ordovician shales of the Billings Formation. Although these strata contained an average of 4 % pyrite, it was most noticeable in the hydrothermal veins. The original building showed no evidence of distress, but when an extension was constructed in 1961, the basement floor slab suffered heave. This was first noticed in 1965 but subsequently some 100 mm was reported, at an estimated rate of 6–21.6 mm per year. The joints and bedding partings in the shale underlying the new extension were found to contain pyrite, which the authors considered to be of hydrothermal origin. These authors noted that in the most affected areas the majority of the pyrite had decomposed. They considered the Thiobacillus *ferro-oxidans* group of bacteria was an important factor in the rate of oxidation. The unaltered shale had a pH in excess of 7, but where the heave was most pronounced the rock was more broken in the area of a fault and here the pH was only 2.8–4.4, a condition conducive to the proliferation of the Thiobacillus bacteria.

An attempt was made to arrest the heave at the Bell Canada Building using significant quantities of potassium hydroxide as a neutralising agent. Over 12 t of potassium hydroxide in some 16,000 litres of water a day was introduced over a period of approximately 15 months during which time the pH rose from between 2.8–4.4 to 6.4–7.1. In most situations such chemical treatment would be a highly impractical as well as an extremely expensive potential solution; in the case of the Bell Canada Building it was not completely successful.

Quigley et al. (1973a) suggested that the heave at the Bell Canada Building could be attributed solely to the growth of selenite crystals. Examination showed that the side pinacoids of the crystals developed in the planes of the discontinuities. The crystals themselves often formed star shapes, which are now frequently referred to as rosettes.

Penner et al. (1973) noted that heave occurred in materials which contained as little as 0.1 % by weight of pyrite. Whilst in general the expansion was not evident until some two years after the material had experienced oxidation, in some cases the interval was as short as six months. They assessed the role of gypsum in the heave process and, in addition to the flat crystals discussed by Quigley et al. (1973b), noted the needle-like structure. Penner et al. (1973) also pointed out that little gypsum had formed beneath the walls and/or columns within the Bell Canada Building. They considered this may be a consequence of the depth to which the walls/columns extended (below the groundwater level) or the natural migration of gypsiferous fluids to areas of low stress where precipitation took place.

Grattan-Bellew and Eden (1975) refer to the heaving in the basement of St Luke’s Church in Ottawa which was constructed on the Ordovician Eastview Formation. They report the Formation contained 8.2 % calcite and 4.25 % pyrite; the latter occurring as separate crystals and as fossil replacement. Abundant gypsum was found in the altered shales, both as bundles of fibres growing normal to the laminations and as flat-bladed crystals parallel to the laminations.

Grattan-Bellew and Eden considered the main heave was caused by the growth of the fibrous crystals which precipitated from mobile calcium sulphate-rich fluids. They noted the areas of maximum heave were often localised and considered this was because once cracks had developed in the host material, the pressure gradient would enhance movement of the solution towards areas of lower pressure (in the cracks) where precipitation was most likely. Grattan-Bellew and Eden (1975) also reported that gypsum and jarosite had developed in the excavated shale beneath the Ottawa Children’s Hospital after only a year.

Coveney and Parizek (1977) reported that up to 200 mm of heave in mine floors was noted in Kansas City some 2–5 years after mining had taken place above the Carboniferous Hushpuckney Shale. This Shale contained up to 3 % by volume of mainly framboidal pyrite. Gypsum constituted 10 % by volume of the weathered shale, occupying veinlets where it occurred as flattened rosettes parallel to the bedding planes and in joints. The authors calculated that, assuming all the potential chemical reactions took place and that the gypsum crystals occupied only some 25 % of the bedding and joint surfaces, the heave of the Hushpuckney Shale could be as much as 100 mm per 1.5 m.

Grattan-Bellew and McRostie (1982) described methods of heave prevention from research undertaken at a building in Ottawa. These authors suggested that cleaning the shales and coating them with 50 mm of concrete had been effective in a number of buildings in Ottawa. However, levelling and monitoring of crack development in houses showed it had not been entirely successful. Examination of the shale beneath the ground floor slab revealed gypsum on the edges of the concrete some 300 mm below the level of the slab. It was believed that oxygen passed into the shale via the junction between the slab and the rising walls.

Bérubé et al. (1986) recorded heave of 100 mm in a college building at Sainte-Foy, Québec, within 12 years of its construction on black Cambrian shales in 1971. At the time the paper was published, the heave was still continuing at the rate of some 10 mm per year. The pyrite occurred as both cubes and framboids and varied in concentration from 1 to 5 %, averaging 2 %. In the altered shale, the gypsum occurred dominantly as flat bedded crystals parallel to the fractures, commonly forming rosettes although some fibrous crystals perpendicular to the bedding were also present. Noting heave was minimal under the footings and pillars, Bérubé et al. favoured the mechanism of sulphate-rich solutions migrating by capillary action, driven by a combination of temperature and pressure gradients, until precipitation occurred in areas of lower pressure.

Since 1986 a number of other papers have been published, notably related to concrete deterioration and swell tests, which will not be reviewed here. For further details see Maher (2013 this book).

United Kingdom

In the UK, much of the early work related to sulphates was concerned with sulphate attack on concrete. In the 1950s a number of problems with concrete were reported and as a consequence the British Standards Institute prepared report 882:1954 entitled *Coarse and fine aggregate from natural sources for concrete.* This states: *Aggregates shall not contain harmful materials such as iron pyrites, coal, mica, shale or similar laminated materials, or flaky or elongate particles, in such a form or in sufficient quantities to affect adversely the strength and durability of the concrete or, in addition to the above for reinforced concrete any materials that might attack the reinforcement.*

One of the main buildings affected was the 750-bed St Helier Hospital, Surrey, constructed in 1938. In 1959 it was found that some of the foundation concrete placed in the brown London Clay had seriously deteriorated. The remedial work in the early 1960s involved supporting the hospital on piles (Legget and Karrow 1983).

Lea (1968), noting the significance of pyrite oxidation, refers to an example of a tunnel at Bexley (south of London) which was constructed in the pyritiferous Woolwich Beds using compressed air to restrict water ingress. Although the tunnel was built using a pre-cast concrete segmental lining made of sulphate-resisting cement, problems occurred following the end of the compressed air work when water with a pH of only 1.8 began seeping through some of the bolt holes. It is clear that the compressed air forced into the bedrock had induced oxidation of the pyrite and the production of ferrous sulphate and sulphuric acid. Subsequently the pH of the groundwater increased to 3.5 after a few weeks and 4.5 after three years. A secondary lining was installed which prevented further oxidation.

The earliest comment on sulphate-generated heave was by Bickerdike and Allen (1972). As mentioned above, they discussed the distress in properties in northern England where builders used coal mine waste as fill beneath ground-bearing floor slabs. They reported up to 75 mm of heave in the middle of some rooms, with associated spider cracking.

Building Research Establishment

Nixon (1978) described a situation where waste from the Cleveland Ironstone Formation of Jurassic age was used as underfloor fill in the Teeside area of north east England. Properties constructed in the 1960s were showing signs of distress within a decade, which had become widespread by 1975. Platelets and rosettes of gypsum were identified beneath the slabs. Investigations indicated up to 2 % by volume of fine grained pyrite was dispersed throughout the shale, both as discrete particles and as framboids. As the distress became particularly apparent in 1975/1976, Nixon postulated that the hot dry summers of those years may have enhanced/accelerated the oxidation process and consequential heave; see also Hawkins 2013.

In 1978, the BRE was invited to investigate a four-storey property in Glasgow, built some hundred years previously. Collins (1990) reports that approximately 300 m^2 of the floor in the main hall had risen by up to 125 mm above the general level. In the distressed area the floor was supported by a low rising wall resting on the dark Upper Limestone Group of Lower Carboniferous age. These interbedded limestones and shales/mudstones are similar to much of the strata in the Dublin area. In the basement, where the floor rested on bedrock, some arching was evident. Trial pitting and X-ray analysis identified pyrite and it was concluded that gypsum and jarosite had formed as a consequence of the chemical decomposition of iron sulphides in the strata below the shallow “sleeper wall”. The remediation involved supporting the sleeper wall on piles and the removal of the pyritiferous material from beneath the basement floor.

In February 1979, BRE Digest 222 *Fill and hardcore* stated (page 5) *Ideally, materials used as hardcore should be chemically inert and not affected by water but few of the materials available at reasonable cost satisfy these requirements completely. The main hazards to be avoided in choosing a material for hardcore are chemical attack on concrete and brickwork mortar in contact with the hardcore….*

On page 6, under the heading *Swelling due to oxidation of pyrites in shales*, it states *Sulphides in the form of pyrites can oxidise to form soluble sulphate in the presence of air, moisture and possibly bacterial action. They can therefore contribute to problems of sulphate attack on concrete. In addition, if pyrites are present together with calcite in a fill or hardcore, there is a danger of expansion due to the growth of gypsum crystals formed by reaction between calcite and sulphuric acid from the oxidation of pyrites.*

The last paragraph is reiterated in the August 1983 Digest (276) entitled *Hardcore.* On the front page of this Digest is a photograph showing typical spider cracking in the floor of a sitting room. On page 2 it discusses *Swelling due to chemical and volume changes in the material* and points out that the methods of recognising potentially troublesome shales are discussed by Nixon (1978). It notes *The observable indications that such an action is taking place are similar to those associated with sulphate attack: cracking, lifting and hogging of floors, movement and cracking of internal partitions and outward movement of external walls.*

BRE Digest 361 (May 1991) entitled *Why do buildings crack?* states *Sulphate attack on ground floor slabs is quite common, usually as a result of using inappropriate fills. Hardcore or fills containing appreciable amounts of sulphate must not be used below concrete floor slabs. Gypsum products are sometimes inadvertently used in hardcore but the most widespread reported cases of failure have involved burnt colliery shales, often referred to as red shale. These often contain considerable quantities of soluble sulphates.* [Their] Fig. 13 *shows how sulphate attack of the underside of a concrete slab can cause it to arch and crack, and the walls to bulge. In cases like this, if the stability of the structure is impaired, the fill should be replaced by sulphate-free materials.* It points out that floor heave can be caused by the use of steel slags, pyritic shales, magnesite bricks and some older high-sulphate blast furnace slags.

Llandough Hospital, Cardiff

The most quoted example of heave in the UK literature is that which occurred at Llandough Hospital, Cardiff, described by Hawkins and Pinches (1986, 1987a, 1987b, 1997). When the hospital was built the ground was levelled to allow the construction of a long east–west corridor. In the north east part of the hospital this necessitated an excavation of some 2–3 m into the dark, very thinly to thinly bedded mudstones of the Westbury Beds.

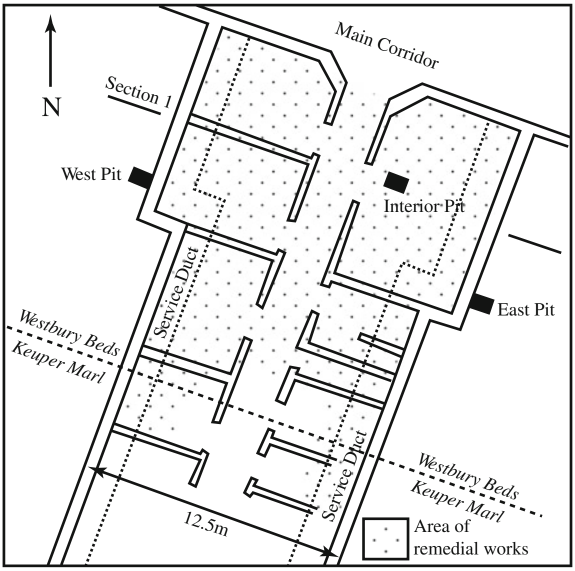


Fig. 39 Trial pit locations and areas remediated

In April 1982, a maintenance worker inspecting the roof area at Llandough Hospital realised that in the northern part of the eastern wing, the walls were moving outwards such that the stability of the roof was in question. The walls were immediately supported with scaffolding and following discussion between the consultant and the Authority, a major structural and geotechnical study was undertaken.

It was apparent that the area of distress (Fig. 39) coincided with the outcrop of the Upper Triassic Westbury Beds. When monitoring points were levelled relative to a datum point established in the main corridor, it was found that the maximum difference in elevation of the floor slab was 81 mm and at a number of points it was in excess of 70 mm (Fig. 40).

The hospital was constructed between 1927 and 1933 but records show that by the 1950s the building was experiencing significant distress. As a consequence, it was decided to install a 1.5 m high, 1 m thick concrete plug against the eastern wall of the building to act as a lateral buttress (Fig. 41).

In discussions with the hospital maintenance staff, it became apparent that for more than 20 years they had been cutting off the bottoms of some doors to prevent them snagging on the floor. In addition, some years previously they had applied formica to cover a 40 mm crack in one of the walls (Fig. 42).

Trial pits were dug to both the east and west of the distressed wing of the hospital and one was excavated beneath the ward floor (Fig. 39). The external pits showed effectively no evidence of oxidation while the internal pit encountered a sleeper wall in which the joints had opened/dilated. In addition, extensive oxidation of the Westbury Beds was noted between 0.9 and 1.7 m below the floor slab at the level of the heating pipes in the service ducts. In this zone, flat gypsum

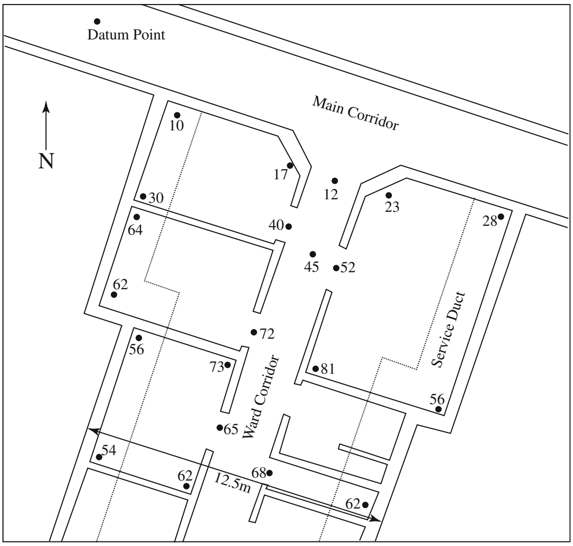


Fig. 40 Floor levels relative to datum set up in the main corridor

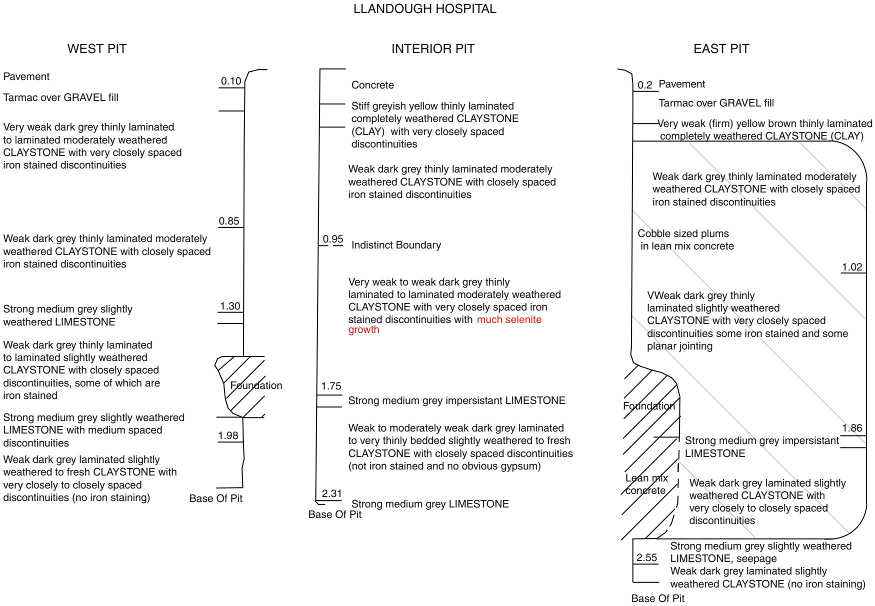
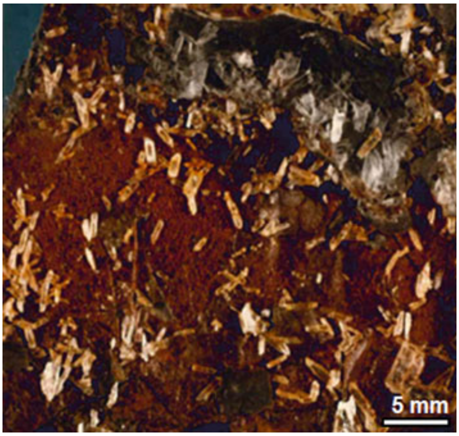


Fig. 41 Geological section across the wards showing the concrete placed in the 1950s and the zone of high selenite growth in the interior pit

Fig. 42 Crack in ward wall exposed when formica removed

Fig. 43 Selenite crystals up to 8 mm long on a bedding surface at 1.6 m depth (Westbury Beds)



crystals were seen over some 20 % of the surface of the bedding laminations (Fig. 43). The growth of these crystals had clearly caused expansion of the in situ strata, resulting in heave of the overlying floors and damage/distress to the ward above. Outward deflection of the walls also occurred as the inner leaf had been constructed on the floor slab.

The structure at Llandough Hospital was very similar to that at the Rideau Health Centre (Fig. 44), described previously by Quigley and Vogan (1970). In

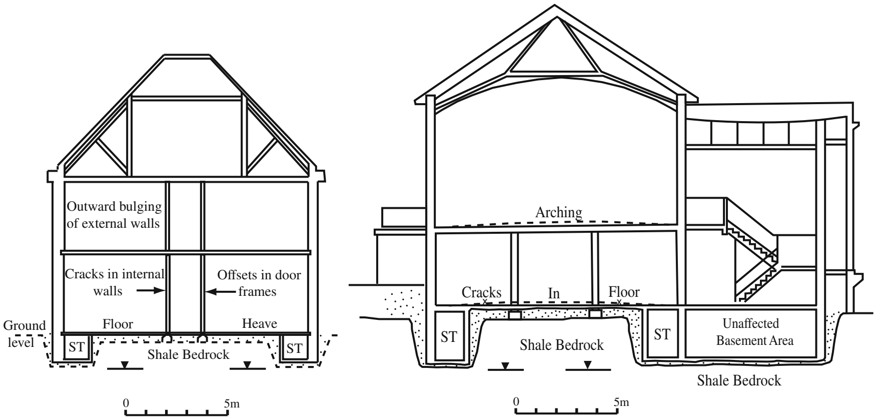


Fig. 44 Similarity between the layout of Llandough Hospital (*left*) and Rideau Health Centre (*right*); *ST* service tunnels

both cases, service ducts passed around the perimeter of the building, such that the ground beneath the slab was heated.

In addition, the groundwater level was some 1.5 m below the floor level. In view of the depth at which the gypsum crystals had grown and the fact that a building error had resulted in an internal wall being constructed on the floor slab (not on a rising wall), it was considered the most cost-effective solution at Llandough would be to remove the pyritiferous material and construct a new reinforced suspended floor on mini-piles.

Subsequently further testing was undertaken on samples from 1.5 m below ground floor level at Llandough Hospital which had been left in unsealed bags in a laboratory for some seventeen months (Table 6).

From Table 6 it can be seen that:

1. The acid soluble sulphate in the exterior samples had increased some four times while the high initial value in the interior pit had almost doubled.
2. The water soluble sulphate had effectively doubled in the exterior and interior pits.

Table 6 Changes in soil chemistry in samples from the Westbury Beds at Llandough Hospital stored in open bags between November 1982 and March 1984

	West Pit			Inside Pit			East Pit		
	Nov 82	→	Mar 84	Nov 82	→	Mar 84	Nov 82	→	Mar 84
ASS (% SO_4)	0.34	→	1.44	2.64	→	4.98	0.43	→	1.92
WSS (mg/l SO_4)	1,500	→	3,840	5,640	→	9,360	1,860	→	2,880
pH	7.1	→	6.25	3.75	→	2.65	7.10	→	5.3

Table 7 Development of sulphate in samples from the Westbury Beds kept in stacked cups at room temperature for up to 74 days (after Hawkins and Pinches 1987b)

	Acid soluble sulphate (%SO_4)			
Cup level	7 days	14 days	28 days	74 days
5 (top)	0.66	1.12	1.24	2.23
4	0.83	1.06	1.33	2.28
3	0.78	0.94	1.34	2.20
2	0.94	1.03	1.23	2.27
1 (bottom)	0.64	0.65	0.90	2.10
Mean (initially 0.64 %)	0.77	0.96	1.21	2.22
Groundwater[a] (water soluble)	223	290	374	342

[a] Tap water sample—results in mg SO_4/litre

3. Although the pH was already low in the interior samples, during the seventeen month period it dropped from 3.75 to 2.65 while in the samples from the east exterior pit it dropped from 7.1 to 5.3.

As a consequence of the appreciation of how quickly acid soluble sulphates can form, Hawkins and Pinches (1986) recommended testing at site investigation stage should measure the total sulphur present. Assuming all the sulphates had been derived from iron sulphides, the potential development of acid soluble sulphates could be established (now referred to as total potential sulphate). Further, by subtracting the sulphur in sulphate from the total sulphur, the amount of remaining oxidisable sulphide could be assessed.

As noted above, Hawkins and Pinches (1987b) undertook a number of experiments to determine the significance of temperature on the generation of sulphates (see Tables 1, 2, 3 and 4) and reported increases in acid soluble sulphates of 236 % (at 18.5 °C), 281 % (at 29.5 °C) and 338 % (at 41.5 °C) over a period of 15 weeks.

A further experiment reported in their 1987b paper involved breaking mudstone samples from the Westbury Beds into small fragments (3–10 mm) and placing them in stacked polystyrene cups with the base of the lowest cup standing in water. Table 7 gives the values obtained converted to SO_4. The mean of the five acid soluble sulphate values increased from 0.64 to 0.96 % SO_4 in 14 days while by 74 days the value had risen to 2.22 % SO_4. At the same time, the pH dropped from 6.5 to 3.8 within 14 days and to 2.3 in 28 days.

Advocating undertaking chemical testing as quickly as possible after sample collection in order to obtain a realistic indication of the potential sulphates which could develop in the natural ground after oxidation, Hawkins and Pinches (1987b) proposed two simple, inexpensive methods:

1. Placing some samples in an oven at 35–40 °C, taking care to ensure the atmosphere remains moist, and re-examining/testing them after 3, 5 and 8 weeks. If sulphates are likely to form in the material, some visible evidence should be seen within this time, e.g. white pinheads of gypsum. If necessary

confirmatory chemical testing can be undertaken. This is now referred to as the "accelerated test".

2. Leaving some samples exposed to the atmosphere for 2–4 months at room temperature, ensuring they do not dry out. A visual assessment can then be made to determine whether sulphates have developed. If necessary this can be confirmed with chemical tests.

To summarise, the problems which occurred at Llandough and the associated research in the 1980s drew attention to a number of significant points:

1. Dark mudrocks invariably contain pyrite and hence where possible should be avoided in engineering construction.
2. If building must take place on dark mudrocks, it is preferable to construct on the weathered/oxidised ground. If it is necessary to build on unweathered material, the time the ground is exposed should be kept to a minimum.
3. Ground-bearing floors slabs should not be placed on dark grey/black pyritiferous bedrock or fill. The use of suspended floor slabs is advocated, with sufficient underfloor space to allow for heave/expansion.
4. The acid soluble sulphate content of a pyritiferous fill is not constant. It may vary in different samples and increase with time if oxidising agents can reach unoxidised material.
5. The speed of oxidation and hence the production of sulphates will be increased in warmer conditions and, particularly in acidic conditions, by bacteria.
6. By obtaining the total sulphur content it is possible to assess the total potential sulphate and the remaining oxidisable sulphide, assuming all the sulphate is derived from iron sulphide.

Hawkins and Pinches (1986) noted that black mudstones are poor engineering materials and must be treated with caution. They pointed out that the total mineralogy/chemistry rather than a few sulphate tests is necessary to establish whether gypsum/jarosite growth may result in heave. During this research the condition of the concrete was only visually assessed; no substantial study of the effect of the sulphates on the sub-floor concrete was undertaken.

Radstock

Following the work at Llandough, when a new housing estate at Radstock (south west of Bristol) was proposed in the 1980s, it was recognised that part of the development would be constructed over the Westbury Beds. The initial site investigation identified needle-like crystals in these black laminated mudstones. It was recommended that suspended floor slabs should be used (Fig. 45), such that any heave which developed as a consequence of oxidation of these mudstones could be accommodated. In addition, inert granular backfill was placed against the rising walls in order to reduce the risk of damage as a consequence of any sulphate

Fig. 45 Suspended floor slabs recommended for houses constructed over pyrite-rich Westbury Beds at Radstock, N Somerset

in the groundwater passing into the concrete. Although the houses were built on the pyritiferous Westbury Beds and the Cotham Beds, which are known to contain expanding lattice clay minerals, no distress has been reported in the 30 years since they were constructed.

Barry, South Wales

In contrast to Llandough Hospital which was built on in situ ground, the Town Hall in the nearby town of Barry was constructed on the site of an old quarry. Wilson (1987) recorded that some 20–50 mm of heave had occurred and showed a photograph of a splitting mudstone fragment. Although the load-bearing structure was extended to the original quarry floor, the ground-bearing floor slabs consisted of unreinforced concrete resting on up to 6 m of dark shaly mudstone fill—the material discarded when the Lower Lias limestones were quarried from the interbedded sequence. Pyrite grains of up to 1 mm were visible in cores and in the in situ mudstones. Beneath the floor slab, most of the mudstone particles were encrusted with small gypsum crystals and some showed evidence of having been split apart by crystals growing in the bedding laminations.

Hucclecote, Gloucestershire

In 1980, a development of 39 houses was constructed at Hucclecote near Gloucester. Within three years house owners were contacting the National House Building Council (NHBC) as cracks were developing in the interior walls, the floors were rising, doors were jamming and cracks were opening in the external

Fig. 46 Crack through the brickwork below bedroom window

walls. The floors typically had spider cracking and in one house the floor arched by 75 mm within eight years, producing a pronounced crack with an associated "step" of over 40 mm. An example of a crack in the external brickwork is shown in Fig. 46. This widened upwards above the patio window which itself had separated from the adjacent wall.

The houses were constructed on the Lias Clay which has a plasticity index of 30–40 % and is known to be a medium to highly shrinkable/swellable clay. As a consequence NHBC anticipated that the problems encountered were related to seasonal shrink/swell and engaged Tomlinson as an advisor to work with the author on the problems.

The buildings at Hucclecote were designed to have ground-bearing floor slabs. In some cases these were constructed directly onto the Lias Clay and in others, where the houses extended over an old clay pit, on fill placed around concrete columns. In view of the severity of the distress, levelling surveys were undertaken which showed that in addition to the arched floor, some of the others had risen by up to 68 mm. The ground investigation involved machine dug pits, both adjacent to the rising walls and at some distance from the properties, in order to establish the geological and chemical profiles.

In this area the Lias Clay is typically a very weak dark grey mudrock in which pyrite is visible. As seen in Fig. 47, extensive gypsum development had occurred in the sedimentary bedding and joints. In some cases this formed as individual crystals occupying 15–25 % of the surface area and in others the vertical crystals

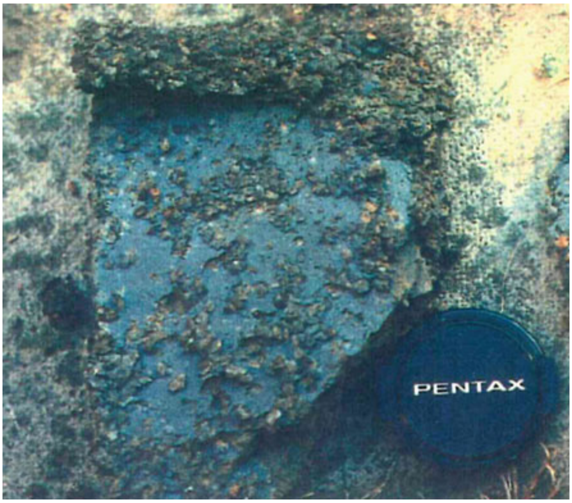


Fig. 47 Isolated gypsum crystals on Lias Clay exposed during the investigations

Fig. 48 Gypsum growth in bedding and joints in the Lias Clay at Hucclecote

were almost touching and appeared like veins (Fig. 48). Where these new crystals were present the "pseudo veins" accounted for 8 % of the vertical profile.

It was agreed that sulphate development was the prime cause of the distress and a decision was made to remediate all 39 houses by removing the Lias Clay and/or fill within a metre of the floor and installing reinforced dense concrete mini-piles to support the new concrete slab (Fig. 49). Although every effort was made to keep inconvenience to the occupiers to a minimum, in some cases the houses had to be

Fig. 49 Remediation included installation of piles to support suspended floor slabs at Hucclecote

vacated for more than six months. It was following this study that Tomlinson included sulphate-generated heave in the 6th edition of his book *Foundation Design and Construction* (1995), referencing the problems at Llandough.

Swindon

At the same time, work was undertaken on some houses in Swindon which had been constructed on the Kimmeridge Clay in 1966/1967. By 1968 they were showing signs of structural distress and a decision was made to underpin with columns extending to 2.44 m. By 1971 it was clear that the underpinning had not been successful and in 1972 a further underpinning exercise was carried out involving 12 mass concrete bases installed to 4.25 m. The author understands that significant gypsum was encountered during these excavations, although at the time this was effectively ignored in view of the decision to underpin.

Between 1974 and 1975 levelling showed the properties were still rising, particularly in the central part of the structures, in the vicinity of the boilers. Between September 1980 and October 1981 demec gauges over the crack in the sitting room of No 32 (Fig. 50) indicated the distress was still occurring, while a levelling exercise showed that the middle part of the bungalow had risen by some 40 mm. Various ground investigations took place before the author was asked to make a detailed study in 1987/1988. This included an extensive examination of the problems of No 30 which, as seen in Fig. 51, had a distinct arch at the front. Samples from trial pits around the outside of the house indicated acid soluble sulphate contents of between 1.8 and 2.7 % SO_4, with the highest value at 9.0 % SO_4 in a very gypsiferous horizon.

Although the problems at this site may well have been related to a concentration of gypsum at approximately ground water level, new gypsum crystals/selenite had clearly formed in the central part of the property which were not identified in the outside pits. It is considered that following the construction of the building, the heating had concentrated sulphate development in the middle of the bungalow.

Fig. 50 Crack through sitting room wall in bungalow on Kimmeridge Clay at Swindon

Fig. 51 Significant arch in front facade of the same bungalow as in Fig. 50

Harrow on the Hill, London

Following an appreciation of the influence of the temperature at Llandough Hospital and in the middle of the properties at Swindon, it was considered there was likely to be an effect associated with the heat of hydration when piles are installed into mudrocks containing pyrite/gypsum. In 1990, the opportunity was taken to sample the London Clay exposed between piles in the basement car park of a shopping centre at Harrow on the Hill, London.

Samples were taken at 10 mm spacings between two piles and the acid soluble sulphates measured. As shown in Fig. 52, some 20–30 mm away from the piles the acid soluble sulphate contents in the basal part of the brown London Clay reached over 2 % compared with a general value of 0.5 % SO_4 at this elevation. It was concluded that during the warming of the host material by the heat of hydration when the CFA piles were installed, the natural ground sulphates had mobilised and become concentrated in the shear zone created by the auger torque (Hawkins and Higgins 1997a).

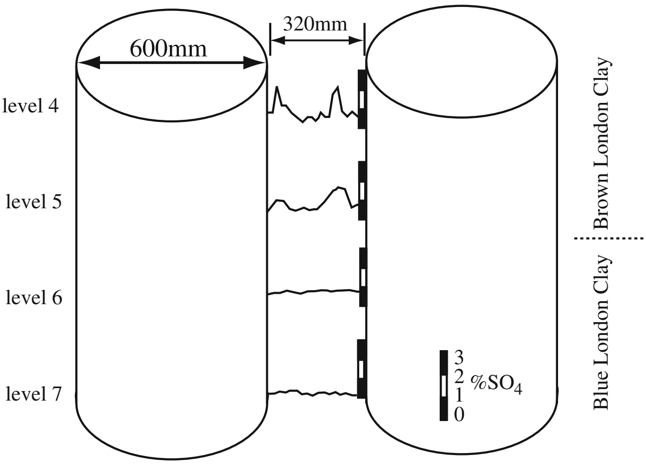


Fig. 52 Increase in sulphate content in the brown London Clay related to the heat of hydration when concrete piles were installed (after Hawkins and Higgins 1997a)

Parc Pensarn, West Wales

In the early 1990s, a supermarket was planned at Parc Pensarn, near Camarthen. The strata recorded on the geological maps and in academic papers (Fortey and Owens 1978) was dark grey shales and mudstones. The Ordovician strata in this part of South Wales would clearly have experienced some regional metamorphism hence the rocks fall into that difficult group between fissile mudstones/shales and weakly cleaved slates where pyrrhotite is typically found. Being on the limb of the Towy anticline, the strata dip varies between 70° and vertical at the site. In this area the argillaceous rocks have experienced periglacial conditions resulting in dilation and weathering of the upper 1–2 m to a silty clay with lithorelicts of mudrock/slate.

As the site required extensive re-grading to form a cut and fill platform, a high backslope was to be constructed in the rock, which showed evidence of some stress release. A 30 m deep borehole was drilled and samples for chemical testing taken at 2 m intervals below a depth of 4 m. At that time the presence of pyrrhotite was not specifically investigated.

1. The total sulphur was negligible in the upper 6 m. Below this it varied with depth, rising to 3 % S at 24 m.
2. The calcareous content was generally negligible except in three thin bands at 10, 24 and 30 m.
3. Acid soluble sulphates were negligible in the upper 6 m but below this values of up to 2 % SO_4 were recorded in the vicinity of the calcareous bands at 10 and 26 m. It is considered these higher values were associated with sulphates having formed in a zone where air could enter the rock mass due to some dissolution and hence oxidise the pyrite/pyrrhotite in the mudstones/slates.
4. The pH was <4 in the upper 6 m, below which it varied between 5 and 7.

At desk study stage, the consultants considered the possibility of old mine workings in the area, as lead and zinc veins are known to exist in the Vale of Towy where many of the more prominent discontinuities are iron stained. Two sets of samples were collected in 1992 to assess the significance of sulphate generated heave; in part to explain why the fill areas had not experienced the anticipated settlement during a year of self weight consolidation. Some of the samples collected were subjected to accelerated testing and some were tested over a longer period (Hawkins and Higgins 1997b).

1. Twenty samples were tested using an accelerated method to establish the rate of sulphate generation. This involved placing the samples in an oven at 30 °C with a relative humidity of 100 % for 8 weeks. Figure 53 shows the acid soluble sulphate values for fresh material which had been taken from 20 locations at the level of the construction platform and the values for the same material at the end of the testing programme. It can be seen that the maximum increase at any individual position was 167 % while the average increase for the 20 samples after eight weeks was 45 %.
2. Four samples were assessed over a period of nine months, again having been placed in an oven at 30 °C with a relatively humidity of 100 % (Table 8).
    (a) The weathered sample showed a five-fold increase in acid soluble sulphate while the pyrite content almost halved.

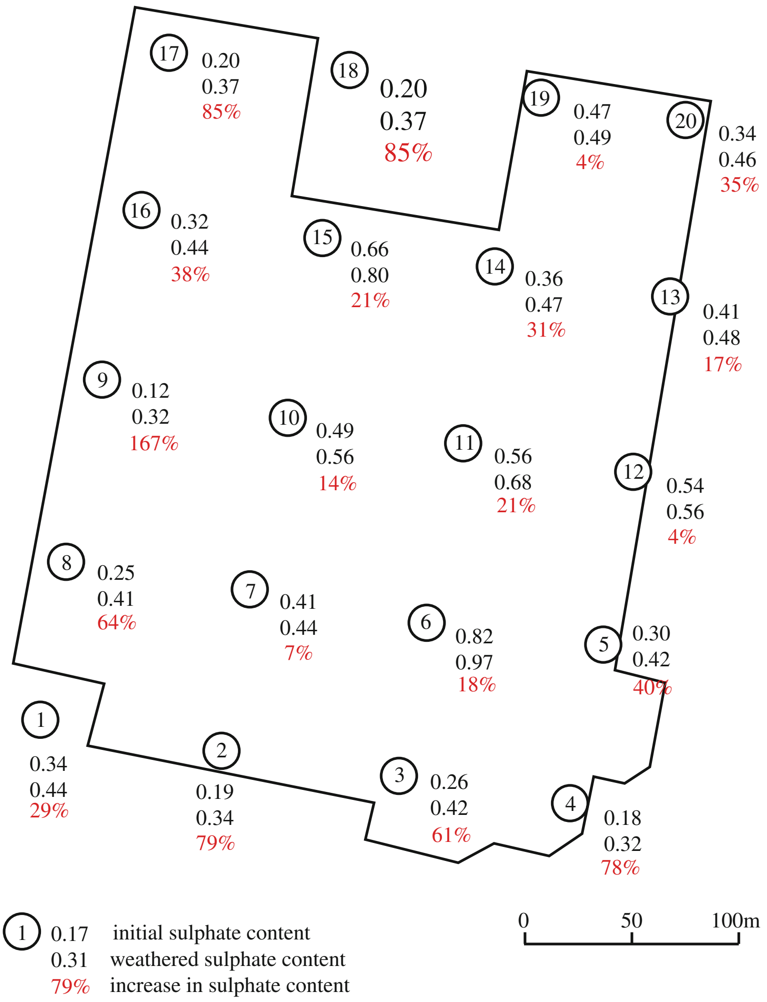


Fig. 53 Change in acid soluble sulphate when samples from 20 locations in the Ordovician mudrock/slates were kept in a moist oven at 30 °C for eight weeks

Table 8 Results of long term weathering test, Ordovician shale from Parc Pensarn

Original sample condition	Sulphate (% SO_4)		Pyrite (%)		Calcite (% $CaCO_3$)	
	Initial	Weathered	Initial	Weathered	Initial	Weathered
Weathered	0.06	0.30	0.88	0.48	0.18	0.00
Fresh excavation	0.08	0.47	2.72	1.98	0.00	0.00
Fresh excavation	0.19	0.80	4.87	3.15	0.36	0.00
Drainage pit excav.	0.12	0.83	3.64	2.07	1.40	0.95

(b) The two fresh samples showed an increase in acid soluble sulphate of 4–6 times while the pyrite content dropped by a third.
(c) The fresh in situ sample taken from the drainage pit increased in acid soluble sulphates by approximately seven times while the pyrite content dropped by almost a half.
(d) The calcite content in the weathered and fresh samples was reduced to zero while in the drainage pit, where the initial calcite content was higher, it dropped by a third.

Lime Stabilisation of Pyritiferous Material

Greaves (1996) noted that the lime stabilisation of clay has been used in construction for thousands of years. In the USA it increased in popularity rapidly in the 1950s, mainly for highway and runway construction, but was rarely used in the UK until the 1970s, again mainly for airfields. Sherwood (1967) indicated that for the London Clay the plastic limit increased from 24 to 43 % with the addition of 4 % lime. However, there were problems with the lime stabilisation of ground containing pyrite, as highlighted by Mitchell (1986) and Hunter (1988). Despite this, lime stabilisation was used on a number of road contracts in the UK during the 1980s; two major case studies where problems occurred are discussed below.

London to Birmingham M40

Snedker (1996) reported the difficulties experienced during a contract to construct part of the M40 near Banbury where the geology is the Lower Lias Clay. The main works took place in 1989, which was a particularly dry year. In April 1990 the south carriageway in a cutting area was found to be out of tolerance, with many fine diagonal cracks. Following a level survey it was clear that the carriageway had heaved in three distinct areas, in some cases by as much as 150 mm. Inspection pits were undertaken and it became evident that the expansion had occurred within the 250 mm deep lime stabilised zone.

Figure 54 shows the sulphates measured during the pre-contract investigation (hence relative to the existing topography) and the values at approximately formation level in the investigation following the main earthworks. It is of interest that the areas of heave did not necessarily coincide with areas of elevated levels of pyrite, which reached as high as 7.7 %. Snedker (1996) considered this was because the conditions required for oxidation were not present in these areas. However, as now appreciated, as well as the zone of aeration/saturation, the nature of the iron sulphides (cubes/framboids) and the size of the individual crystals/microcrystals would have affected the rate of chemical decomposition and sulphate growth.

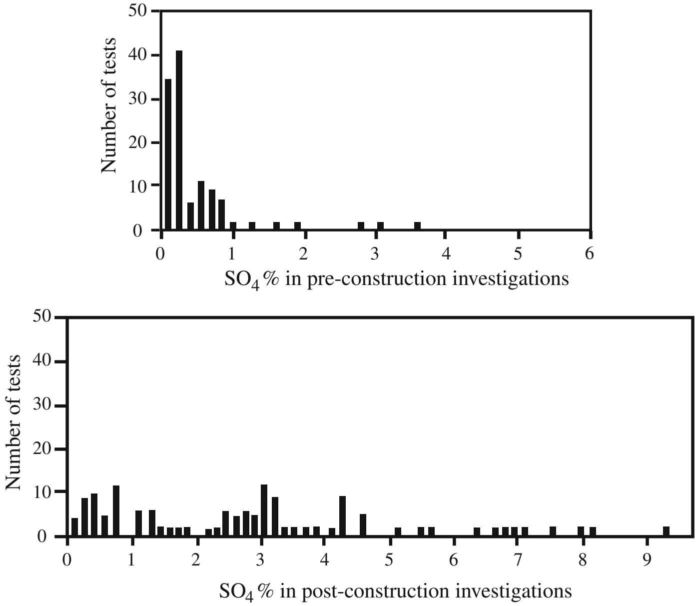


Fig. 54 Sulphate levels on the M40 determined before and after the earthworks (re-drawn after Snedker 1996)

As a consequence of these problems, the UK Highways Agency reviewed many of their documents dealing with sulphates. For example, HA74/00 (Clause 3.38) notes *The oxidation of sulphide minerals, principally pyrite, and the associated formation of sulphuric acid and sulphates takes time* (*Hawkins and Pinches* 1986; *Hawkins and Wilson* 1990; *Sandover and Norbury* 1993). *Therefore laboratory tests for sulphates will tend to show higher values than occur in situ, the longer the testing is delayed. Also the pH will decrease, that is the sample will become more acidic, the longer the testing is left. These changes will affect the interpretation of the acceptability of materials as higher total and water soluble sulphate contents will be recorded in the laboratory tests than in the undisturbed soils. This can lead to an inaccurate assessment of total and water soluble sulphate contents of the material for lime stabilisation.*

Hertfordshire, A10

Despite the warnings by such workers as Sherwood (1993), Barber (1996) and Perry et al. (1996) as well as numerous papers from other parts of the world, a further major problem occurred with lime stabilisation on the A10 north of London where 25 % of the 7.5 km long new dual carriageway buckled, cracked and ridged (see Fig. 55).

Fig. 55 Distress in the A10 (north of London) following lime stabilisation of sulphate-rich soils (New Civil Engineer 25 March 2004)

Although the original site investigation indicated the presence of some sulphur and sulphates, a decision was made to lime stabilise the glacial boulder clay to form the capping layer. During the general earthworks, pyritiferous boulder clay was exposed and further sulphates developed in the warm, conditions of 2003, which was the fourth driest summer in England and Wales since records began in 1914 (see Hawkins 2013).

By November 2003, the road had been black-topped and the road marking undertaken in anticipation of opening in December, some eight months ahead of schedule. However, in late November undulations were noted in the road surface and extensive investigations were undertaken in early 2004. As with the M40, ettringite and thaumasite were identified in the capping layer—a clear indication that the lime had reacted with the sulphates and aluminium clay minerals in the boulder clay, resulting in heave. During the ensuing discussions, attention was drawn to a Technical Memorandum produced by the National Lime Association of the USA and Canada in 2000. This identified five classes of risk related to the amount of sulphate present in material to be lime stabilised (Table 9).

It is significant that at the time of the contract HA74/00 drew attention to a threshold of 1 % SO_3 (1.2 % SO_4) in ground to be stabilised and to the need for

Table 9 Risk for lime stabilisation (after the Technical Memorandum 2000)

Soluble sulphate (% SO_4)	Suitability for lime stabilisation
<0.3	No significant risk
0.3–0.5	Moderate
0.5–0.8	Moderate to high
>0.8	High to unacceptable
>1	Soils generally not suitable

caution where the sulphate content was above 0.25 % SO_3 (0.3 % SO_4). They also highlighted the necessity to undertake a detailed, appropriate investigation if lime stabilisation was envisaged.

Unfortunately HA74/00 did not adequately describe the pitfalls of lime stabilising in dry spells when it would be difficult to keep the material sufficiently wet to ensure all the potential ettringite/thaumasite growth took place in the mellowing period. This is particularly significant in hot dry weather when, in addition to surface evaporation, water may be sucked downwards into the desiccated ground beneath the layer being stabilised.

It is well known that when assessing soils for stabilisation it is important not only to consider the sulphate contents measured at site investigation stage but also to take due cognisance of the total potential sulphates in the design of the lime stabilisation works. Unless there is adequate moisture available, sufficient rotavation is undertaken and an appropriate mellowing time is allowed for all the potential ettringite/thaumasite to form naturally, there is a real possibility that not all the associated expansion will take place and hence the material will not be chemically stable prior to the final compaction/rolling.

The Highways Agency pointed out that testing samples some time after collection would give an elevated value for acid soluble sulphate, but they did not emphasise the danger of undertaking the earthworks early and leaving the formation/protective layer exposed such that oxidation would take place and the sulphate content increase above that taken into account when assessing lime stabilisation.

Research is currently being undertaken to establish the role of fly ash added to material during the process of lime stabilisation of sulphate-rich soils (McCarthy et al. 2011, 2012).

Sulphate-Generated Heave in Dublin Since 2000

As discussed in the examples given elsewhere in this book, a number of structures in the Dublin area have experienced significant distress which has been attributed to sulphate-related heave. However, instances of heave associated with the generation of ground sulphates were unrecorded in Ireland until 2006/2007 (Maher et al. 2011; Pyrite Panel Report 2012). This may have been because:

1. Instances of sulphate-related heave were mis-diagnosed and the distress considered to be due to other causes;
2. In the past, the fill used beneath ground-bearing floor slabs was typically strong resistant rock derived from fluvial gravels or gravels from glacial tills. However, it is difficult to compact natural rounded gravels to meet modern standards of compaction and this, together with the limited resources, means it is now common to purchase angular crushed material from quarries.

3. In order to obtain maximum densification, the National Roads Authority of Ireland (NRA) require the size fraction of Clause 804 granular Type B material to fit within a specified envelope.
4. In the late 1990s, Homebond (who provide house owners' warranties), highlighted the need to adequately compact the material. NRA required that the material should be laid and compacted at a moisture content within the range of optimum to 2 % below optimum. As a consequence, since 2000 the material placed below a floor slab would be close to its maximum density and hence less likely to be able to accommodate any expansion.
5. During a housing boom, some material is likely to be stockpiled on site to avoid delays with site works and/or protect against an inability to obtain a sufficient supply when required. It is unlikely that building contractors would have followed the NRA recommendation that *The material should be maintained within the moisture content range specified in sub-clause 804-3 whilst awaiting overlaying*. Where material stored on site experiences wetting and drying, the potential for oxidation and the development of sulphates is exacerbated (Nixon 1978).
6. With the huge demand from house builders in the early 2000s, quarries may have exploited different strata from those which they had been excavating previously. In strata which can vary considerably in lithology in a relatively short distance, it is likely that in a boom period some quarries would have extended into poorer quality material without necessarily appreciating the significance of this.
7. It is possible that quarries which had traditionally supplied material for one purpose (e.g. asphalt) were now supplying a more general fill, without having undertaken an appropriate re-appraisal of the resource for that purpose.

In addition, there were also changes in the design and construction of houses in the late 1990s and early 2000s. As a consequence, modern buildings are more likely to manifest distress which might have been obscured/accommodated in the past:

(a) With the widespread availability of polythene damp-proof membranes, suspended floors were increasingly being replaced by ground-bearing floor slabs.
(b) Although there is less maintenance with concrete floors, under stress a concrete floor will crack whereas a timber floor has more flexibility.
(c) Tiled floors, which became increasingly popular in the 2000s, are more easily laid on concrete surfaces. In addition, as the finish is less important if tiles are to be laid, this was advantageous to builders who often allowed purchasers to choose their own tiles.
(d) Underfloor heating systems and radiators with underfloor pipes became more common. In addition, modern houses tend to be kept at higher temperatures than in the past, albeit the insulation is likely to be better.
(e) Many walls are now finished with a dry lining, the base of which frequently extend onto/over the floor slab.

(f) Whilst not best practice, pouring a continuous ground floor slab has considerable time/cost benefits, particularly on large-scale housing developments. Remediation has confirmed that in many cases the floor slab has not been poured in individual rooms but extended over rising walls. As a consequence larger areas, including the upper floors, will be affected if the underfloor fill experiences expansion.

(g) Modern, lighter building materials have allowed internal walls and even rising walls to be as narrow as 100 mm in some domestic structures. This has implications for the integrity of the building if significant cracking occurs and/or sulphates penetrate into the concrete.

(h) Modern cement is more brittle than the lime mortar used in the past, hence stress cracking is more likely to be evident.

Recorded Evidence of Sulphides in the Dublin Area

The stratigraphy/biostratigraphy of the Dublin Basin has recently been published by Kalvolda et al. (2011). In particular these authors reviewed the geology at Bay Lane Quarry and Feltrim and have slightly revised the lithostratigraphy (Fig. 56).

There is much in the geological literature to indicate that rocks quarried in the Dublin area are likely to contain pyrite. In *The Geology of Meath,* McConnell et al. (2001) record a number of aggregate producing quarries. This Memoir notes that *the Lower Carboniferous carbonate rocks of the Sheet 13 map area are host to substantial base metal mineralisation.* They state significant Zn-Pb deposits have been identified in the region and give eight specific locations, noting *These deposits, collectively referred to as Irish-type, share the following common characteristics.*

1. *Mineralisation is for the most part strata bound and confined to either the basal Carboniferous mixed sequence of carbonate and clastic rocks (the Navan Group) or Waulsortian facies rocks.*
2. *They occur along, or immediately adjacent to, northeast to east northeast extensional faults that are postulated to have served as conduits for ascending ore fluids…*
3. *…Logwood and Oldtown additionally contain abundant iron sulphides (pyrite, marcasite) and barite.*

Under the heading *Navan* the Memoir notes *The bulk of the ore at Navan occurs as a stacked series of stratiform to stratabound sulphide lenses aligned approximately northeast, parallel to major faulting. Sphalerite and galena are the dominant constituents of the orebody, with generally subsidiary amounts of pyrite, marcasite, barite, dolomite and calcite. The ore exhibits a wide variety of mineral replacement textures including disseminations, complex replacement styles, breccia vein fillings and layered sulphide sediments.*

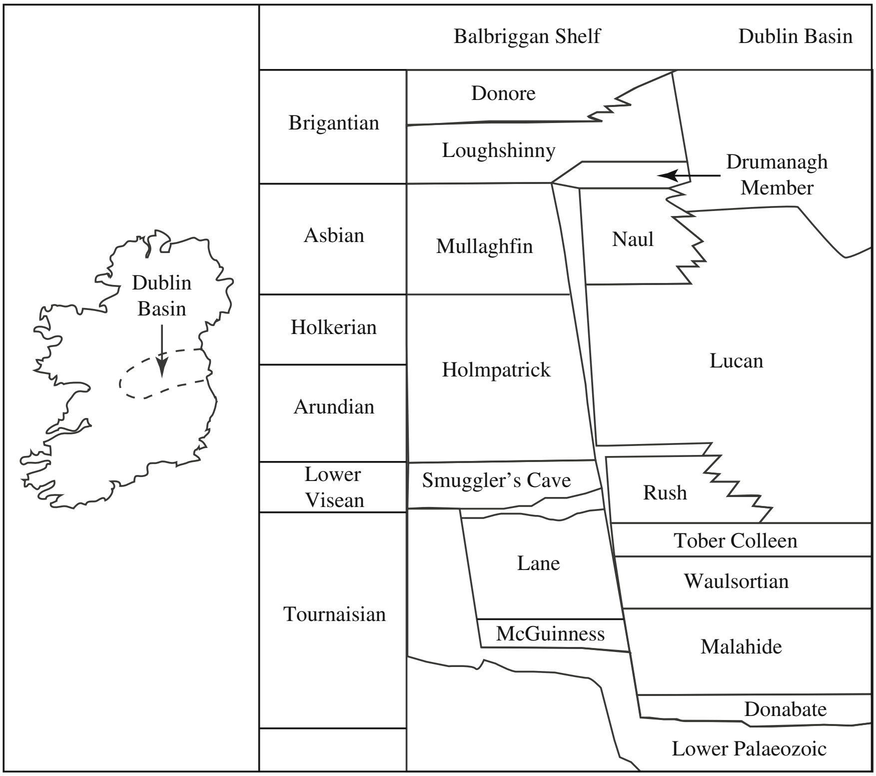


Fig. 56 Lithostratigraphy of the Dublin Basin area (after Kalvolda et al. 2011)

The presence of a basal conglomerate is recorded and *Localized portions of the conglomerate host pyritiferous massive sulphide mineralisation that amounts to at least 1.75 Mt grading 12.2 % Zn, 2.5 % Pb and 23 % Fe…*

At Tatestown, some 3 km to the northeast of Navan, the Memoir records *sulphide mineralization is generally stratiform and thickens in the immediate hanging wall of a northerly dipping east–west normal fault that transects the orebody.* At Longwood Quarry, the Memoir records *Massive pyrite occurs in the upper part of the Waulsortian limestones, accompanied by 2–3 % Zn over 1–2 m intervals.*

The Memoir records that one quarry in the Loughsbury Formation at Hollywood, near Garristown, produced 250,000–500,000 tonnes per annum for *Building aggregate and rock fill.* It describes the Loughsbury Formation as…. *Laminated to thinly bedded, argillaceous, pyritic, locally cherty micrites and graded calcarenites, interbedded with dark grey to black shale.* The Memoir notes that in 1997 some 35 million tonnes of aggregate were obtained from hard rock quarrying and points out that *Within the map area several different lithologies, including limestone, greywacke, shale, basalt and sand and gravel, are worked to be used as aggregate.*

It is clear, therefore, that the sedimentary rocks in the Dublin area need very careful assessment prior to their use as aggregate. Such an assessment should involve not simply the chemistry of the strata and the water within the quarry, but also an appropriate petrographic study (see Eden 2013), as well as detailed examination/logging of the quarry face to observe any sulphide mineralisation in the vicinity of faults or master joints.

Standards and Codes Related to Sulphates with Special Reference to the Dublin Area

It would be extremely unusual for a house-builder to provide his own specification for hardcore or undertake any testing and, in Ireland, it was common practice for both builders and engineers to order 3″ down or 804 for placement beneath ground-bearing floor slabs and for estate roads/pavements. As might be expected, most house-builders would traditionally obtain such "fill" or "aggregate" or "hardcore" from a main supplier and assume that it would be suitable for the purpose intended. In Ireland, they would take note of the advice given in the Homebond House Building Manual, as compliance would be a condition of a Homebond warranty to the house purchasers.

The Homebond Manual was first published in 1993 with subsequent editions in 1999, 2001, 2004 and 2006 (before the pyrite problem was appreciated). In each edition the requirement with regard to hardcore was for *Good quality hardcore: clean, crushed, well graded stone… Hardcore material should be clean, graded, crushed stone, free from shale and 100 mm max. size…*Homebond also note *sulphate can cause expansion and disruption of concrete, particularly on filled sites.*

Irish Building Regulations 1977, Technical Guidance Document C (2004), notes *The hardcore bed should be at least 150 mm thick and should be of broken stones, broken brick or similar suitable material well compacted and clean and free from matter liable to cause damage to the concrete.* Building Regulations 2000, Technical Guidance Document D (2005) states *All works to which these Regulations apply shall be carried out with proper materials and in a workmanlike manner… The materials should be of a suitable nature and quality in relation to the purposes and conditions of their use…*

Until the early 2000s most standards/guidance documents referred to appropriate levels of water soluble sulphate, as it was assumed that the problems were caused by dissolved sulphate moving into concrete in the groundwater. In the 2000 editions of their respective documents, both the Highways Agency (UK) and the NRA (Ireland) considered that for material within 0.5 m of concrete the appropriate water soluble sulphate threshold should be 1.9 g/l SO_3 (equivalent to 2.3 g/l SO_4).

When investigations were made following the problems related to the bridge piers at Junction 11 on the M5 motorway east of Gloucester UK, it was appreciated that the outsides of piles in Liassic mudrock had suffered severe thaumasite attack (Report of the Thaumasite Expert Group 1999). As a consequence it was appreciated that it was insufficient to measure only the sulphate which may be dissolved in water and it became more common to analyse the acid soluble sulphate in the ground, considering also the potential for direct attack by sulphates. Subsequently, in the 2004 specifications by the UK Highways Agency and Irish NRA the criterion was changed to acid soluble sulphate with the recommended maximum level being 0.2 % SO_3 (0.24 % SO_4).

As noted above, ground heave resulting from the development of sulphates had been appreciated since the middle of the 20th century, but no guidance values were available regarding the assessment of this possibility. An attempt was made by Hawkins and Pinches (1997), who cautioned that if the pyrite content was >1 % and the difference between the total sulphur and the percentage sulphur in sulphate above 0.5 %, the material would be susceptible to ground heave as a consequence of pyrite degradation.

European Standards

From the 1990s the suppliers/quarrying industry were aware that the European Union were preparing new documents regarding aggregates. An article in Quarry Managers Journal (January 1992) states *The Construction Products Directive is an ambitious and far-reaching Directive which will affect all producers, exporters, suppliers and retailers of construction products and the construction industry generally.* [EN documents are listed under British Standards Institution in the references]

The first significant document was EN 13242:2002, (BSI 2008a) entitled *Aggregates for unbound and hydraulically bound materials.* This was approved by CEN on 23rd September 2002 and was to be given the status of a National Standard on or before June 2004. Each country would provide their own Guidance on this document, making it relevant to the particular conditions in that area.

In the case of Ireland, SR 21 entitled *Guidance to the Use of IS EN 13242:2002,* came into effect on 29th July 2004. Ireland chose attestation level 4 for aggregates, i.e. further testing of samples taken at a factory (quarry) according to the prescribed test plan and certification of factory production control were not required. In addition, Ireland, together with the UK and Sweden, did not consider it mandatory to CE mark products. A CE mark is given as confirmation that all the recommended testing/requirements have been undertaken and the results proved satisfactory, such that the product can be assumed to be fit for purpose. Without this, reliance has to be placed on the supplier's own system of quality control.

Although EN 13285:2003, entitled *Unbound mixtures—Specification,* was approved slightly later (12th December 2002), it was to be given the status of a

National Standard on 18th July 2003. As with EN 13242:2002 (Annex C), it drew attention to the responsibilities of producers in respect of the quality of their product. Clause D.3.3 of EN 13242:2002, *Knowledge of mixtures,* points out *It is the producer's responsibility to ensure that if any dangerous substances are identified, their contents do not exceed the limits in force according to the provisions valid in the place of use of the unbound mixture.*

EN 13242:2002 recommended categories for various properties of the material and provided examples, e.g., if the maximum acceptable value for acid soluble sulphate content was considered to be 0.2 %, it would be designated $AS_{0.2}$ while if no threshold was considered relevant it would be specified as AS_{NR} (not required). Under chemical requirements, Para 6.2 refers to acid soluble sulphate and Para 6.3 to total sulphur. A Note to Para 6.3 states *Special precautions are necessary if pyrrhotite, an unstable form of iron sulphide (FeS), is present in the aggregate. If this mineral is known to be present a maximum total sulphur content of 0.4 % as S should apply.*

As noted above, SR 21:2004 was produced as a *Guidance to the Use of IS EN 13242:2002* in the Irish context. A discussion of all the information given is beyond the scope of this chapter, but it is relevant to note that:

1. There is a difference between the 2004 edition and that which came into force on 7th December 2007 with regard to total sulphur (Clause 3.4.2). Although it still includes the comment *Pyrrhotite, an unstable form of iron sulphide, is an uncommon constituent of aggregate in Ireland…* it points out that *Producers and specifiers should be aware that the recommended category S_1 for total sulphur may not of itself completely exclude the risk of swelling due to the presence of a reactive form of pyrite. Where it is envisaged that material from a quarry may be used for this purpose it is advised that a suitably experienced petrographer carry out a detailed mineralogical examination covering the proposed area of extraction in order to*
   (a) *ascertain the material's suitability for this end use, and*
   (b) *establish an appropriate test frequency for total sulphur from an assessment of the variability of the quarry deposit. This assessment may need to be repeated where there is a significant change in quarry characteristics.*

SR 21 does not define a *suitably experienced petrographer* nor how the suitability of the material should be assessed. However, this is referred to in ASTM C295 (2012), Applied Petrography Group of the Geological Society of London (2010) and Eden (2013 this book).

2. The 2007 edition of SR 21 also included a new Annex E related to granular fill for use under concrete floors and footpaths. The Los Angeles value is given as 40, compared with the value of 30 given in the 2004 edition (Annex D), which many Engineers used as the criteria for underfloor fill.

Table 10 BRE recommendations regarding the assessment of sulphur/sulphate test results to establish the worst credible conditions

No of samples	Characteristic value
1–4	Highest measured result
5–9	Mean of two highest results
>10	Mean of highest 20 % of results

British Research Establishment

In British Research Establishment (BRE) Special Digest 1 (2005) entitled *Concrete in aggressive ground*, separate recommendations were made for material containing pyrite. In natural ground not containing pyrite (Clause C.5.11) it was recommended that the water soluble sulphate content and pH should be obtained while for natural ground containing pyrite, Clause C.5.12 points out that *it is essential to take account of the total potential sulphate content which might result from oxidation following ground disturbance.* In this situation, in addition to water soluble sulphate and pH, it was recommended that acid soluble sulphate (%SO_4), total sulphur (%S), total potential sulphate as %SO_4 (three times total sulphur) and oxidisable sulphides as %SO_4 (total potential sulphate minus acid soluble sulphate) should be determined.

A box on page 30 of Special Digest 1 highlights *Practical notes on pyritic ground*. It states: *Concrete in pyritic ground which is initially low in soluble sulphate does not have to be designed to withstand a high potential sulphate class unless it is exposed to ground which has been disturbed to the extent that contained pyrite might oxidise and the resultant sulphate ions reach the concrete. This may prompt redesign of the structure or change to the construction process to avoid ground disturbance; for example by using precast or cast* in situ *piles instead of constructing a spread footing within an excavation.*

Of particular note is the caution: *The sole determination of the acid soluble sulphate content, as employed in some recent European Standards, will not detect pyrite which might be oxidised to sulphates as a result of ground disturbance.* BRE also make recommendations as to how the test results should be assessed to determine a characteristic value (Table 10) for comparison with given thresholds.

Transport and Road Laboratory

Transport and Road Laboratory (TRL) 447 Reid et al. (2001) provided an indication of the necessity to appropriately assess material adjacent to structures in their report entitled *sulfate specification for structural backfill*. They recommended different values for material within 0.5 m of concrete and backfill adjacent to galvanised steel. In the case of concrete, they recommended thresholds of 2.3 g/l SO_4 for water soluble sulphate, 0.6 % SO_4 for total potential sulphate and 0.46 % SO_4 for oxidisable sulphides. Adjacent to galvanised steel elements, the threshold was 0.3 g/l SO_4 for water soluble sulphate and 0.06 % SO_4 for oxidisable sulphides.

In the 2005 edition of TRL 447, however, the threshold values for backfill against concrete or cement-bound materials were reduced to 1.5 g/l SO_4 for water soluble sulphate and 0.3 % SO_4 for oxidisable sulphide; the total potential sulphate threshold remained at 0.6 % SO_4. For material adjacent to galvanised steel elements, for water soluble sulphate the threshold was 0.3 g/l SO_4 and for oxidisable sulphide, 0.06 % SO_4.

TRL also considered the significance of the framboidal form of pyrite, stating *If pyrite is present in framboidal form…the material should be classified as unacceptable as structural backfill, because of the known tendency of this form of pyrite to oxidise rapidly in engineering situations…The use of the material may be permitted as structural backfill if it can be established to the satisfaction of the overseeing organisation that:*

1. *the material has been used in the past as structural backfill without leading to problems with sulfur compounds; and*
2. *the reason why the material will not cause a problem is known, based on an understanding of its chemistry and mineralogy.*

National Roads Authority of Ireland

The NRA Specification for Roadworks 800 Series is the Standard generally used for engineering works in Ireland. As noted above, engineers and builders frequently request "804" (now "808") material for hardcore beneath floor slabs and estate pavements, referring to stone which meets the requirements of Clause 804/808 in this document.

The March 2000 edition included a general note (Clause 801) which stated that material to be placed within 0.5 m of concrete should have a water soluble sulphate value not exceeding 1.9 g/l sulphate, expressed as SO_3 (equivalent to 2.3 g/l SO_4). It also stated the material should be placed in layers not greater than 225 mm in thickness and that the minimum compactive thickness should be greater than 110 mm. In addition, the material should satisfy the following conditions:

1. The particle size distribution should fit within a grading envelope such that the proportions of coarse and fine material would compact to form a dense layer.
2. The liquid limit should be <21 %, such that the amount of shrinkable/swellable clay minerals would be limited.
3. The material should be placed with a moisture content in the range of optimum to optimum minus 2 %.
4. The 10 % fines values should be at least 130 kN.
5. The flakiness index should be <45.
6. The water absorption value should be <2 %.

Table 11 Relevant part of Table NG1/1—recommended frequency of testing for the requirements set out in the NRA 800 Series (2004)

Clause	Work, goods or material	Test	Frequency of testing
801	Unbound sub-base and road base material (other than slag) adjacent to cement bound materials, concrete pavements, structures or products	Acid soluble sulphate content	1 per 400 tonnes or per location if less than 400 tonnes*
804	Granular material Type B	Grading Moisture content	1 per 1,000 tonnes or min. 2 per day*
		Methylene blue Liquid limit Flakiness index	1 per week*
		OMC Los Angeles	2 per year*
		Magnesium sulphate soundness	1 per 2 years*
		Water absorption	As required (<2 %)

* *See text below*

The Specification was revised in May 2004 when the measurement of sulphate was changed from water soluble to acid soluble. The threshold given was 0.2 % SO_3 (equivalent to 0.24 % SO_4). This was based on testing following EN 1744-1:1998 (British Standards Institute 2010) which gives the results as SO_3. In addition, the 10 % fines value was replaced by the Los Angeles test and the concept of the Methylene Blue test was introduced. A new sub-clause 804-4 was included which required the material to be maintained within the moisture content range specified in sub-clause 804-3 whilst awaiting overlaying. In addition to updating the Specification for Roadworks, in May 2004 the NRA also issued a Notes for Guidance document. Table NG1/1, headed *Typical Testing Details*, gives the frequency of testing for the various requirements of the Clauses in the 800 Series. The relevant data are given here in Table 11.

The key to Table NG1/1 notes that the asterisk *indicates that the frequency of testing is given for general guidance and is only indicative of the frequency that may be appropriate (i.e. no frequency is given in the SRW or reference documents). Where materials are known to be marginal or if initial test results show them to be such, the frequency of the testing should be increased. Conversely where material properties are consistently in excess of specified minimum requirements or well below specified maximum limits then the frequency of testing should be reduced.*

In December 2010 the NRA issued a further revision of the Specification which included a new clause (809) entitled *Unbound Materials Placed Adjacent to*

Metallic Structural Elements. The following requirements apply to steel which is not protected by/enclosed in concrete.

1. A water soluble sulphate threshold of 300 mg/l SO_4, equivalent to 0.3 g/l.
2. The oxidisable sulphides should not exceed 0.06 % sulphate (as SO_4) determined by deducting the acid soluble from the total potential sulphate.

Concrete

As noted above, the deterioration of concrete due to the crystallisation and expansion of sulphates is well known and extensively described in the literature. Bessey and Lea (1953) report work on cement products buried or partly buried in the ground which was undertaken by the Research Committee of the Institution of Civil Engineers. In the 1930s, test beds were set up in the Keuper Marl, Lias Clay, Oxford Clay, Kimmeridge Clay and London Clay, but unfortunately the work had to be temporarily abandoned in the 1940s.

BRE Special Digest 1: 2005, *Concrete in aggressive ground,* draws attention to many of the points raised in TRL 447 (2001; 2005). In addition to reproducing an excellent photograph of the thaumasite attack on the concrete pile of a 30 year old highway bridge exposed to wet, pyritic clay fill, it notes:

1. *When porous concrete is in contact with saturated ground, the water phase is continuous across the ground/concrete interface and sulphate ions will be readily carried into the body of the concrete.*
2. *Migration of sulphate ions from unsaturated ground into the concrete can take place by diffusion provided there is sufficient water to coat the particles of soil, but the rate will be slow and dependent on the sulphate concentration.*
3. *The reactions have been demonstrated to depend on the type of cement, on the availability of reactive carbonate in, for example, the aggregate and groundwater, and on the temperature.*
4. *Two separate forms of sulphate attack on Portland cement concrete are described… the 'conventional form of sulphate attack' leading to the formation of ettringite and gypsum* and *a more recently identified type producing thaumasite… In practice both can operate together to some extent in buried concrete under field conditions.*
5. *Sulphate attack can only be diagnosed when the concrete in question is showing physical signs of degradation such as expansion….surface erosion or softening of the cement paste matrix.*
6. *The identification of abnormally high levels of sulphate (significantly greater than about 4 % by weight of cement) within the surface of a visually sound concrete does not automatically imply that sulphate attack has taken place; it may only be a warning of potential attack in the future.*

The Digest draws attention to the importance of temperature for the development of thaumasite in concrete. It notes that *thaumasite formation is most active below 15 °C* and points out that, in England, foundations placed in the upper 1.2 m are likely to experience a minimum temperature of 4 °C in March and a maximum of 17 °C in September. At a depth of 3 m the temperature varies between a minimum of 8 °C in April and a maximum of 12 °C in October. The Digest also points out that in an environment where the sulphides can oxidise to produce sulphuric acid, the pH can become low and the acid may cause deterioration of both concrete and any reinforcement.

It is of note that EN 12620:2002 + A1:2008 (Biritish Standards Institute 2008b) draws attention to the more severe criteria necessary if pyrrhotite is present in concrete aggregates. In Clause 6.3.2 it points out *Special precautions are necessary if pyrrhotite, (an unstable form of iron sulphide FeS), is present in the aggregate. If this mineral is known to be present, a maximum total sulphur content of 0.1 % as S shall apply.* Chinchón-Paya et al. (2012) suggest that while pyrrhotite is extremely important, 0.1 % is too restrictive and will make the sourcing of aggregates in some areas very difficult. As noted above, however, the presence of pyrrhotite is known to have resulted in significant problems (e.g. Trois Rivières Maher, this book) and current research indicates it may be far more extensive than had previously been appreciated. Indeed, although not mentioned in the Irish literature, pyrrhotite has recently been identified in the area of Dublin airport. In view of this, the possible presence of pyrrhotite and not just pyrite should always be considered and the implications of this taken seriously.

A number of authorities stress the importance of the chemistry within 0.5 m of cementitious material. However, this may not take adequate cognisance of water movement when the ground/fill has a high pyrite content. Such moisture movement may follow preferential pathways, e.g. discontinuities in mudrocks (note the oxidation in Fig. 10), faults etc. Bessey and Lea (1953) show that in the London Clay, in some cases the gypsum occurs coincident with levels of granular silty/sandy bands. This is not surprising as such bands would facilitate the preferential lateral movement of water in wet periods and oxygen in dry periods. In an interbedded limestone mudstone sequence the stronger, more brittle limestones will fracture such that, in a similar manner, the joints allow both water flow and, in the unsaturated zone, the penetration of oxygen into the host material. In both cases, there may be visible evidence of oxidation (brown coloration), particularly at the upper margins of these more permeable horizons.

Any foundations which extend into the bedrock, therefore, should take due cognisance of the presence and potential change in state of the iron sulphides/sulphates. It is important that the dark pyritiferous material is not exposed for longer than necessary and that a very dense concrete is used such that it inhibits ingress of sulphate-rich solutes. The material must be assessed carefully to establish the potential danger.

1. The pyritiferous aggregate/natural ground in which the concrete is placed may result in deterioration of the concrete as a consequence of the formation of

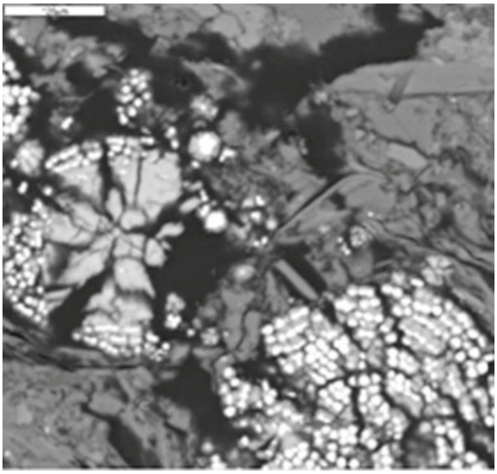


Fig. 57 Variable weathering of framboids in the fine fraction attached to concrete. Scale bar 20 µm

gypsum, ettringite and/or thaumasite. The role of ferrous sulphate has not yet been elucidated. An example of the deterioration of a concrete beam can be seen in Fig. 28 of Hawkins and Stevens (2013 this book). Figure 57 shows two weathered framboids in the fine fraction adhering to a concrete core.

2. Whilst many Codes refer to concrete per se, concrete blocks are even more prone to the penetration of sulphate-rich solutes as they typically contain approximately 15 % voids. The movement of the sulphate minerals is affected by the carbonation of the concrete but there is significant evidence that in many instances sulphate has moved extensively into/through blocks as well as into structural concrete. An example of thaumasite infilling voids in a concrete block is shown in Fig. 58; 10.9 % SO_4 was recorded at a distance of 16 mm into the block. Figure 59 shows the ingress of sulphates from the outer and inner sides of a horizontal block. Values of 7–10 % SO_4 were obtained between 23 and 33 mm from the outer face while 10.5 % was recorded at 17 mm from

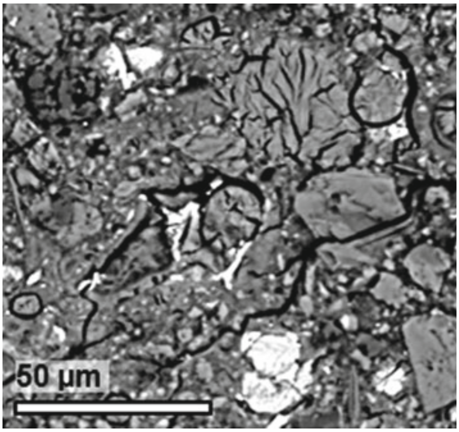


Fig. 58 Thaumasite infilling voids, 16 mm from the surface of a block where the SO_4 content was 10.9 %

Fig. 59 Sulphate penetration into concrete block; upper graph from the outside, lower from the inside face

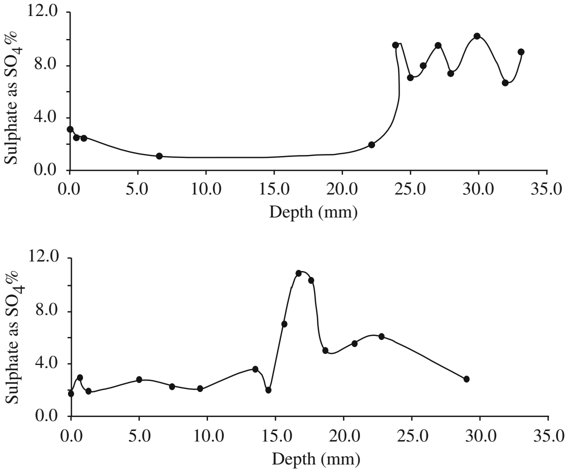
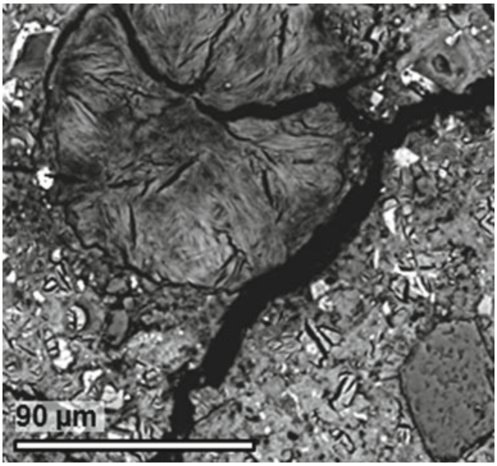


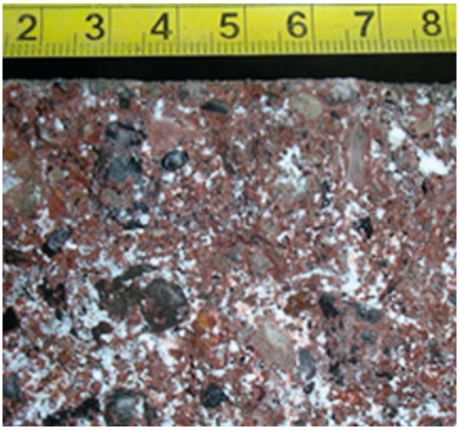
Fig. 60 Thaumasite infilling a void at a depth of 9.4 mm into a concrete block



the inside face. Figure 60 shows thaumasite has developed at a depth of 9.4 mm into a concrete block where the sulphate content was up to 19.4 % SO_4. Figure 61 shows a core from a flat-lying concrete block which indicates significant deterioration of the concrete had taken place within five years of placement. It was not possible to obtain a good quality core either because of a lack of cement in the middle part of the block and/or the presence of thaumasite which weakened/disintegrated the material.

Fig. 61 Degraded concrete with thaumasite developed in poor quality block in a rising wall

Fig. 62 Thaumasite exposed on a broken block close to that shown in Fig. 61



In one recently remediated house the concrete blocks at approximately the groundwater level showed such extensive thaumasite development that the blocks could be broken by hand pressure (Fig. 62).

3. In addition, the aggregate from which the concrete is produced may contain pyrite or pyrrhotite which may oxidise to produce sulphates and result in a deterioration of the quality of the concrete. This is similar to the Mundic problem in south west England and the Trois Rivières situation in Canada, both referred to above. It is not surprising, therefore, that in an area where pyrite is so abundant as in Dublin, it has also been identified in the aggregate within concrete blocks (Fig. 63).

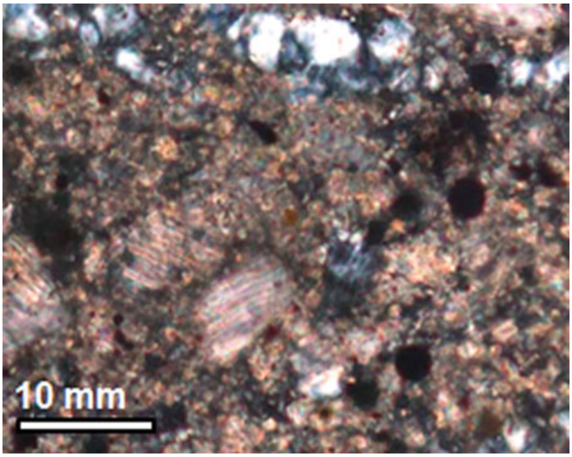


Fig. 63 Oxidised pyrite contained in fragments within concrete aggregate

Investigating for Potential Sulphate-Related Problems

Assessing a Greenfield Site

For many years, engineers have been encouraged to establish the ground chemistry as part of their site investigation specification. However, apart from contamination testing, this is generally limited to the sulphate content and pH of the soils. Too often samples are taken at random, without due cognisance of the likely depth at which the sulphides/sulphates are likely to be present in the ground being investigated.

Frequently the need to undertake specific rather than general sampling is not appreciated. For example, engineers commonly refer to the brown and the grey London Clay but do not always appreciate the advice given in such documents as HA74/00 (Clause 3.30) that this colour change is likely to be coincident with a sulphate-enriched zone.

As seen in Fig. 64 (modified after Hawkins 1998), in the aerated zone above the winter groundwater level, most of the sulphides have already oxidised and as a consequence the soils have changed from grey to brown while the sulphates have been leached downwards by percolating rainwater. In the dark grey material below the summer groundwater level, i.e. in the saturated zone, sulphides are still present while between the summer and winter groundwater levels the soils are invariably mottled brown/grey; it is in the lower part of this mottled zone that sulphates typically accumulate.

Figure 65 shows the high sulphates typically found in the mottled zone at approximately the lowest groundwater level. It is clear that at this site in south Gloucester a sample taken at 1 m would give a very low sulphate value compared with a sample from the enriched zone between 1.4 and 1.6 m. Whilst these figures are specific to the particular site in the Lower Lias Clay, which in this area is

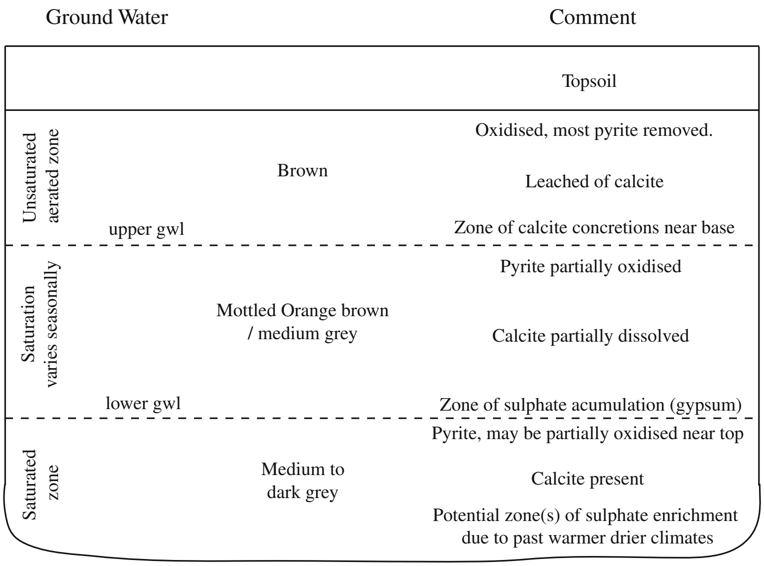
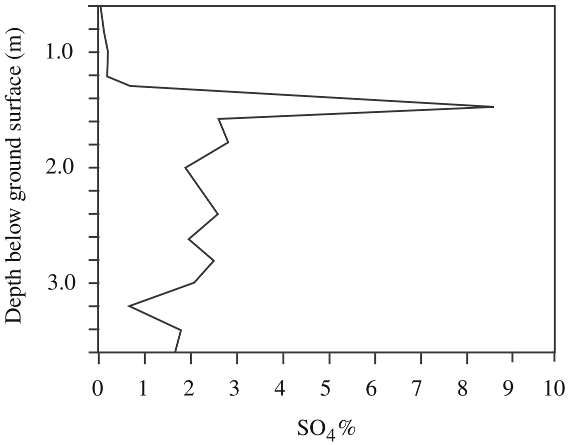


Fig. 64 Sketch illustrating the horizon which is likely to be enriched with sulphates

Fig. 65 Acid soluble sulphate profile from the Lower Lias, south of Gloucester



known to be rich in pyrite, it illustrates a typical pattern of sulphate variation. It is important that this is appreciated if appropriate sampling is to be undertaken and realistic sulphate values obtained which can be taken into account when assessing the potential aggressivity of material in the vicinity of concrete and/or metal.

When Hawkins and Higgins (1997a) recorded the acid soluble sulphates in the London Clay at Harrow on the Hill, a maximum value of 3.6 % SO_4 was obtained for a sample at a depth of 7.5 m. Hawkins and St John (2013b) report two profiles in the London Clay from a site in south east London. Although the acid soluble

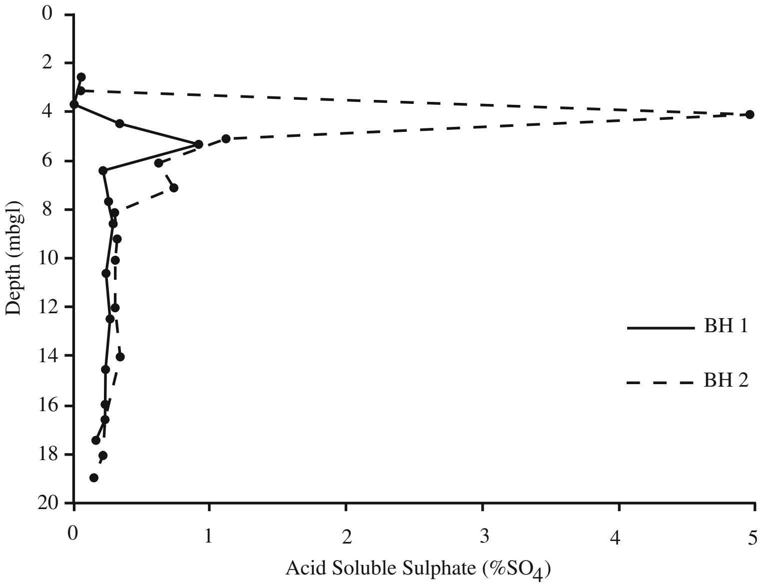


Fig. 66 Variation in ground sulphates between two boreholes within 35 m of each other in the London Clay in south east London

Table 12 Changes in acid soluble sulphate levels at different depths and distances from an 8 m high elm/hawthorn hedge

SO_4 (%) at distances from elm/hawthorn hedge				
Depth (m)	1 m	4 m	8 m	11 m
0.3	0.8	0.5	0.4	0.5
0.5	0.8	0.5	0.5	0.2
0.7	2.3	0.6	0.4	0.1
1.0	1.1	0.6	0.8	0.1
1.3	1.1	0.5	0.4	0.0

sulphate values showed a peak at the brown/grey boundary in both profiles, the maximum values (5 and 0.8 % SO_4) were very different (see Fig. 66). This emphasises the importance of not only studying the laboratory results but also of looking carefully at the overall situation in order to assess the worst credible conditions.

It is also important to appreciate that in greenfield sites sulphate-rich waters are drawn towards trees/hedges by the nutrient-seeking roots (Table 12) and that gypsum crystals are often noted in old, decayed root systems. The extent to which this effect is significant varies according to the species and to the seasonal conditions; the roots extending deeper and/or further from the tree when moisture is scarce.

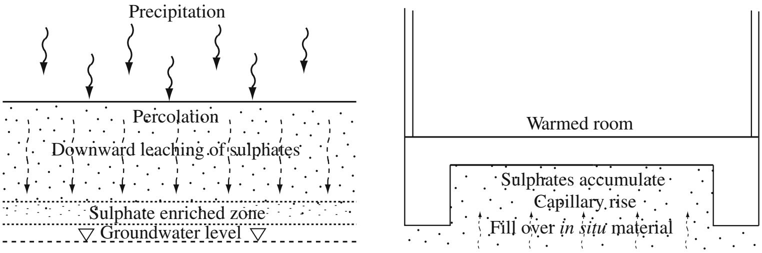


Fig. 67 Comparison of moisture movement in greenfield site and beneath a ground-bearing floor slab

As there is a significant increase in the acid soluble sulphate near the tree, sampling and testing should take this into consideration. This is particularly important if lime stabilisation is being considered as whilst the general sulphate contents measured in the open field may be acceptable, in the vicinity of hedges/ trees the higher levels may mean the soils are unsuitable for this method of ground treatment.

It is also necessary to consider the new environmental conditions which will be created as a consequence of the engineering works. When gravity services are installed, they generally reduce the groundwater level, exposing to oxidation material which has previously been saturated. In addition, when the ground surface is covered by houses or a non-porous road pavement is constructed, there will be a reduction in the downward percolation of rainwater in these areas. Indeed, warm houses may cause upward movement of ground salts by capillary action such that there may be a concentration of sulphates beneath the underfloor membrane. Figure 67 shows schematically such a change in conditions and emphasises the potential dangers of underfloor heating and the inappropriate location of ground floor boilers.

Assessing Fill Beneath Buildings

The concentration of sulphates will also vary in fill material. In view of the influence of temperature, the development of sulphates will be affected by the particular location in the house; bedrooms are likely to be cooler than sitting rooms and kitchens, while the floor beneath a fire place/boiler is likely to be particularly warm. The significance of this must be considered both when deciding where test samples should be taken and in the interpretation of the results. The location of sample points and the procedures for sampling are discussed by Lombard (2013 this book).

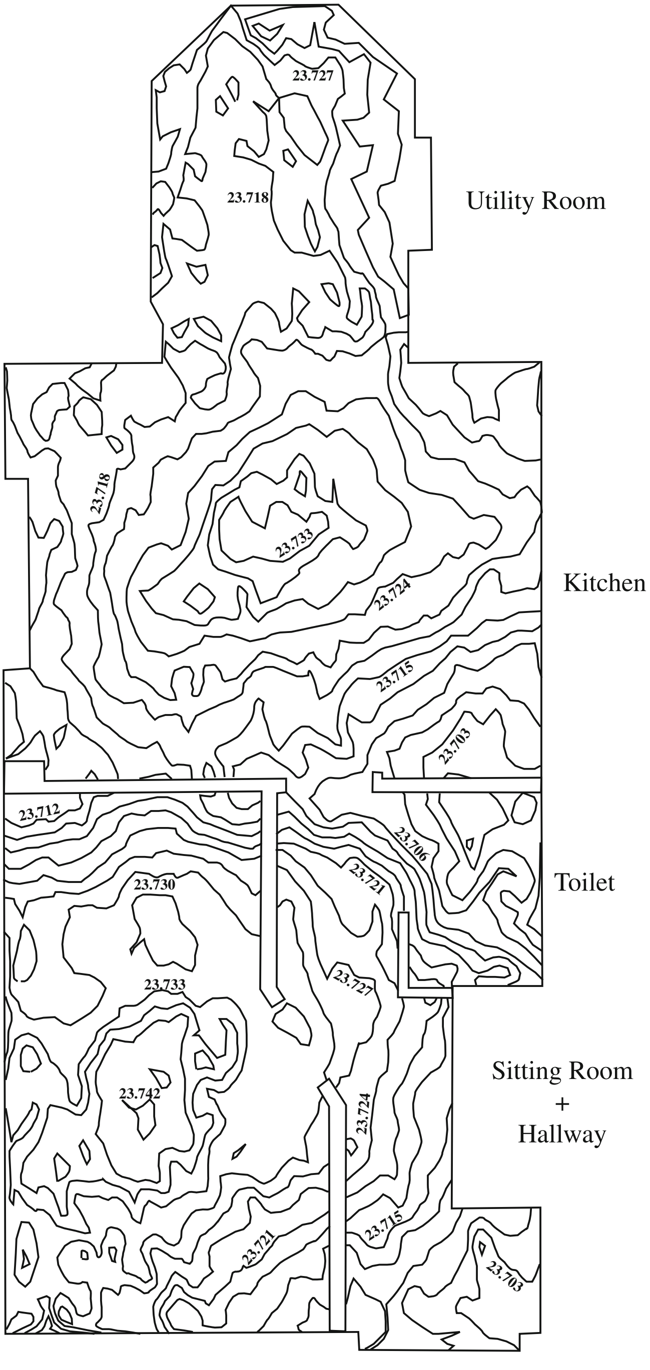


Fig. 68 Laser scan of a ground floor affected by sulphate-generated heave. Note the dome shape in the kitchen and the rise extending across the sitting room/corridor constructed on a single slab

Assessing Sulphate-Related Movement in Buildings

Appreciating the difference in level of a ground-bearing floor slab is a valuable indication of the extent of vertical expansion which typically takes place as pyritiferous bedrock/fill oxidises, ferrous sulphate is produced and gypsum crystals are formed. Depending on whether the floor slab is reinforced, it may rise as a single entity with pronounced cracks/lips around the periphery and some minor spider cracking within the room, or where there is no reinforcement a dome shape is created.

A laser scan can indicate the topography of the floor at a given point in time. Figure 68 shows levelling contours produced by laser scanning in a house on an estate in Dublin. The arching of the floor slab is particularly noticeable in the kitchen, which was constructed on concrete laid between rising walls. However, in the front part of the house the sitting/dining room and adjacent hallway were all built off a single floor slab and hence the dome effect extends across the internal walls such that the rise shown in the hall/corridor is similar to that in the sitting room. Extensive cracking occurred above the doorway into the sitting room and as a consequence of the internal walls being built off the slab, the damage extended to the upper floors.

Generally, level monitoring is undertaken when there is already evidence of distress in the building. This form of monitoring uses studs fixed into the floor which are tied into a substantial external datum. Particularly when buildings are in use, however, the location of these points is often constrained and they may be disturbed during the monitoring period. Further, the points measured on an unreinforced slab may not record the maximum heave as this is not always in the same location and/or at the same rate. Where the building is not in use, it is preferable to establish a significant number of points on a close grid system at circa 0.5 m centres such that the variable nature of the movement can be better understood.

When monitoring is undertaken using a grid system, it is often possible to identify those areas of a floor with the greatest rise compared with the average heave. An example is given in Fig. 69 which shows the rate of rise over time of the maximum point, compared with the average of the 160 points installed in the same floor slab. At the Ballymun Youth Centre, after the initial set of levelling studs were monitored it was appreciated that not all the areas of significant heave were being recorded. As a consequence, some 7 months after monitoring began, a further set of points were installed. Over a 13 month period a maximum rise of 10.5 mm was recorded in the entrance lobby while in some other rooms the heave was much more limited.

At another site, where a large reinforced slab was being pushed up, monitoring was undertaken over an eight month period (Fig. 70). It can be seen that during this time the floor rose by some 4.5 mm (equivalent to 7 mm/year). This is consistent with the fact that within some four years of construction the floor rose between 20 and 30 mm.

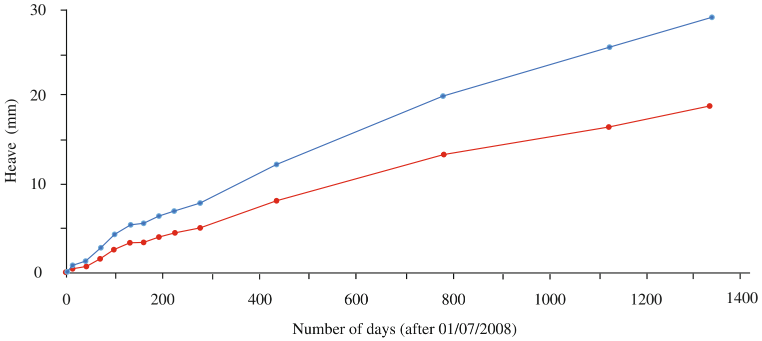


Fig. 69 Maximum rise (*blue line*) and average of the 160 monitoring points (*red line*) in same house. Slab laid February 2006

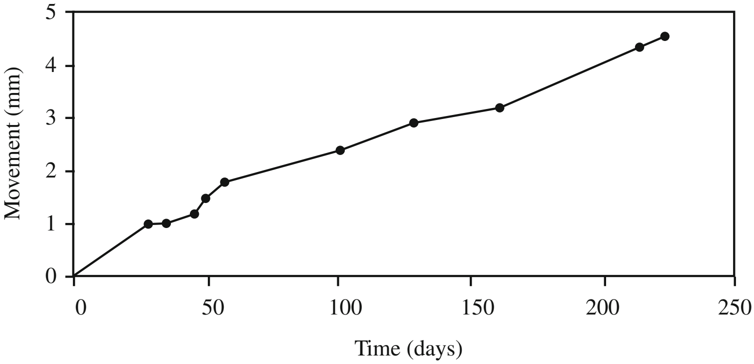


Fig. 70 Levelling of a point on a large reinforced concrete floor slab

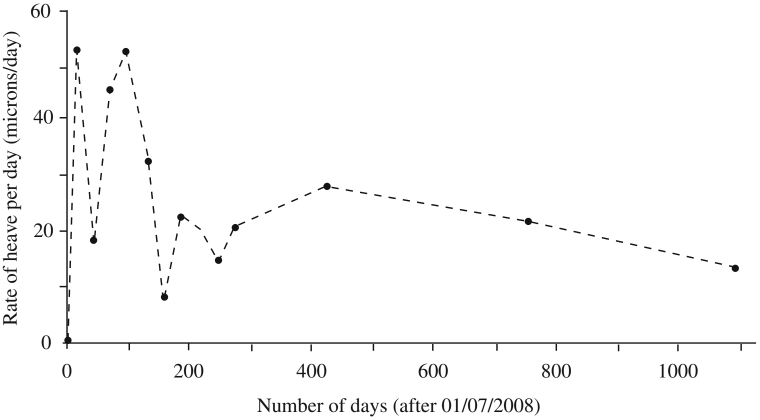


Fig. 71 Calculated notional average rates of rise per day for the blue line in Fig. 69

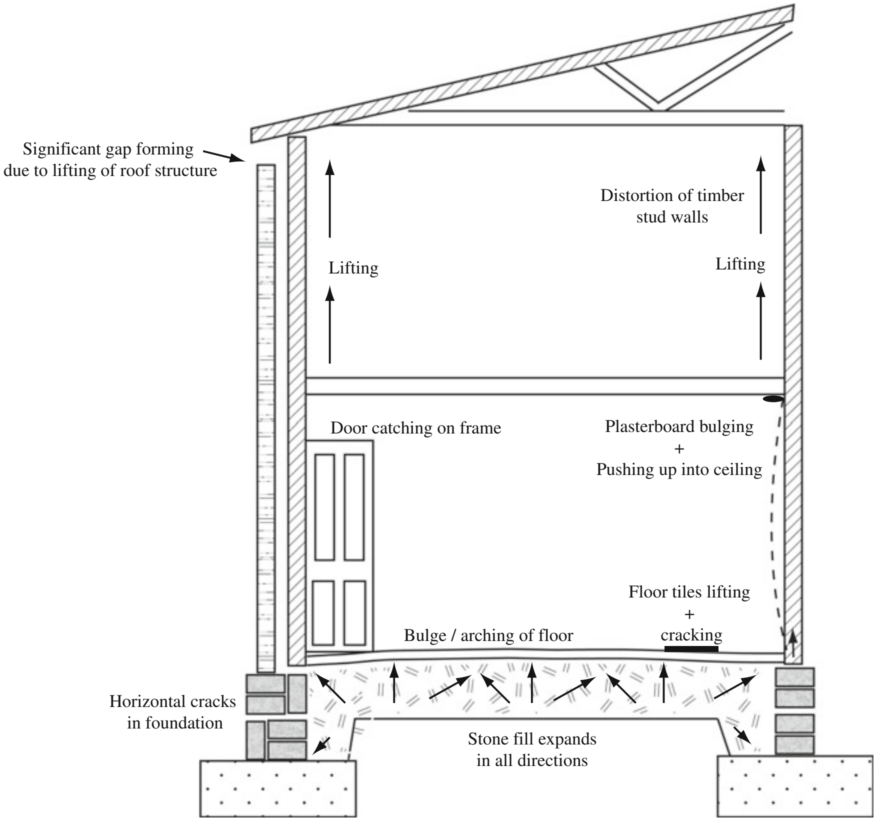


Fig. 72 Typical types of distress due to sulphate-related heave

Rise in this floor slab was significantly faster in the first 150 days of monitoring. When the survey data were analysed in detail to produce a nominal average daily rise, it appears that despite an anomalously low value after some 40 days, the notional average rise over a 97 day levelling period (four readings) was 43 μm/day. Subsequently, for the five readings in the following twelve months the notional average rise was only 22 μm (Fig. 71).

These levelling data are consistent with the suggestion, postulated above, that it is the development of significant ferrous sulphate rims in the early stages of oxidation in the calcareous-rich rocks of the Dublin area which has resulted in the initial, rapid heave (Hawkins 2012). This is exacerbated by the early development of selenite crystals which cause the opening of fractures within the aggregate fragments.

The kinds of damage that are typically seen as a consequence of sulphate-generated heave are shown schematically in Fig. 72.

The recent problems in Dublin have drawn attention to the pressure produced by the expanding pyritiferous fill and its capacity to lift houses/terrace blocks by

Fig. 73 Rise of a manhole biscuit/cover slab of up to 13 mm due to the expansion of the surrounding pyritiferous fill (*left*). In the manhole wall itself gaps of up to 10 mm were noted (*right*) where the upper wall remained cemented to the biscuit

up to 20 mm (Finnegan and Hawkins 2013 this book; Forde 2013 this book) such that the superstructure is separated from its support/load-bearing walls. In order to determine how much the walls have risen it is necessary to install monitoring points in the internal walls. Whilst this may be done by screws or nails socketed into the wall, an elbow bracket provides a more substantial point to level. Again, it is essential to establish a fixed datum point, external to any influence of the deleterious fill, to which the levelling data can be related accurately.

As noted by Forde (2013), the design and construction of a building will influence its response to the swelling of material beneath the floor slab. If the upper storey/roof is supported by structures built on the ground-bearing floor slab, when heave takes place the distress is transferred upwards. In the example given by Forde the roof initially rose by some 20 mm and the gap between the top of the external wall and the eaves was infilled by the builder within thirty months. Subsequently the roof continued to be pushed up such that the rise at the time the photograph was taken was almost 40 mm (Forde Fig. 20).

At Avila (Finnegan and Hawkins 2013 this book) the internal walls, which also supported the roof, were constructed on the ground-bearing floor slab while the external walls were built on the strip footings. Within a year the roof construction had begun to rise, leaving horizontal separation cracks between the upper part of the external wall and the eaves. In 2008 this crack was some 18 mm wide but subsequently extended to 25 mm. When an internal load-bearing wall was removed, the 25 mm crack effectively closed in a matter of seconds.

During investigations/remedial work at Clancarthy, the whole super-structure, which was designed to rest on the rising walls, was found to be separated from the lower part of the rising walls by 5–10 mm. Again, when the fill was removed the horizontal cracks rapidly closed. In addition to the vertical movement of buildings, the expansion of pyritiferous fill may also be manifested in lateral movement. Eden (2013 this book) shows the severity of the cracking which can occur on the lower external walls of buildings. In view of the random presence of pyrite within a rock mass or aggregate and the arbitrary locations in which forceful gypsum growth takes place, it is not possible to predict whether the more severe expansion will take place laterally or vertically.

Finnegan and Hawkins draw attention to the necessity to level monitor manholes etc. Where pyritiferous fill is used in road formations, horizontal cracks may develop in shafts and the manhole biscuits may be separated from their supporting walls (Fig. 73).

Factors to be Considered When Assessing Potential Pyrite-Related Problems

Many Standards (e.g. BS 5930), Specifications (e.g. Highways Agency) and text books discuss good practice in terms of sampling and testing, hence this chapter only draws attention to some points particularly relevant for investigations to identify sulphate-related problems and the assessment of the data obtained.

Prior to any assessment, it is important to be aware of whether the data obtained represent index properties (which by definition should not change) or properties which may vary with time and/or related to environmental conditions. It is also important to appreciate that unless the rock is strong, inert and durable, there is likely to be a change between the test data obtained on fresh samples and those obtained some years later when the material has been subjected to a changed environment.

The data can be considered in two categories: those related to the physical properties and those related to the chemistry of the material.

Physical Properties

1. *Lithological identification*

It is not easy to correctly identify the lithology of a sample of rock aggregate in hand specimen. This is particularly true when all the rocks are carbonaceous, i.e. dark in colour. It is then very difficult to distinguish a mudstone from a calcareous mudstone, argillaceous limestone or limestone, and hence to determine their relative proportions in the fill mass.

(a) There will be a natural tendency to look preferentially at the coarser material (i.e. with particles greater than some 10 mm), which can be easily handled. With the aid of a hand lens and hydrochloric acid, an assessment is made based on the colour, texture etc. of these fragments. In an interbedded lithology, it is easy to over-emphasise the proportion of coarser, stronger rocks but it is often the characteristics of the weaker finer fraction which are more significant from an engineering point of view. Unless the material is broken down to an approximately consistent size (say 5 mm) and examined under a microscope, the proportions of the various lithologies present may not be determined accurately.

(b) Argillaceous lamellae within limestones are frequently not visible to the naked eye and hence are likely to be missed in hand specimen. However, the rate of oxidation of pyrite/pyrrhotite in the stronger sedimentary rocks is partly related to the presence of such clay lamellae, which can only be identified by a microscopic examination of the material.

(c) In general, the amount of sulphides is greater in mudrocks than in limestones. In addition, in mudrock the pyrite/pyrrhotite is more likely to be in the form of microcrystals/framboids, while in the highly calcareous rocks cubes/lumps are common. If the proportions of the different rocks are not appropriately determined, this will have implications when considering both the extent and rate of oxidation.

2. *Particle size*

The particle size distribution (PSD) determined before the material is placed and compacted cannot necessarily be equated with the PSD obtained from material collected from beneath pavements or ground-bearing floor slabs.

(a) The quarrying process induces incipient fractures which may then extend through the fragments, in part related to on site compaction.

(b) Frictional abrasion of angular fragments during compaction causes an increase in the fine fraction.

(c) Many materials experience stress release within a matter of months of being removed from the confining overburden as a consequence of quarrying. This is particularly relevant where clays are present. Any clay minerals in the rock will cause and/or assist delamination.

(d) If the rock contains pyrite/pyrrhotite, dilation created by chemical reactions opens the rock while the development of gypsum is likely to result in a change in the size and shape of the aggregate particles. In addition, the release of sulphuric acid in calcareous materials causes a degree of chemical decomposition of the rock mass as a consequence of the dissolution of the binding cement.

3. *Atterberg limits*

In geotechnical engineering, the liquid and plastic limits are usually considered to be index properties which do not change. This has been shown not to be the case in calcareous mudstones where the calcium carbonate can be removed by dissolution (Hawkins and McDonald 1992). It is also not the case when quarried material is allowed to weather.

(a) When material is quarried and crushed, all the particles are fresh and the fine fraction is dominantly a rock flour consisting of silt- rather than clay-sized fragments, i.e. any clay minerals are held within the particles. As a consequence, the Atterberg limits obtained on freshly quarried material (rock flour) are likely to be non-plastic.
(b) When the material is weathered and oxidised, clay minerals recover their adsorbed layers, hence the liquid limit will increase and "non-plastic" material may become plastic.
(c) Some dark, carbonaceous, pyritiferous rocks, such as those in the Dublin Basin, contain smectite, an expanding lattice clay mineral. The de-confinement of this mineral associated with the breakdown of the aggregate particles can have a major effect on both the liquid and plastic limit and the shrink/swell potential of the material.
(d) In pyritiferous rocks, the presence of sulphuric acid will increase the rate of breakdown of the aggregate, releasing clay minerals. As a consequence, care must be taken in relating results obtained after the material has oxidised to those obtained on the material at source.

4. *Los Angeles value*

It is difficult to obtain a representative Los Angeles value from an interbedded sequence such as that commonly found in Carboniferous strata.

(a) The fragments used in the test will vary in shape, from more flaky mudstone particles to more angular, rougher particles from stronger rocks.
(b) In a rotating drum, the effect of the steel balls will differ with the two particle shapes and hence the selection of the fragments to be tested needs careful consideration.
(c) As the weaker mudstones experience de-stressing and the development of incipient discontinuities during the quarrying process, this material will break down more easily than the limestone particles. It is important, therefore, to ensure the test sample properly represents the proportions of the different lithologies in the source material.
(d) The test result represents the rocks in that particular state; subsequent oxidation of pyrite/pyrrhotite can cause a breakdown of the material such that a later test will give a different value from that obtained on the original, less weathered sample.

5. *Water absorption*

Whilst strong, durable, inert rock fragments may not change their water absorption capacity with time, this does not necessarily pertain with many weak to medium strong sedimentary rocks, including limestones with clay lamellae, or some metamorphic rocks.

(a) In its in situ condition, a rock is likely to be experiencing a significant overburden stress and be in its most dense state. As a consequence it has little capacity to take in more water than may already exist in any pores.
(b) In construction engineering, it is essential to examine cores in weak or medium strong rocks within hours of their retrieval, in order that such data as RQD and bedding thickness can be accurately assessed relative to the in situ rock mass and not the increasingly desiccated, de-stressed material in the exposed core. However, the opposite is true for material which is to be used for aggregate.
(c) As noted above, when quarried, sedimentary rocks experience de-stressing and the development of incipient fractures which with time can extend through the aggregate fragment. The development of such fractures has a significant effect on its water absorption.
(d) When the rock is sufficiently de-stressed, hydration takes place and the clay minerals attempt to re-establish their electrical balance (develop adsorbed layers). Tests undertaken on material after it has experienced this de-stressing and all the rehydration and re-establishment of the adsorbed layers has taken place, will give a different result than would be obtained on material which has been confined for millennia. This is particularly important when expansive lattice clay minerals are present in the aggregate.
(e) Water absorption is an important property when constructing roads and railways as it may affect the breakdown of material, particularly if the surface experiences dynamic loading. It is generally less important for fill placed beneath ground-bearing floor slabs when the load is relatively static. However, the presence of moisture is an important factor in the oxidation process, hence water absorption cannot be overlooked.

6. *Swell tests*

Swell tests have long been used to assess potential heave in the construction industry related to both pyritiferous fill used on building sites and lime stabilisation. However, they are not without problems; Notman (2011) assesses and criticises the BS 1924:1990 CBR swell test which is recommended in TRL 505. Swell tests generally only simulate conditions over a short period hence care must be taken when assessing the data obtained in terms of heave beneath floor slabs which may continue for many years. When pyritiferous rocks are being considered, the following points are particularly important.

(a) In order to obtain realistic results on pyritiferous material, it is essential that there is a continuous supply of oxygen, which can be inhibited if the test material is placed in an effectively impermeable container with the open base standing in water.

(b) In order to have international comparisons of swell test results it is necessary to ensure the uniformity of the test environment, as well as consistent water chemistry, temperature and humidity.
(c) Unrestricted upward movement of the fill, without frictional drag or other lateral impairment, should be ensured.
(d) The sample tested should be representative of the lithologies present in the general material and its chemistry at the commencement of the test must be properly established.
(e) Meaningful results can only be obtained if the material is placed in the swell mould within a very short time of its removal from its in situ conditions, i.e. it has not had time to experience stress release and/or suffer any oxidation. It is not realistic to compare the results from a swell test on fresh material with those obtained from material that has been beneath pavements/floor slabs for some time, such that the earlier (and possibly more dramatic) heave has already taken place (see Figs. 70 and 71).
(f) The chemistry of the sample should also be determined at the end of the test, to obtain an indication of the amount of sulphide which has oxidised. However, as noted above, it is too simplistic to assume that this can be related directly to either the total amount of heave which may occur in the future and/or the speed at which future reactions may take place.
(g) At the end of the test, the reason for the swelling should be established. This should take into account the influence of any swelling clay minerals, the thickness of the ferrous sulphate rim, the presence and nature of selenite crystals and whether gypsum-filled veins are present. In the latter case it is important to determine petrographically whether the gypsum has simply in-filled an existing crack or the vein has developed as a consequence of active/forceful growth.

7. *Shrink/swell*

It is well known that in many countries the ground level varies seasonally. With summer evaporation of the free and adsorbed water in the clay fraction, the unsaturated zone deepens and the ground shrinks; in winter the soil is re-hydrated and the ground swells.

(a) Such a situation will occur in pyritiferous materials if they are weathered and contain appreciable amounts of clay minerals, notably illite and smectite. It is important, therefore, to separate seasonal shrink/swell, which also causes extensive cracks in floor slabs and walls, from the continuous rise and ongoing/increasing distress caused by the sulphate-induced, irreversible expansion of a pyritiferous material.
(b) The author experienced an example of such a rise related to shrink/swell which occurred in 1976 (Hawkins 2013). A floor slab in a partially constructed building on the pyritiferous Oxford Clay rose by 37 mm in two months

(September and October) after rain following a particularly dry spell. It is for this reason that the NRA has a liquid limit threshold of 21 % for aggregate, although this is not a requirement in some other specifications.

(c) During the investigation of a distressed house in Dublin, X-ray diffraction indicated that 9 % of the clay minerals in the underfloor fill were interstratified illite:smectite. Although at this location the presence of 3 % pyrite and 10 % gypsum in the sample from beneath the ground-bearing floor slab indicated sulphate generation to be the significant cause of the heave, the likelihood that seasonal shrink/swell also played a part cannot be discounted.

Chemical Properties

1. Most rocks containing iron sulphides will have a low sulphate content if tested immediately after the sample is retrieved from its confined, saturated state. On exposure, oxidation begins very quickly (within days) hence caution is required in interpreting the results of tests undertaken some time later.
    - (a) Material containing pyrite should not be left stockpiled in the quarry where it is exposed to moisture and oxygen. This is particularly important if it experiences wetting and drying cycles, as these conditions are likely to accelerate the oxidation process. Tests have shown that > 3 % SO_4 developed in material stockpiled in Dublin over a period of some 30 weeks.
    - (b) A similar situation occurs if the material is stockpiled on a construction site and/or spread to produce a formation for the ground-bearing floor slab but not covered immediately.
    - (c) In the case of road construction, care must be taken to ensure that fresh material containing sulphides is not left exposed in cuttings and/or the fill forming embankments, particularly if lime stabilisation is to be undertaken.
    - (d) The temperature experienced by fill material is important as higher temperatures accelerate the development of sulphates.
        - i. The material may be exposed to direct sunlight.
        - ii. Houses are generally maintained at a relatively high temperature. This is particularly important if there is a floor-standing boiler, hot water pipes pass beneath the ground floor slab and/or there is an underfloor heating system.
        - iii. As noted above, the depth at which the material is placed influences the seasonal changes in temperature it will experience. This is significant in the formation of such minerals as thaumasite in both the fill and any contained concrete.

  - iv. Heat may emanate from a natural underground source, often associated with faults and/or master joints in the underlying rock structure. Locally, this may be evidenced by the presence of thermal springs (Hawkins and St John 2013a).
  - v. In a fill where the fine fraction is dominated by silt/sand grade particles the moisture will initially rise as vapour from the underlying saturated in situ material. When clay minerals are released as a consequence of the weathering of the aggregate, capillary rise via the adsorbed layers will become significant, hence the rate of moisture movement will be greater.

2. Sulphate values may be given as water soluble or acid soluble sulphate. Although many of the tests quoted in the Standards result in a value being obtained as SO_3, most of the literature now refers to SO_4 ($1.2 \times SO_3$). Many of the documents produced in the early 2000s refer to a threshold value but do not clarify whether it is given as SO_3 or SO_4.
3. Most of the commonly used laboratory tests identify sulphates but do not distinguish those which have developed from iron sulphides from those which have developed from other minerals contained in the host material. Of particular importance is the distinction between sulphates which have a low solubility (e.g. barytes) which may significantly influence the test value reported but are unlikely to contribute to heave or concrete attack.
4. The total potential sulphate (calculated as 3 times total sulphur) does not distinguish whether the sulphur is related to iron sulphide and/or other sulphide minerals which may be present in the test sample.

   - (a) Particularly in the very dark coloured rocks with a high carbon content, organic sulphur may be present. Organic sulphur is less problematic as regards concrete attack (Czerewko et al. 2003a).
   - (b) Where the sulphur is related to iron sulphide, it must be appreciated that this may be in various forms. The rate of reaction/formation of sulphate will depend on both the nature of the pyrite/pyrrhotite (cubes/lumps or framboids) and the size of the microcrystals/seeds.
   - (c) As the total sulphur test is undertaken on only a small quantity of material, even if properly prepared it is possible that it may contain a disproportionate amount of sulphide related to a single pyrite cube. In this case, it is highly unlikely that in the general fill, the calculated total potential sulphate will form within a relevant time period.

5. Extreme caution should be exercised when calculating the proportion of iron sulphides which have oxidised. It is now common practice to establish the oxidisable sulphides which remain in the host aggregate by deducting the acid soluble sulphate from the total potential sulphate. However, as noted above, there are considerable difficulties in establishing both the total potential sulphate and the appropriate acid soluble sulphate values.
6. Care should be taken in relating the proportion of material which has already chemically oxidised with the time it will take for the remaining sulphides to be

converted. Experience has shown that the oxidation process and the manifestation of heave is non-linear, hence it cannot be assumed that at a calculated point, all the expansion will be completed and/or the aggressive action on concrete will cease. The rate at which the chemical reactions take place is unlikely to be consistent while the extent to which they cause heave will depend on a number of environmental factors as well as the nature of the iron sulphides present.

(a) The first material to oxidise is likely to be pyrrhotite, if present. This may take place in a matter of weeks. Nicholson and Scharer (1993) suggest the rate of reaction with pyrrhotite can be one hundred times quicker than with pyrite.
(b) Fractured microcrystals, whether in framboids or as separate grains, will oxidise more quickly than unfractured, perfectly formed microcrystals.
(c) Unorganised framboids will oxidise and split apart more quickly than organised clusters.
(d) When the microcrystals and framboids are weathering, the formation of a ferrous sulphate rim may result in a slowing of the oxidation process, (depending on the presence and role of bacteria) and/or an increase in initial expansion.
(e) Iron sulphides not in the form of framboids will have a lower specific surface and hence will oxidise at a slower rate. In some cases these grains (cubes, lumps, octahedra etc.) will have fractured, which will affect the size of the oxidisable surface and hence the rate of degradation.
(f) The overall characteristics of the aggregate are important. As discussed above, the presence of laminations in mudstones and clay lamellae in limestone is particularly significant. The nature of the aggregate will also affect whether the formation of gypsum or jarosite accounts for all the sulphuric acid released or whether the groundwaters become increasingly acidic. This is particularly relevant for concrete and reinforcing steel. For this reason, most Standards have a different threshold value for assessing the potential for damage to concrete and/or corrosion of steel.

7. The calculation of equivalent pyrite is also used to assess the potential for further heave as a consequence of oxidation. As given in CTQ-M200 (2001) equivalent pyrite is determined as 1.87 × [total sulphur minus (0.334 × water soluble sulphate)]. It should be noted that the Canadian WSS is akin to the ASS used in UK and Ireland. NSAI 398:2013 now recomend equivalent pyrite = 0.623 × OS. The results are then related to the potential for swelling as shown in Table 13. If equivalent pyrite is used, for a meaningful result care must be taken to ensure (as far as practical) that the more stable sulphides and/or sulphates are not present/included in the results. When a material is obtained directly from the bedrock, i.e. soon after quarrying, it is likely that there will be very little sulphate and hence the material may appear satisfactory. With oxidation, however, ferrous sulphate and sulphuric acid are formed and subsequently calcium sulphate which will affect the result obtained.

Table 13 Relationship between equivalent pyrite and chemical swelling potential as given in CTQ-M200, 2001

Pyrite equivalent (%)	Chemical swelling potential
0–0.5	Negligible to low
0.5–1	Low to medium
1	Medium to high

8. As noted above, due cognisance must be taken of the location from which the material is sampled. Sulphates can be mobilised and concentrated related to the heat of hydration when concrete is placed in the ground and the presence of a general or localised heating system. In a greenfield situation, the presence of a natural ground heat source, seasonal groundwater levels and the presence of trees etc. will influence the location and concentration of sulphates.

Recommendations

This chapter has discussed the significance of the oxidation of iron sulphides, with particular emphasis on the potential for sulphate-generated heave and the movement of sulphates into concrete. In the context of aggregate placed beneath ground-bearing floor slabs, the following recommendations would reduce the potential problems for new build and remediation projects.

1. Builders are advised to order only inert fill. To meet this requirement and provide effectively inert material, suppliers should be able to demonstrate the chemical characteristics in Table 14 as well as the physical properties given in documents provided by such appropriate authorities as the Highways Agency in the UK and the NRA in Ireland. If these criteria are met, the material would fall into the category of negligible to low risk in CTQ-M200 (2001).
   (a) The supplier should be able to demonstrate that a minimum of ten total sulphur, acid soluble sulphate and water soluble sulphate tests have been undertaken. In each case the average of the highest two results should be considered the representative value to be compared with the thresholds in Table 14.

Table 14 Suggested threshold values for acceptable sulphur/sulphate levels

Test	Threshold	Comment
Total sulphur	<0.2 % S	Takes account of the presence of pyrite and/or pyrrhotite and gives a maximum total potential sulphate of 0.6 %.
Acid soluble sulphate	<0.2 % SO_4	Is consistent with current practice in the UK and Ireland for material placed within 0.5 m of concrete.
Water soluble sulphate	<0.3 g SO_4/litre	A low value but an important early indication that sulphides are oxidising.
Oxidisable sulphide	<0.3 % SO_4	Total potential sulphate (i.e. 3 × total sulphur) minus acid soluble sulphate.

   (b) The tests should be undertaken on a regular basis. It is likely that this will be every month or every 1,000 t but confirmatory tests should be undertaken whenever a new part of the quarry/new horizon is to be worked.
   (c) If material is stockpiled in a quarry for more than a month it should be retested, such that purchasers can be assured that the test certificates are current for the material as sold.
2. Clearly, in some cases the criteria in Table 14 may not be met but the material still be satisfactory for use beneath ground-bearing floors slabs. The characteristics in Table 15 may allow material which does not meet the thresholds in Table 14 to be accepted, based on an informed judgment undertaken by a consultant/engineer suitably experienced in pyrite problems. Accelerated testing may assist this decision.
3. The consultant/engineer acting for the supplier must ensure that the samples submitted for petrographic study are properly representative of the material produced by the supplier and take into account material within or adjacent to faults/sulphide-rich veins. It is important that these further studies are undertaken by a petrographer who has a background of experience related to sulphate-generated heave and concrete degradation.
4. The design of the building can be modified to accommodate the use of material otherwise deemed unacceptable/marginal for placement directly beneath a ground-bearing floor slab. Such design modifications may include the use of suspended floors, rising walls which are smooth-sided/covered such that fill cannot adhere to the wall, the use of a void former to absorb lateral pressures, minimising any potential warming of the fill from the heating system etc.

When making a judgment, the consultant/engineer should take into account all the available information and appreciate that the rate and extent of any heave will depend on a number of different factors, including environmental considerations which will vary from country to country, site to site.

Summary/Conclusions

The chapter discusses the origin of iron sulphides, which are found in most rocks, highlighting the significance of pyrite and pyrrhotite. These minerals can oxidise in the presence of moisture and oxygen; the associated chemical reactions resulting in expansion and the potential for degradation of concrete. Engineering construction can initiate/accelerate these natural chemical processes by changing the environment, e.g. exposing fresh (unoxidised) material and/or changing the groundwater level.

While the early literature from Canada and the UK largely reported distress in structures placed on pyritiferous bedrock, the recent problems in Ireland have largely been caused by the use of aggregate containing pyrite/pyrrhotite as fill beneath ground-bearing floor slabs. Pyrrhotite has now been identified in the north

Table 15 Characteristics which should be considered in a petrographic examination

Characteristic	Area of interest	Comment
Nature of the iron sulphides	Presence of pyrite/pyrrhotite	Pyrrhotite reacts more quickly; some sulphides are effectively non-reactive
Type of pyrite/ pyrrhotite	Cubes/lumps or microcrystals/ framboids	Affects specific surface and area available for oxidation; microcrystals/seeds react more quickly
Presence of other sulphides/ sulphates	Organic sulphur/stable minerals (barytes etc.)	May affect chemical results but not be problematic as regards heave/ concrete attack
Cubes/lumps	Fractures, surface irregularity	Affects area available for oxidation
Microcrystals/ framboids	Size	Affects rate of oxidation
Framboids	Ordered/disordered; tight/open	Affects rate of oxidation
Microcrystals	1. Shape, defects (e.g. strain shadows)	Affects rate of oxidation
	2. Euhedral/fractured	Affects rate of oxidation
	3. Single crystals or themselves framboids	Affects rate of oxidation
Pyrite/pyrrhotite in the fine fraction (<0.25 mm)	Proportion in fine fraction	Pyrite/pyrrhotite commonly more abundant in the fine fraction and more readily oxidised than that contained in larger fragments
Evidence of oxidation	Presence of oxidation products; degradation of crystals;	Indication that oxidation has taken place/ potential for ongoing reactions
	Alteration rim largely ferrous sulphate or reduced to iron oxide	Initial expansion may be less likely to be ongoing
Presence of calcium carbonate	Sufficient proportion for the formation of significant gypsum	Necessary component for production of gypsum; affects acidity, activity of bacteria
Presence of gypsum	Amount and nature in fine fraction and/or fragments, infilling veins etc.	Indication of expansion/potential for concrete attack; Infilling veins (passive) or isolated crystals/props (expansive)
Presence of clay minerals	Ubiquitous or in lamellae/ bands	Affects de-stressing, rate of ingress of oxidizing agents
Presence of expanding lattice clay minerals	Likely to require X-ray confirmation following glycolation	Can cause expansion independent of sulphate-generated heave
Organics/carbon content	Abundance; any indication of graphite	Increases rate of oxidation and thaumasite generation

Dublin area and it is likely its presence is more common than is generally appreciated.

Pyrite/pyrrhotite occurs both as cubes/lumps and as framboids. During the quarrying process, the "lumps" of pyrite/pyrrhotite may be damaged. The resultant fractures create an increased surface area available for oxidation. As a consequence, cubes/lumps of iron sulphide, which are generally considered to be less reactive, may still give rise to sulphate-generated heave. The framboids vary significantly in size, purity and degree of ordering, which again affects the rate of oxidation. In addition, the microcrystals also vary in size and may be fractured; it is suggested such fracturing is related to tectonic disturbance.

The chapter emphasises that the extent of sulphate-related heave will depend on many factors including whether the iron sulphides were initially pyrite or pyrrhotite, the form and nature of the crystals/microcrystals, whether the host material is laminated, whether the ground/fill is saturated/unsaturated, the presence of calcium carbonate within the host material/aggregate, the pH, abundance of acidophilic bacteria, temperature etc.

Although ground heave of over 100 mm has been recorded in North America, most ground-bearing floor slabs in the Dublin area have risen by tens of millimetres. Again, while much of the literature records heave which has occurred after/over a number of years, one of the features of the Irish situation is the speed with which the reactions have taken place. In many cases, significant damage was recorded in the first two to three years after the deleterious fill was placed. Although some floor slabs have risen by 10 mm/year, typically the rate of rise is in the order of 4–7 mm/year.

The highly calcareous nature of the lithologies used for aggregate in Ireland is likely to be one of the reasons why ferrous sulphate rims are so widely developed compared with those where acidophilic bacteria are prolific. This initial expansion caused by the extensive ferrous sulphate development is particularly significant and is likely to be a major factor in the early manifestation of distress in the Dublin area.

In the boom period it was common practice in Ireland to install the ground-bearing floor slab over the whole of a house rather than in individual rooms between the rising walls. As a consequence, when heave occurred, in addition to spider cracking in the floor slab, the distress was passed upwards through the internal walls. Particularly where the dry lining rested on the floor slab, very extensive buckling and sudden severe cracking has been reported. In addition, lateral expansion has occurred in many structures, resulting in an outward movement of the lower part of the external walls.

A previously unrecorded effect of sulphate-generated expansion of the fill beneath ground-bearing floor slabs in Ireland has been the development of horizontal cracks around the perimeter and internal rising walls. In some properties, where the expanding fill gripped the walls it was able to lift the superstructure by up to 20 mm. During the remediation it has been noted that when the fill is removed and the associated expansion pressures eliminated, the superstructure has usually settled within a matter of minutes or hours such that only lateral unfilled bedding joints are visible.

Pyrite/pyrrhotite has also been found in the aggregate used in concrete/concrete blocks. Recent work in Canada has highlighted cases of distress in concrete due to the oxidation of pyrrhotite contained in the aggregate. In Ireland, to date the main problems with concrete appear to have been caused by the ingress of sulphates into the pore spaces, particularly in the case of concrete blocks. However, iron sulphides have also been identified in concrete aggregate.

The paper proposes some criteria to confirm an aggregate is effectively chemically inert and will not result in significant damage to a structure due to heave. It is appreciated, however, that where these criteria are not met, the fill may be deemed acceptable on the basis of further detailed petrographic analysis and informed engineering judgement. Nevertheless, attention has been drawn to the caution which must be exercised when interpreting both the physical and chemical test values of material which is not chemically inert.

Acknowledgments The author is grateful to Menolly Homes, Ballymun Regeneration, Dublin City and many others for agreement to use the photographs and information in the chapter. Particular acknowledgement is given to Mike Eden of Sandbergs who took many of the SEM photographs, Austin Murphy for his meticulous record-keeping and help with the data and Simon Powell for some of the photographic work. Much of the work in Ireland could not have been done without the help, encouragement and constructive criticism of James Lombard. I am also grateful for the assistance of Marcus Hawkins who prepared many of the diagrams and Tom St John who helped with the research and the manuscript. The contribution of past Ph.D students is acknowledged.

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