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Foreword

During the late 1980s/early 1990s, I was fortunate to lead an enthusiastic team of Ph.D. students undertaking research related to various aspects of ground chemistry, including the generation of sulphates. In 1992, I convened a meeting at the University of Bristol, which brought together a number of authorities interested in the effect of ground chemistry on construction. Some of the papers were published in *Ground Chemistry: Implications for Construction*.

Some 20 years after the 1992 Conference, in view of the problems which were occurring in Dublin it seemed apposite to organise a follow-up meeting which would consider specifically the oxidation of pyrite and the risks associated with the use of pyritiferous material beneath ground-bearing floor slabs and estate pavements. Rather than holding it in Bristol again, it was decided to have the symposium in Dublin. Trinity College offered to host this as part of their Trinity Week programme, when the University reaches out to the community with lectures and discussions on topics of public interest.

The meeting, held in April 2012, was attended by some 300 participants, including engineers, architects, builders and lawyers, as well as people who had personal experience of the problems created by sulphate-generated heave.

More than 10,000 houses known to have had, or currently experiencing distress in Dublin, were constructed using infill produced from the dark grey/black highly carbonaceous mudstones and limestones which form the interbedded geology of much of the Dublin Basin. Most of these rocks contain pyrite, either as cubes/lumps or as microcrystals which may be grouped together in framboids. The chemical reactions associated with the oxidation of pyrite frequently result in expansion, both when ferrous sulphate is produced and when the released sulphuric acid reacts with calcium carbonate to form calcium sulphate (gypsum).

The book provides a background to the formation of pyrite and the processes involved in its oxidation. It then considers appropriate sampling and testing to determine whether the material is suitable for use beneath ground-bearing floor slabs and in the vicinity of concrete. The nature of the problems which can occur is discussed, including examples of the development of distress in structures in Dublin. The ways in which pyritiferous material has proved problematic in Canada and the eastern USA are also presented. Finally, some current research into the possible influence of pyrrhotite (a more unstable form of iron sulphide), the nature of the microcrystals and the influence of ground temperature are discussed.

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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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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,

Pyrite
(cubic FeS_2)

Pyrrhotite
($Fe_{1-x}S$)

Marcasite
(orthorhombic FeS_2)

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*

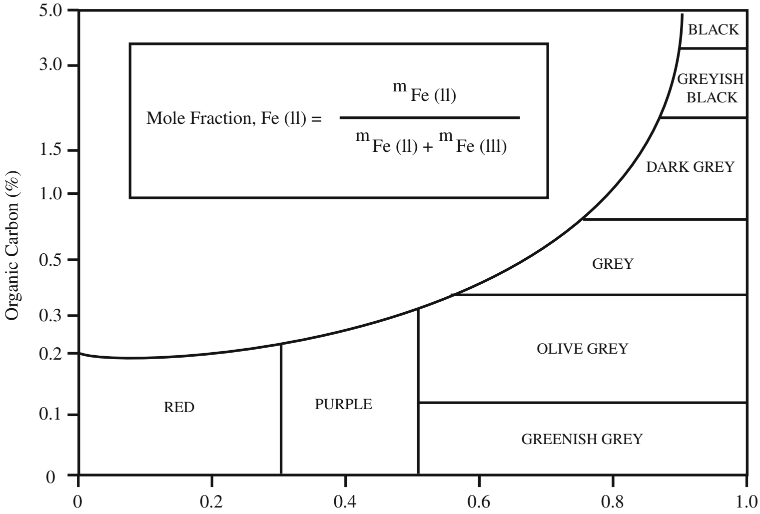


Fig. 2 The colour of mudrock as a function of the organic content and the Fe^{2+}/Fe^{3+} contents (after Potter et al. 1980)

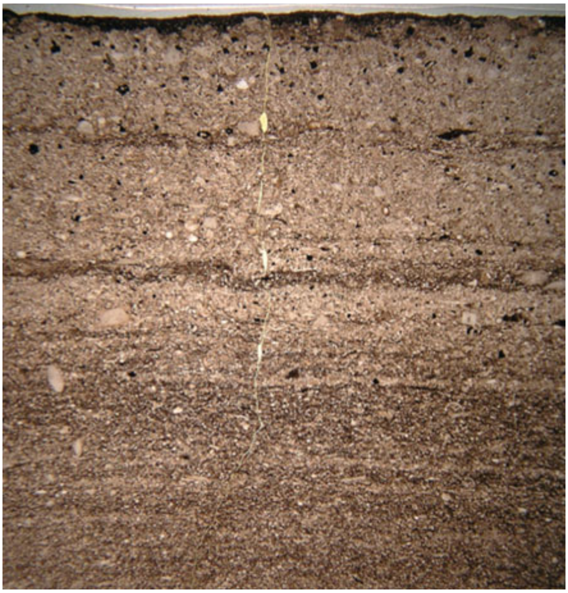


Fig. 3 Clay lamellae in calcareous mudstone/ argillaceous limestone (height of photo 25 mm)

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

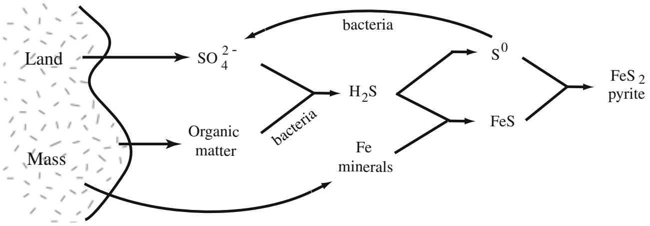


Fig. 4 Main steps in sedimentary pyrite formation (re-drawn based on Berner 1984)

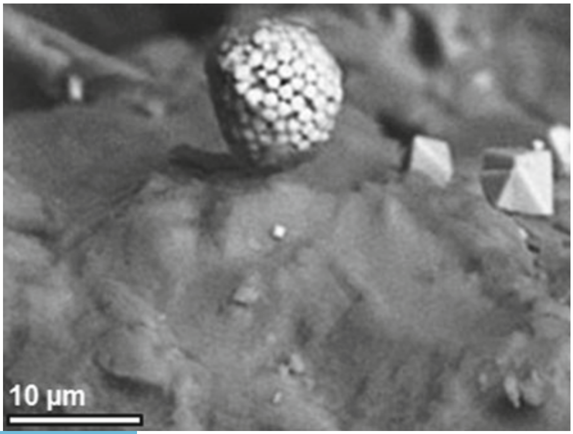
[e.g. pyrrhotite] *which during early diagenesis readily transform to pyrite under most conditions.*

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.*

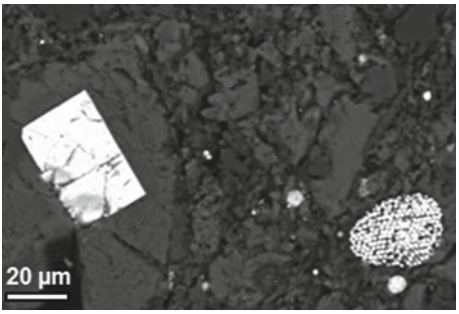


Fig. 6 Both cubic and framboidal pyrite in a calcareous mudrock sequence

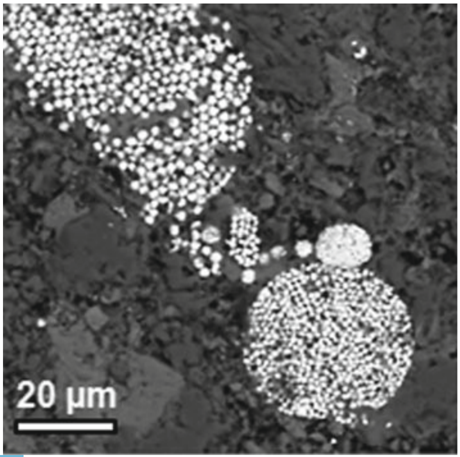


Fig. 7 Variously sized pyrite microcrystals in framboidal form

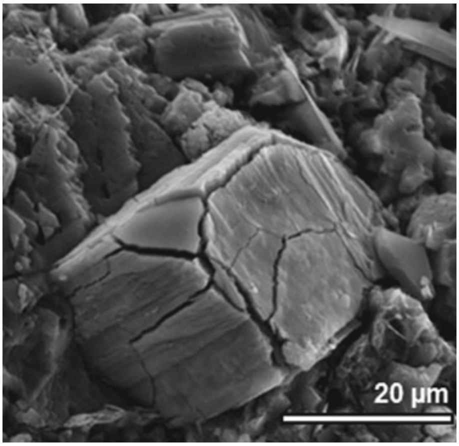


Fig. 8 Fractured lump of pyrite; note striae/corrugations on sides

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.

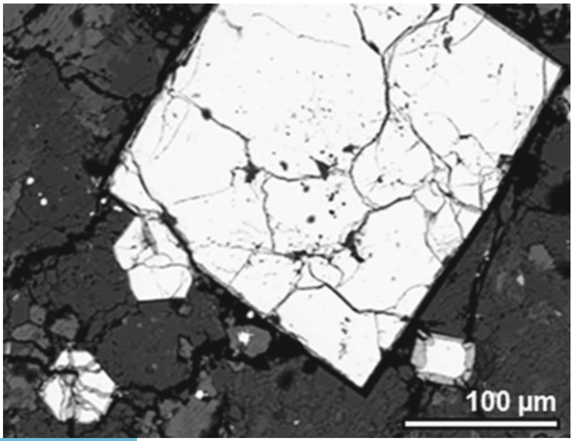


Fig. 9 Commencement of oxidation on fractures in pyrite cubes/lumps

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:

Fe_2O_3	+	$4SO_4^{2-}$	+	$8CH_2O$	+	$\frac{1}{2}O_2$	→	$2FeS_2$	+	$8HCO_3$	+	$4H_2O$
Ferric iron oxide	+	Sulphate	+	Organic matter	+	Oxygen	→	Pyrite	+	Bi-carbonate	+	Water

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

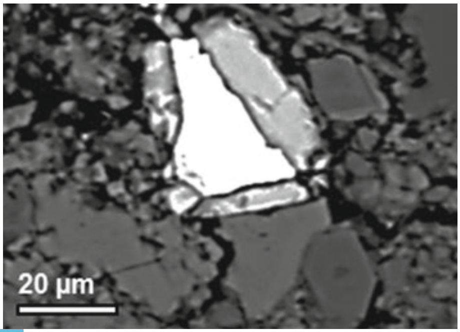


Fig. 11 Alteration on outer edges of a pyrite lump

Fig. 12 Pyrite lump oxidising along internal fractures

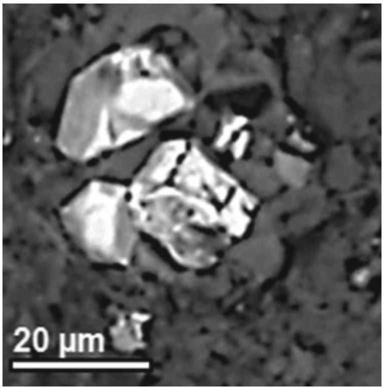


Fig. 13 Oxidizing framboid; note cracks in microcrystals and separation of the seeds in the outer part

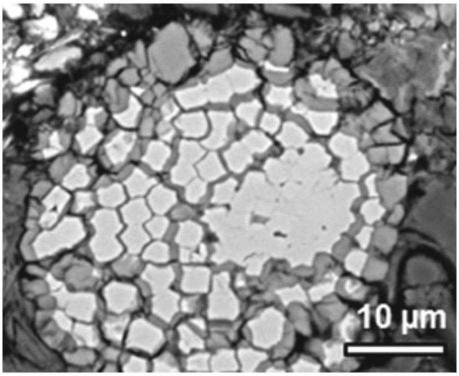
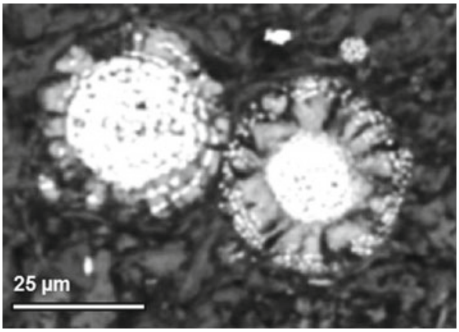


Fig. 14 Framboids showing varying degrees of oxidation and corresponding thicknesses of alteration rims; note seeds moved out as alteration rim formed



(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

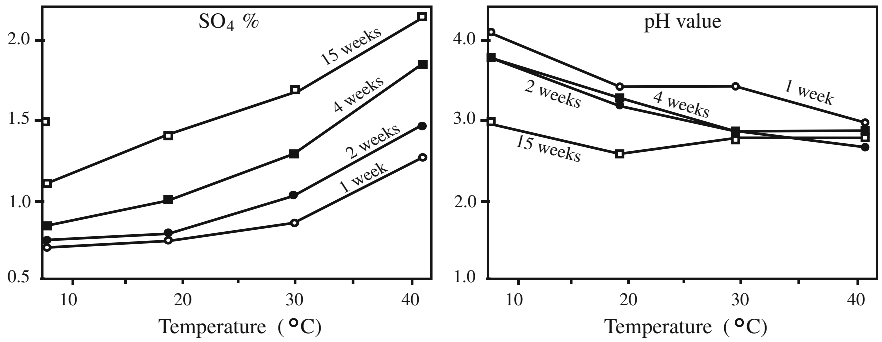


Fig. 15 Changes in acid soluble sulphate (%SO_4) and pH values at different temperatures; Westbury Beds samples from Chipping Sodbury (see Table 1)

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

Clay Formation	Pyrite %	Calcite %	Changes in acid soluble sulphate (% SO_4) 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.

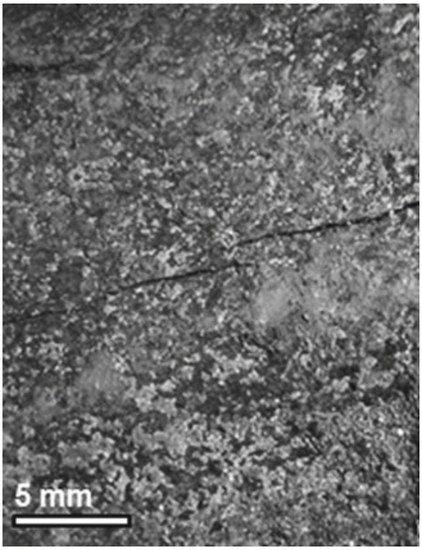
Porosity/Permeability

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

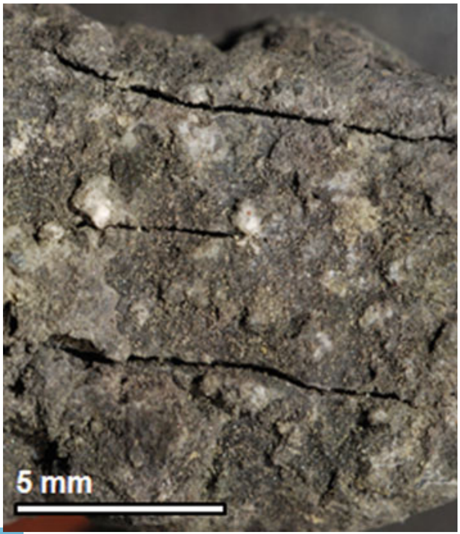
Fig. 16 Cracks developing in argillaceous limestone, Dublin



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

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

pyrite + water + oxygen → ferrous sulphate + sulphuric acid

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*

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

ferrous sulphate + oxygen + sulphuric acid → ferric sulphate + water

b) Oxidation of pyrite

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

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O \rightarrow 15FeSO_4 + 8H_2SO_4$$

ferric sulphate + pyrite + water → ferrous sulphate + sulphuric acid

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

$$Fe_2(SO_4)_3 + FeS_2 \rightarrow 3FeSO_4 + 2S$$

ferric sulphate + pyrite → ferrous sulphate + elemental sulphur

c) Generation of sulphuric acid

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

$$S + 1.5O_2 + H_2O \rightarrow H_2SO_4$$

elemental sulphur + oxygen + water → sulphuric acid

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

$$2S + 6Fe_2(SO_4)_3 + 8H_2O \rightarrow 12FeSO_4 + 8H_2SO_4$$

elemental sulphur + ferric sulphate + water → ferrous sulphate + sulphuric acid

3. Formation of gypsum

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4.2H_2O + CO_2$$

sulphuric acid + calcite + water → gypsum + carbon dioxide

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

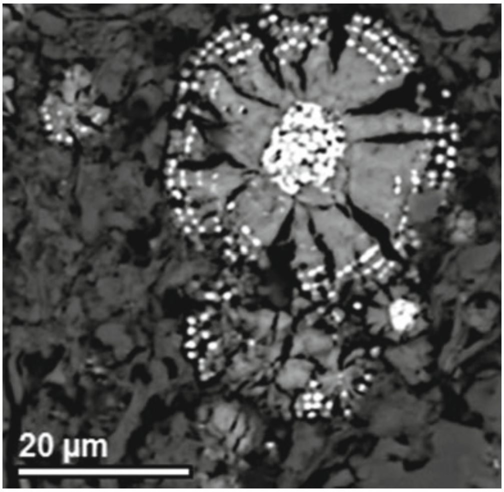


Fig. 19 Alteration rim around a framboid containing microcrystals moved outwards as the rim is formed (after Hawkins 2012)

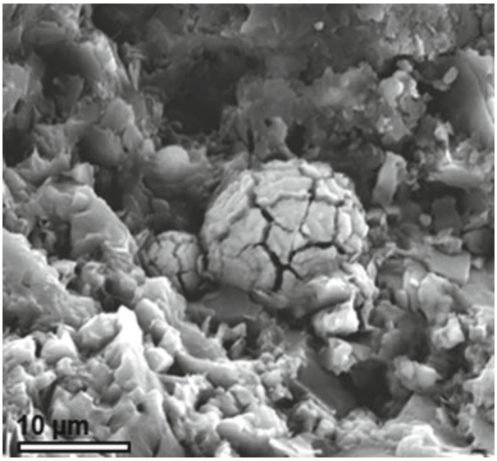


Fig. 20 3D view of alteration rim resembling a cracked sphere/football (after Hawkins 2012)

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

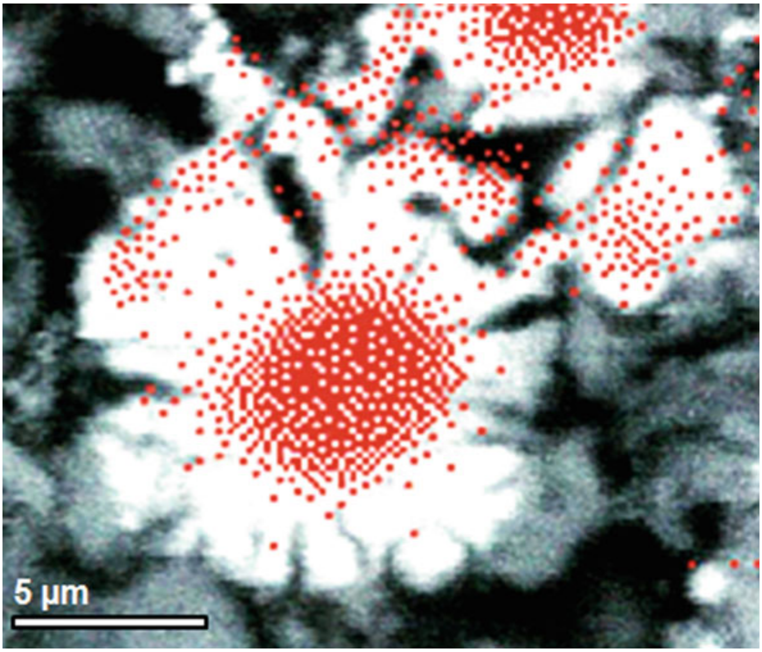


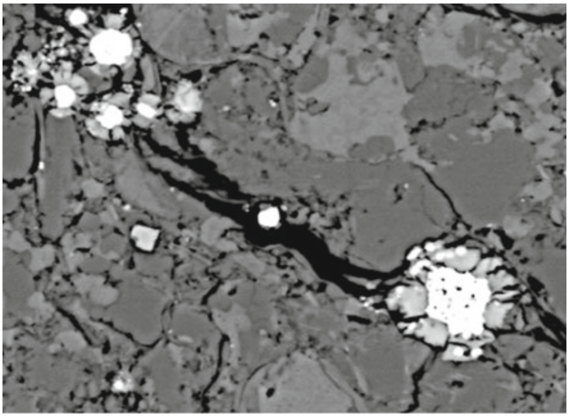
Fig. 21 X-ray map showing the oxidation product (*white*); some of the microcrystals are suspended in the alteration rim (the *red* indicating sulphur)

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

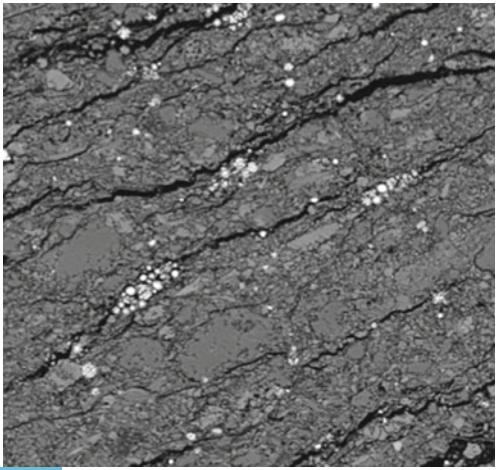


rim around framboids and its effect on the host mudstone. In these weaker strata the pressure exerted during the development of the ferrous sulphate rim is capable of fracturing the rocks, causing an initial dilation. In brittle rocks the framboids are often aligned, hence when they oxidise the resultant 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



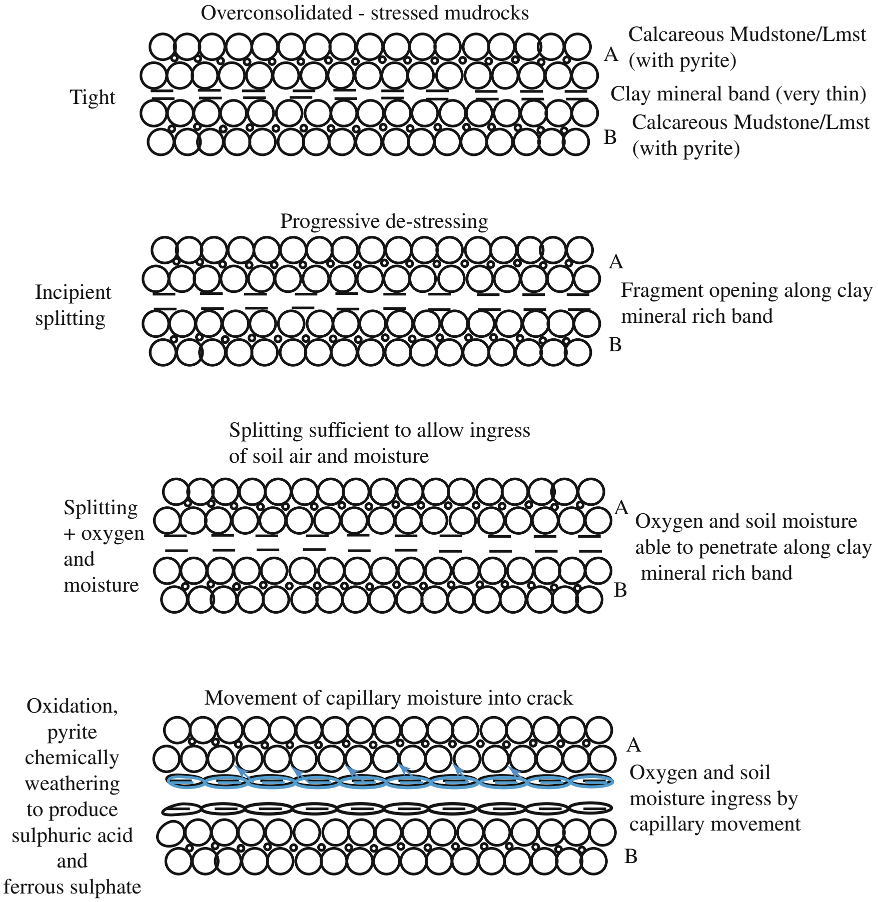


Fig. 24 Diagram to illustrate the progressive splitting of a relatively strong rock which includes very thin clay lamellae with pyrite/pyrrhotite (see Fig. 3)

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

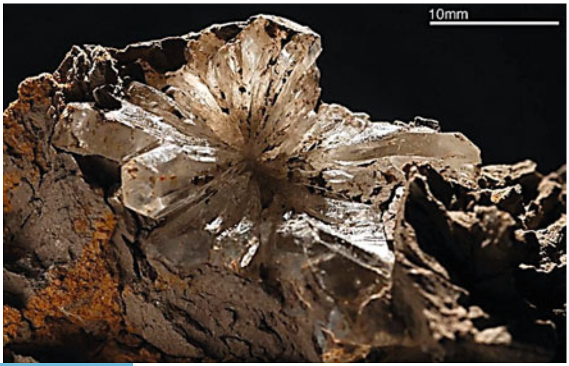


Fig. 26 Gypsum crystals from a 2012 site investigation in the London Clay (6–7 m depth)

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

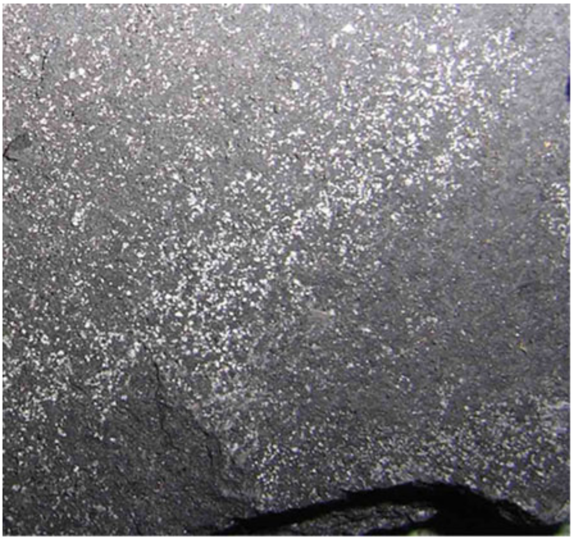


Fig. 27 Random growth of crystals exposed when lamination prised open (photo 40 mm)

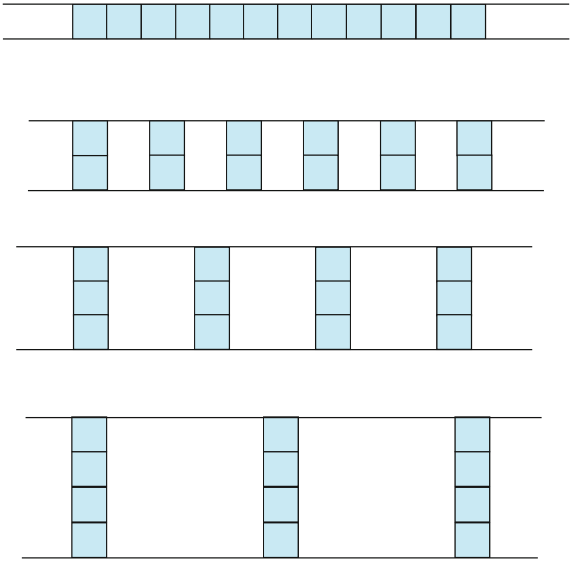
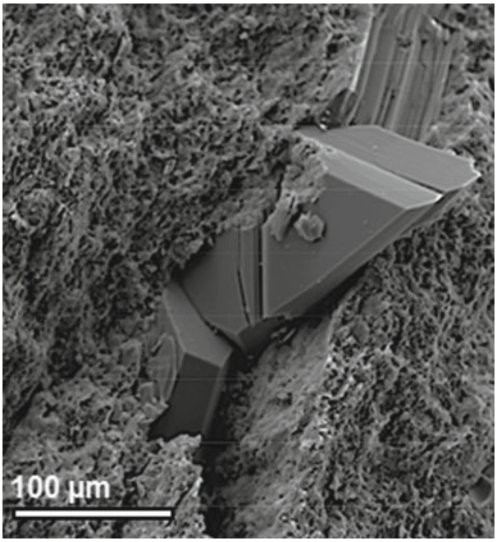


Fig. 28 Different amounts of dilation with same volume of gypsum

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

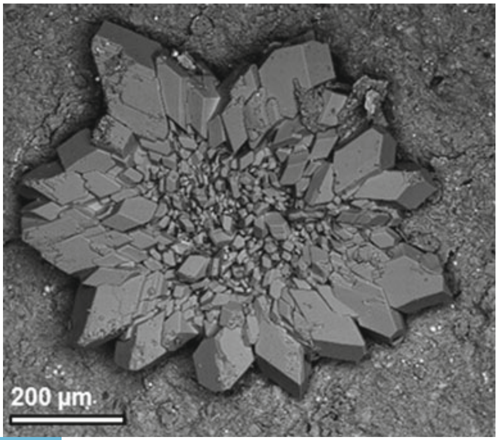
Fig. 29 Developing rosette pushing through the mudstone



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



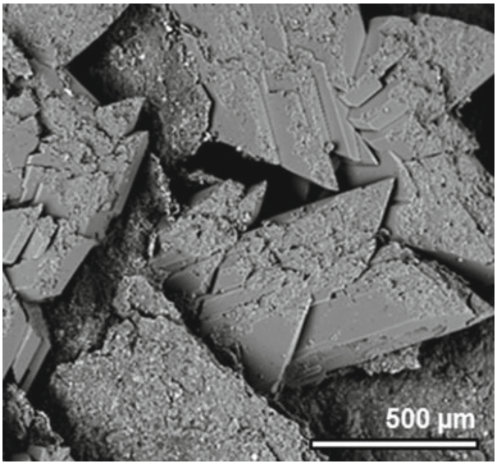


Fig. 31 Parallel-sided crystals growing in calcareous mudstone

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

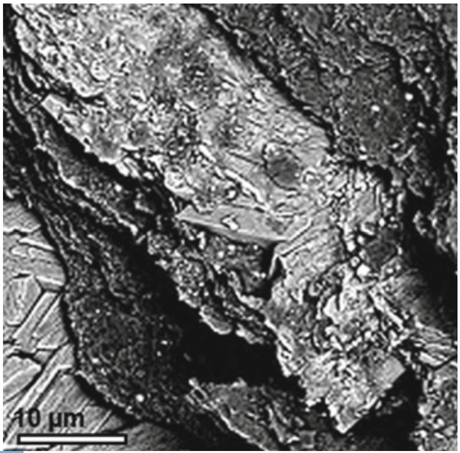
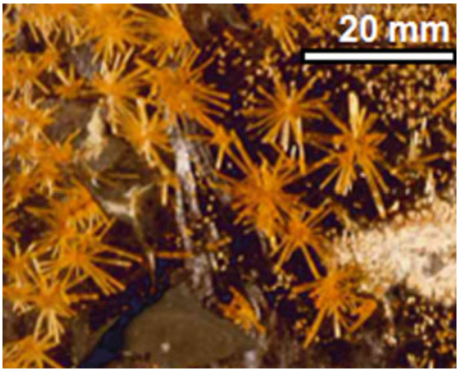


Fig. 32 Crystals growing at different levels within the calcareous mudstone (after Hawkins 2012)

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

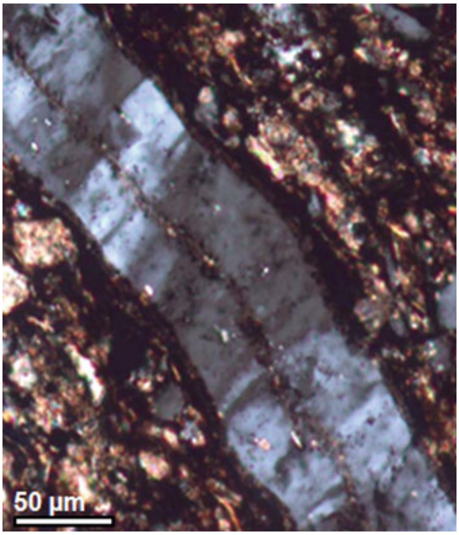


Fig. 35 Gypsum-filled vein; note median line

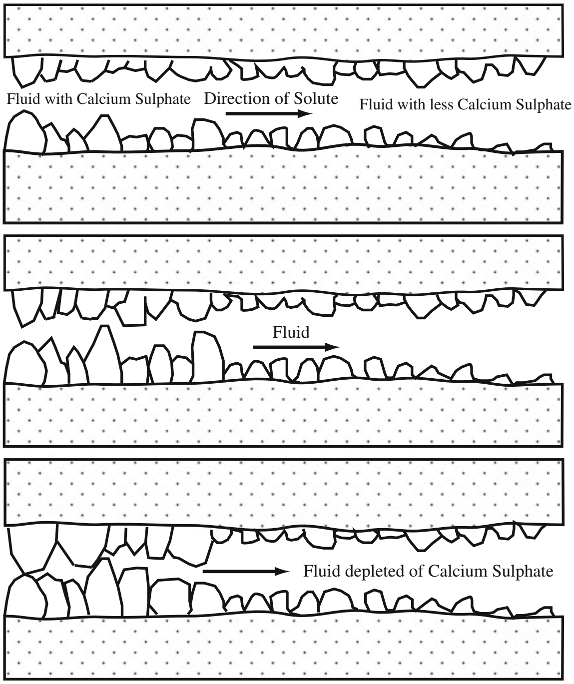


Fig. 36 Direction of solute and crystal growth (after Hilgers et al. 2003)

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.

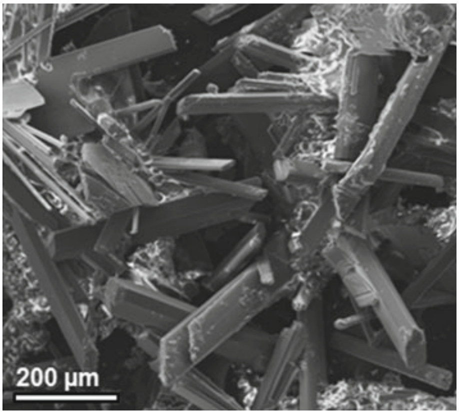


Fig. 37 Elongate gypsum crystals which developed after evaporation of 1 litre of water which had drained through pyritiferous fill into a borehole

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 *ferrooxidans* 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.

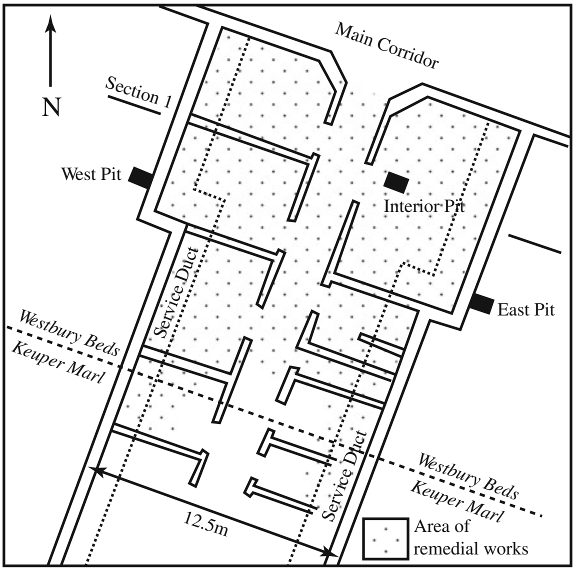


Fig. 39 Trial pit locations and areas remediated

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

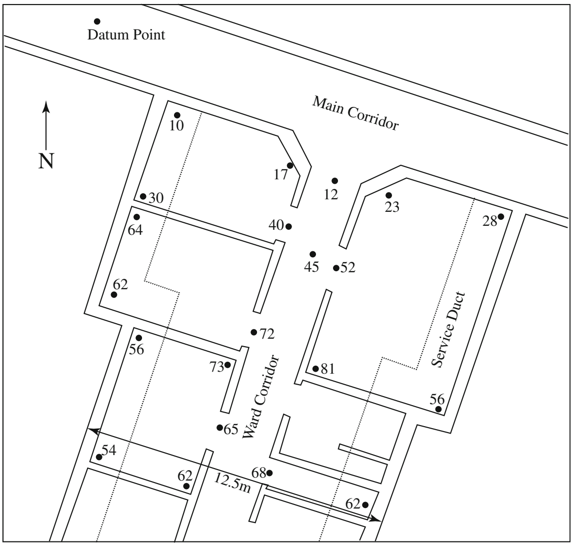


Fig. 40 Floor levels relative to datum set up in the main corridor

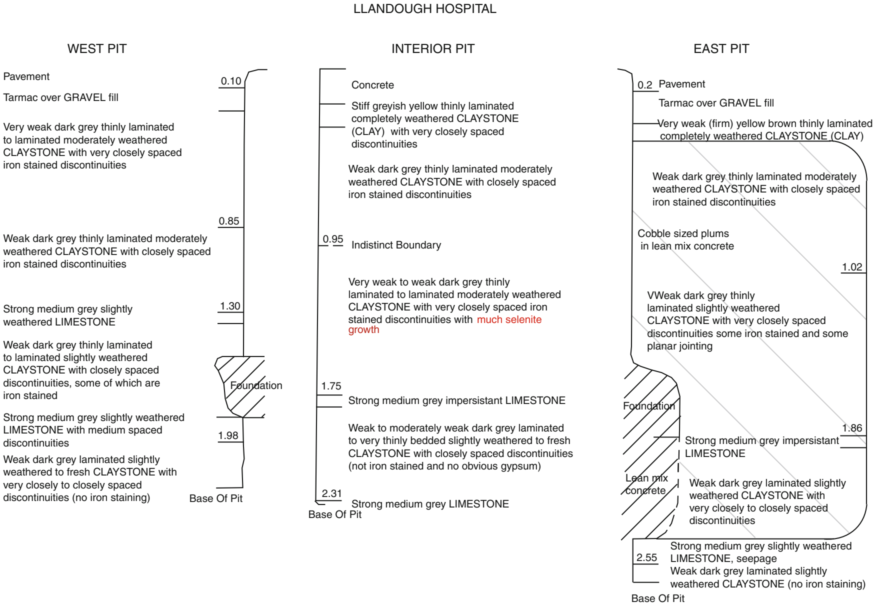


Fig. 41 Geological section across the wards showing the concrete placed in the 1950s and the zone of high selenite growth in the interior pit

Fig. 42 Crack in ward wall exposed when formica removed

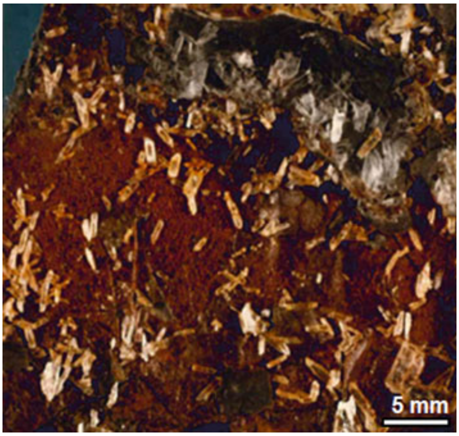


Fig. 43 Selenite crystals up to 8 mm long on a bedding surface at 1.6 m depth (Westbury Beds)

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

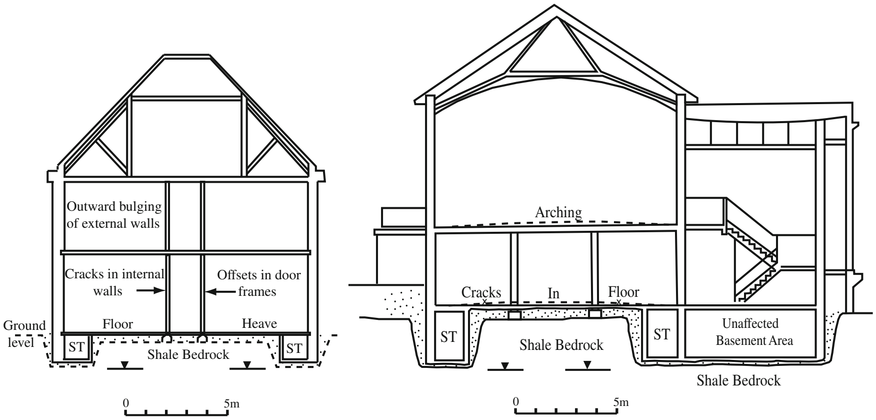


Fig. 44 Similarity between the layout of Llandough Hospital (*left*) and Rideau Health Centre (*right*); *ST* service tunnels

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

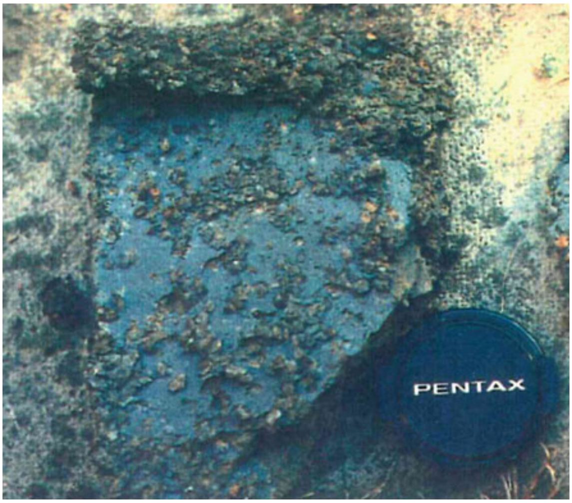


Fig. 47 Isolated gypsum crystals on Lias Clay exposed during the investigations

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).

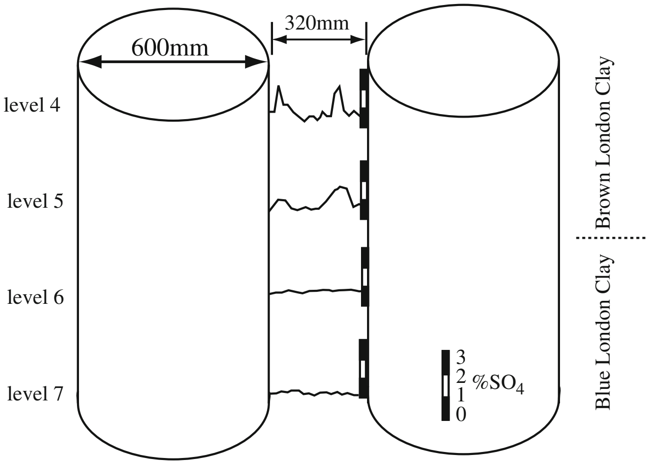


Fig. 52 Increase in sulphate content in the brown London Clay related to the heat of hydration when concrete piles were installed (after Hawkins and Higgins 1997a)

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.

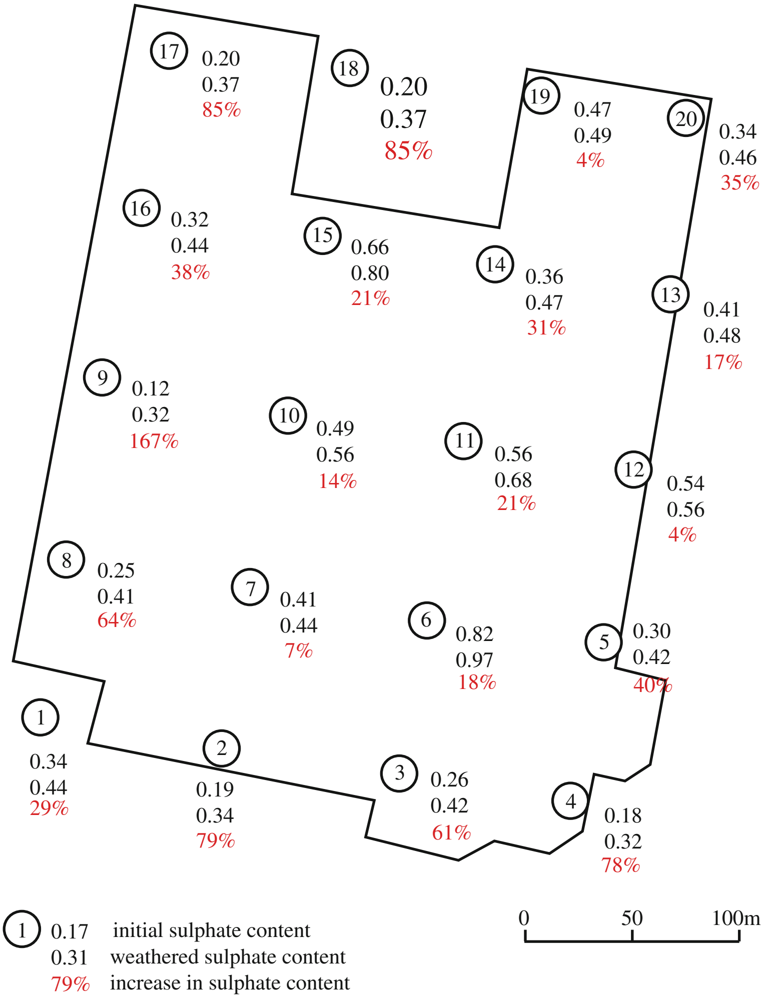


Fig. 53 Change in acid soluble sulphate when samples from 20 locations in the Ordovician mudrock/slates were kept in a moist oven at 30 °C for eight weeks

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.

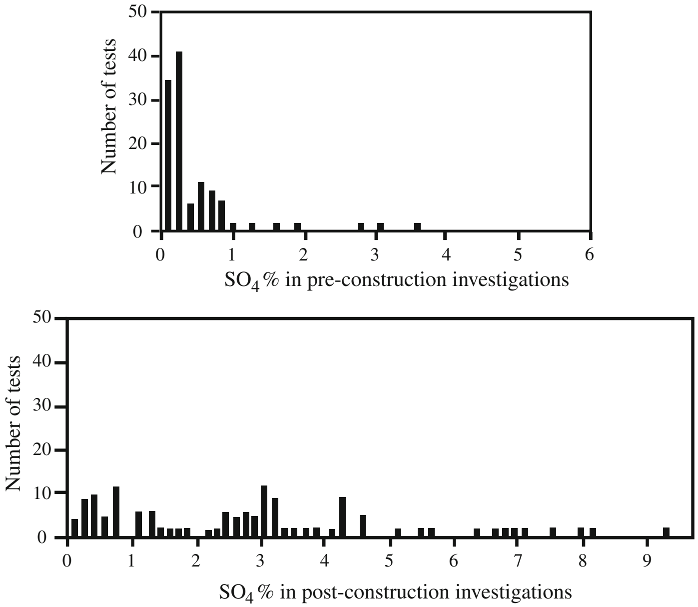


Fig. 54 Sulphate levels on the M40 determined before and after the earthworks (re-drawn after Snedker 1996)

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.*

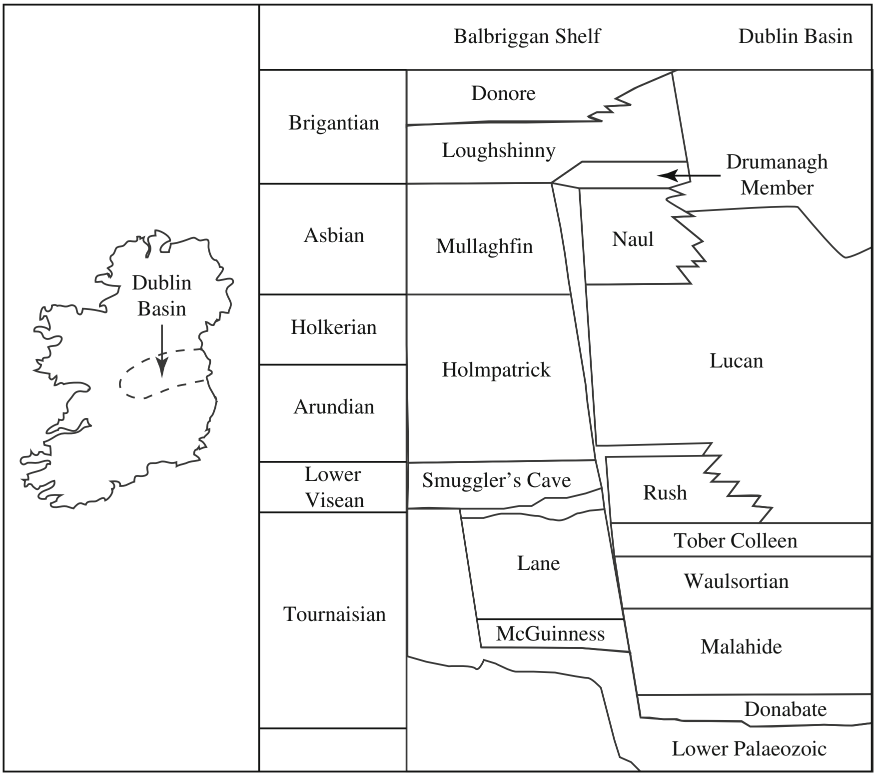


Fig. 56 Lithostratigraphy of the Dublin Basin area (after Kalvolda et al. 2011)

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

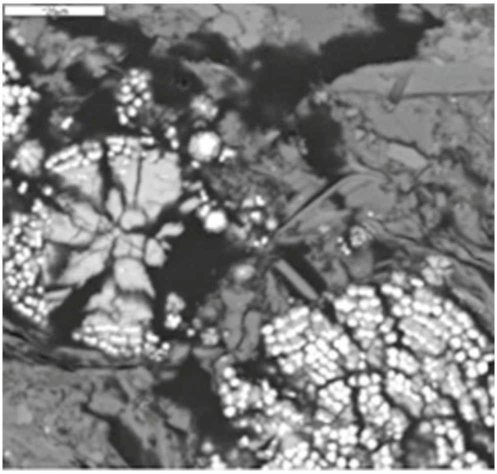


Fig. 57 Variable weathering of framboids in the fine fraction attached to concrete. Scale bar 20 μm

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

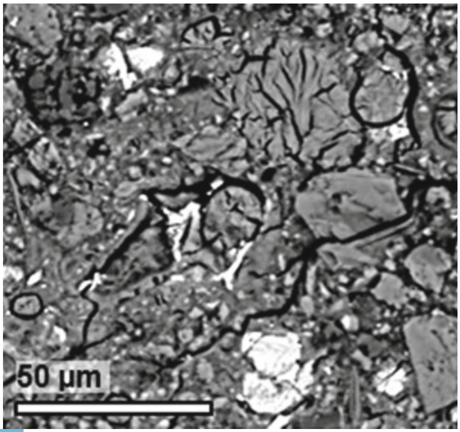


Fig. 58 Thaumasite infilling voids, 16 mm from the surface of a block where the SO_4 content was 10.9 %

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

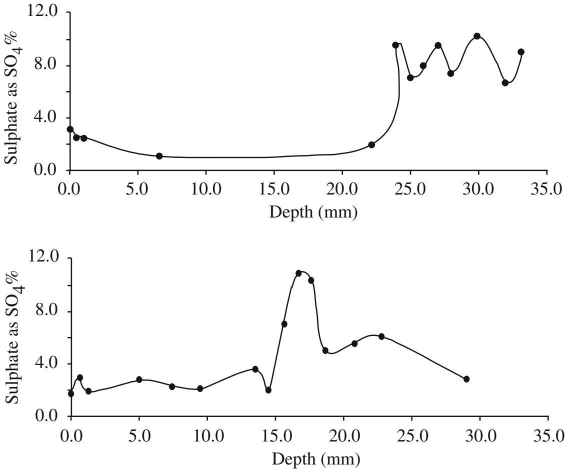
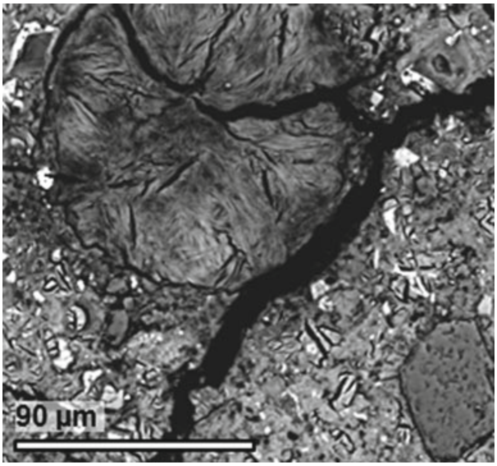


Fig. 60 Thaumasite infilling a void at a depth of 9.4 mm into a concrete block



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

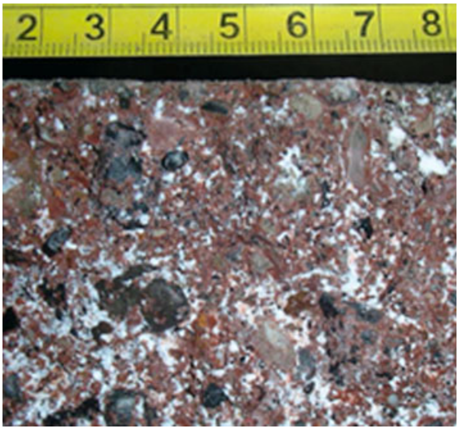


Fig. 62 Thaumasite exposed on a broken block close to that shown in Fig. 61

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).

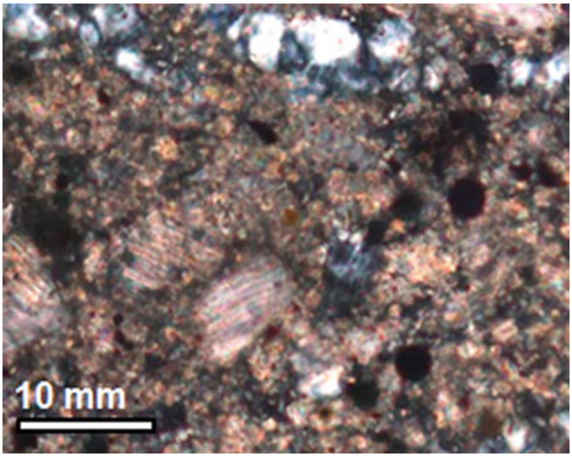


Fig. 63 Oxidised pyrite contained in fragments within concrete aggregate

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

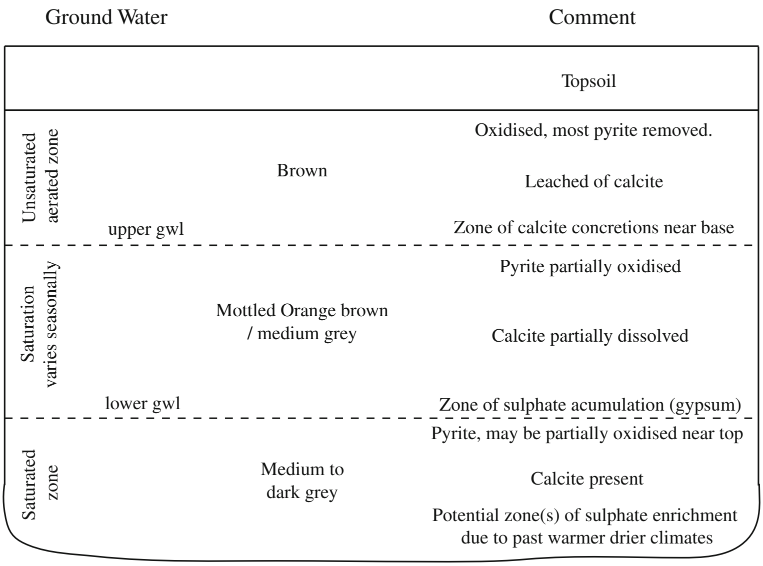
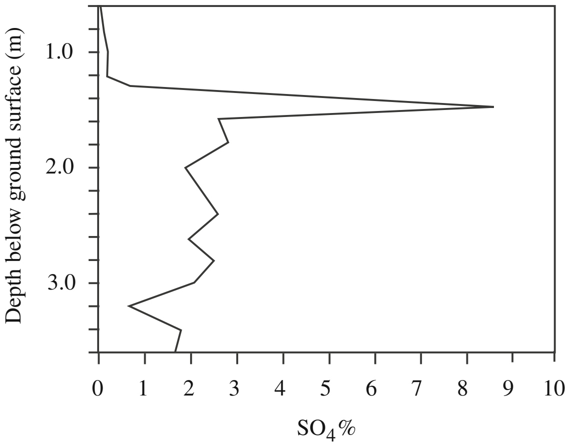


Fig. 64 Sketch illustrating the horizon which is likely to be enriched with sulphates

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

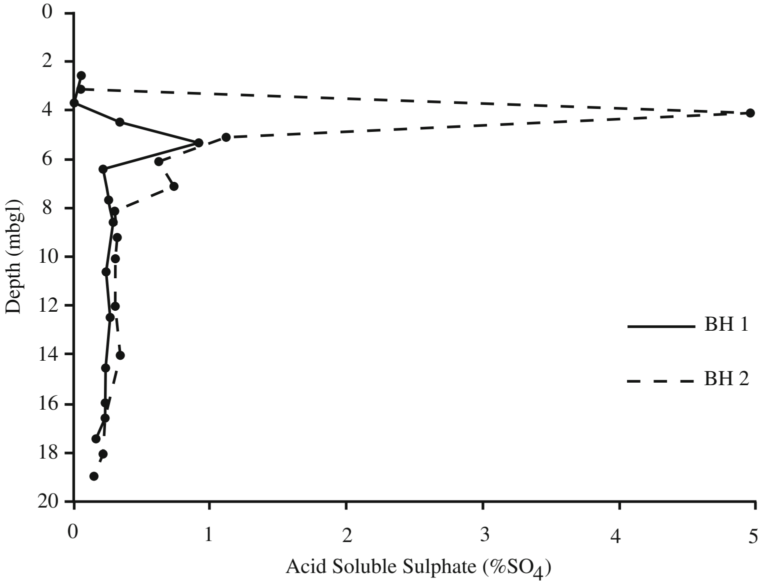


Fig. 66 Variation in ground sulphates between two boreholes within 35 m of each other in the London Clay in south east London

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.

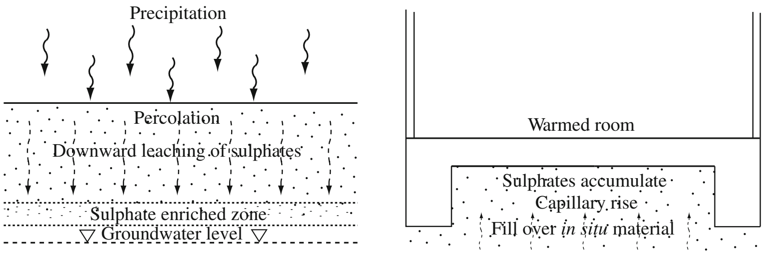


Fig. 67 Comparison of moisture movement in greenfield site and beneath a ground-bearing floor slab

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).

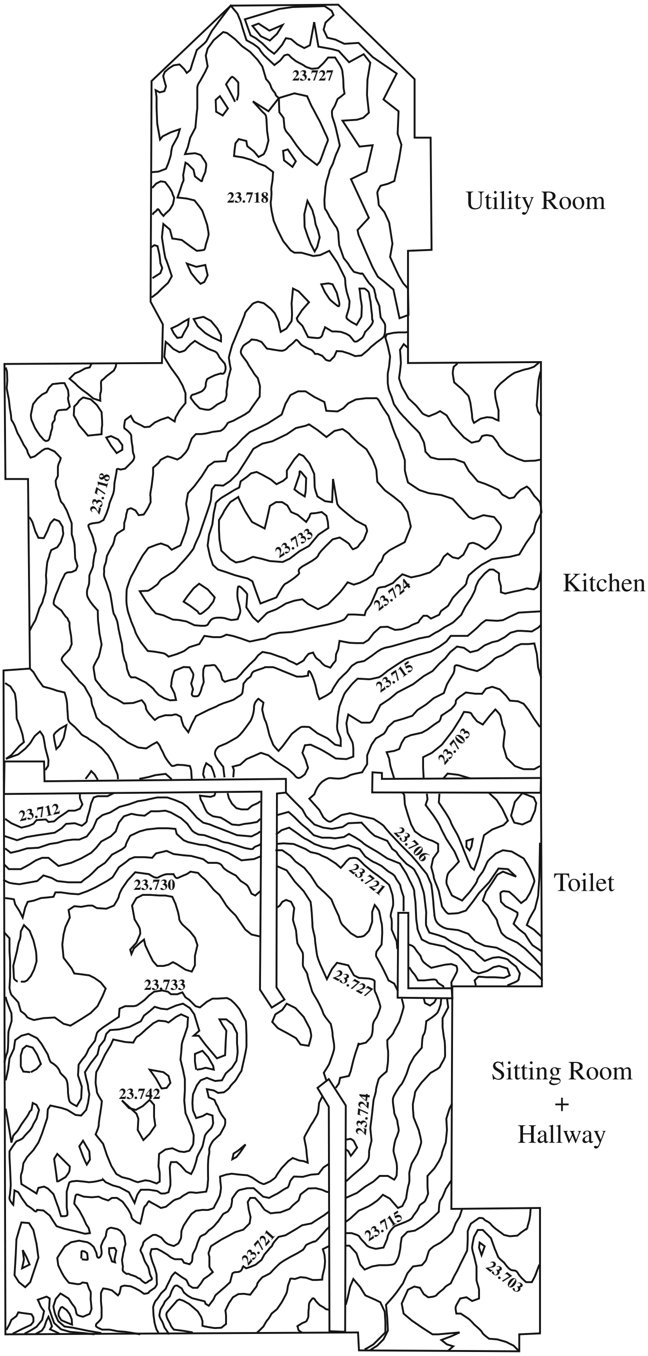


Fig. 68 Laser scan of a ground floor affected by sulphate-generated heave. Note the dome shape in the kitchen and the rise extending across the sitting room/corridor constructed on a single slab

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.

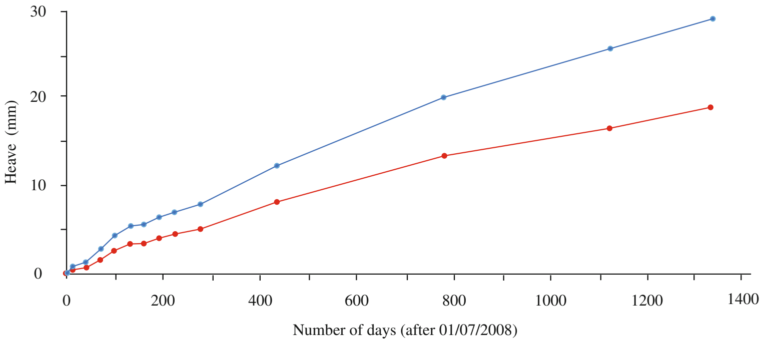


Fig. 69 Maximum rise (*blue line*) and average of the 160 monitoring points (*red line*) in same house. Slab laid February 2006

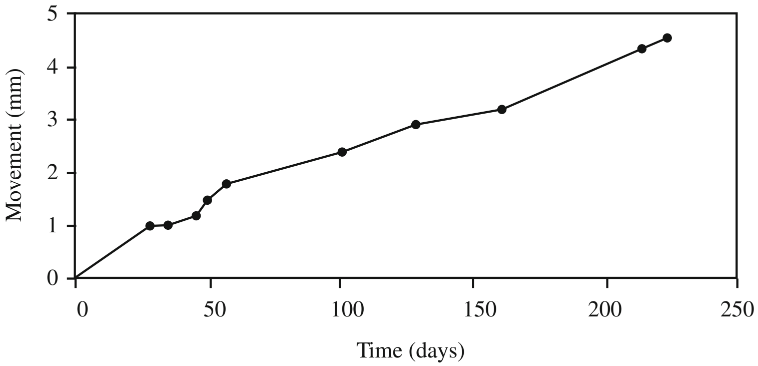


Fig. 70 Levelling of a point on a large reinforced concrete floor slab

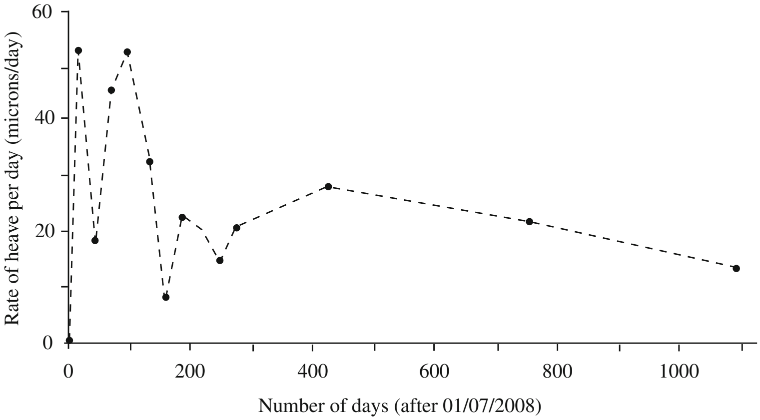


Fig. 71 Calculated notional average rates of rise per day for the blue line in Fig. 69

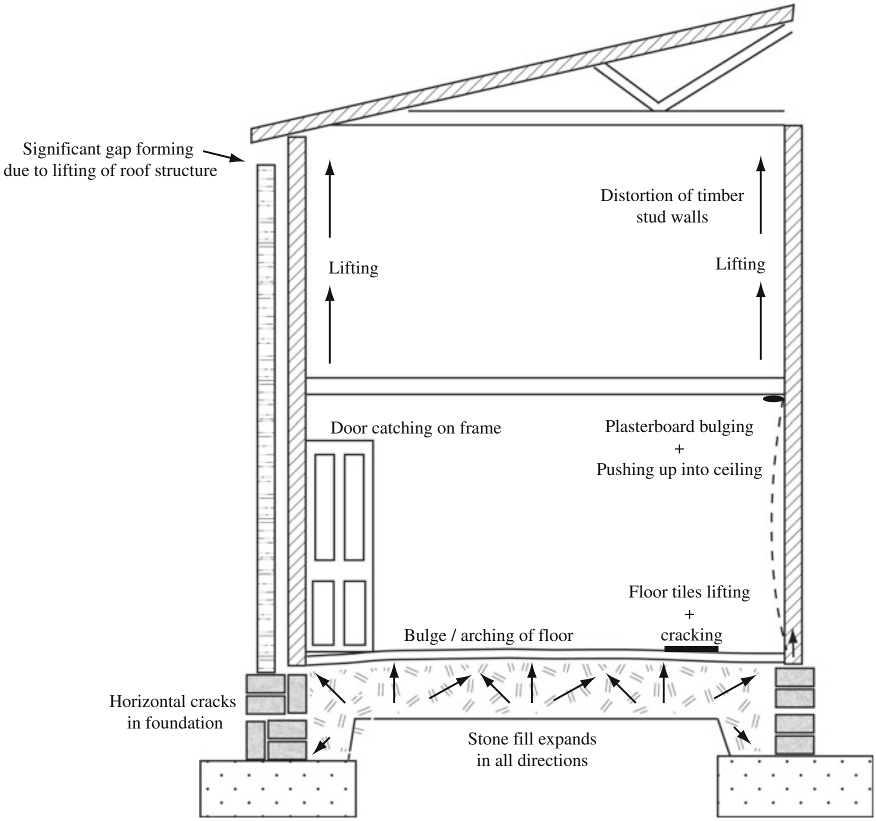


Fig. 72 Typical types of distress due to sulphate-related heave

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 re-tested, 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 largelly 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.

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Sampling Potentially Pyritiferous Materials

James Lombard

Introduction

Since 2006 it has become apparent that a number of properties in the Dublin area are suffering distress as a consequence of expansion of pyritiferous fill placed beneath ground bearing floor slabs. The location and method of sampling and the appropriate storage of the material are important in order to reliably determine whether such expansion has taken place and/or may take place in the future.

In many instances the distress is very obvious, with large cracks developing in dry-lined walls, doors jamming, floors and window cills arching etc. In others, the evidence is more limited, such that it could potentially be related to other causes. A further concern is for the structural integrity of concrete/concrete blocks which may be attacked by sulphates, although this is probably more problematic with larger structures than estate houses.

In the current climate, in order to put forward an insurance claim it is generally necessary not only to confirm evidence of damage to a property but also to demonstrate the cause. This is usually done by providing evidence that sulphates have developed in the underfloor fill and there is a potential for the associated chemical reactions to continue. Similarly, in order to obtain finance/insurance, a purchaser is commonly required to demonstrate that the property is "pyrite-free". Sampling may also be required when purchasers wish to establish the suitability of a potential aggregate material, particularly if a new quarry is to be opened, or if a new face/stratum in an existing quarry is to be worked.

This chapter discusses the sampling required to obtain appropriate material on which the necessary chemical testing and petrographic analyses can be undertaken, as described by Eden (2013). It draws attention to the ways in which important evidence can be missed or destroyed and how, without proper care, the samples acquired can result in misleading data.

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Sampling Locations

In order to allow a proper analysis of the nature of the fill beneath house floors, it is necessary to obtain samples which are representative of the fill mass, such that all the relevant characteristics can be assessed. It is desirable to obtain samples from areas where the distress has been greatest. Unfortunately this is invariably in the middle part of a floor and, in an occupied home, this may cause the owners some distress even if every attempt is made to minimise the disturbance to the finishes. In this case, a judgment will need to be made as to the most appropriate and practical location for the test pit/s. However, as seen in Fig. 1, it is clearly not appropriate to sample adjacent to or through the rising walls (external or internal) where the samples may be dominated by coarser (less mudstone-rich) material and the aggregate is likely to be less dense.

In most cases, one or two sampling locations will be sufficient to confirm a pyrite problem when distress associated with heave is evident in the property. However, as the pyrite will be present at random locations within the host material and will vary in its susceptibility to oxidation (and associated expansion), it is likely the Engineer will require at least two samples to confirm that the fill will not give rise to problems in the foreseeable future.

A number of different factors affect sampling locations in a greenfield site when the in situ ground is being assessed for potential sulphate problems. This is considered in Hawkins (2013) and hence is not discussed further here.

Where a new quarry is being assessed, it is important that the advice of an experienced geologist/engineering geologist is sought at the outset; they will be responsible for specifying the sampling regime. Subsequently, it will normally be recommended that visits are made to the quarry at regular intervals in order to confirm that the material being extracted has not changed significantly as different levels are reached and/or faces opened up. This will depend on the nature of the strata being exploited.

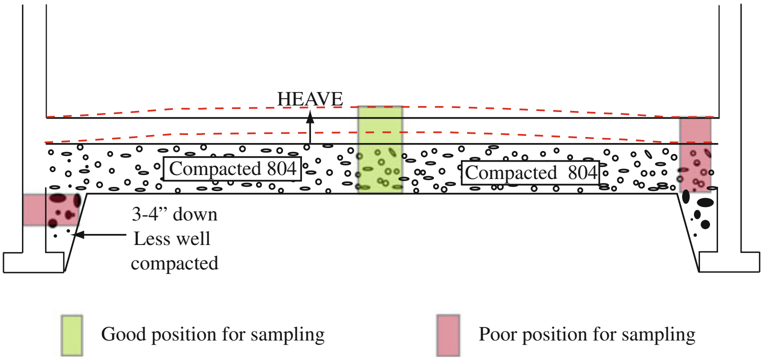

Fig. 1 Significance of locations for taking fill samples from below floor slabs

Sampling Methods

Wherever possible, in order to observe the nature of the fill, a small, approximately 0.5 m square, inspection pit is opened. If the property is empty, this can be undertaken using a kango hammer. When the property is occupied, it is generally better to break through the concrete floor slab using a series of c. 150 mm diameter perimeter holes to allow the central plug to be lifted out (Fig. 2). It is important that during the break-through and drilling the minimum of water is used, both to avoid any effect on the fill material and to reduce the disturbance to the home owners. The uncut membrane should be photographed and the date recorded.

It is essential that the sampling engineer is in attendance before the radon barrier is cut diagonally and carefully bent back such that it can be replaced and securely taped when the hole is reinstated (Fig. 3). The thickness of the concrete should be noted, and whether there is any reinforcement. The thickness of any sand (blinding) present should be recorded and very carefully scraped away as crystals of gypsum and/or calcite may be present directly below the membrane. Should any evidence of crystallisation be seen, samples will be taken for laboratory study. A photograph should then be taken of the exposed fill.

Fig. 2 Cored inspection pit with exposed membrane

Fig. 3 Membrane cut such that it can be securely taped back during reinstatement

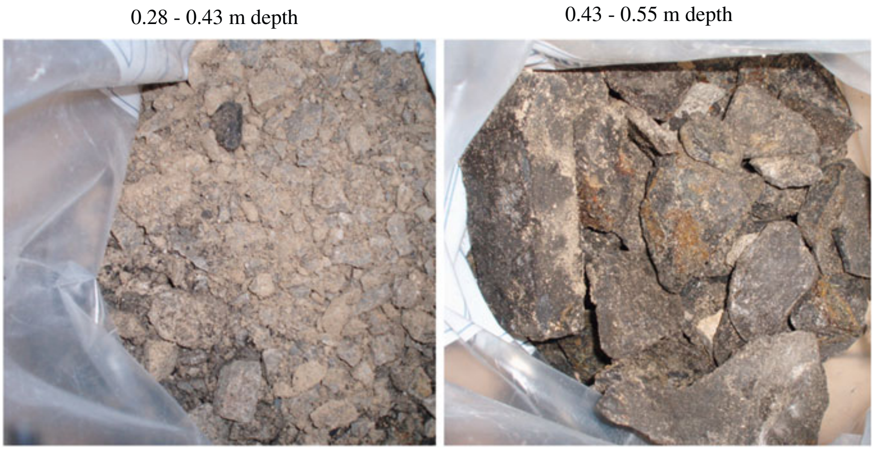

Fig. 4 Variation in fill taken from two different depths in the same inspection pit

The exact depth of the hole and extent of the sampling will depend on the nature of the material exposed. In general, coarser material (3–4″ down) is put into the trenches dug for the strip footings while the finer (Clause 804) material is commonly placed beneath the slab (Fig. 1). It is likely that the finer material will contain a greater proportion of mudstone and hence is likely to be the most problematic.

Any layering related to a difference in the placed material should be photographed and samples taken from each horizon (Fig. 4). The size and density of the fill should be visually determined as an assessment may need to be made as to whether the material was appropriately compacted at placement stage; a loose fill may result in settlement.

At all stages it is important to ensure that the individual fragments of the fill are not damaged or allowed to disintegrate during the sampling process as this will affect subsequent particle size distribution analysis. It is also extremely important to obtain the fine fraction as this will affect the liquid limit and plasticity results. If samples are collected by hand through a cored borehole, it is likely the "grabbed" sample will contain dominantly the coarser material in preference to the weaker/finer material. This will influence the Los Angeles and water absorption results.

Whenever possible, the pit should be extended to the underlying in situ strata and a sample taken from this material. However, this is often not practical during this investigation stage when the house is occupied. In this case, the approximate depth of fill can be determined using a hand held drill.

Size of Samples

Various Codes and Standards indicate the size of the sample required for various grades of material. Clearly, if a borehole is undertaken rather than a test pit it will be difficult to obtain a representative sample, particularly at depth. If coarse material is present it may be impractical to obtain a sample of the recommended volume/weight from an occupied home. In this case, it is essential that the photographs realistically indicate the nature of the fill such that an approximation can be made of the relative proportions of the gravel/cobble and smaller sized clasts. It should be noted that British Standards Institute (2002) recommends a 17 kg sample for coarse grained material (37.5 mm).

An appreciation of the recommended sample sizes is important if the testing may form part of the evidence in legal proceedings.

Number of Samples Required

In some instances the commissioning engineer will specify the number of samples required. This is most often the case when there is a dispute and in this situation the size of the samples and how they should be distributed between the various parties will also be a consideration. More frequently, however, the number and size of the samples will be determined on site in the light of the conditions encountered.

Although the blinding sand is not generally tested, unless there is some evidence that crystals are present, it is good practice to take a small (c. 200 g) sample in the event of subsequent information suggesting testing would be appropriate (Fig. 5).

Fig. 5 Blinding sand is carefully removed and a small sample taken immediately after the membrane has been cut and bent back

In general, two large (c. 15–20 kg) samples should be taken of each compacted layer where more than one can be identified, but as noted above, in some situations it may be particularly important to ensure the volume of material taken is appropriate for the size of the aggregate clasts.

Prior to reinstatement, the test pit should be photographed and logged.

Sampling Concrete

It is often necessary to take samples to establish the strength/quality of the concrete used in the floor slab and whether there is any reinforcement, as this will affect how heave is manifested in the property.

One cored sample will be required to assess the strength and composition of the concrete, including the proportion of cement and whether there is any evidence of pyrite in the contained aggregate. This sample may be one of the cores removed when the test pit was opened.

If cracks are present in the floor slab, it is valuable to take a sample including the crack. It can then be examined to determine whether it extends through the full depth of the concrete and/or is more open near the upper surface, which would indicate heave. A core containing a crack may also be requested in order to determine if there are sulphate minerals growing in the crack, which would indicate an unsatisfactory membrane between the fill and the concrete.

Testing of structural concrete in the foundations/rising walls may also be required. However, as this is normally specified during the remedial works, it is not discussed here.

Post-sampling

A drawing should be prepared detailing the property, room and location where each sample was taken and the date.

A test schedule will be drawn up reflecting both the site conditions and the requirements for the particular project. This may involve splitting samples between interested parties. After the samples have been logged, as much air as possible should be removed from the sample bags and they should be securely sealed and labelled. If they cannot be tested immediately, they should be stored in a cool environment (say 5–10 °C), away from direct sunlight.

Samples for immediate testing should be dispatched as quickly as possible and the laboratory notified, such that preparation for testing can be undertaken as soon as possible. This is extremely important as changes in the environment will affect the chemical reactions which take place in the material. Where additional samples are to be held for future use, the conditions in which they are to be kept should be agreed and recorded. At a minimum a cool environment away from direct sunlight is required, but instructions may be given for the material to be kept at a lower temperature and/or for the moisture content to be obtained and the sample then dried in an oven at in the order of 40 °C or air dried under a lamp.

Summary and Conclusions

This chapter has drawn attention to some important considerations when sampling potentially pyritiferous material, with particular reference to fill beneath structures which are showing evidence of distress. In order to ensure that the appropriate testing can be carried out and to minimise the likelihood of misleading results, a number of factors must be taken into account.

1. The location of the sampling points can directly influence the results obtained. Samples taken in warmer areas (near fire places, radiators, underfloor hot water pipes etc.) are likely to show enhanced gypsum growth compared with areas near rising walls where it is likely the temperature will be cooler and the fill less compacted. This information must be recorded.
2. Sampling should be undertaken from a carefully excavated inspection pit in order that:
    a. The nature of the concrete slab and whether it is reinforced can be determined;
    b. The full nature of the material can be visually assessed, including the thickness and density of the various fill layers;
    c. A suitably sized sample of material can be taken which is representative of the fill, including the coarse and fine fractions;
    d. The depth of the fill and where necessary the nature of the underlying in situ material can be determined.
3. Care should be taken to minimise any disturbance suffered by the sample as this will affect both the assessment of the material in its current condition and potentially accelerate further oxidation.
4. When samples of concrete are required to assess its quality, it is valuable if one of the cores can extend across a crack, if present. This not only allows information to be obtained on the strength/composition of the concrete but, if the crack can be seen to widen upwards, provides useful evidence that heave is taking place.

The positions of the inspection pits should be recorded and a log and photographs obtained. Samples should also be photographed and dated prior to the air being excluded and the bags sealed. Storage should be kept to a minimum as any changes in environmental conditions can affect the chemical reactions which may be taking place. When necessary, samples should be kept in a cool environment, away from direct sunlight, prior to transportation to the laboratory.

If additional samples are to be kept for future use, the conditions in which they are kept should be agreed and recorded. In most cases a low temperature will be required, or it may be decided that the moisture content should be obtained and the sample oven/air dried.

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Testing of Potentially Pyritiferous Material

Mike Eden

Introduction

The widespread occurrence of pyrite-related heave in buildings constructed with fill containing mudstone is of major concern in the Dublin area, Ireland. Most of the problems encountered relate to buildings constructed within the last decade, at a time when demand for aggregates was very high. A high proportion of the affected properties are domestic dwellings and there are several examples of entire housing estates that have required extensive remediation, involving the complete removal of the pyritic fill and replacement with inert material. The remediation process is both costly and highly disruptive to those involved. A typical example of the effects of pyritic heave on the walls of a domestic property in the Dublin area is shown in Fig. 1.

Heave related to pyritic fill is most commonly attributed to the growth of the sulphate mineral, gypsum ($CaSO_4.2H_2O$), on a microscopic scale within compacted pyritic mudstone (Penner et al. 1972). On exposure to air and moisture, sulphates are generated in abundance in pyritic mudstone, as a result of the oxidation of the pyrite. Calcium is readily available from groundwater saturated with calcium ions and from calcite contained within the limestones/calcareous mudstones generally present in the Dublin fill.

From the microscopic analysis of several hundred examples from the Dublin area examined by the author it is clear that the expansion responsible for heave results not only from gypsum formation but also from the expansive growth of alteration rims around the surfaces of pyrite framboids. The potential for heave seems to be exacerbated by mudstone with laminations and also by the presence of swelling sheet silicate minerals in pyritic mudstone.

Concrete foundations in contact with pyritic mudstone fill are often exposed to high levels of sulphate as a consequence of pyrite decomposition and moisture

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Fig. 1 *Horizontal* and *vertical* displacement due to pyritic heave in a domestic property in the Dublin area. The *vertical* displacement is of the order of 5–7 mm and the *horizontal* displacement is in excess of 10 mm

movement within the fill. It is therefore perhaps not surprising that sulphate attack has been identified in some concrete foundation structures backfilled with pyritic material and several cases of thaumasite-related sulphate attack in concrete have been encountered in the Dublin area, including the Ballymun Youth Facility.

It is clear that in order to assess the integrity and potential long-term durability of foundation structures containing potentially pyritic fill, consideration needs to be given to both the characteristics of the aggregate and the condition of the concrete foundations exposed to groundwater that may have percolated through the fill. The purpose of this chapter is to review the techniques required for the reliable analysis of potentially pyritic fill and for foundation concrete which is/has been in contact with such fill.

Laboratory Testing of Fill for Potential for Pyritic Heave

The Selection of Appropriate Test Methods

Many published standards, including the Irish Guidelines in SR21 (National Standards Authority of Ireland 2004, 2007), rely heavily on chemical testing for sulphur and sulphate, and basic physical testing including grading and soil index properties for the determination of the suitability of fill for use in construction. It is important, however, to bear in mind that as the mechanisms responsible for pyritic heave take place on a microscopic scale, testing for the susceptibility of fill to heave without the use of the microscope has the potential to give misleading results. For example, whilst it is possible to infer the presence of pyrite indirectly from chemical analysis for total sulphur and sulphate, it is not possible from the chemical analysis alone to determine whether the pyrite is in the more reactive framboidal form, whether it occurs as relatively innocuous pyrite cubes, or whether it is (in part) related to a less significant mineral.

Table 1 Laboratory techniques for the identification of risk factors for heave in fill beneath ground-bearing floor slabs

Risk factor	Definitive/preferred test method	Secondary techniques
Does the fill contain pyritic mudstone?	Petrographic examination	Electron microscopy
How much pyritic mudstone does the fill contain?	Petrographic examination	None
How much pyrite does the fill contain?	X-ray diffraction analysis of bulk sample	Electron microscopy/ X-ray microanalysis
Does chemical analysis of the sample show high potential sulphide >0.4 s	Calculation from measurements of acid soluble sulphate and total sulphur (total sulphur—sulphate sulphur)	None
Is the pyrite in a framboidal form?	Electron microscopy	Reflected light petrography
Is there evidence for pyrite decomposition generating sulphates?	Electron microscopy or petrographic examination	None
Is gypsum formation occurring in cracks or laminations?	Petrographic examination	Electron microscopy
Can pyrite decomposition be shown to be causing cracking?	Electron microscopy	Petrographic examination
Are there other factors that could be giving rise to heave e.g., the presence of swelling sheet silicate minerals?	X-ray diffraction analysis of clay fraction of fill	Index testing (LL/PL)

The risk factors that directly influence the potential for crushed rock fill to give rise to heave are listed with the appropriate test methods in the Table 1. This is based on experience gained from the examination of several hundred fill samples over eight years.

The use of a combination of test methods is essential for the reliable analysis of heave susceptibility as the results from each method of analysis can be considered in the light of the results from the other analytical techniques. For example, if high levels of pyrite are indicated by, for example, conventional chemical analysis, a combination of X-ray diffraction, electron microscopy and reflected light optical microscopy should be undertaken to confirm the extent and nature of the pyrite and its significance in foundation material and/or material in the vicinity of concrete.

Petrographic Examination

Sample Preparation Considerations

The standard test methods for the petrographic analysis of aggregates, such as BS 812, Part 104 (British Standards Institute 1994) or BS EN 932-3 (British Standards

Fig. 2 A typical fill sample containing a range of rock types including pyritic mudstone, limestone and phyllite; note the difficulty in visually distinguishing the different rock types

Institute 1997), rely on hand sorting of aggregate samples with or without the use of thin sections to provide verification of the rock types. Analysis of this type has the potential to give misleading results for the following reasons:

(a) The rock types commonly encountered in the Dublin area are very fine grained and cannot always be reliably distinguished visually (Fig. 2).
(b) It is often on the surfaces of the fill particles in the fine fraction that the deleterious effects of pyrite alteration are most likely to be seen.
(c) Although washing may improve the visual identification of the rock types, it is likely that degraded fill particles and fines will be lost during that process.

For these reasons it is important that when carrying out petrography on fill samples, the thin section examined with the petrological microscope represents the full sample, including the possibly degraded finer material.

For the analysis of a representative sample, the preferred method of sample preparation for petrographic examination of pyritic fill involves laboratory crushing of an air-dried subsample. The procedure is summarised as follows:

(a) The initial subsample of around 1.5 kg is obtained by riffling from a much larger sample weighing around 15 kg. This is then crushed to pass 5 mm.
(b) The laboratory crushed material is then air dried.
(c) The size fraction examined petrographically is that retained on a 0.25 mm sieve but passing a 5 mm sieve. The size fraction passing 0.25 mm is separately examined with the electron microscope.
(d) The prepared thin section subsample is embedded in epoxy resin prior to preparation of a thin section suitable for analysis with the petrological microscope. Figure 3 shows a petrological photomicroscope which has the capability to operate in both reflected and transmitted light modes. Figure 4 illustrates a typical 50 × 70 mm thin section.

Fig. 3 Example of a research-grade petrological photomicroscope suitable for examining thin sections of pyritic mudstone fill

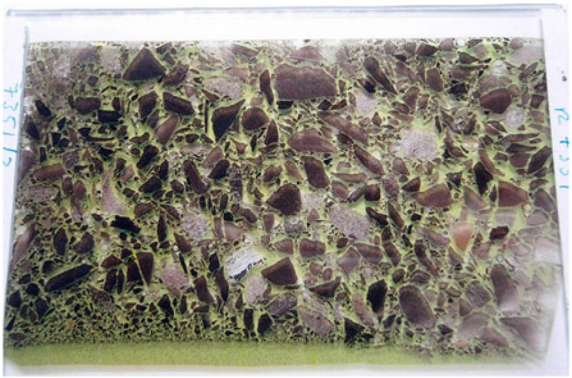


Fig. 4 Petrographic thin section (50 × 70 mm) of an embedded laboratory-crushed fill sub-sample

Thin section preparation is carried out as soon as possible after sampling and without the use of water, to avoid the possibility of post-sampling alteration of pyrite (Czerewko and Cripps 2006).

Measurement of the Proportions of the Rock Types in Crushed Rock Fill

The fine grained nature of the rock types in the fill, coupled with the necessity to take into consideration both the weaker degraded particles more likely to be found in the fine fraction as well as the more robust rock types more likely to be found in the coarse fraction, make the petrographic examination of thin sections indispensable for the measurement of the proportions of the rock types in mudstone fill.

The most convenient way of measuring the volume proportions of the rock types in a fill sample is by carrying out a point count analysis of a thin section prepared from a representative laboratory-crushed fill sub-sample, such as that illustrated in Fig. 4, using the petrological microscope fitted with an automated point counting stage.

Using this method it is possible to measure the proportions of laminated and non-laminated mudstone, the quantities of mudstone containing pyrite and the proportions of mudstone particles with and without gypsum-filled cracks. These measurements are critical in assessing the extent to which the fill may have expanded and for determining whether the fill may have the potential to give rise to pyritic heave.

The Petrographic Identification of Pyrite in Mudstone and Other Rock Types

The pyritic fill used in the Dublin area generally has two distinct lithologies, limestone and mudstone. The proportions vary but the limestones may be argillaceous and the mudstones calcareous. The non-calcareous mudstones commonly contain swelling sheet silicate minerals such as illite–smectite, are laminated and have a very high organic carbon content. The calcareous mudstones rarely contain swelling sheet silicate minerals (smectites) and may be laminated or non-laminated. All the mudstone varieties in the Dublin area contain abundant clay-grade sheet silicate minerals (kaolinite and illite) and organic/carbonaceous matter, and have varying amounts of framboidal and non-framboidal pyrite and quartz. The quartz occurs as both clay-grade and silt-grade particles. Despite their fine grain size the various types of mudstone can be readily distinguished in thin section.

Pyrite framboids can also be identified in thin sections and are visible as spherical clusters of much finer crystals—too fine be resolved individually. A typical example is seen in Fig. 5 which shows an unaltered pyrite framboid in calcareous mudstone. It should be noted that in transmitted light the pyrite

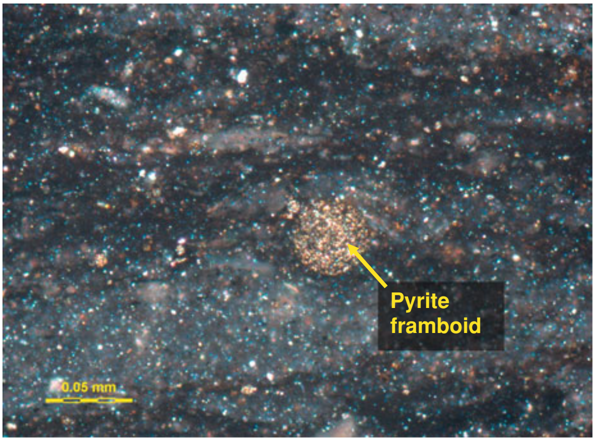


Fig. 5 View showing unaltered *framboidal pyrite* in *reflected light*

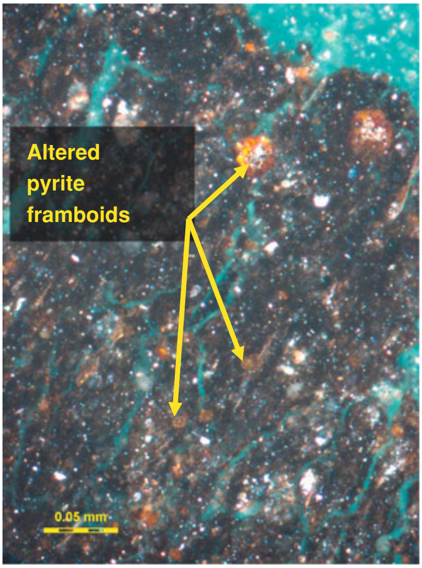


Fig. 6 Altered *framboidal pyrite* in porous calcareous mudstone with abundant internal cracking (*highlighted* in Fig. 7)

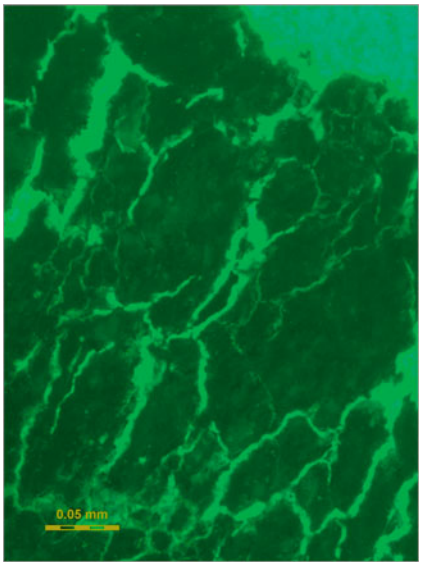


Fig. 7 Internal microcracking as commonly seen in pyritic mudstone with altered framboidal pyrite (same field of view as in Fig. 6)

framboids may be very difficult to distinguish from the similarly opaque carbonaceous matter that is commonly abundant in the mudstone; to identify framboidal pyrite with the petrological microscope, reflected light examination is essential.

Under polarised reflected light, the alteration of framboidal pyrite can be recognised from the growth of distinctive reddish orange alteration rims (Fig. 6). Fluorescence microscopy is an effective method for the detection of the

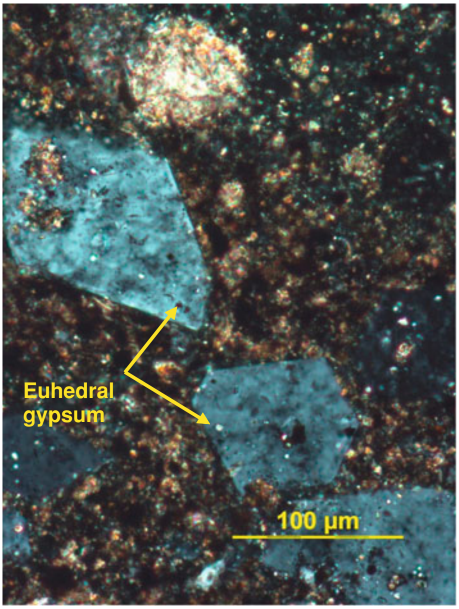


Fig. 8 Photomicrograph of a thin section showing the growth of *euhedral gypsum* crystals in finely crushed calcareous mudstone fill

characteristic microcracking and porosity enhancement that commonly accompany the alteration of framboidal pyrite in mudstone. This is illustrated in Fig. 7 which shows a fluorescent light image of the identical field of view to that shown in Fig. 6.

Petrographic Identification of Gypsum Formation in Pyritic Fill

By the far the most common mode of occurrence of gypsum in the fill is as euhedral gypsum crystals around the surfaces of fill particles—commonly in a matrix of mudstone fines, see Fig. 8. Euhedral gypsum can also sometimes be found growing within openings along the laminations in laminated mudstone particles.

Gypsum can also commonly be found within veins or cracks (Fig. 9). In some cases it is difficult to confirm whether the gypsum in cracks is of recent origin. Observations of mudstone aggregate particles with gypsum-filled cracks in concrete blocks, however, show that gypsum-filled cracks at least have the potential to develop on an engineering timescale.

Electron Microscopy (SEM) and X-ray Microanalysis (EDS)

Introduction and Sample Preparation Considerations

The ability to work at much higher magnifications than are possible with optical light microscopy and to undertake chemical analyses of objects smaller than

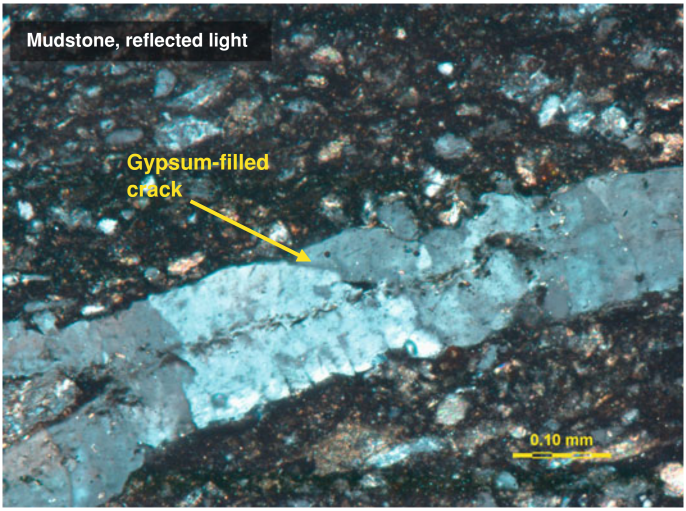


Fig. 9 Photomicrograph of a thin section showing the growth of gypsum crystals in a vein in finely crushed calcareous mudstone fill

Fig. 10 Scanning electron microscope fitted with an energy dispersive X-ray microanalysis system for making chemical analyses

0.005 mm in diameter, make SEM/EDS (Fig. 10) an indispensible tool for the analysis of pyritic mudstone and framboidal pyrite. X-ray mapping techniques, image analysis and X-ray micro-chemical analysis allow the quantities of pyrite in individual rock types to be measured and the mechanisms of pyrite alteration and gypsum formation to be observed directly.

The same sample preparation considerations apply for fill samples examined with the SEM as for the samples examined petrographically. It is essential that the whole sample is represented, in order to allow a full picture to be gained of the extent of pyrite alteration and gypsum formation. Typically, polished surfaces are prepared from the same embedded block used for the thin section. In addition, it may be useful to examine fracture surfaces to determine any gypsum growth or pyrite alteration on laminations and on the outer edges of fill particles.

Framboidal and Non-Framboidal Forms of Pyrite

Framboidal pyrite typically occurs as spherical clusters of pyrite crystals that may individually measure <0.001 mm in diameter. The framboids are commonly of the order of 0.005–0.050 mm in diameter. The typical form of an unaltered pyrite framboid seen on a broken surface of a mudstone particle is illustrated in Fig. 11. The framboid is surrounded by flaky crystals of sheet silicate minerals and very fine granular particles of quartz and calcite.

The significance of framboidal pyrite is that it is much more reactive than non-framboidal pyrite due to its very high specific surface area. A 0.01 mm diameter pyrite framboid composed of 740 individual 0.001 mm diameter pyrite crystals would have a surface area that would be in the order of eight times greater than that of a single pyrite crystal of identical volume. This does not take into account the potential contribution to surface area from micro-fractures and flaws within the individual pyrite crystals that make up the framboids.

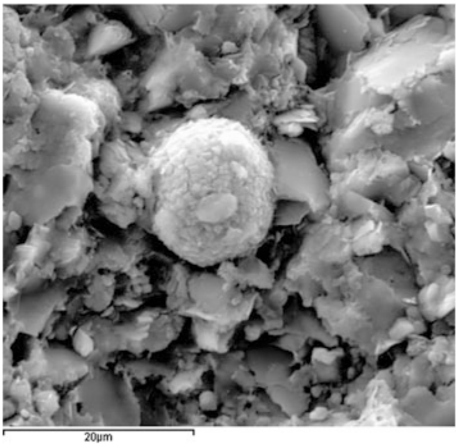


Fig. 11 Secondary electron image showing a spherical unaltered pyrite framboid on a mudstone fracture surface

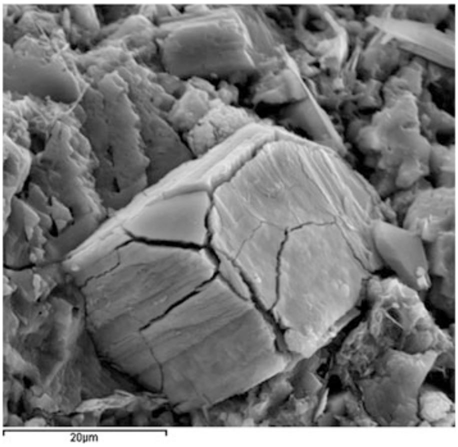


Fig. 12 Secondary electron image showing an altered pyrite cube with a partially delaminated surface skin indicating the alteration process

It is also possible, however, for pyrite to occur on a very fine scale as pyrite cubes rather than in a framboidal form, as illustrated in Fig. 12 where the pyrite cube is surrounded by abundant crystals of calcite and small amounts of flaky sheet silicate crystals. Non-framboidal pyrite is most commonly found as sporadic coarse crystals, sometimes visible to the naked eye in the more calcareous fill particles—especially the sandy limestones and argillaceous limestones.

Pyrite Alteration

The alteration of framboidal pyrite commonly leads to the formation of distinctive “daisy”-like structures, as seen in Fig. 13 where the unaltered pyrite appears whitish grey and the alteration rims around the surfaces of the framboids appear light grey.

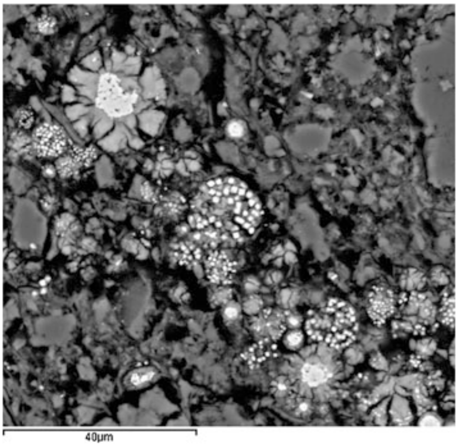


Fig. 13 Backscattered electron image showing altered pyrite framboids in calcareous mudstone

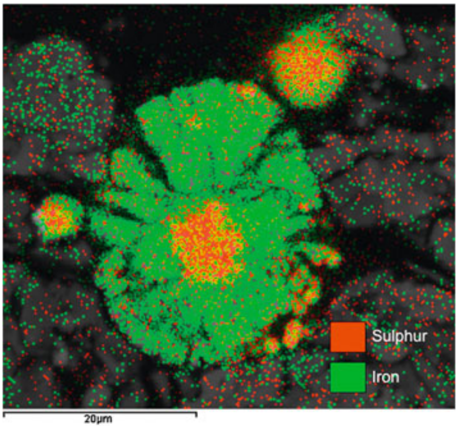


Fig. 14 Backscattered electron image of an altered pyrite framboid with superimposed X-ray maps showing the relative abundance of sulphur and iron

These structures commonly have an inner core of unaltered pyrite framboids with an iron-rich alteration rim. The low sulphur content of the pyrite alteration rims is illustrated in the X-ray map shown in Fig. 14, and is indicative of the migration of sulphate away from areas of active pyrite alteration. In some cases some residual unaltered pyrite can be found around the periphery of the alteration rims. The hydrated iron-rich alteration rims formed around the surfaces of altered pyrite framboids commonly have radial shrinkage cracks which may be original features and/or caused by desiccation during examination of the samples under vacuum in the electron microscope. It is very common for altered pyrite framboids to occur in porous mudstone particles associated with internal cracking. In addition, pyrite alteration products sometimes appear to have opened cracks along the sedimentary laminations.

Gypsum Formation

Gypsum formation typically takes place on a scale that is readily visible with the petrological microscope. An advantage of using the electron microscope however is that it is possible to observe gypsum which has formed directly on fracture surfaces or in cracks and to make chemical analyses of the crystals to confirm their identification. The growth of euhedral gypsum crystals on/in laminated surfaces in mudstone particles—commonly as rosettes—is highly indicative of expansion resulting from gypsum formation in weaker rocks. A typical gypsum rosette growing on a lamination surface in mudstone particle is shown in Fig. 15.

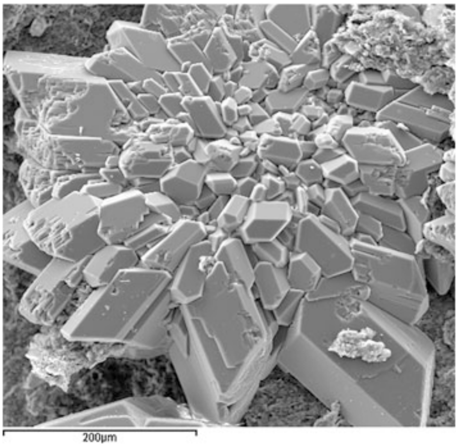


Fig. 15 Backscattered electron image of a gypsum rosette on a lamination surface

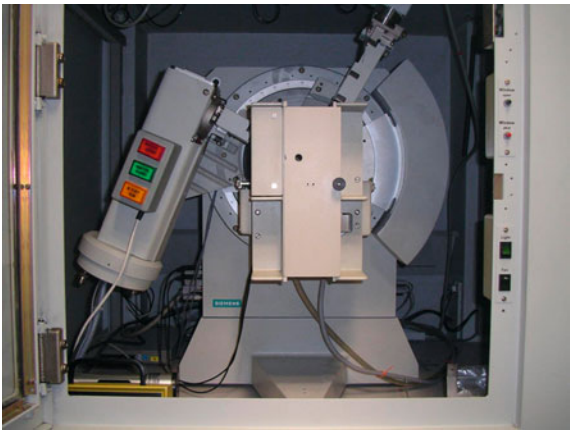


Fig. 16 A Siemens D5000 Diffractometer

X-ray Diffraction

Introduction

X-ray diffraction (XRD) is the definitive method for identifying and measuring proportions of very fine grained crystalline substances, such as clay minerals or some forms of pyrite that are too fine to be identified by other means. The X-ray diffraction technique involves exposing a sample (typically in a powdered form) to a beam of X-rays and measuring the intensity and angles of the X-rays that are diffracted by the mineral crystals contained within the powdered sample. Each mineral has its own unique fingerprint of diffraction angles and relative intensities and these are used to identify the minerals present and to measure their abundance. A typical X-ray diffractometer is illustrated in Fig. 16.

Sample Preparation and Examination Considerations

Sample preparation and the data collection parameters used for the diffractometer are critical for a reliable quantitative analysis of the proportions of minerals by X-ray diffraction.

The circular assembly in the background in Fig. 16 is the goniometer that precisely controls the angle between the X-ray source (shown on the left of the view) and the X-ray detector (shown at the top right of the view). The diffractometer shown is fitted with an automated sample chamber (the rectangular box at the front centre of the view).

Poor sample preparation and/or data collection parameters can adversely affect:

(a) Quantitative measurements of the proportions of the minerals;
(b) The limits of detection for minerals present in small quantities;
(c) The identification of the sheet silicate minerals and in particular the swelling sheet silicate minerals;
(d) The proportions of sheet silicate minerals detected.

The key parameters for sample preparation are particle size, which should ideally be less than 0.010 mm, and the method of loading the sample holder, which to a large extent will affect the orientation of flaky particles such as sheet silicate minerals within the mounted powder sample. The amount of heat generated during the grinding of the sample needs to be kept to a minimum as excessive heat can break down the structure of some types of sheet silicate minerals such as smectite. Comprehensive information relating to methods of sample preparation can be found elsewhere in the literature (see for example, Brindley and Brown 1980).

Identification of Mineralogical Composition by X-ray Diffraction

The use of databases such as the ICDD PDF 4 Minerals database in conjunction with software such as Brucker Diffrac plus EVA is an established technique for interpreting the raw data obtained from powdered samples with the X-ray Diffractometer. Figure 17 is a typical X-ray diffractogram with the identified minerals annotated.

Identification of Swelling Sheet Silicate Minerals

Some types of mudstone used contain significant quantities of the swelling sheet silicate mineral, smectite. The smectite is generally interlayered with the non-swelling sheet silicate mineral, illite. The significance of the presence of swelling sheet silicate minerals in pyritic mudrock is that these minerals are known to cause heave and subsidence as they undergo expansion when wetted or shrinkage when dried. Although these changes are independent of the presence of pyrite, it is likely

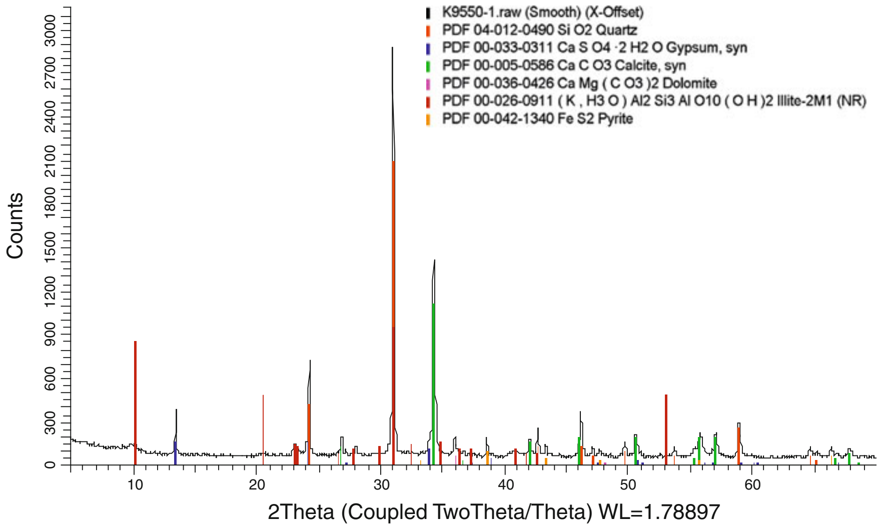


Fig. 17 Random powder X-ray diffractogram plot showing intensity as the vertical axis and degrees 2-theta as the horizontal axis. Each identified peak in the diffractogram is colour coded and referenced in the key

that small scale cracking along laminations generated by moisture movement in swelling clay minerals may accelerate rates of pyrite decomposition.

It is generally possible to detect swelling sheet silicate minerals in fill where they are present in significant quantities. The interlayering of smectite with other sheet silicate minerals, however, hinders its identification and quantification in random powder X-ray diffraction samples. For a more detailed evaluation of the clay mineralogy by X-ray diffraction it is desirable to separate the clay fraction from the fill and analyse this independently as a sedimented clay fraction, before and after treatment with ethylene glycol vapour. The purpose of the ethylene glycol treatment is to determine whether or not the sheet silicates are of a swelling type. Ethylene glycol absorption by swelling sheet silicate minerals causes a diagnostic expansion in their d-spacing that can be readily detected by X-ray diffraction.

Quantification of Mineralogical Proportions by X-ray Diffraction

Using software that employs the Rietveld refinement such as Sietronics Siroquant or Brucker Diffrac + TOPAS it is possible to measure the semi-quantitative proportions of the minerals identified from the raw diffraction data file. The way in which the XRD data is collected as well as the way in which the sample is prepared will both affect detection limits and the degree of precision achievable for the quantification of the minerals.

The key data collection parameters that affect detection limits for the individual minerals are the efficiency of the X-ray detector and the period of time over which the signal from the diffracted X-rays in the powder specimen is collected. It is common for basic mineralogical examination by X-ray diffraction to collect data over a period of an hour for a scan of 60°. For the reliable detection and quantification of small quantities of pyrite by X-ray diffraction, however, extended periods of data collection are essential. The use of an X-ray tube with a cobalt target rather than the more common copper target can be beneficial in the detection of iron-rich minerals such as pyrite.

The range of minerals present within a given sample will also affect the accuracy of the quantification, as the coincidence of X-ray peaks for certain minerals—particularly the sheet silicate minerals—hinders both their identification and quantification. With prolonged periods of data collection and with efficient sample preparation techniques, the error in the quantification of pyrite in mudstone is likely to be of the order of ±0.5 %.

Chemical Analysis

The principal tests for the chemical analysis of pyritic mudstone are acid and water-soluble sulphate (2:1 extract) and total sulphur. The most commonly employed test method is that given in BS EN 1744-1 (British Standards Institute, 2009). TRL 447 (Reid et al, 2001, 2005) recommends ICP analysis in conjunction with microwave digestion for the measurement of acid/water-soluble sulphate and total sulphur but does not provide a standard test method for these procedures. With either method of analysis it is useful if the analyst is familiar with the chemistry of the mudstone and the potential pitfalls in analysing these types of materials for sulphate and sulphur.

In carrying out chemical analysis of pyritic mudstone it is important to take into consideration the following:

(a) Both BS 1744 and TRL 447 are similar in that they require an extraction phase followed by an analytical phase. The extraction phase of either method requires some degree of practical dexterity and some of the methods involve multi-step extraction procedures and so are best undertaken by an experienced analyst.
(b) Additionally the TRL 447 methods involve analysis of the extracted solutions by ICP-AES and this would need to be undertaken by an analyst familiar with the operation of these instruments and the use of elemental standards for calibration purposes.
(c) Both methods recommend the use of good laboratory practice involving the analysis of duplicate samples and the meeting of reproducibility criteria.

(d) With both methods it is useful to have some understanding of the material under investigation. For example, in the case of the determination of acid soluble sulphate the analyst should be aware that the material may contain sulphide sulphur and so use the appropriate method given in the standard for materials containing sulphide. Failure to undertake this precaution may well lead to an over estimation of the acid soluble sulphate and consequently an under estimation of the total oxidisable sulphide.
(e) Experienced analysts will also be able to look at the results for the analysis of the fill material and know if they make "analytical sense" i.e., the total sulphur content must include all of the sulphur in the acid soluble sulphate and so should not be a smaller value.

Chemical analysis is of fundamental importance in assessing the potential for pyritic heave. There are, however, many cases where it is not possible to make a reliable interpretation of the chemical analysis results without reference to microscopic methods. Some of the limitations of relying solely on chemical methods of analysis are:

(a) The calculation of total oxidisable sulphide is based on chemically measured values for total sulphur and acid soluble sulphate. There are errors attached to both of these measurements that might be compounded in the calculation of oxidisable sulphide.
(b) The calculation of total oxidisable sulphide relies on the assumption that all the sulphur is either in the form of pyrite or sulphate. The likelihood of organic sulphur compounds is not taken into account.
(c) The lack of a standard method for the microwave digestion and ICP procedures recommended in TRL 447 (2005) contribute to a potential for interlaboratory variation in methodology and test results.
(d) Chemical analysis cannot provide an indication of the potential reactivity of the sulphide compounds, i.e., it cannot distinguish highly reactive framboidal pyrite.
(e) Some types of fill, such as those with high proportions of phyllite, contain non-framboidal pyrite. However, as this is usually locked in an effectively impermeable matrix, it is less likely to decompose and contribute to expansion/heave. Without petrographic analysis or electron microscopy the mode of occurrence of this type of pyrite cannot be characterised.
(f) High total sulphur results can sometimes occur in limestones containing non-deleterious forms of sulphate such as barium sulphate or strontium sulphate.

Assessing the Effects of Pyritic Fill on Foundation Concrete

Introduction

The chemical reactions that result in pyrite decomposition and gypsum formation in pyritic fill generate sulphate and carbonate ions, both of which are potentially deleterious to concrete. Groundwater in contact with pyritic mudstone fill almost invariably has high levels of sulphate and frequently contains calcium and calcium ions. This is confirmed by the abundance of euhedral gypsum and calcite crystals which are commonly found around the surfaces of fill particles removed from foundation materials.

The key environmental risk factors that contribute to the potential for sulphate attack on sub-surface concrete/concrete blocks are:

(a) *Availability of sulphate*:

Groundwater in contact with pyritic fill is often saturated with sulphate ions generated by the decomposition of the pyrite.

(b) *Carbonate ions:*

Dissolved carbonate ions in conjunction with sulphates contribute to the potential for the development of the thaumasite form of sulphate attack (TSA). TSA is by far the most commonly encountered form of sulphate attack in foundation concrete in contact with pyritic fill in the Dublin area, probably due to the abundance of dissolved carbon dioxide in the groundwater as well as the high levels of sulphate.

(c) *Availability of moisture*:

For sulphate attack to occur in sub-surface concrete/concrete blocks, a source of moisture is required to transport the sulphate and carbonate ions from the fill into the concrete. Without moisture the potential for sulphate attack to develop is negligible.

(d) *Moisture movement*:

Severe sulphate attack is most likely where moisture movement can provide a steady supply of sulphate and carbonate ions.

As well as the environmental risk factors for sulphate attack, there are also risk factors that relate to the characteristics of the concrete and the design of the concrete foundations. Figure 18 illustrates the typical configuration of a foundation structure in a domestic property where the fill has been removed during remediation works.

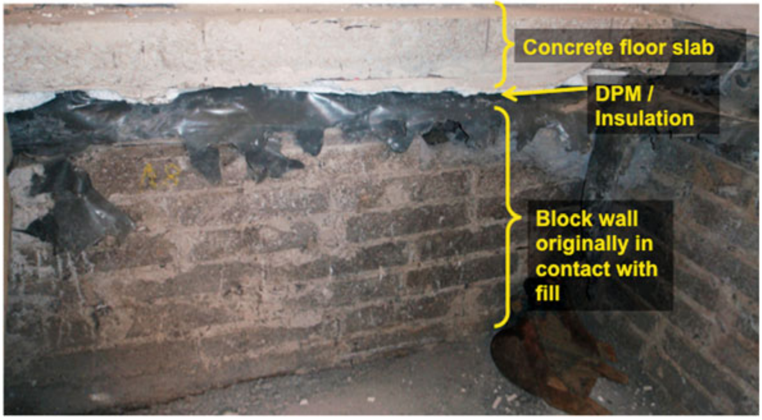


Fig. 18 Exposed internal foundations constructed from concrete blocks on a concrete footing

The key concrete and foundation design risk factors are:

(a) *Low cement content:*

Many concrete foundations are constructed from concrete blocks that have cement contents of significantly less than 10 % by weight of concrete and it is not uncommon for the cement paste to include a high proportion of calcareous dust. Whilst blocks of this type have been used widely in concrete foundations without problems, where the cement content is low, the weakening effects of sulphate attack on the cement paste in concrete blocks are exacerbated.

(b) *Concrete defects—poor mixing:*

Poor mixing during the manufacture of concrete blocks can result in a large variation in compressive strength due to the uneven distribution of the cement binder. Areas of concrete with unusually low cement contents are especially susceptible to sulphate attack. On occasions there can be ambiguity over the interpretation of whether or not the weakened condition of a concrete sample results from the block being inherently weak or whether the block has become weakened as a result of sulphate attack.

(c) *High permeability/void contents:*

Many of the commonly used concrete blocks have high void contents and contain abundant interconnected voids. This promotes the ingress of moisture which, if carrying sulphates and dissolved carbon dioxide into the concrete, accelerates the rate of deterioration.

(d) *Narrow wall thicknesses:*

The structural significance of surface weakening in concrete blocks resulting from sulphate attack can be accentuated by narrow wall thicknesses, especially in walls where concrete blocks are laid on their edges with a wall thickness of around 100 mm or less.

Most documented cases of structurally significant sulphate attack in buried concrete foundations describe concrete that is several decades old. In the majority of the properties in the Dublin area with foundations constructed with pyritic fill, however, the buildings are rarely more than ten years old. Nonetheless, the early signs of sulphate attack can sometimes be found in the form of sulphate ingress and thaumasite formation in voids in concrete blocks. In some instances the early stages of cracking resulting from the thaumasite form of sulphate attack can be seen.

In carrying out laboratory testing of foundation concrete with suspected sulphate attack it is important to take into consideration the likelihood that the early stages of sulphate attack may only be visible in the outermost few millimetres of the foundation. It is therefore essential that a petrographic and/or SEM examination of the surface concrete be carried out. The most appropriate test methods for examining foundation concrete with suspected sulphate attack are discussed below.

Detecting the Early Signs of Sulphate Attack in Concrete

Sampling

Sulphate attack on foundation concrete, especially the thaumasite form, often develops in a very patchy manner and it is not uncommon to find areas of severely deteriorated concrete adjacent to areas of sound concrete showing no signs of sulphate attack. For this reason, prior to selecting sampling locations for laboratory tests, an initial visual inspection is essential to look for such early signs of deterioration as surface softening or the abundant growth of white crystalline deposits on concrete surfaces. Areas of concrete that are sometimes saturated with groundwater that has been in contact with pyritic fill are particularly susceptible to sulphate attack.

Diamond core drilling or the removal of intact concrete blocks is necessary to provide samples suitable for a thorough laboratory investigation of concrete surfaces for sulphate attack.

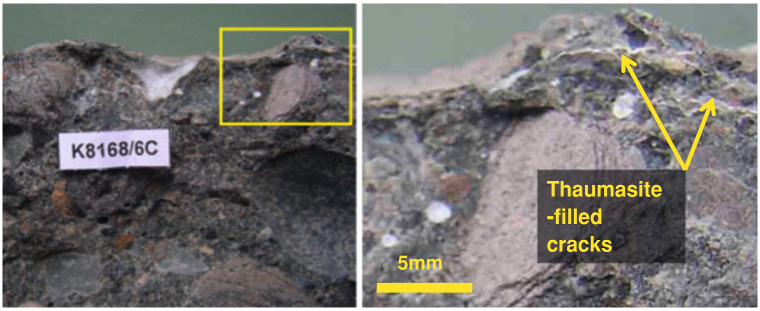
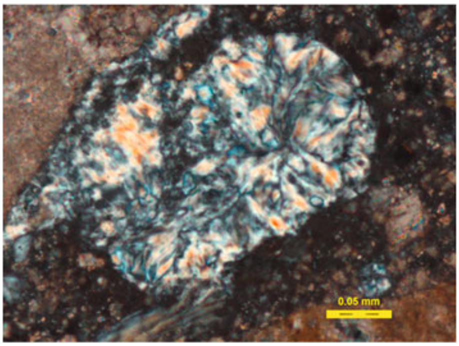


Fig. 19 Low magnification view of split surface through a concrete strip foundation (*left*); close up indicating very fine cracks developed just below the surface (*right*)

Fig. 20 Typical thaumasite-filled void in the cement paste in a concrete block



Petrographic Examination for Detecting Sulphate Attack

The methodology for the petrographic examination of concrete for potential sulphate attack is set out in detail in APG-SR2 (2010). Further guidance is given in CSTR No 71 (2010) and in the Report of the Thaumasite Expert Group (1999).

Fig. 21 Thaumasite-filled cracks around surfaces of coarse aggregate particles in a concrete block

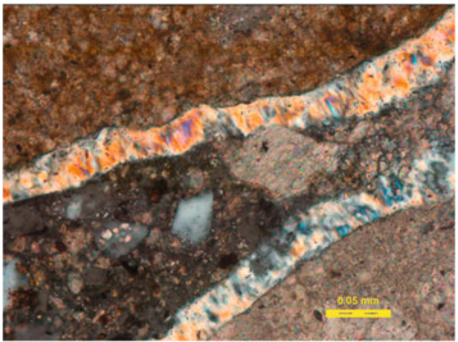


Table 2 Summary of the petrographic indicators for sulphate ingress and sulphate attack in the foundation concrete (based on petrographic observations made by the author)

Stage of sulphate attack	Petrographic characteristics:				Degree of weakening of the concrete
	Portlandite Note 1	Ettringite Note 2	Thaumasite Note 3	Porosity	
Stage 0 (unaffected concrete)	Normal levels of portlandite	Small amounts of secondary ettringite occur in voids[Note 4]	None found	Normal levels of porosity—consistent with w/c ratio	None
Stage 1 (1st onset of sulphate ingress)	Substantial portlandite depletion	Abundant ettringite filled voids and pores	Thaumasite may or may not be present in voids	Often very little change in porosity due to pore fillings of ettringite	Very low
Stage 2 (1st onset of cracking due to sulphate attack)	No portlandite seen in the paste	Abundant ettringite filled pores commonly present	Thaumasite growth in microcracks around aggregate surfaces	Minor porosity enhancement	Low
Stage 3	No portlandite seen in the paste	Abundant ettringite filled pores commonly present	Thaumasite abundant in cracks through the paste as well as around aggregate surfaces and through aggregate particles	Moderate porosity enhancement	Moderate degree of weakening—possibly a 20 % strength reduction
Stage 4	No portlandite seen in the paste	Abundant ettringite filled pores commonly present	Thaumasite partially or fully replaces the cement hydrates in the paste	Very high degree of porosity enhancement	High degree of weakening—concrete can be crumbled by hand

Note 1: Calcium hydroxide—a normal constituent of cement paste in concrete
Note 2: A hydrated calcium-aluminium-sulphate compound found in most concrete
Note 3: A carbonate sulphate mineral containing silica, calcium and sulphate
Note 4: Secondary ettringite formation in voids is a normal characteristic of concrete placed in a damp environment and its presence does not necessarily indicate deterioration or weakening

Much information can be gained from a preliminary visual examination of a freshly broken cross section through a concrete surface which has been in contact with mudstone fill (Fig. 19).

It is often possible to observe abundant crystalline void infillings in concrete blocks exposed to sulphates.

Petrographic examination can be readily used to identify thaumasite and other minerals formed due to sulphate attack. Petrography can also be used to determine depths of sulphate penetration and the distribution of the various sulphate compounds that can be formed as a result of the sulphate attack, such as thaumasite, ettringite and gypsum.

The first signs of sulphate ingress observed petrographically in the foundation concrete are most commonly the development of unusually abundant ettringite in voids and pores in the cement hydrates and the growth of thaumasite within pre-existing voids in the concrete. This infilling of sulphate within the voids does not generally in itself cause weakening of the concrete. A typical example of a thaumasite-filled void is shown in Fig. 20 where the thaumasite appears mottled yellow-blue-grey.

The first sign of weakening resulting from sulphate attack is the development of thaumasite–related cracking such as that illustrated in Fig. 21 where the fibrous crystals of thaumasite appear as various shades from blue to pink. In its most severe form thaumasite attack can result in the partial or complete replacement of the cement paste in the concrete with thaumasite, resulting in substantial weakening.

A summary of the petrographic evidence for sulphate attack and its associated severity is given in Table 2.

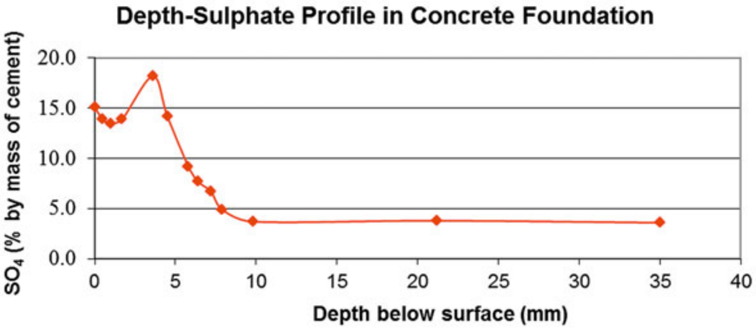


Fig. 22 Typical sulphate profile for in situ cast concrete

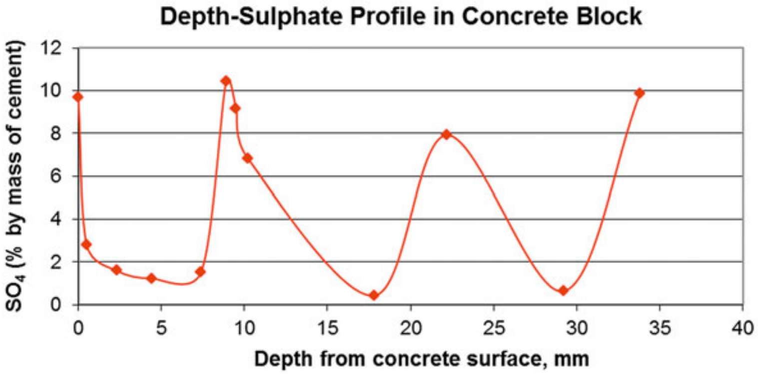


Fig. 23 Typical sulphate profile for a concrete block

Electron Microscopy and X-ray Microanalysis for Detecting Sulphate Attack

The electron microscope coupled with an X-ray microanalysis system can be used to measure the extent of sulphate ingress into concrete surfaces on a microscopic scale. Analysis of this type is particularly valuable for sub-surface concrete as it is possible to analyse representative areas of cement paste excluding aggregate particles by X-ray microanalysis. A typical example of one of these profiles from an in situ cast concrete ring beam is shown in Fig. 22. The profile is made up from analysis of a 0.1 × 0.1 mm area of cement paste at various depths below a concrete surface in contact with pyritic fill.

The low cement contents of the concrete blocks and abundance of aggregate dust contribute to the difficulty of measuring depth/sulphate profiles in concrete blocks. The high voidage of the concrete blocks and patchy sulphate ingress lead to very widely varying sulphate contents for the paste as shown in Fig. 23 where again the profile is made up from analysis of a 0.1 × 0.1 mm area of cement paste at various depths below a concrete surface in contact with pyritic fill.

Conclusions

The Analysis of Pyritic Fill

A combination of test methods including petrography, chemical analysis, X-ray diffraction and electron microscopy is required to reliably classify the potential for pyritic fill to cause heave in foundations. The microscopic methods of analysis, including petrographic examination and the scanning electron microscopy, are indispensible if a realistic analysis of the crushed rock fill is to be undertaken to assess the potential for heave.

Identification of the rock types and their proportions requires petrographic examination. This should ideally be carried out in such a way that the finer degraded fill particles are not excluded from the portion of the sample examined petrographically, as it is often in the fine fraction of the fill that the chemical reactions responsible for heave are occurring.

The interpretation of chemical test results, such as acid and water soluble sulphate and total sulphur, often needs to be made in the light of test results obtained from other methods of analysis such as X-ray diffraction or X-ray microanalysis.

Sulphate Attack in Foundation Concrete in the Vicinity of Pyritic Fill

The conditions for sulphate attack exist in foundations in contact with pyritic fill as long as there is a source of moisture.

By far the most common form of sulphate attack is thaumasite-related. This is because of the high levels of dissolved carbon dioxide and sulphate in groundwater that has passed through pyritic fill.

In the Dublin area, concrete used for foundations adjacent to pyritic fill is typically less than ten years old. As a consequence, specialist techniques, including petrographic examination and electron microscopy, are required to detect the early stages of the development of sulphate attack in the concrete.

Acknowledgments Brian Hawkins, HM Geotechnics; James Lombard, Ground Investigations Ireland; and Gavin Mayers, Sandberg LLP.

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Problems Associated with the Use of Pyritiferous Fill at Ballymun Youth Facility, Dublin

A. Brian Hawkins and Matthew Stevens

Introduction

Although there had been a recreational centre in Ballymun since 1998, as part of the regeneration of the area it was decided by Ballymun Regeneration Limited to extend the existing 240 m^2 centre off Sillogue Road to provide a new Central Youth Facility (Fig. 1). Also known as the "Reco", the youth centre is now managed by the Ballymun Regional Youth Resource. The new 1,120 m^2 extension includes further offices, a restaurant and various activity rooms at ground and first floor levels, as well as store rooms either side of the entrance to an enclosed courtyard (Fig. 2). In addition, to the north an exercise room/gymnasium adjoins the original sports hall. A roof garden is present at first floor level on the south of the extension. The detailed layout of the ground floor of the new extension is shown in Fig. 3.

In 2002 a ground investigation was undertaken consisting of four trial pits which extended to a depth of c. 2.9 m. Below a variable thickness of made ground there was a horizon of typically brown, firm to stiff, glacial deposits (Dublin Boulder Clay). Below some 2.6 m, the material was unoxidised and is commonly referred to as the Dublin Black Boulder Clay. These glacial deposits underlie much of Dublin and provide the founding strata for most of the significant buildings in the city (e.g. Farrell et al. 1995; Skipper et al. 2005; Long and Menkiti 2007).

On 16th August 2004, James Elliott Construction began work at the site, clearing some scrub vegetation, diverting services and preparing to place fill to provide a good working surface. Based on the ground investigation report, Moylan (now Waterman Moylan, the Client's Consulting Engineers) recommended that

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Fig. 1 Ballymun Youth Facility

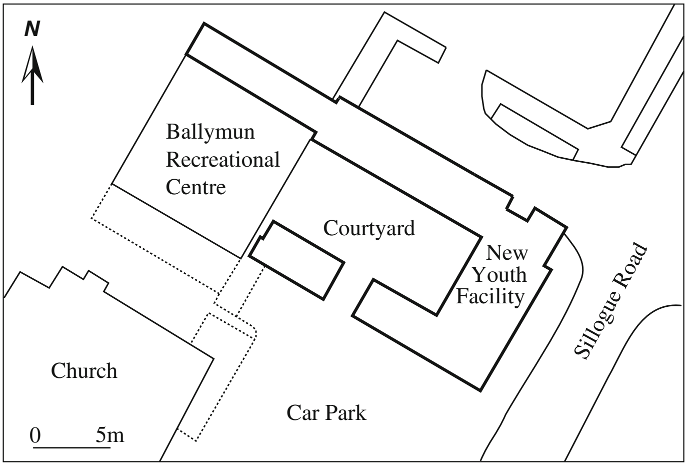


Fig. 2 Layout of the new Ballymun Youth Facility

the new buildings should be constructed on large mass concrete pier foundations extending down to the Black Boulder Clay (Fig. 4). Moylan recommended the use of ground-bearing floor slabs and that the placed aggregate fill beneath the slabs should have properties compliant with Clause 804 of the NRA 800 Series—Specification for Roadworks.

Between 3rd November and 13th December 2004, thirty-nine 1.8 × 1.8 m lean mix concrete piers were installed to varying depths, although all extended to the Black Boulder Clay.

Having constructed the 0.6 × 0.5 m ground beams and initial columns, fill was placed in 150–225 mm lifts. As seen in Fig. 5, in the larger areas the fill was compacted with a roller while in more restricted spaces a whacker was used.

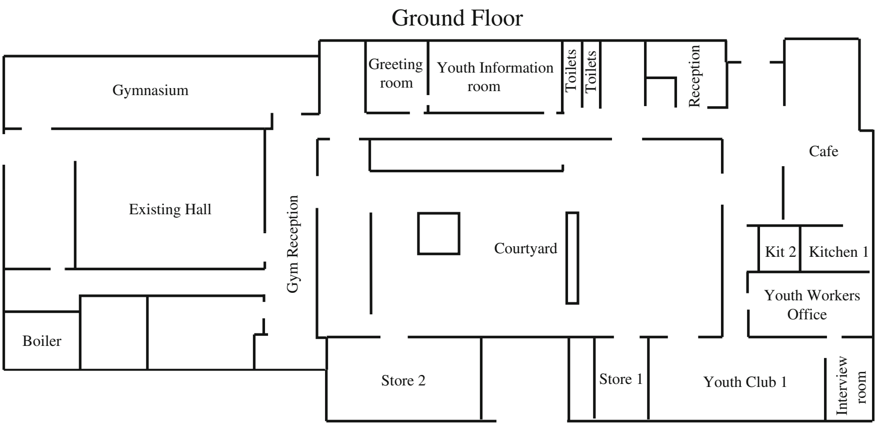


Fig. 3 Ground floor layout, Ballymun Youth Facility

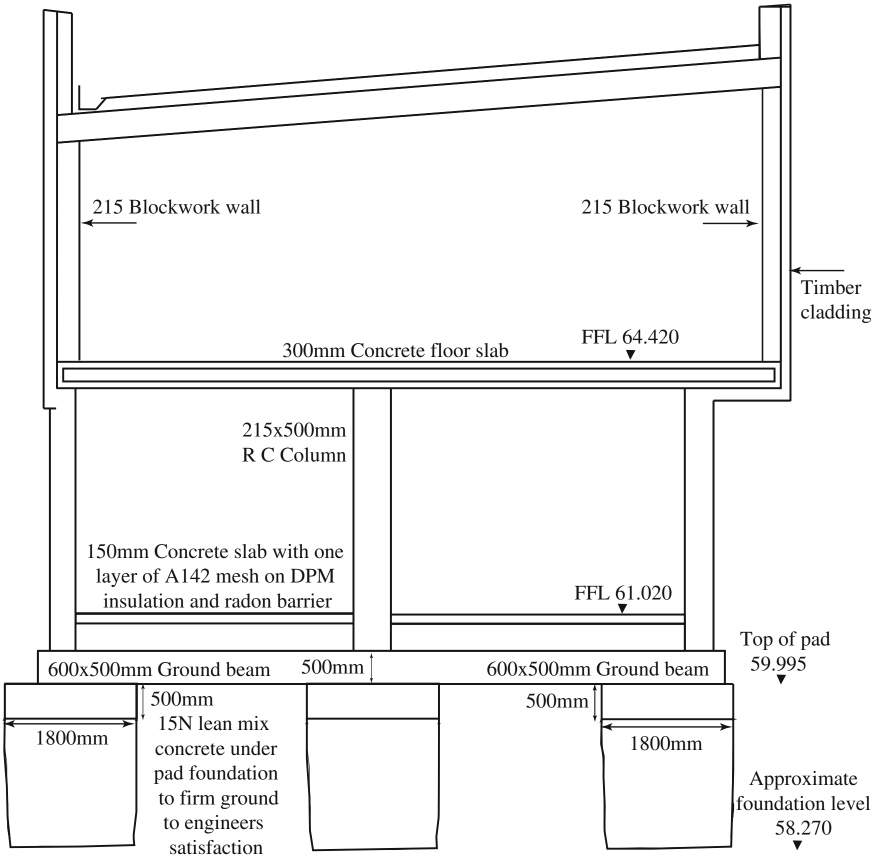


Fig. 4 Section showing structure and foundation layout

Fig. 5 Fill being compacted by roller, December 2004

Having placed the radon barrier and insulation layer, the 150 mm reinforced concrete slab was poured and allowed to harden over the Christmas period.

This chapter discusses:

(a) The visible development of the distress in the building;
(b) The investigation undertaken in 2007/2008;
(c) The chemistry and other tests carried out on the fill material, both before and after the remediation;
(d) The levelling/elevation survey undertaken between March 2008 and April 2009 to assess the rate/extent of the heave;
(e) The methods the contractors used to remove and replace the deleterious fill;
(f) The effect of the pyritiferous fill on ground concrete, including that observed as the remediation was being undertaken.

Visible Development of the Distress

On 23rd August 2005, a snag list was prepared, as is commonly done towards the end of the construction period. This was updated on 1st September 2005 and contained a number of items typical of those frequently requiring attention before a building is taken over. Practical Completion of the Youth Facility was signed by the Ballymun Architect on 2nd September 2005 and the Centre was formally opened that month. As with most contracts, following Practical Completion there was a year when any defects observed would be repaired by the builder in an interval known as the Defects Liability Period.

Within a month of acceptance of the building, cracks had appeared, and on 6th October 2005 the Client prepared another snag list which drew attention to a number of these. Those recorded were mainly in the stairwell and below windows in the Club Room, Youth Workers' Office and ground floor corridor. In hindsight it is likely that where the dry lining extended for the full height of the wall only limited bulging was visible, but where the upwards pressure was restricted (e.g. by window cills), overstressing resulted in the visible bulging and cracking appearing more significant.

During early 2006, doors were jamming and dry-lined walls, notably in the Reception area, showed extensive bulging and cracking. Although it is likely there was some cracking of the ground-bearing floor slabs, with fixed floor coverings this would have been difficult to assess and understandably was not examined/ recorded. On 3rd August 2006, a further snag list was prepared (Table 1). This identified the positions and lengths of cracks at some 100 locations, many of which extended for over a metre in length.

Table 1 Snag list: 3rd Aug 2006

	Room	No of items/cracks	Max. crack length (mm)
Ground floor	Reception area	16	1,300
	Cafeteria	9	600
	Kitchen	3	1,500
	Corridor to youth workroom	5	700
	Youth workers' office	5	1,000
	Youth workroom	9	1,000
	Interview room	4	"full height of room"
	Corridor by stairs	5	"full height of room"
	Toilets	3	"full height of room"
	Corridor by youth information	6	"full height of room"
	Youth information	3	600
	Multipurpose	6	"full height of room"
	Corridor/stairs	3	1,500
	Gym	5	"couple of metres"
First floor	Internet public	4	1,000
	Internet classroom	2	1,000
	Lobby	3	2,000
	Conference	4	2,000
	Special Needs toilet	1	2,000
	Corridor by lift	9	2,000
	Toilets	7	Not stated
	Corridor by art room	4	3,000
	Art Room	2	2,000
	Staff canteen	1	1,500
	Lobby stairs	4	1,500

Whilst minor cracking of plaster/plasterboard is common in new buildings, the large number and the length of the cracks recorded compared with the previous snag list in October 2005 caused considerable concern. Only eleven months after Practical Completion significant ongoing repairs were necessary to allow the continued full use of the building as a youth facility.

The 3rd August 2006 snag list did not include the pronounced upward bend and crack in the ceiling of the Gym adjacent to the mirror wall (Fig. 6). However, it is clear that in the area where the Gym adjoins the original building, as the floor rose it forced the dry lining upwards into the ceiling and, as a consequence, a crack developed parallel to the internal wall. Evidence of the rise in the dry lining of this wall is indirectly recorded in the snag list as *Make good wall at top of socket.* A photograph taken in February 2008 (Fig. 7) shows 4–5 mm of upward rise at the position of the fixed electrical socket.

Unfamiliar with the symptoms of sulphate-induced heave, neither the Client nor the builder appreciated the cause of the distress and the likelihood that the problems caused by sulphate-generated heave become worse with time. As a consequence, between September and November 2006 the builder carried out a number of repairs. The distress continued and repairs were continually undertaken by the Youth Centre staff. In this busy environment, however, details of the individual repairs undertaken “in house” were not recorded and no further detailed snag lists were prepared.

In view of the ongoing problems, in October 2007 the Ballymun Regional Youth Resource commissioned an independent consultant’s assessment. In their report, Donnelly Troy suggested the distress may be a result of sulphate heave, which had been identified elsewhere in the Dublin area in 2007. Ballymun Regeneration Ltd then contacted their Engineering Consultants and requested them to undertake a more detailed investigation.

In early November 2007 Moylan undertook a photographic and damage survey. Only some 26 months after the facility was opened, it was noted that the damage included:

(a) Extensive bulging of the plasterboard panels (Figs. 8, 9, 10 and 11);
(b) Cracking in the plasterboard lining (Figs. 12 and 13);

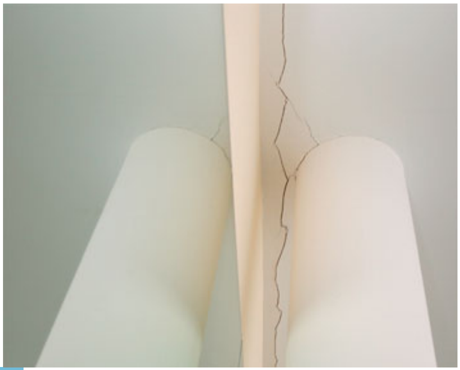


Fig. 6 Crack in ceiling above mirror approx. 100 mm from rear wall of Gym

Fig. 7 Dry lining displaced relative to plug, February 2008

Fig. 8 Bulging of plasterboard in Reception area (November 2007)

(c) Severe cracking of the lining to the east of the window and arching of the cill in the corridor to the Gym (Figs. 14 and 15);
(d) A 5–6 mm rise in the floor relative to the threshold at the doorway from the lift area into the courtyard (Figs. 16, 17 and 18);
(e) Spider cracking in the floor of Store 1 (Fig. 19).

In July 2007 the suppliers of the fill (Irish Asphalt) informed the builder that pyrite was present in some of their product and that this had led to heave on some sites. In view of this and the distress observed at the Central Youth Facility, Moylan instructed Ground Investigations Ireland (GII) to obtain samples of the material from beneath the floor slabs and undertake appropriate geotechnical and chemical analyses to establish if the fill contained deleterious material.

Fig. 9 Bulging and cracks in corridor (November 2007)

Fig. 10 Bulging in part restricted by electric points; Youth Information Room (November 2007)

Investigation 2007–2008

A total of seven sampling pits were excavated by GII on 17th November 2007, five within the building and two in the courtyard (Fig. 20). The interior trial pits were some 0.5 m square and excavated through the concrete floor slab, insulation and underlying radon barrier. In the courtyard, the sampling pits were dug after the 65 mm thick porous brick paving and sand screed had been removed.

Fig. 11 Door frame displaced by bulging plasterboard; Youth Workers' Office (November 2007)

Fig. 12 Cracking in plasterboard which has bulged and displaced the skirting board (November 2007)

Representative samples were taken in each sample pit (see Table 2). The "A" samples were sent to Geomaterials Research Services (GMRS), now part of Sandberg LLP, while the "B" samples were retained by GII. Samples were also taken by Arup, who were working on behalf of the builder.

Assessment of Samples

In addition to determining the lithology of the material obtained by GII in Nov 2007, a number of physical tests (particle size distribution, PSD), Atterberg limits,

Fig. 13 Severe crack in the plasterboard in the entrance lobby (November 2007)

Fig. 14 Bulge in plasterboard on the north side of window in Fig. 15

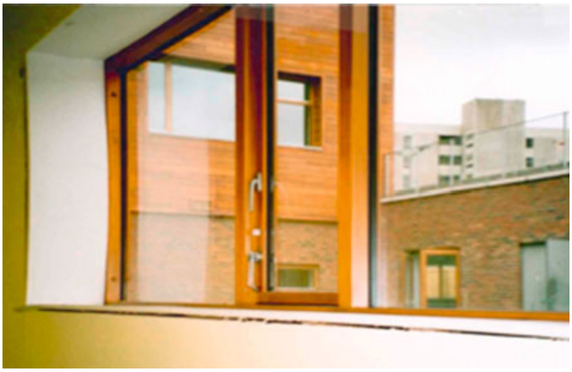


Fig. 15 Gap developing as window cill arches, between corridor from the Gym and the courtyard

water absorption and Los Angeles) were undertaken (Table 3). The chemical testing included total sulphur, acid soluble sulphate and water soluble sulphate.

As seen in Table 3 and discussed below, the material in the interior pits (TPs 1–5) was significantly different from that in the exterior pits (TPs 6 and 7), in

Fig. 16 Damage to threshold at doorway from Reception into the courtyard (March 2007)

Fig. 17 Rise of floor against the threshold into the stairwell (November 2007)

regard to colour, physical properties and chemistry. It is understood that the courtyard area was used as a compound during construction and that some of the fill material used to level off the area had been imported from a different source. The fill was therefore a mixture of materials rather than stone from a single source.

From Table 3 it can be seen that:

1. The material in TPs 1–5 was very dark grey to black compared with that in TPs 6 and 7 which was much lighter and browner in colour.

Fig. 18 Detail of height difference shown in Fig. 17

Fig. 19 Cracking of the floor slab in Store 1 (November 2007)

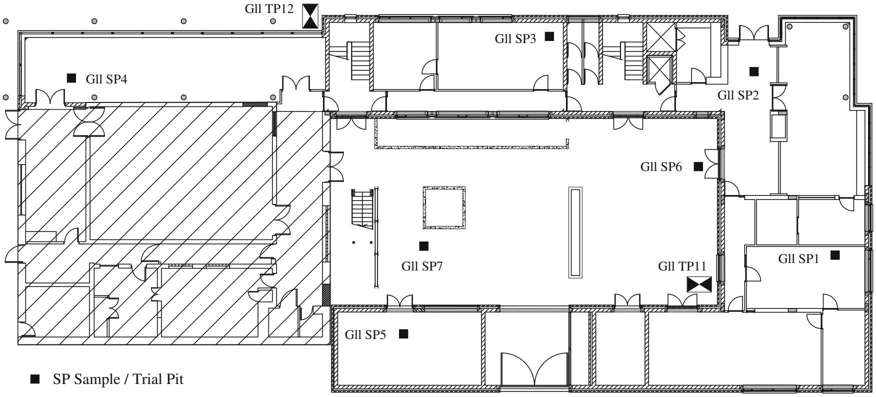


Fig. 20 Locations of seven sampling pits undertaken in November 2007 and trial pits 11 and 12 undertaken in May 2008. Pits referred to as Trial Pits in text

Table 2 Locations and depths of samples taken in Nov 2007

	Interior pits					Exterior pits	
Location	TP 1	TP 2	TP 3	TP 4	TP 5	TP 6	TP 7
Concrete/ Paving brick	0.00–0.19	0.00–0.21	0.00–0.18	0.00–0.23	0.00–0.18	0.00–0.07	0.00–0.07
Insulation	0.19–0.24	0.21–0.26	0.18–0.23	0.23–0.75	0.18–0.23		
Sand	0.24–0.26	0.26–0.27	0.23–0.45	0.75–0.90	0.23–0.25	0.07–0.1	0.07–0.13
Sample A	0.28–0.32	0.28–0.35	0.25–0.3	0.30–0.35	0.25–0.3	0.15–0.2	0.16–0.2
Sample B	0.45–0.50	0.50–0.55	0.50–0.55	0.40–0.45	0.40–0.45	0.30–0.35	0.30–0.4
Depth of pit (m)	0.76	0.84	0.65	0.65	0.67	0.75	0.83

Table 3 Summary of physical properties of samples taken in November 2007

	Interior pits					Exterior pits	
	TP 1	TP 2	TP 3	TP 4	TP 5	TP 6	TP 7
Depth (mm)	280–320	280–350	250–300	300–350	250–300	150–200	1555–200
Colour	Very dark grey-black					Med-light brown/ grey	
Lst. + dolomite (%)	8	8	8	8	6	70	63
Carb. + bit. Lst. (%)	36	33	29	28	27	17	29
Mudstone (%)	8	1	9	–	6	1	1
Calc. + carb. Mdst. (%)	43	57	54	59	60	6	6
Grading							
Passing 16 mm	78	75	70	81	80	51	73
8 mm	51	45	47	52	56	30	52
4 mm	33	28	29	30	35	19	32
2 mm	25	20	20	22	27	14	23
1 mm	18	15	13	16	20	10	16
0.5 mm	14	12	9	13	16	8	12
0.063 mm	6	6	4	8	9	4	6
Atterberg Limits							
<0.425 mm (%)	15	12	12	15	19	15	15
Liquid limit (%)	28	30	27	27	27	25	23
Plastic limit (%)	NP	NP	NP	NP	NP	NP	NP

2. The particle size analysis (Fig. 21) indicated that the material generally fell within the grading envelope required for Clause 804 as specified, but that Samples 4 and 5 had slightly more fines (<0.063 mm) than stipulated. However, such a small increase in the fraction may well be a consequence of the placement/compaction processes and would not necessarily have a significant influence on the behavior of the fill if it was inert. As seen in Fig. 21, the middle fraction of Sample 6 (between 2 and 11 mm) was slightly coarser than detailed in Clause 804. Again this would not be considered problematic.

3. The Atterberg Limit tests, which are undertaken to determine the nature of any clay minerals present and their potential to swell, are assessed only on the material <0.425 mm. The liquid limits obtained, therefore, were based on only 12 to 19 % of the total sample. As seen in Table 3, the results varied between 23 and 30 %—above the thresholds of 20/21 % set in Clause 804. Whilst clearly non-compliant, these values are not sufficiently high to indicate the presence of expansive lattice clay minerals. In addition, all the samples were non-plastic, implying a very low percentage of clay minerals and hence a low swell potential.
4. After the initial examination and particle size distribution analysis, each of the samples was crushed to pass through a 4 mm sieve. The material was then passed over a 0.2 mm sieve and a thin section made of the 0.2–4 mm fragments. The lithologies were determined by point counting using a petrographic microscope.

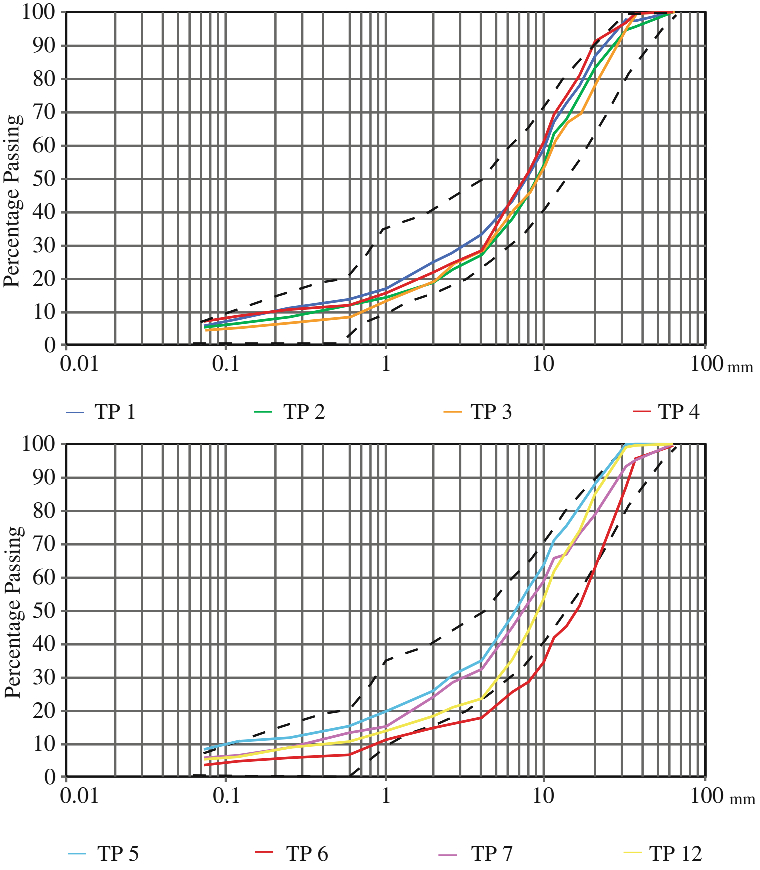


Fig. 21 Particle size of fill from TPs 1–7 and TP 12 relative to the Clause 804 grading envelope

(a) The microscopic examination indicated that Samples 6 and 7 contained >60 % pure limestone while the other samples contained mainly carbonaceous/bituminous limestone (Table 3).
(b) In all the samples the material identified as pure mudstone accounted for <10 %. However in the interior samples calcareous and carbonaceous mudstone accounted for 43–60 % of the material.
(c) Some of the very calcareous mudstones/argillaceous limestones were laminated with clear bedding partings (shales) and many of the "more massive" calcareous mudstones contained layering/sedimentary banding where the clay-rich horizons were only some 1 mm apart (Fig. 22). These bands were also notably darker in colour and would be expected to be weaker than the general material.
(d) Pyrite, both as cubes/lumps and as framboids, was observed during the microscopic examination. The 5–7 μm framboids were often oxidised with alteration rims up to 10 μm thick. It was noted that some of the framboid seeds were on the outer edges of the alteration rim, suggesting they were transported outwards as ferrous sulphate developed during the oxidation process.

X-ray diffraction analyses (XRD) were undertaken on a representative proportion of the sample. After 35 g had been crushed and milled, a representative 2 g sample was tested to establish a semi-quantitative assessment of the proportions of the various minerals present.

As recommended by Hawkins and Pinches (1987) the sulphide remaining and available to oxidise was established by determining the total sulphur minus the sulphur in sulphate (Table 4).

1. The pyrite content in the interior samples was 2–3 % while in the exterior samples only 1 % was recorded in Sample 6 and no significant pyrite in Sample 7.
2. The calcite content for Samples 1–5 varied between 32 and 35 % while for the two external samples, 77 and 79 % were recorded.
3. Between 2 and 4 % gypsum was recorded in Samples 1–5 and 1 % in Sample 7. No gypsum was detected in Sample 6.

Fig. 22 Layers of clay-rich material in a calcareous mudstone

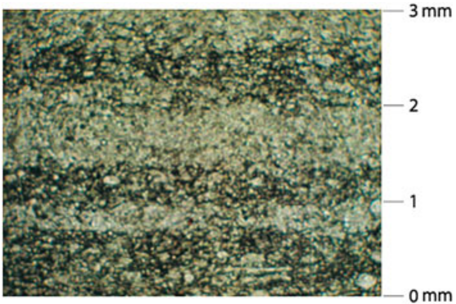


Table 4 Summary of mineralogy and chemistry of samples in Table 3

	Interior pits					Exterior pits	
Percent	TP 1	TP 2	TP 3	TP 4	TP 5	TP 6	TP 7
Calcite	33	33	35	34	32	79	77
Dolomite	8	9	8	9	7	4	6
Pyrite	2	2	2	2	3	1	<1
Gypsum	4	3	2	2	3	ND	1
<0.2 mm fraction	10	17	13	15	7	14	9
Pyrite (SEM)	10	7	10	12	9	2	3
Chemistry							
Total sulphur	1.38	1.41	1.34	1.51	1.56	0.35	0.24
Acid sol. sulphate (% SO_4)	0.55	0.46	0.46	0.51	0.43	0.08	0.06
Water sol. sulphate (mg/l SO_4)	1,614	1,575	1,612	1,589	1,603	538	144
Sulphur minus sulphur in sulphate (% S)	0.83	0.95	0.88	1.00	1.13	0.27	0.18

4. The 0.2–4 mm and <0.2 mm fragments were mixed and examined under the scanning electron microscope (SEM). This allowed an optical estimation of the percentage of pyrite in the fine material. As seen in Table 4, this varied between 6 and 14 %. Clearly the fine fraction, being dominantly derived from the mudstones, is likely to contain more pyrite than the coarser material which is likely to be formed of the stronger limestone lithologies.

The chemistry was determined from a representative part of the samples, following BS EN 1744-1 (Table 4).

(a) In Samples 1–5 the total sulphur ranged between 1.34 and 1.56 % S (average 1.44 %), while for Samples 6 and 7 the average was 0.3 % S.
(b) In Samples 1–5 the acid soluble sulphate ranged between 0.43 and 0.55 % SO_4 (average 0.48 %), while for Samples 6 and 7 the average was 0.07 % S.
(c) In Samples 1–5 the water soluble sulphate results ranged between 1,575 and 1,614 mg/l SO_4 (average 1,599 mg/l SO_4), while for Samples 6 and 7 the average was 341 mg/l SO_4.
(d) The total sulphur minus the sulphur in sulphate (i.e. the sulphur remaining to be oxidised) varied between 0.83 and 1.13 % S in Samples 1–5 but was only 0.27 and 0.18 % S in Samples 6 and 7 respectively.

The NRA 800 Series (2000) recommended that for material within 0.5 m of concrete/concrete products, the maximum water soluble sulphate content should not exceed 1,900 mg/l SO_3, equivalent to 2,300 mg/l SO_4. However, as from May 2004 (i.e. before the fill was purchased) the NRA no longer required the water soluble sulphate content to be established but instead stipulated that the acid soluble sulphate content should be measured and should not exceed 0.2 % SO_4.

The samples from the courtyard (6 and 7) met both of these requirements and all the water soluble sulphate values met the 2000 criteria. However, all the interior samples had acid soluble sulphate contents of more than double the recommended 0.2 % SO_4.

The 800 Series did not consider values/thresholds that could be utilized when assessing sulphate-induced heave; it is assumed this omission was because the writers of the 800 Series anticipated the unbound material would be chemically inert.

After receiving the reports from GMRS in January 2008, an analysis of the results was undertaken and a visit made to the Youth Facility in February 2008. From the assessment of the laboratory results and the field observations it was concluded that the distress was related to sulphate-generated heave as a consequence of the oxidation of pyrite in a dominantly dark grey to black, frequently laminated, calcareous mudrock.

As discussed in more detail in Hawkins (this book), during the chemical process of oxidation ferrous sulphate is formed and sulphuric acid released. The formation of the ferrous sulphate itself causes the initial heave and much of the early fracturing of the mudstone fragments. At the same time, the released sulphuric acid combines with any available calcium carbonate to form calcium sulphate (gypsum). These new minerals may develop in existing cracks within the aggregate fragments, on the aggregate surfaces and/or as euhedral selenite crystals in the open spaces between the fragments.

In these situations, the newly formed gypsum may not cause significant expansion of the fill material. However, the sulphuric acid moving within a fragment may combine with in situ calcium carbonate to form isolated selenite crystals. Such crystals may grow as mobile liquids penetrate into the dilating fragments and/or new crystals may be precipitated in/on laminations in the mudstones and within weak clay-rich horizons in argillaceous limestones.

It is the growth of these selenite crystals which prises open the “layers”, causing dilation of the individual particles and resulting in heave of the compacted fill (Figs. 23 and 24).

The SEM examination of the fill material confirmed the presence of ferrous sulphate rims which had clearly created expansion and cracking of the individual fragments. The growth of selenite crystals within the incipient discontinuities could also be seen. It is these crystals which caused the main dilation and heave. In addition, the chemical analyses indicated that significant unoxidised sulphide remained in the fill, which could react in the future and result in further expansion.

Fig. 23 Cracks opened by crystal growth

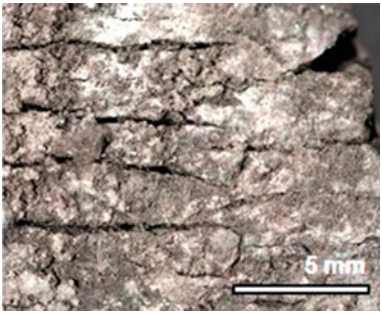
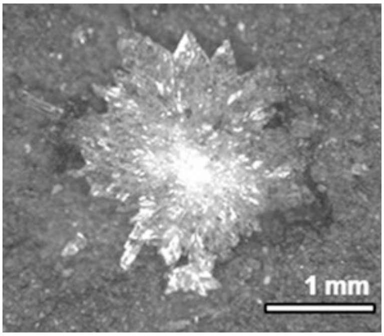


Fig. 24 Typical selenite crystal formed in a dilating crack



Additional Investigation: May 2008

Prior to any decision regarding remediation, it was necessary to confirm the founding level of the mass concrete piers and assess the nature of the material on which the piers were placed. As a consequence, on 21st May 2008 two additional external pits (TPs 11 and 12) were excavated adjacent to concrete piers (Fig. 20). In order to reach the Black Boulder Clay, they were extended to depths of 2.5 and 3 m respectively.

In TP 12, the Brown Boulder Clay extended to 2.55 m. At that depth a 0.15 m thick partially weathered zone separated the Brown from the Black Boulder Clay. The material at the base of the concrete pier was effectively dry, over-consolidated Black Boulder Clay and was estimated to have an undrained shear strength of more than 150 kPa.

A sample of fill was taken from between 0.2 and 0.35 m (see Table 5). Examination of this showed framboidal pyrite was present in the fragments of calcareous mudrock and euhedral selenite crystals were noted in the fine material coating the surface of the particles. The lithologies in the material from TP 12 closely resembled those in TPs 1 to 5 of the previous investigation.

A sample of the Black Boulder Clay was also taken in TP 11, at a depth of 1.9 m (base of the pier). As seen in Table 5, analysis indicated that the total sulphur content was 0.02 % S, the acid soluble sulphate content 0.13 % SO_4 and the water soluble sulphate content 166 mg/l SO_4.

Level Survey and Monitoring

Following the February 2008 inspection, a digital levelling survey was initiated. Two external datum points were established and the levelling began on the 5th and 11th March 2008. However, the measurements clearly could not take into account the heave which had already taken place; some instances of which are recorded in the photographs from November 2007 (e.g. see Fig. 18).

Table 5 Details of the samples taken from the fill material in the external pits (TPs 11 and 12) and from the underlying Boulder Clay at 1.9 m in TP 11 and 2.7 m TP 12

Trial pit	TP 11	TP 11	TP 12	TP 12	TP 12
Depth (m)	0.6	1.9	0.2–0.35	0.52–1.0	2.7
Colour	V dk grey	Brown	V dk grey	V dk grey	Brown
Grading					
Passing 16 mm	72	–	–	57	–
8 mm	48	–	–	24	–
4 mm	31	–	–	13	–
2 mm	25	–	–	10	–
1 mm	20	–	–	8	–
0.5 mm	17	–	–	7	–
6.3 µm	9	–	–	3	–
Lithology (%)					
Mudstone	9	–	–	10	–
Calc./carb. mudstone	58	–	–	61	–
Limestone	6	–	–	4	–
Bit./carb. limestone	27	–	–	25	–
Atterberg limits (%)					
<425 µm	28	63	–	32	–
Liquid limit	30	35	–	33	–
Plastic limit	24	19	–	24	–
X-Ray analysis (%)					
Calcite	34	–	–	35	–
Illite/muscovite	15	–	–	14	–
Pyrite	3	–	–	3	–
Gypsum	3	–	–	2	–
Chemistry (% by mass)					
Total sulphur (S)	1.45	0.02	1.32	1.14	0.02
Acid sol. sulphate (SO_4)	1.19	0.13	1.50	0.8	0.09
Water sol sulphate (mg/l SO_4)	1,420	166	1,606	1,367	100
Sulphur minus sulphate sulphur (S)	1.05	–	–	0.87	–

The locations of the level/monitoring points were constrained by the fact that the building was in use as a Youth Facility and it was important to consider both the safety of personnel and the possibility of damage to monitoring points during the daily activities of the Centre. Initially 45 monitoring points were chosen and studs fitted on floors and ceilings. In addition, in order to establish the relative movement within the rooms, in some places levelling points were positioned on both the ground bearing floor slab and an adjacent concrete cap supporting one of the columns which extended to some 2 m below ground floor level. Studs were also placed on each side of the external doorways to determine the variation in level between the floor slab and the door threshold.

Between 11th March 2008 and 14th April 2009 sixteen readings were taken at the 45 monitoring points and the two datum points. Unfortunately, at some locations the points were damaged such that a total of 11 were only read for part of the 13 month period. Rather than provide all the detailed data here, Table 6 gives an indication of the more significant changes over this period. It should be noted that this is in addition to the rise which had already occurred prior to Mar 2008. The points which had risen by more than 3 mm between March 2008 and April 2009 are shown in Fig. 25.

In view of the results obtained in the first six months when five showed a rise of more than 4 mm, a further 57 monitoring points were installed and read between 17th November 2008 and 14th April 2009. At nine points the floor rose by at least 2.5 mm over this 143-day period (Fig. 26). The maximum rise of 3.4 mm (L 49) was in the Reception area where there were also rises of 2.6 and 2.9 mm (L 48 and 96). In the café, at L 45, 50 and 55, the rise was 2.6, 3.1 and 2.5 mm respectively while in the Youth Workers' Office (L 64), there was a rise of 2.6 mm and in the Youth Information Room (L 94 and 95) the rise was 2.5 and 2.8 mm.

A time versus rise graph has been prepared for the six points which rose by more than 5 mm in 402 days (Fig. 27). Even allowing for possible inaccuracies related to the surveying, it is clear that the relative heave was not consistent.

In particular:

(a) There was a relatively sudden rise between 18th June and 9th July 2008. In this 21-day period the average rise of the six points was 1.4 mm. At three points (the café, and Locations 15 and 16 in the entrance lobby) the rise was at least 1.8 mm.

Table 6 Summary of significant rises at various dates after installation on either 5th or 11th March 2008. Number of days in italics refer to installation dates in italics

Date			28/05/08	22/08/08	24/11/08	09/02/09	14/04/09
Days since installation			79/*73*	165/*159*	232/*226*	309/*303*	402/*396*
Location	Survey point	Date of installation	Rise (mm) in days after installation				
Entrance Lobby	15	05/03/08	2.4	4.6	8.1	8.9	10.5
	16		2.7	4.8	7.7	7.9	9.5
Youth Club 1	41	*11/03/08*	1.0	2.0	3.9	3.9	4.6
Café	19	05/03/08	1.1	2.4	3.1	4.3	5.0
Gym corridor	10	05/03/08	0.6	1.8	3.1	2.8	4.3
Gym	34	05/03/08	0.6	2.0	4.7	3.7	5.5
Store 1	38	*11/03/08*	1.5	3.2	5.5	4.7	6.3
Store 2	44	*11/03/08*	0.7	1.7	3.5	2.5	3.7
Courtyard	7	05/03/08	2.6	4.6	7.4	6.5	9.1
Courtyard	8	05/03/08	2.7	4.3	7.4	6.8	9.4
Outside of Gym	2	05/03/08	1.4	2.9	3.9	4.2	5.3
Outside of Gym	3	05/03/08	1.7	4.3	6.2	7.3	8.6

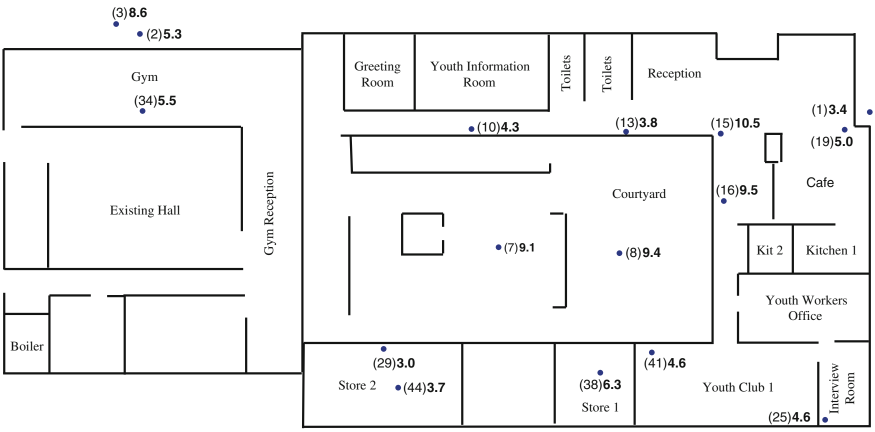


Fig. 25 Levelling points showing a rise of >3 mm between March 2008 and April 2009

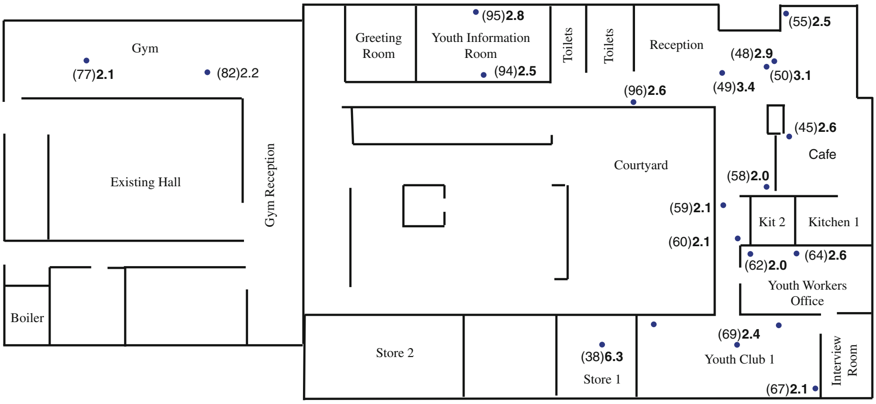


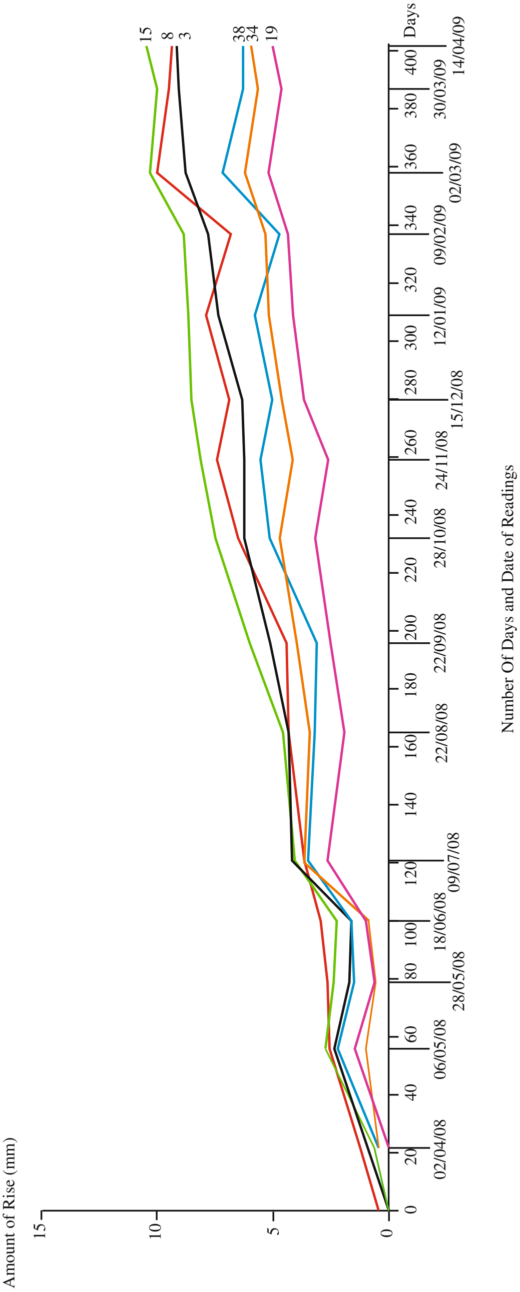
Fig. 26 Points showing a rise of >2 mm between November 2008 and April 2009

(b) Between 9th July and 22nd September 2008, the rise was not generally as fast as the overall average.

(c) There was an apparent drop at two internal and two external locations between 12th January and 2nd March 2009. The records shows that on 9th February 2009 there was an apparent drop of 1.1 mm in Store 1 (Location 38) and 1.6 mm in the Gym (Location 34) while in the courtyard (Locations 7 and 8) apparent drops of 1.4 and 1.1 mm were recorded.

The accuracy of the survey is believed to be within 0.8 mm hence minor “blips” may be associated with the survey techniques. The sudden rise in June/July 2008 would appear to be a consequence of quicker expansion, possibly related to a period of warmer weather. The reason for the apparent drops has not been established. Without further evidence it is considered likely to be related to the survey techniques, possibly a change in staff and/or instrumentation.

Fig. 27 Six monitoring points which rose by >5 mm over 402 days



Assessment of Concrete, 2008

When TPs 11 and 12 were dug in May 2008, it was noted that some of the concrete showed signs of deterioration and some gypsum crystals were present on the surface of the concrete. As a consequence, on 3rd July 2008, the upper parts of the pits were re-opened and a number of samples were cored from the support beam and mass concrete pillars. Figure 28 shows the poor state of the upper part of the beam in the corner of the courtyard (TP 11) where more than 25 mm of the concrete at the top external corner of the beam could be removed with finger pressure.

Based on the GMRS report dated 14th August 2008, on the concrete samples from TP 11 it is noted:

(a) Patches of gypsum up to >50 µm thick were present, coating part of the outer surface of the concrete (Fig. 29);
(b) Ettringite extended up to 8 mm into the top of the ground beam (Fig. 30);
(c) In core 6, ettringite was present in voids. As seen in Fig. 31, there was 10.6 % SO_4 at 1 mm and 7 % SO_4 at 3 mm into the core;
(d) Thaumasite was present to a depth of 2.8 mm in the top of the ground beam and in cracks up to 1.8 mm into the concrete (Fig. 32);

Fig. 28 Deterioration of concrete at the top of the beam, TP 11, and the nature of the dark deleterious fill adjacent to it

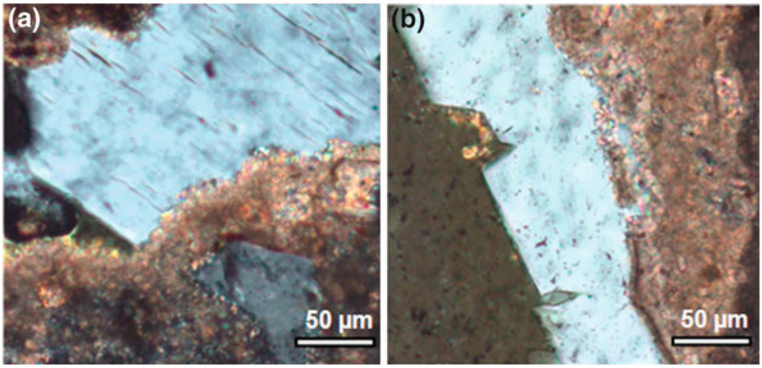
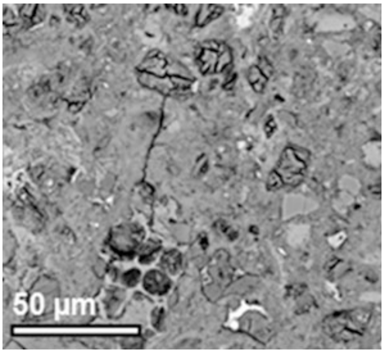


Fig. 29 Growth of gypsum crystals on surface of concrete

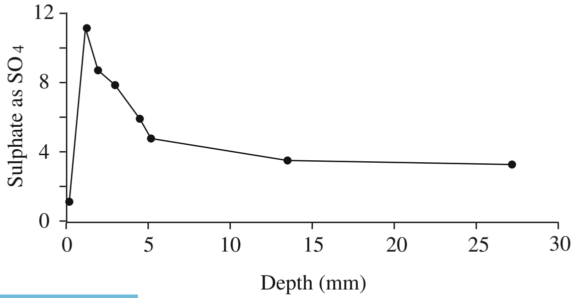
Fig. 30 Abundant ettringite-filled voids, note crack in concrete



(e) At the top of the mass concrete pier, ettringite penetrated into pores and cracks by up to 5 mm. The sulphate profile from the outer surface indicates up to 11 % SO_4 by mass of cement (Fig. 33) and elevated sulphates up to 3 mm into the pier.

Analysis of the GMRS report on samples from TP 12 (outside of the Gym) also indicated high values of sulphate near the outer edges of the concrete.

Fig. 31 % Sulphate extending into concrete pier



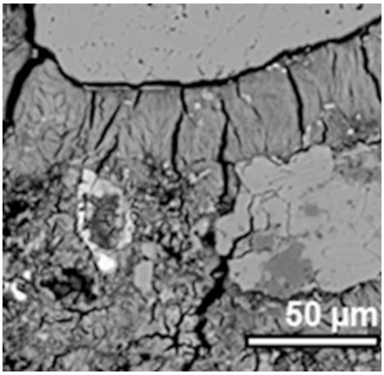


Fig. 32 Fibrous thaumasite in crack around quartz particles, note crack in concrete

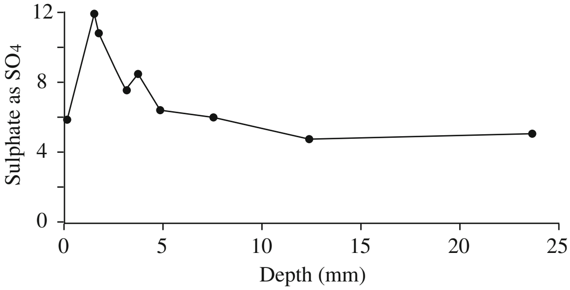


Fig. 33 Relationship between % SO_4 and distance from top of concrete pier

(a) Thaumasite was recorded up to 2 mm from the edge of the concrete at the top of the beam where the sulphate content was 12 % SO_4 by mass of cement;

(b) High levels of ettringite were recorded (up to 12 % SO_4 by mass of cement) extending up to 5 mm into the mass concrete pier;

(c) An infilled crack 3 mm from the surface was seen in a core from the top of a mass concrete pier (Fig. 34). The profile of SO_4 content relative to the concrete surface of the pier is shown in Fig. 35.

(d) Despite the high percentage of sulphates in the concrete, there was little evidence that significant sulphate attack had already taken place although cracks can be seen in Figs. 30, 32 and 34. However, with such high sulphate contents already present, any further sulphate ingress would be likely to cause disintegration of the affected concrete.

Decision to Remediate

Whilst the level monitoring results were informative, the ongoing distress evident in the building itself was such that it was becoming extremely difficult for personnel to continue to use the facility. In addition to the trip hazards at door

Fig. 34 Crack filled with thaumasite and ettringite, note crack in concrete

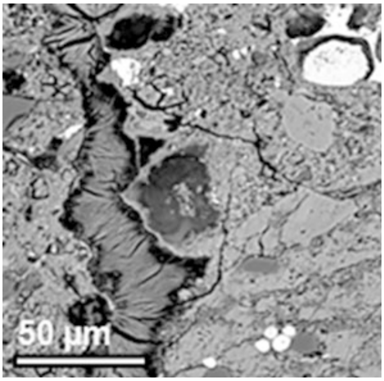
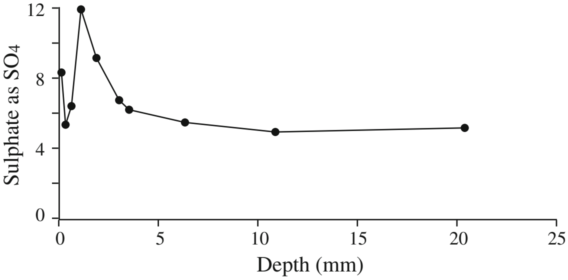


Fig. 35 Relationship between % SO_4 and distance from concrete surface

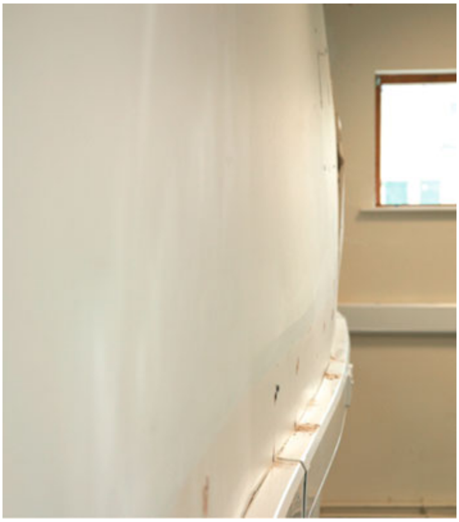


thresholds, the jamming of doors, the unsightly cracking, the stress in the area of electric sockets etc., the shock of hearing a sudden loud noise when the bulging dry lining became so stressed that it cracked made it unrealistic for staff to continue to work in such an environment (Figs. 36, 37 and 38).

The only known practical way of dealing with significant heave due to the generation of sulphates beneath a ground-bearing floor slab is to remove the material containing the pyrite. As described in Canada by Penner, Eden and Grattan-Bellew (1972) in Northern England by Nixon (1978) and in South Wales

Fig. 36 Distortion of plasterboard in office

Fig. 37 Distorted electric service duct



by Hawkins and Pinches (1987), preventing the oxidation of pyrite in the aggregate and hence the subsequent formation of sulphates which would cause further heave is extremely difficult.

Although flooding and inducing chemical reactions have been considered, flooding is generally impractical and to date, the chemical solutions which have been attempted have been found to be both extremely expensive and dubious in terms of their long term success. Further research work is being undertaken, but as yet there is no substantiated evidence of a practical and effective solution to the problem, other than the complete removal of the pyritiferous material or a change in the design of the structure to accommodate the potential heave. As a

Fig. 38 Plasterboard pushed away from plug

consequence, Ballymun Regeneration Ltd decided to remediate the building by removing the imported fill.

Remedial Works

Having provided alternative temporary accommodation for the youth facilities, the original builder commenced remedial works in May 2009. The services were disconnected/removed and, for logistical convenience, the building was divided into three zones (Fig. 39).

The floor was marked out and then cut into 400 mm blocks which could be handled efficiently by site staff (Figs. 40 and 41).

The radon barrier and insulation were taken up and the fill removed using small tracked backactors to load the material onto conveyors for disposal off-site (Fig. 42). Figure 43 shows layers of the replacement fill being compacted.

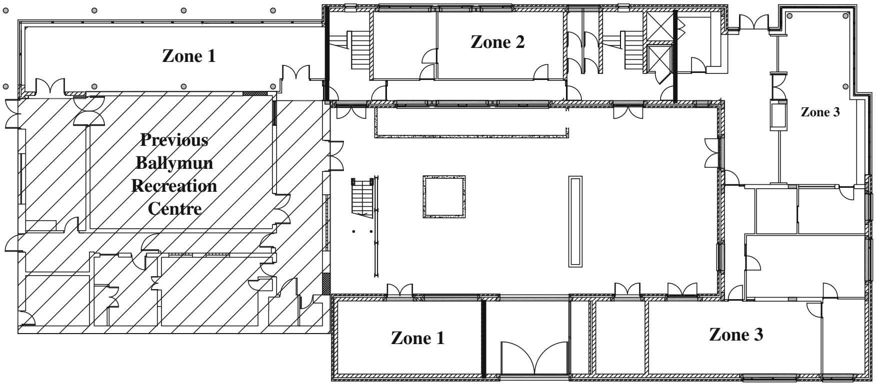


Fig. 39 Zones for the remediation delineated by the builder

Fig. 40 Floor marked for cutting into manageable blocks

Fig. 41 Saw cutting the marked blocks prior to removal

Fig. 42 Removing the fill using a conveyor system

In order to confirm that the observed differential movement was not related to settlement, at each stage of the works the material supporting the walls and pads was assessed to ensure they had been placed on the Black Boulder Clay and that the bearing capacity of that material was adequate to support the load. This was particularly important in the Reception/café area where existing services had been removed at the time of construction and hence the deleterious fill extended to a depth of some 2.5 m.

During the remedial works, numerous samples of the underfloor fill were taken on behalf of both the Client and the builder, for immediate testing and/or storage for future reference. In addition, while the foundations were exposed the opportunity was taken to check whether the deleterious fill had affected the concrete.

On 11th June 2009 samples of concrete from beneath the fill in Store 2 were taken and sent to GMRS for analysis. Their report indicated:

(a) Samples of the mass concrete foundation pad taken from either side of the room had sulphate values of 9 and 12.6 % SO_4 at 1.6 and 1 mm respectively.
(b) The sample from the overlying ground beam had an acid soluble sulphate content of 7.1 % SO_4 up to 0.4 mm from the surface while values of >4 % SO_4 were measured at a depth of up to 2.7 mm from the surface.

Fig. 43 Roller compacting the replacement fill

(c) Up to 10.6 % SO_4 was present in the outer 0.4 mm of a concrete block taken from the rising wall, with >4 % SO_4 extending to a depth of 6 mm from the surface.
(d) No ettringite or thaumasite was identified in the samples from Store 2.

On 1st July 2009, samples were also taken in the area of concrete ground beams beneath the Gym which extended from the original Sports Hall towards the road. Again these were sent to GMRS who reported:

(a) Up to 17.8 % SO_4 was found in the foundation pads supporting the beams, extending up to 8 mm into the concrete. Thaumasite-filled cracks were identified up to 4 mm into the concrete.
(b) A concrete chip from the beam at the southern end of the Gym had sulphate values of up to 14 % SO_4 and thaumasite-filled cracks were observed close to the surface (Fig. 44). Elevated levels of sulphate extended up to 10 mm into the concrete beams.
(c) A sample block from the outer rising wall had sulphate values up to 6.1 % SO_4 with >4 % sulphate recorded up to 25 mm into the block.

On 29th July 2009 concrete samples were taken from beneath the Youth Information Room and lift shaft area. The GMRS analyses indicated:

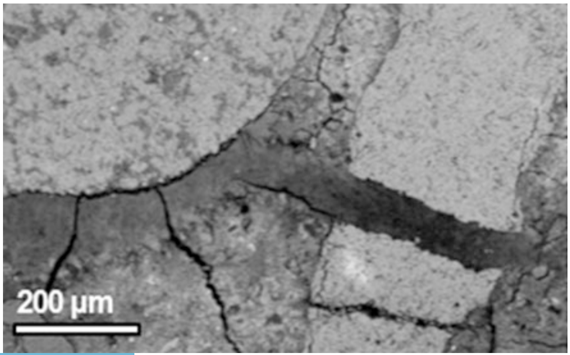


Fig. 44 Thaumasite in beam

(a) Samples 1 and 2 had sulphate values of >4 % SO_4 up to 6 mm into the concrete.
(b) The concrete chippings in core 4 had >4 % SO_4 extending up to 11 mm into the concrete.
(c) In concrete blocks examined from Zone 3, thaumasite was seen to fill pores up to 6.1 mm into the block (Fig. 45).

On 8th October 2009 concrete samples were taken from Store 1. The results of the analyses indicated:

1. A maximum sulphate content of 16.6 % SO_4 with >4 % SO_4 extending into the concrete for up to 10 mm.
2. Thaumasite and ettringite up to 5 mm from the outer face of the concrete.

In view of the extent of sulphate penetration into the concrete/concrete blocks a decision was made to scabble the ground beams where the concrete was exposed during the remedial works. In part this was to ensure that sulphates did not extend as far into the beams as the steel reinforcement. After the outer 1–5 mm had been removed by scabbling, the concrete was coated with a Fosroc product to inhibit further moisture entering into the cementitious material and thus minimise the potential for any future development of sulphate.

Although the concrete block rising walls were also scabbled to remove the high percentage of sulphate in the outer few millimetres, the addition of a Fosroc product was considered desirable to reduce any further ingress of moisture into/through the concrete which could affect the carbonation process in the concrete. Although only limited cracking which could be specifically related to sulphate attack was evident and it was considered that, having minimised the potential for any future chemical reactions, should the outer part of the blocks experience some deterioration this would not compromise the longevity of the structure.

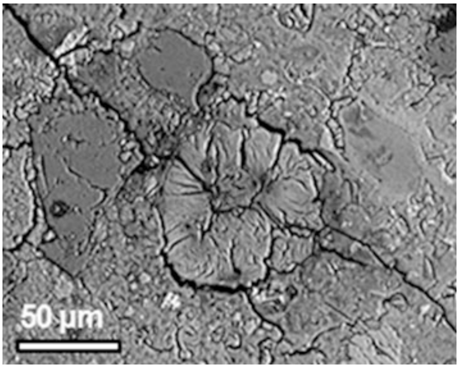


Fig. 45 Thaumasite filling void 6.1 mm from concrete surface

Horizontal Crack

During the remedial works, particularly in Zone 3, it was noted that a horizontal crack with an aperture of some 1–5 mm was present around much of the outer wall particularly beneath the Games Room and Kitchen/Café area. This horizontal crack had no relationship with the damp proof course but indicated a clear parting of the rising wall approximately 0.5 m below ground level.

It became apparent during the works that the sulphates had not only caused a rise in the ground-bearing floor slab by vertical expansion, but horizontal expansion pressures had also been generated. The expanding fill, pressing against the external wall, where there was no smooth-sided gap between the floor slab and the rising wall, caused the whole superstructure to be lifted away from the lower part of the supporting walls.

When the fill was taken out, and hence the lateral pressures removed, the superstructure settled back. The maximum aperture of the horizontal crack is not known but elsewhere in Dublin openings of up to 23 mm have been observed.

Quality of Replacement Backfill

Before a decision was made as to which quarry should be used for the replacement fill, test certificates were requested. On the basis of the results, the quarry selected as potentially suitable was visited by the Client's team. Having satisfied themselves that the quarry was dominantly limestone, with some chert nodules, samples were selected by the team and independently tested. The results of the chemistry testing on the replacement fill (prior to and at the time of placement) are given in Table 7.

As can be seen from this table, the results indicate the replacement fill is effectively chemically inert. In addition, the SEM imagery did not detect any

Table 7 Chemistry of replacement fill

Position	Date Tested	Lithology (%)		Total Sulphur (% S)	ASS (% SO_4)	WSS (mg SO_4/l)	S–S in sulphate (% S)
		Pure Lst.	Chert/ Sil. Lst.				
Stockpile 1	05.10.09	95	5	0.06	0.08	12	0.03
Zone 1	02.11.09	97	3	0.04	0.06	40	0.02
Zone 2	02.11.09	100	0	0.05	0.09	38	0.02
Zone 3	02.11.09	98	2	0.06	0.13	42	0.02
Stockpile 1	07.12.09	97	3	0.05	0.02	34	0.04
Stockpile 2	07.12.09	99	1	0.13[a]	0.02	67	0.12

[a] This sample was further examined and the presence of barite (an insoluble sulphate) identified
Sil. Lst siliceous limestone; *ASS* acid soluble sulphate; *WSS* water soluble suphate
S–S in sulphate sulphur minus sulphur in sulphate

Table 8 Comparison of chemistry of original fill (2007 and 2009) and replacement fill

		No. samples	Av. Calcite (%)	Av. Pyrite (%)	Av. Gypsum (%)
2007	Interior pits	1-5	33.4	2.2	2.8
2009	Zone 1	8	27.8	1.1	5.0
	Zone 2	4	30.4	1.98	5.3
	Zone 3	4	24.7	0.93	5.4
	Average of 16		27.6	1.4	5.3
2009	Replacement	2	82.8	0.15	0.2

significant pyrite, although small cubes/lumps were observed, locked into a dense limestone.

A comparison with the original fill taken at various dates during the remediation is given in Table 8. It can be seen that some 1.5–2 years after the initial samples were taken in November 2007, the 16 samples tested in 2009 had lower average pyrite contents while the average gypsum had increased from 2.8 to 5.3 %.

Summary and Conclusions

Within months of the completion of the Ballymun Youth Facility in 2005, significant cracking occurred and doors began to jam. Within a year of Practical Completion a snag list identified more than 130 cracks, some of which extended for the full height of the room. At the 100 locations recorded in the snag list, damage included cracks in plasterwork, bulging of walls, separation of skirting boards and arching of window cills. Initially the cause of the damage was not clear and it was assumed to be related to normal plaster shrinkage or workmanship issues. However, despite ongoing repairs, the distress continued.

Chemical analyses of five samples of fill taken from beneath the building in late 2007 indicated high levels of total sulphur, acid soluble sulphate and water soluble sulphate while the X-ray diffractograms showed 2–4 % pyrite. The SEM studies proved an abundance of framboidal pyrite in the calcareous mudstone which formed the dominant lithology in the fill. In places the pyrite had already oxidised such that ferrous sulphate rims had formed around the framboids/framboid seeds, causing expansion and cracking of the individual particles. Gypsum in the form of selenite was seen as crystals within incipient discontinuities in the aggregate particles, where clearly the crystal growth had caused dilation. Gypsum was also seen in some veins and as euhedral crystals in the fine material around the individual aggregate fragments.

As the chemistry indicated the potential for further significant heave in the future, Ballymun Regeneration Ltd decided to move the Youth Centre into temporary accommodation and replace the deleterious fill. The source for the replacement fill was chosen based not only on the test results provided by the quarry, but also a site visit by the Client's consultants when they selected samples for independent testing to confirm the suitability of the aggregate.

During the removal of the pyritiferous material, the opportunity was taken to examine concrete which had been in contact with the fill. Although the structural integrity of the concrete had not been compromised, the development of sulphates (including ettringite and thaumasite) had extended sufficiently into some concrete/concrete blocks that it was considered prudent to scabble and coat the outer surfaces to ensure the development/movement of sulphates could not cause a problem in the future.

The remedial works were successfully completed in December 2009 and the Youth Facility was formally re-opened on 14th January 2010 by President Mary McAleese.

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Remediation of Senior Citizens' Dwellings Affected by Pyrite-Induced Heave

Peter Finnegan and A. Brian Hawkins

Introduction

In June 2003 Dublin City Council commenced the development of twenty senior citizens' dwellings in Donnycarney, west of Clancarthy Road (Fig. 1). In addition to the 2-storey apartment blocks there is a communal laundry and a boiler house which provides central heating for the three blocks (Fig. 2).

The construction was completed in September 2004 but within 18 months cracks appeared in the ground floor walls. Distortion was noted in the kitchens and in some cases the water in the shower trays did not flow towards the drains.

Following the appreciation that damage which had occurred in buildings in other areas in Dublin (notably to the ground-bearing floors slabs) was related to defective stone fill, it was decided to remove the floor coverings. After observing the severity of the distress, samples of the stone aggregate beneath the ground-bearing floor slab were taken. Testing indicated excessive levels of pyrite and the presence of gypsum.

This chapter describes the site and the design of the structures, the nature of the distress, the characteristics of the fill and the remediation process. Of particular note were the horizontal cracks in the rising walls, which effectively separated the superstructure from the wall foundations.

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DOI: 10.1007/978-3-319-00221-7_5,

Fig. 1 View from Clancarthy Road into the development

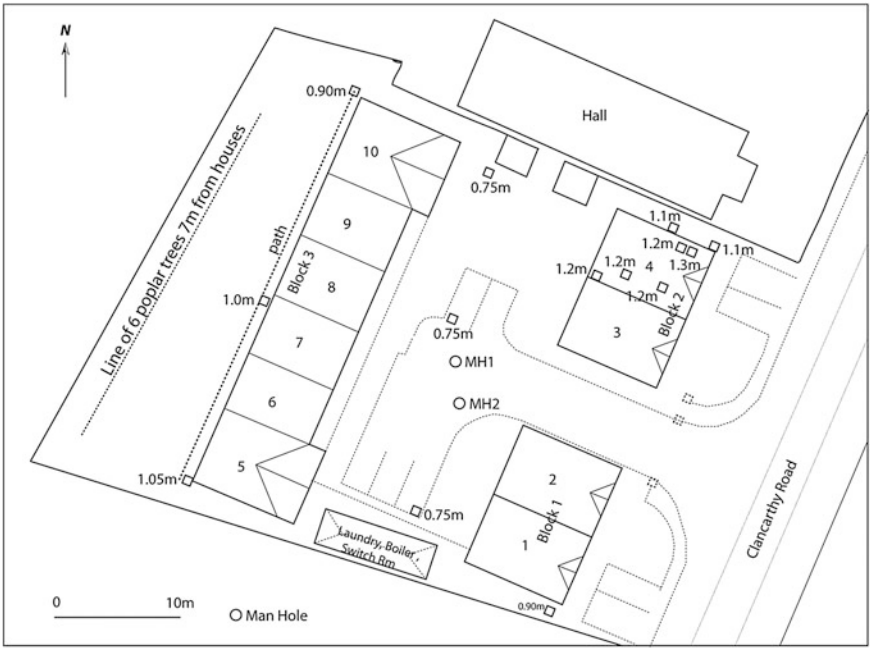

Fig. 2 Layout of the development and the location of the pits where the fill thickness was measured

The Site

The original site had a gentle fall to the east. In order to provide an effectively flat area for the courtyard/car park, it was necessary to excavate at the rear of the properties and to create a relatively steep slope at the entrance to the site, off Clancarthy Road (Fig. 1).

Each of the three apartment blocks consists of ground floor flats and upper maisonettes. The two blocks which front onto Clancarthy Road are separated by the site entrance, while at the rear there is a 35 m long terrace consisting of six flats and six maisonettes. To the south of the site there is a communal laundry and a boiler room/switch room which serves all three apartment blocks. To the north of the parking facility there is a small building in which waste bins are housed.

The buildings are constructed of load-bearing masonry on strip footings. The ground floors consist of an upper screed underlain by a reinforced concrete slab beneath which is an insulation layer and a thick polythene sheeting over imported fill material. Trial pits were dug around the site to establish the thickness of the fill. As seen in Fig. 2, beneath Block 2 (adjacent to Clancarthy Road) the maximum thickness of fill was in the order of 1.2 m, decreasing to some 0.75 m in the courtyard area. Beneath the long terrace block at the rear of the site the fill was in the order of a metre thick; the area having been overdug to simplify the installation of the services.

As seen in Fig. 3, all the upper maisonettes have balconies. In the front blocks these are concrete structures; the weight of the concrete being counterbalanced by an in situ strip of floor. The small steel balconies to the rear of the apartment block are counterbalanced by an in situ strip extending into and running the length of the structure. The front walkway is supported by steel columns. To the west of the long terraced block there is an excavated slope and a pathway. Close to the site boundary some six Lombardy poplar trees are present, but these are approximately 7 m from the rear of the flats (Fig. 2).

Nature of the Distress

The individual floors were floated within the rising walls, i.e., the floors did not span over the rising walls. Initially the most obvious forms of distress were the cracking of tiles (Fig. 4) and the change in water flow direction in the shower rooms. In the kitchens, where the ends of work surfaces were held down by tiles, the rise in floor level was accommodated by an arching of the middle of the worktops, often up to 20 mm (Fig. 5). In other rooms, the rising floor pushed radiators upwards such that they were lifted off of their supporting brackets (Fig. 6) and wardrobe doors were jammed against the ceiling (Fig. 7). The floors themselves were often domed, with significant gradients towards the edges of the

Fig. 3 Block 3, front elevation showing manholes and rear elevation showing location of trial pits

Fig. 4 Cracking of tiles in a shower room

Fig. 5 Deflection of the kitchen worktop by 9–10 mm

Fig. 6 Vertical displacement of radiator relative to wall fixing brackets

Fig. 7 Wardrobe doors pushed upwards against ceiling

Fig. 8 Floor cracking in Apartment 8

rooms. In a number of the flats there was a clear rotation of the internal lintel due to lifting of the partition walls.

When the covering was removed from the ground-bearing floor slabs, significant "spider cracking" was seen in the screeding (Figs. 8 and 9). Subsequently, cracks were proved to extend down through the underlying concrete slab. In some rooms, such as the sitting room in No. 2, the doming was not so apparent but the reinforced slab rose as a single entity, leaving a pronounced lip of some 48 mm

Fig. 9 Floor cracking in Apartment 10

Fig. 10 Floor slab rising, causing lipping by the wall (Apartment 2)

Fig. 11 Horizontal crack in manhole

adjacent to the bathroom wall (Fig. 10) and up to 18 mm against the rear external wall.

In the entrance corridor of No 2, the bottom of the gable wall had been pushed outwards by some 20 mm. On the external side of this wall, a brick footpath showed compression with the bricks arched in the middle such that a pronounced separation of the bricks could be seen.

Externally, a number of cracks were seen in the walls at the location of the balcony supports and at the base of the lintels to the ground floor French doors. When the manholes in the courtyard were lifted, horizontal cracks were observed with apertures of up to some 20 mm (Fig. 11). It was clear, therefore, that the biscuit of the manhole had risen such that the surface was separated from the main chamber. Around the manholes the tarmac showed some deflection and distinct tear cracking. Very severe cracking was observed in the boiler room. Here, vertical poles had been constructed on the floor slab to support the pipework. When the floor rose, the vertical poles pushed up the roof structure such that it was lifted off the perimeter walls by up to 15 mm.

Sampling and Testing

In view of the severity of the distress being experienced by the buildings, Dublin City Council instructed Ground Investigations Ireland to undertaken some sampling and analysis of the material beneath the ground-bearing floor slabs.

Initially, on 6th March 2009, a 0.45 × 0.45 m trial hole (TP 2a) was excavated at the entrance to No. 2. A tub sample was taken at 0.26 m below floor level; two bag samples between 0.26 and 0.5 m and a further bag sample between 0.5 and 0.61 m. In the light of the test results, in December 2009 further samples were obtained from trial pits in Nos 2, 4 and 10 and from the store room. At the same time, an external sample was taken from beneath the pavement outside of No 7. The locations of the samples are shown in Fig. 12 and the depths of the tested samples are given in Table 1.

When TP 2a was inspected, a horizontal crack was observed at 680 mm below floor level. A trowel pushed into the crack met no resistance until 225 mm when it encountered fill on the far side of the concrete block wall. Subsequently a trial pit was undertaken at the rear of the properties, approximately halfway along the terrace block (Fig. 3). A 8–10 mm horizontal crack was observed some 650 mm below the damp proof course. As seen in Fig. 13, a saw could be pushed into the crack for 350 mm. Where the mortar was missing the aperture was some 20 mm (Fig. 14).

Nature of the Fill

The samples of fill were sent to Geomaterials Research Services Ltd (GMRS) who were asked to undertake both chemical and X-ray analyses and to provide a petrographic description of the material. For convenience, the results are summarised here in Table 1. This includes the six samples taken from interior pits and the exterior sample from the pavement, referred to as Sample 7.

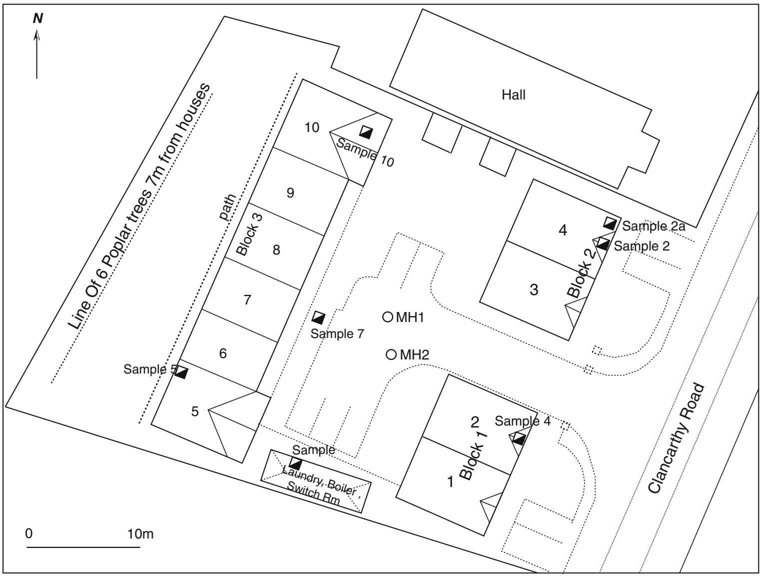

Fig. 12 Location of sampling points

The grading of the fill from beneath the ground-bearing floor slabs was typical of NRA Clause 804 material while the fill from beneath the pavement was much coarser in character, containing more rounded gravel and cobble sized particles. The material was also lighter in colour and clearly represented the backfill of a service trench. Although the results have been included in Table 1, as the material is so different from the general fill from beneath the ground-bearing floor slabs, it is not discussed further in this chapter.

Five of the six interior samples consisted mainly of mudstone (>70 %). When the material was examined in the laboratory, some half of the mudstone was found to have a distinctly laminated structure. Although some pure limestone was present, a number of the fragments were seen with the microscope to have a significant argillaceous or carbonaceous content. The fragments also contained some phyllite. Only 27 % mudstone was recorded in Sample 2A (from adjacent to the front door of Apartment 4) with the main lithologies being limestone (34 %) and phyllite (12 %). Comparing this with the other samples suggests it was a mixed material, some of which may have come from a different quarry.

In the interior samples, the X-ray analysis indicated that generally between a quarter and a third of the material consisted of calcite; the analysis showed that the fine platy minerals present were illite and mica. The X-rays indicated that all the interior samples had >1 % pyrite while the proportion of gypsum varied between 2 and 6 %; the maximum being in the storeroom material.

Table 1 Lithology and chemistry of the trial pit samples

	Internal Samples						External
	2A	2	4	5	10	Storeroom	7
Sample depth (m)	0.25–0.50	0.30–0.53	0.28–0.55	0.30–0.53	0.30–0.58	0.20–0.43	0.05–0.28
Moisture content	4.14	6.18	5.84	6.18	6.66	7.05	5.63
Colour	Dark grey	Dark grey	Dark grey	Dark grey	Dark grey	Dark grey	Medium grey
Shape	Flaky/blocky	Flaky	Flaky	Flaky	Flaky	Flaky	Flaky
Calc. lam. mudst	17	51	39	51	46	48	1
Calc. non-lam. mudst	10	22	29	22	27	22	4
Lam. si. carb. arg. lst.	9	1	2	1	1	1	<1
Non-lam, si, carb, arg, lst.	11	4	9	4	7	5	5
Carb. limestone	25	8	9	8	5	8	35
Pure limestone	9	4	7	4	5	10	35
Calc. sst, sandy silty lst	2	4	3	4	5	3	1
Chert/silicified lst.	3	–	1	–	–	–	8
Quartz and quartzite	–	1	–	1	1	–	4
Phyllite	12	5	1	5	–	2	2
Calcite	30	31	28	31	29	27	58
Illite/Mica	18	16	16	16	12	17	6
Pyrite	1	1.2	1.1	1.2	1.1	1.3	<0.1
Gypsum	2	4	4	4	5	6	0
TS (% S by mass)	1.39	1.27	1.20	1.27	1.38	1.71	0.16
ASS (% by mass SO_4)	1.58	1.78	1.54	1.78	2.04	2.14	0.2
WSS (mg SO_4/l)	1602	1,758	1,730	1,758	1,804	1,734	64
Total S minus sulphate (% S)	0.86	0.68	0.69	0.68	0.70	1.00	0.09

Note: *lam*-laminated; *si*-siliceous; *carb*-carbonaceous; *arg*-argillaceous

Fig. 13 Saw pushed 350 mm into horizontal crack (rear wall of block 3)

Fig. 14 8–10 mm aperture where the mortar has not broken away

The chemical analysis indicated:

1. The total sulphur varied between 1.2 and 1.71 % S by mass;
2. The acid soluble sulphate varied between 1.54 and 2.14 % SO_4;
3. The water soluble sulphate varied between 1,602 and 1,804 mg SO_4/l;
4. The total sulphur minus sulphur in sulphate (which gives an indication of the potential oxidisable sulphide remaining in the material) varied between 0.68 and 1 % S.

The scanning electron microscope work indicated framboidal pyrite was present in all the samples from beneath the ground-bearing floor slabs. All five samples contained gypsum, both infilling cracks/veins and as euhedral crystals which had formed on the surfaces of the rock fragments within the fill.

Interpretation of the Results

As discussed below, the material tested was unacceptable as fill beneath concrete floor slabs and/or adjacent to concrete/concrete block rising walls.

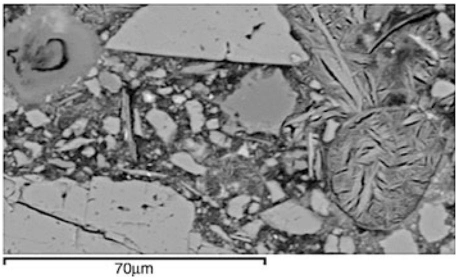

Fig. 15 Ettringite formed in a void 25.5 mm from the outer face of a concrete block

1. The total sulphur was above the 1 % S threshold recommended in the Irish Standard (SR 21:2004);
2. The acid soluble sulphate was above the 0.2 % SO_4 threshold in SR 21 and in the NRA 800 Series;
3. The water soluble sulphate threshold at the time of construction was 2,300 mg SO_4/l but from 2004 onwards the requirement was to test acid soluble rather than water soluble sulphate. The 2005 edition of TRL 447 (Reid et al) limits water soluble sulphate to 1,500 mg SO_4/l within 500 mm of concrete;
4. The sulphur minus sulphur in sulphate threshold is not discussed in the Irish Standards. This gives an indication of the amount of sulphur remaining which could potentially be oxidised. In 1992, Hawkins and Pinches (1997) suggested a threshold of 0.5 % S total sulphur minus sulphur in sulphate. while in 2001 TRL 447 (Reid et al) recommended an oxidisable sulphide limit of 0.46 % SO_4 which was reduced to 0.3 % SO_4 in 2005. As seen in Table 1, all the fill tested had values above 0.68 % S.

In view of the fact that the manholes showed significant signs of distress (biscuits rising), in retrospect it is unfortunate that a sample of the fill in this area was not obtained. However, in order to assess the extent of any sulphate ingress into the concrete block rising walls a number of 143 mm cored samples were taken through the rear wall of Nos 5 and 7 and the side wall of No 10. The analysis is given in Table 2.

With concrete blocks, the sulphates (ettringite and thaumasite) are generally precipitated in voids within the block (Fig. 15). Figure 16 shows the variable distribution of sulphates within the same sample.

Table 2 Sulphate contents in concrete cores measured from inner/outer surface

Location	Outer/inner end	Max SO_4 in paste (wt. %)	Depth of max sulphate (mm)	Max depth >4 % SO_4
No 5 rear wall	Inner	14.5	20.5	36.5
No 7 rear wall	Outer	13	25	29
No 7 rear wall	Inner	7	27	27
No 10 side wall	Outer	10	9	26
No 10 side wall	Inner	10	5	23

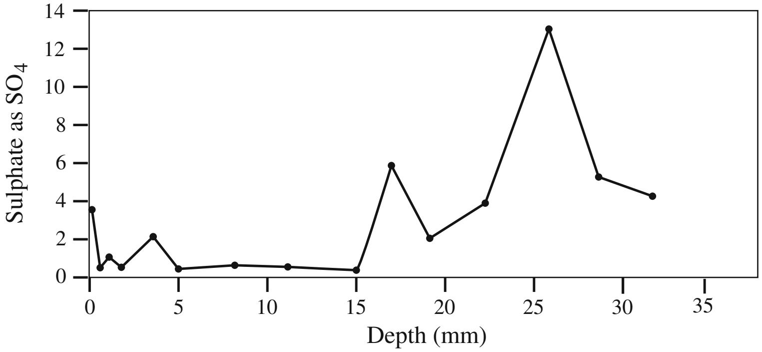

Fig. 16 Variation in sulphate content along a profile from the outer face of a concrete block

Fig. 17 Void near the outer face of the block infilled with ettringite and thaumasite

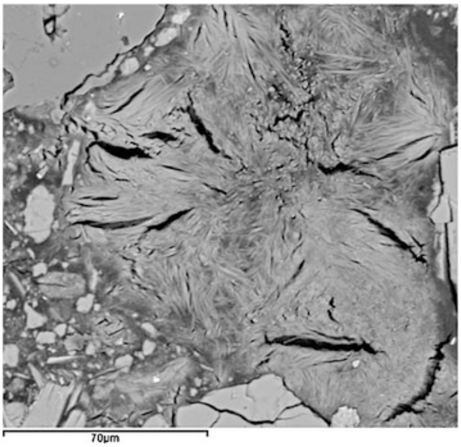

Figure 17 shows ettringite and thaumasite forming in the outer part of the sample from Flat No. 10. The photograph is at a depth of 10 mm. Figure 18 shows the variations in sulphate value along a line from the outer edge of the block. No cracks filled with ettringite or thaumasite were seen in the concrete cores.

The movement of groundwater had clearly taken sulphates into the blocks from the pyritiferous fill such that within seven years many of the voids near the inner and outer surfaces had been infilled with ettringite and thaumasite. However, it was considered that if the deleterious fill was removed such that little further development of sulphate would take place, the structural integrity of the thick rising walls would not be compromised by the amount of sulphate development which had already taken place.

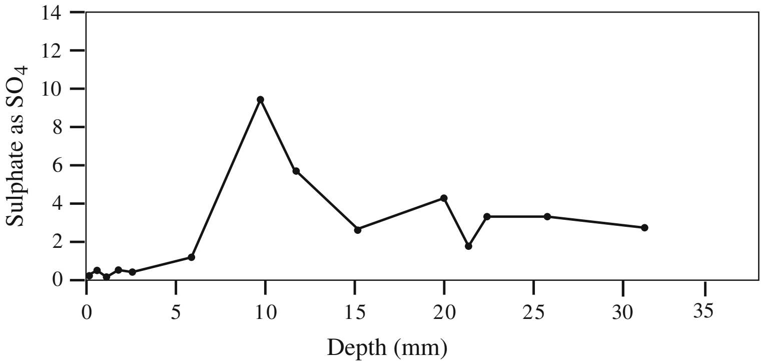

Fig. 18 Variation in sulphate content from the outer surface of the concrete block

Remedial Works

In view of the extent of the structural damage, a decision was made that the only satisfactory long term remediation would be to remove the deleterious fill. In order to do this, it was necessary to temporarily re-house the occupants of the apartments.

The remediation took place between May and August 2011. Following the disconnection of the services and dismantling of all internal fittings (kitchens, showers etc.), all non load-bearing blockwork partitions were demolished to maximise the efficiency of the machinery used to break up the concrete floors and remove the stone (Fig. 19).

The noise, dust and general disturbance created by mechanically breaking up the floor was considerable; the stone had been so well compacted using whacker plates that the small machines had considerable difficulty in loosening and removing the fill (Fig. 20). In hindsight, it would have been preferable to have cut the floor into blocks which could then have been removed by hand.

Fig. 19 Broken up floor slab

Fig. 20 Removal of stone

It was noticed that when the wall partitions were removed, lintel bearings which had appeared slightly open prior to the remediation closed. The external cracks in the balconies also appeared to close, suggesting that the non-loadbearing blockwork partitions may have been attracting load. Although the partitions rested on independent strip footings, the open bed joints observed during the investigations (see Figs. 13 and 14) indicate that the walls had been lifted through the clenching action of the stone. Demolition of the partitions relieved the upward forces on the first floor slabs which were tied to the external walls, allowing the lintels to settle on their bearings.

It was anticipated that the cracking of bed joints in the rising walls would be more extensive and this proved to be the case (Fig. 21).

During the removal of the floor slab, it was noted that perimeter insulation had been omitted in the original construction, allowing direct contact between the slab and the gable wall. In addition, the gable of Unit 2 only had a footpath outside, whereas the opposite gable of the same block was adjacent to the entrance driveway between the front buildings. It appeared that the more confined gable experienced more movement.

Fig. 21 Several cracked bed joints in rising wall

Recording of Information

At the outset of the works it was assumed that once the fill had been removed, the building would "settle" over a period of some 7–10 days, and appropriate periods were built into the tender documents to allow for this. It was intended that during this period, some form of monitoring would take place to record the movement of the building with the closure of the cracks. Several attempts were made to capture the movement on camera, but due to the rapidity of the recovery of the building, this had limited success. Measurement of crack width at the vertical face of the rising wall proved too subjective to provide a realistic rate of closure.

Cracks such as those shown in Fig. 22 were observed following removal of the stone fill on one side of the wall. As a consequence, dial gauges were fixed across the cracks and measuring locations were marked before the fill on the other side of the wall was removed. It is likely that some settlement of the wall occurred during the removal of the stone on the first side of the wall, although that could not be measured.

Initially, attempts were made to record the recovery of the walls using the video function on a pocket digital camera. This was unsuccessful as the removal of the stone on both sides of a wall can take up to 2 h, and the camera did not have sufficient capacity. A second attempt was made using timelapse photography as shown in Fig. 23. Photographs were taken at approximately one minute intervals for the duration of the excavation with the time shown on the clock in the background and the relative displacement shown on the dial gauge. The dial gauges were accurate to one hundredth of a millimetre i.e. one complete revolution of the gauge shown was one millimetre (Fig. 24).

It was noticed that the downward movement of the wall was not gradual, but incremental, with the movement happening in "bursts" of approximately 0.75 mm following a period of no movement. Secondary tell-tales in the form of strips of

Fig. 22 Measuring crack width with calipers

Fig. 23 Timelapse camera set-up

Fig. 24 Dial gauge fixed across cracked bed joint

DPC were inserted into some of the cracks. As the cracks closed, the strips were squeezed in place, indicating that effectively complete recovery of the wall had taken place. Dial gauges were also left in place for up to two days after the excavation, although no significant further closure of cracks was recorded.

The dial gauges were extremely sensitive to any movement of the wall and at times recorded widening of the crack for a short interval when the excavator was working in the immediate vicinity of the wall. This also indicates how fragile the building was at that stage and the importance of the skill of the operator with a small machine. For future similar exercises, a second camera is recommended to record the activity of the machine. This can be correlated with the closure of the cracked joint.

Lessons Learned and Further Work

1. During the excavation it was found the stone was very tightly packed, especially near the rising walls. This was not expected, as normally where the depth of stone is greater above the strip footings, it is unlikely to be as well

compacted as in the centre of the floor slab. It is evident from an examination of the fill and the structural distress which occurred in these buildings that the expansion of the fill takes place both laterally and vertically.

2. Whilst the greatest visible expansion/heave tended to be towards the centre of the floor slabs, it is clear that the rising walls inhibited the lateral expansion of the fill, causing a densification of the material around the outer edges of the rooms. It was the effect of this confinement that resulted in both a densification and the gripping of the rising walls such that when vertical heave took place, movement of the whole structure occurred.
3. The building appeared to recover in three stages. An appreciation of these stages is important when determining and programming remedial works, particularly when terraced properties are involved.
   a. When the partitions (which had become load-bearing) were removed, lintels straightened and cracks in balconies closed;
   b. When the floor slab was broken, reducing the confining pressure, the walls dropped and re-adjusted to their original vertical alignment;
   c. When the stone fill was removed, the horizontal cracks closed as the building settled back effectively to its original position.
4. Where a long terrace is involved, it is important to remember that the removal of the stone fill, both outside and inside the individual properties being remediated, will affect the confining pressure and potential settlement of the adjacent properties. Recovery of one part of the terraced structure may have commenced or be completed in one remediated unit before any movement takes place in adjacent units and as a consequence, secondary cracking can result.
5. It is preferable to saw cut any portion of slab in the immediate vicinity of a rising wall as breaking out can cause damaging lateral forces.
6. The size of machine used to remove stone needs to be carefully considered to limit the damage to the building while maximising machine operations. Damage can result from physical striking of ceiling by the machine "knuckle" or when removing stone from the immediate vicinity of a rising wall. Although the rising walls can be re-used, they are fragile in their cracked state and particularly when stone is being removed from one side.

The Avila Experiment

The effect of the horizontal cracks was also observed at Avila Park where six bungalows had been constructed in 2005. Cracks in the internal plasterwork were reported by the occupants within a year. By September 2006, cracks were also visible in the external elevation. Examination of the design and construction, which was identical to that for houses previously built at the same location, failed to reveal any structural defects to which the cracking could be attributed. Trial pits and foundations were examined by a geotechnical engineer but the outcome was inconclusive.

By 2008, it was becoming widely known that defective stone fill was the cause of distress in many houses in the North Dublin area. As a consequence, the Avila development was revisited, and it was appreciated that the damage was entirely consistent with heave of the stone infill and a consequential lifting of the floor slab. Samples of the fill were taken and tested, which revealed the presence of pyrite (including the framboidal form) and the development of gypsum.

Further investigation revealed that the floor slab had lifted the internal walls, which were "toothed" into the inner leaf of the external walls. When the inner walls were pushed up, the outer leaf of the external walls did not generally lift but a large crack appeared in the course of blockwork above the lintel. This was attributed to the tying of the two leaves of blockwork together, as a single steel cavity wall lintel had been used. In some cases this crack had opened by 18 mm, and by the spring of 2012, one house had a horizontal crack some 25 mm wide.

In August 2011, some experimental works were undertaken in an attempt to relieve the confining forces. Internal walls were removed in some instances and saw cut where they were bonded to the external walls. Blockwork was removed where it was in contact with the bottom chord of roof trusses. A perimeter strip of floor slab was saw cut and removed so that it could not bind on the external wall,

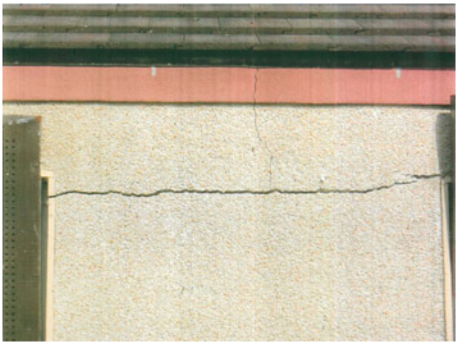

Fig. 25 Crack in external wall prior to removal of internal load-bearing wall taken at 10:30 a.m.

Fig. 26 Closure of crack in Fig. 25 taken at 11:30 a.m. on the same day after removal of the inner wall

as had occurred at Clancarthy Road where the misplaced perimeter insulation allowed contact between the floor slab and the wall. The intention was to relieve the forces on the superstructure and arrest further damage.

The works were carried out over one week in August 2011. Saw cutting of the concrete was successful, except in corners where the radius of the saw blade prevented clean cutting such that these pieces had to be broken out. A two-minute video, made with a pocket digital camera mounted on a stepladder, recorded the 12 mm crack shown in Fig. 25 closing in a period of 10 s (Fig. 26).

Although the house is still a very damaged building, it would appear that the distress has been arrested. To date, no defective stone has been removed from the house. It is to be expected that the rising walls will have many cracked bed joints that will be revealed during remedial works. Ongoing observation and monitoring of this building may throw light on alternative methods of remediation in some structures.

Conclusions

The chapter describes the problems encountered due to sulphate-generated heave at two sites in North Dublin. In both developments the ground-bearing floors slabs were placed over imported pyritiferous fill; the pyrite being present both as cubes/lumps and in the framboidal form.

At Clancarthy the floor slabs rose by almost 50 mm, causing extensive distress to the buildings, while where the expanding fill had "gripped" the rising walls, horizontal bedding joints had opened as the whole building was lifted upwards. The chapter reports experiments undertaken to determine the speed with which the cracks closed when the pressure was released as the fill was removed. Time-lapse photography indicated the closing of the crack occurred quite suddenly; once it had started the crack was effectively closed within minutes.

At Avila, the internal walls were "toothed" into the internal leaf of the external walls founded on pyrifterous fill. As a consequence, when the floor rose the whole roof structure was raised and a pronounced horizontal crack developed just below the eaves of the bungalow. Again, when the forces were relieved by the separation of the internal walls from the rising slab, the horizontal cracks in the superstructure effectively closed within 10 s.

Some "lessons learned" from the remedial works included:

1. Cutting the concrete floor slab prior to removal is preferable to simply breaking up the concrete;
2. Trial pits should be undertaken to ascertain the extent and significance of horizontal cracks on bed joints and to determine whether they are at a consistent level within the blockwork;
3. The advisability of removing the fill on both sides of the rising walls simultaneously to minimise any differential stresses in the superstructure;

4. The importance of considering the effect of any sulphate development in/on concrete/concrete blocks;
5. The characteristics of the building movement, during remediation i.e., its speed and incremental nature;
6. The confining effect of small elements, e.g., plaster etc., which has significant consequences.

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The Effect of Pyrite-Related Heave: A Structural Engineer's Perspective

Paul M. Forde

Introduction

It is well known that structures may suffer distress related to ground conditions, for example as a consequence of mining, dissolution in limestone terrain, landslips, inadequate bearing capacity etc., while seasonal shrink/swell often causes cracks to open in summer and close in winter. However, when a number of new properties in the Dublin area were found to be experiencing significant distress in 2006, none of these more common causes could explain the ongoing problem. After some early misdiagnoses, it was found that the buildings were affected by heave due to sulphate generation in the imported fill.

This chapter presents some experience of dealing with the effects on houses when sulphates developed in a pyritiferous infill placed beneath ground-bearing floor slabs.

Background to the Problem

My first introduction to the problem was on a housing development of over 400 homes in 2006. The houses had only been built in 2003/2004 yet the owners were complaining of cracks opening above door heads in internal walls. These walls had been built directly on a continuous ground-bearing floor slab rather than on individual rising walls. On inspection, the cracks appeared to be far more severe than would be expected in new properties. Subsequently, DBFL were asked to consider a number of other properties which had suffered similar damage.

Initially the problem was misdiagnosed as settlement of deep sections of fill against rising walls (Fig. 1). In the first houses, it was recommended that grout

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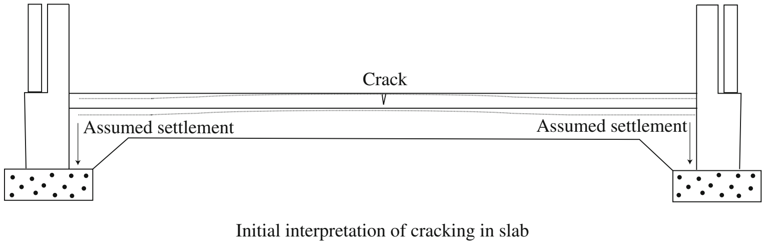


Fig. 1 Initial interpretation of cracking in the ground-bearing floor slab

should be pressure-injected into any voids in the fill. However, when cracking recurred in the same houses, it was clear that a different cause was responsible and it would be necessary to review the previous conclusions.

In late 2006 samples were taken from one of the houses and sent to Trinity College, Dublin. Following testing by Dr. Robbie Goodhue in December 2006 and a report by Dr. Trevor Orr in March 2007, it became apparent that the fill used beneath the floor slabs contained pyrite and that, as a consequence of oxidation of the pyrite, gypsum had formed. It was known that the chemical processes involved cause expansion.

This finding had significant implications as the client had used the same fill under about a thousand homes on three estates built at a similar time in the north Dublin area. The problem did not appear to have been experienced previously in Ireland and hence the critical issue was the necessity to confirm that this was the cause of the damage, and if so, to determine the most appropriate remediation.

From a literature review it became apparent that similar problems had occured in Canada and it was decided Golder should be asked to become involved. It was considered they would be able to deal with the geotechnical aspects as they had considerable world-wide experience and had worked on the pyrite problems in Canada.

Initial Inspection and Prognosis

Engineers and architects face significant problems in identifying pyrite-related damage in the early stages when it can be mistaken for normal shrinkage cracking etc. Most builders will treat the damage as normal snagging and will only become puzzled and suspicious when there is recurring damage. It was this recurrence of remediated damage which led to further investigation of the initial housing development and the same scenario has been encountered on many other sites.

One of the questions raised most frequently by both clients and homeowners at the early stages is whether the damage will stabilise, can be stabilised, or whether it will continue for some time in the future. As a number of factors are involved in the rate of heave as well as where and how it will be manifested, this is extremely difficult to answer satisfactorily and in all cases, significant investigation is required to clarify the extent of the problem.

Methods for Describing, Investigating and Monitoring Damage

Engineers are accustomed to describing wall and floor cracking and its remediation, using the guidance given in BRE Digest 251—*Assessment of damage in low-rise buildings* (1995, revised 2011). While this Digest is a very useful tool in categorising visual damage, I must stress that it is *not*, by its own admission, to be used in determining the appropriate remediation for *progressive* damage.

Under the section *Classification of Damage* it stresses that …*The classification relates only to visible damage at a given time and not its cause or possible progression which should be considered separately*… and also that… *Great care must be taken to ensure that the classification of damage is not based solely on crack width since this factor alone can produce a misleading concept of the true scale of the damage. It is ease of repair of the damage which is the key factor in determining the overall category of damage for the whole building.*

Engineers should proceed with caution during the initial inspection of a property suspected of suffering pyrite-related damage as they will be faced with many critical and potentially contentious considerations. Amongst these are:

(a) Where is the treatment of this problem going, and what significance will my report have?
(b) Am I looking at a property in isolation or is it possible to examine adjacent properties in the development to establish trends?
(c) How much is known of the source of the stone filling (quarry history)?
(d) Should I be advising testing of the stone at this stage, which can be a sizeable expense for a homeowner?

If the problem is likely to go to court or arbitration then a systematic Method Statement should be agreed in advance between the client’s legal advisers and the engineer, who at this stage should have advised the client to engage the services of specialist geotechnical experts.

The inspection should record all damage meticulously on floor plans and wall elevations with the use of sketches and photos. Crack widths should be measured using appropriate methods.

It is also worthwhile to mark and date crack termination points (see Figs. 2 and 3). Any evidence of previous repairs should also be noted, particularly repairs that do not appear to have been successful i.e. where damage has re-appeared.

When preparing these records it should be appreciated that further inspections may be carried out in the future. Indeed, they can be very useful in establishing progression, which is a very significant feature of pyrite-related damage and can be

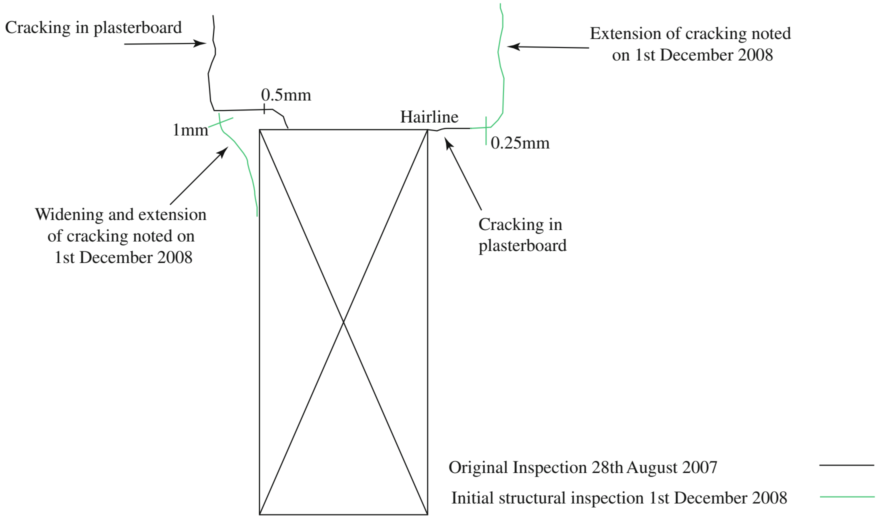


Fig. 2 Damage recorded in an internal wall of a house indicating progression over an interval of 15 months

very important in confirming that the damage is not related to other causes, e.g. consolidation of the fill, drying out of plaster etc.

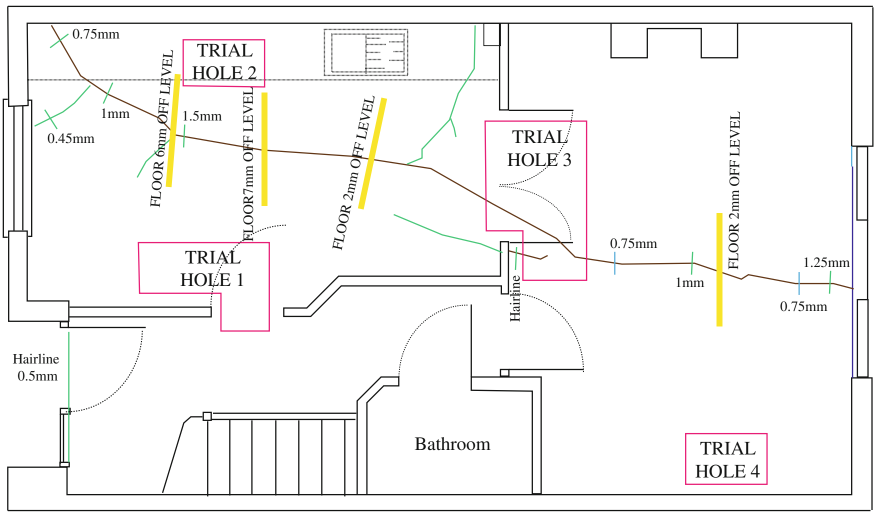
Mechanism of Heave/Response of Structures

Experience of inspection, testing and reporting before, during and after remediation on a wide range of projects since 2007 has indicated that the effects of pyritic stone infill differ, depending on a number of aspects of the structural design. It is clear that a complex interaction takes place between the expanding stone infill, the ground floor, the rising walls and foundations, and the superstructure (Fig. 4).

Where the stone infill is very confined, such as adjacent to party walls and internal rising walls, very large forces are developed which cause the walls to be lifted and the formation of horizontal cracks in the rising walls. Where the stone infill is less confined, such as at external walls where outward movement can occur, the forces generated by the expanding stone infill can be relieved or partially relieved.

Continuing lateral pressure causes outward stress on the external rising walls and this can lead to cracking and lateral displacements (Fig. 5). The movement is not always obvious, but during the remedial works evidence of the lateral pressures exerted by the fill was found in numerous properties.

In some properties, sudden apparent rises were noted in the ground floor slab within a number of days after the removal of the ground floor slab in the adjacent property i.e. on the other side of a common party wall.



Ground floor plan:

Items noted during structural inspection	19th February 2008	—
Items noted during re-assessment on	24th April 2008	—
Inspection on	4th + 5th March 2008	—
Items noted during structural inspection	10th September 2008	—
Positions of Trial Holes dug through floor	15th + 16th September 2008	—

Fig. 3 Damage recorded in a floor slab during four visits over an 8 month period. Progression in the width and extent of cracking is highlighted. The locations of four exploratory trial pits are also shown

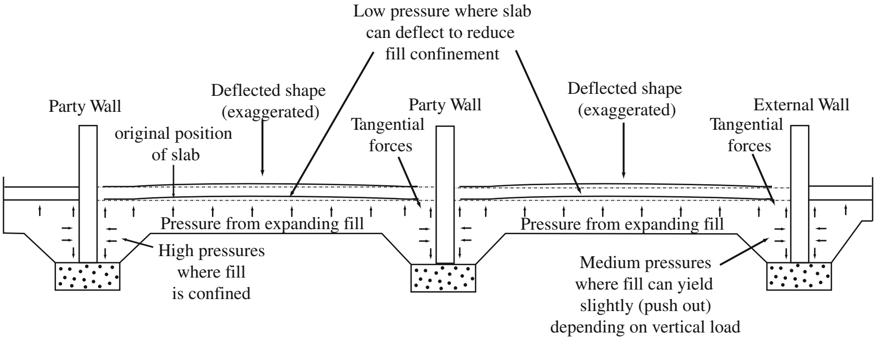


Fig. 4 Section through terrace showing notional sub-floor behaviour

Frictional forces between the expanding stone and rising wall elements can play a significant role in the way the structure responds to the swelling fill. Particularly where it is in a confined state, these can be very large (Fig. 6).

Fig. 5 Cracks created during lateral displacement of a rising wall

Before After

Fig. 6 Effect on the ground-bearing floor slab after the removal of fill in an adjacent property

A number of different values have been suggested in the literature for the expansive forces generated during pyritic heave. Maher et al. (2011) and Maher (2013) report pressures of up to some 600 kPa have been established for fill from remediated properties in Dublin while Bryant (2003) reported expansive forces of over 2,000 kPa. It should be noted that the expansion process can continue for many years; in the case of Llandough Hospital the remediation took place some 40 years after construction (Hawkins and Pinches 1987).

During the removal of the defective stone, horizontal cracking and gaps in the rising wall joints below ground floor level were often observed. These frequently extended through the full thickness of the rising walls and some cracks/gaps continued around the full periphery of the property. Where they passed through the internal rising walls, in some cases the aperture was in the order of 20 mm (Fig. 7).

Fig. 7 Horizontal gaps (up to 20 mm) observed in a rising wall immediately after the fill was removed in a localised trial pit (the balance of the fill beneath the floor slab was still in place at this time)

This in effect meant that frictional forces between the stone and the blockwork were sufficient to:

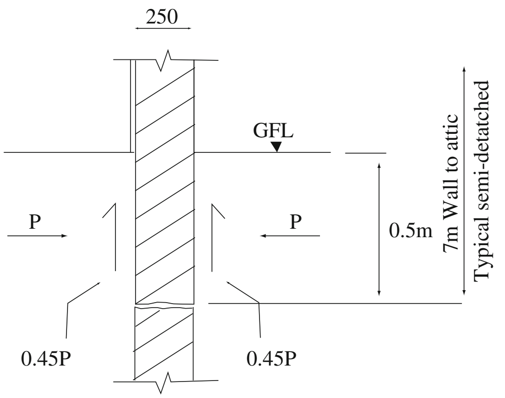
(a) break the mortar bond;
(b) lift the house by 20 mm, and
(c) hold the house up in its raised position.

These cracks/gaps were observed to close almost immediately after the slab and fill were fully removed and the forces that caused the building to rise were relieved, allowing the walls to return to their original positions.

Remedial works undertaken to date have confirmed that the interaction between the swelling stone, the sub-structure and the superstructure is complex and is likely to depend on many factors relating to the fill, its environment, the form of construction and time. Most structural engineers who have not experienced these processes would be very surprised at the pressures that can be developed in the fill if it is in a confined state. These pressures can be sufficient to fully lift a house and hold it in its raised position, as outlined above. The most basic calculation will show that this is possible with swelling pressures in the order of 100–200 kPa where the coefficient of friction between the stone and the blockwork is taken at, say, 0.45 (Fig. 8).

During the initial stages it became clear that remedial works carried out in one property could eventually be compromised to some extent by the continued swelling of an adjacent 'untreated' property. This can make the issue of Certification difficult and as a consequence it is recommended that remedial works are best carried out on a block by block basis.

Fig. 8 Sample calculation of pressure required to lift a party wall



1. Ignoring Mortar

$2\,(0.45P) \times 0.5\text{m} = 7 \times 0.250 \times 22\ \text{kN}/\text{m}^3$
$2\,(0.45P) \times 0.5\text{m} = 39\ \text{kN}/\text{m}$

Add 6kN for incidental loading = 45 kN / m

$P = 45 / 0.45 = 100\ \text{kN}/\text{m}^2$

2. Assuming mortar must be broken first

Take mortar strength at $0.2\ \text{N}/\text{mm}^2$

Required additional force to break mortar and lift house =

$0.2 \times 215 \times 1000 / 1000 = 43\ \text{kN}/\text{m}$

Therefore pressure, P Value, in stone is

$(45 + 43) / 0.45 = 196\ \text{kN}/\text{m}^2$ say $200\ \text{kN}/\text{m}^2$

Experience has shown that structural damage in the Dublin area is normally manifest approximately 2–3 years after the floor slabs have been poured. However, both earlier and later instances have been recorded.

Examples of Damage Caused to Houses and Other Buildings

As noted above, the damage observed in any project affected by pyritic stone infill depends on many factors relating to the fill itself, its environment and also the type and form of construction. However, the following are typical of the damage observed in the Dublin area:

Fig. 9 Crack up to 7 mm wide across a floor which has risen 30 mm within a distance of 2.5 m

Ground Floor Slabs

Concrete ground-bearing floor slabs have risen and cracked. In standard houses, rises of around 25–30 mm across a normal width house are common, with crack apertures of up to 7 mm. A typical example of a crack extending through a sitting room is shown in Fig. 9.

Internal Walls (Cracking)

Cracking is common over door heads and where the internal wall, constructed on the floor slab, abuts the external wall founded on a strip footing (Fig. 10).

Fig. 10 Cracking through plaster and blockwork of internal wall

Fig. 11 Bowing of a stud wall pushed upwards by the rising floor slab

Bowing of Internal Stud Walls

Many of the internal walls in the affected buildings were constructed as plasterboard stud walls. Where the plasterboard rests directly on the floor slabs, the upward pressures cause distinct bowing (Fig. 11).

Skirtings/Architraves

A typical example of the twisting and bowing of timber skirtings is shown in Fig. 12. Door architraves are also frequently distorted by the pressure from the swelling stone.

Kitchen Units/Worktops

The rising/arching of the floor slab causes significant stress on fittings, particularly in kitchens where units may be damaged and worktops lifted/distorted. Figure 13 shows the effect on a worktop under stress from the rising floor but restrained by the wall tiles.

Fig. 12 Displacement of timber skirting

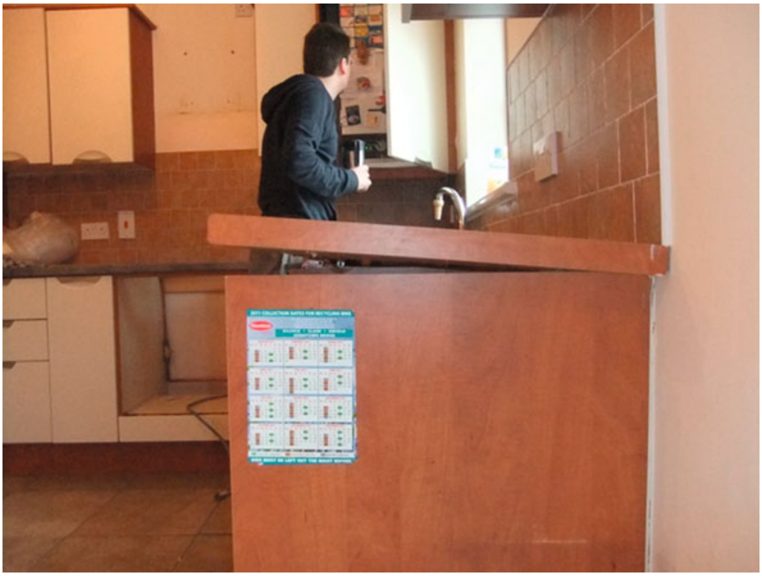


Fig. 13 Kitchen work top prised off its base

Doors Binding

There are many examples of doors binding against the rising ground floor slab (Fig. 14) or external paving (where the same pyritic stone has been used externally). In other situations, the door frame is forced upwards by the rising floor while the architrave in the centre does not rise, hence the door "catches" in the middle (Fig. 15).

Fig. 14 Bottom of door binding against floor

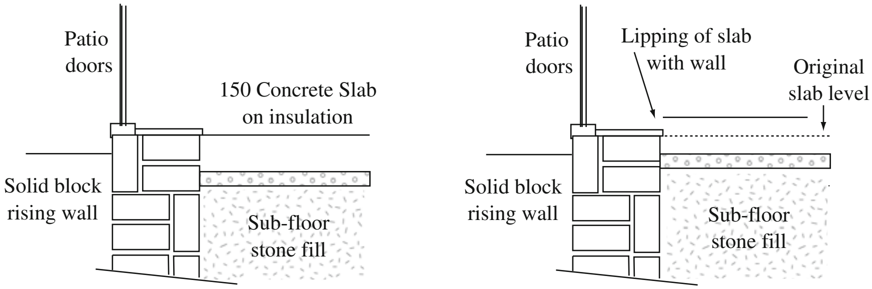
Fig. 15 Top of door binding against architrave

Lipping

Significant lipping can occur in the ground floor, generally at external doors/patio doors where the ground floor slab rises relative to the door threshold (Figs. 16 and 17).

External Plinth

In many types of construction, cracks occur where lateral pressures are applied to the rising walls. Typically these cracks develop where there is a structural



Ground floor slab adjacent to patio doors - before expansion of stone fill

Ground floor slab adjacent to patio doors - after expansion of stone fill

Fig. 16 Ground floor slab adjacent to patio doors, *before* and *after expansion* of the stone fill

Fig. 17 Typical lip at the location of a patio door (7 mm in this case)

weakness in the wall, such as where the damp proof course has been placed. In some instances this is accompanied by differential outward movement across the crack (Fig. 18).

External Leaf: Other Horizontal Gaps/Cracks

Significant horizontal gaps and cracks in the external leaf of cavity constructions have been noted. These develop where the inner leaf has been pushed up relative to the external leaf, notably in timber-framed houses. On one particular project this resulted in a gap of 40 mm at soffit level within 5 years (Figs. 19 and 20). In other situations a similar rise at the underside of cills has been observed.

Fig. 18 Cracking and displacement of external wall (plinth)

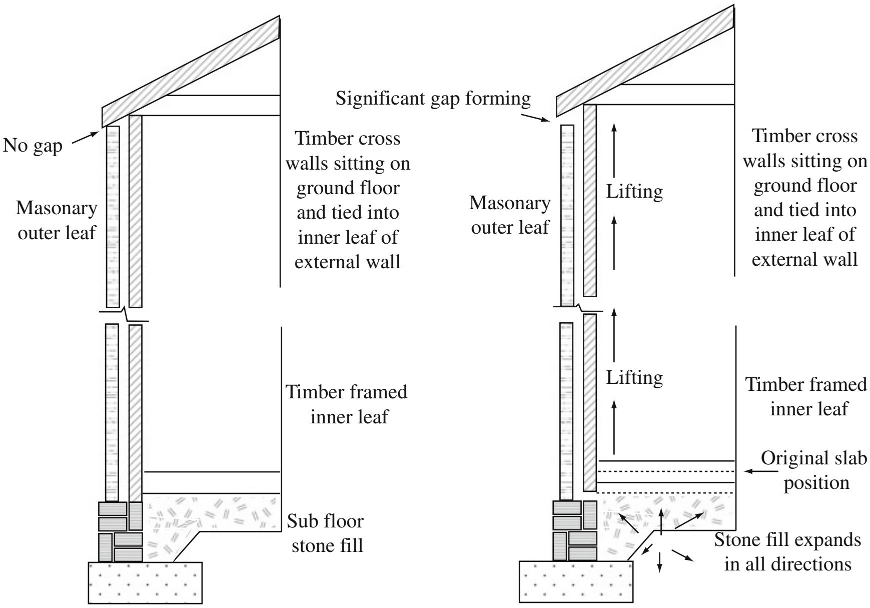


Fig. 19 Sketch indicating external wall *before* and *after* the internal leaf has been pushed upwards by the expanding fill

External Areas

Where pyritic fill has been used in external areas, various types of damage occur including cracking of concrete pavings, lipping at cold joints (between adjacent pours), gaps under kerbs and general lifting and differential movements in paved

Fig. 20 Gap of some 40 mm which developed at eaves level within 5 years of construction

areas. Possible damage to underground services from swelling stone is also a concern. Horizontal gaps have been observed in many manholes and service chambers (Figs. 21 and 22).

Concrete Attack

During the remediation works, evidence of gypsum growing on the rising walls was often observed. It was clear that if the fill were not removed, with time the concrete/concrete blocks could suffer sulphate attack.

Fig. 21 Pavement cracking near manhole

Fig. 22 12 mm gap near top of manhole

Parameters in Defining Appropriate Remediation

The key issues that need to be considered before appropriate remediation can be specified can be summarized as follows:

(a) What level of pyrite is in the stone and at what stage of oxidation is it? Based on these levels, is the oxidation (and consequential swelling) likely to continue in the future, and over what period?
(b) What is the quality of the stone and does it comply with current codes and guidelines (NRA SRW, SR 21, BRE Special Digest 1, TRL 447, Canadian Standard CTQ M200) with regards to aggregate grading and strength, sulphide, total sulphur and pyrite/equivalent pyrite.
(c) Is the observed damage consistent with swelling of the sub-floor fill?
(d) Is the level of sulphates in the stone sufficient to raise concerns about the possibility of chemical attack on concrete elements in close proximity to the stone e.g. block rising walls, foundations etc.?
(e) Is there any evidence of progression in the observed damage?
(f) Is there any evidence of damage to the external walls of the building?

There is to date very little definitive guidance available to engineers from Government or other regulatory sources. The guidance currently available in the form of SR21 is open to some question and is certainly not definitive. It is important that engineers, both structural and geotechnical, and other specialists practising in the field, should be brought together to aid Government in the formulation of definitive guidelines and recommendations.

Remediation and Certification

To date, remediation has entailed the complete removal of the defective stone and its replacement with stone of approved quality. The remediation work demands careful planning and an agreed practical method statement and quality control measures should be in place in advance of the works commencing on site. A variety of issues are likely to emerge during remediation which may include:

(a) Sequencing of the works to minimise possible further damage to retained elements of the structures while allowing the remediation to proceed as expeditiously as possible.
(b) Temporary stability, particularly of sub-structure works, at all stages.
(c) Replacement/retention of underground services.
(d) Addressing items of sub-standard construction exposed by the remedial works.
(e) Repairs to cracking etc. in elements to be retained.

Some of these issues can give rise to 'differences of opinion' between the Engineer and the Contractor and also possibly with the owners' technical advisers. Despite the fact that the Contractor may be his client, the Engineer must steer a fair and impartial course during the remediation and must be mindful that, firstly, it is the homeowner's interest that is paramount and secondly that it is the Engineer who ultimately must certify the works.

Certification

This will be based on confirmation that:

(a) The house has been so constructed that there is adequate bearing for the loads imposed, it is structurally sound and fit for habitation.
(b) The deleterious material has been removed and the new inert hardcore has been properly installed.
(c) Structural concrete has not been adversely affected and/or has been dealt with appropriately.
(d) Any significant building defects have been addressed.
(e) Services have been correctly reinstated.

Expert Witness and Expert Reports in Respect of Legal Actions/Arbitrations

Expert Witness

The brief of the Expert Witness will be provided by the legal team, but the following points are relevant in all cases:

1. The Expert Witness is required to provide information which is likely to be outside the experience and knowledge of others appearing at the Court/Arbitration.
2. The Expert's duty is, first and foremost, to the Court.
3. The Expert must be properly qualified to give an Opinion.
4. Even the most distinguished Experts may disagree and hence the Expert Witness must be able to rigorously defend their Opinion under formal examination by the Court, if required.
5. Prior to a court hearing, the Expert will be asked to provide a report which will give the facts as he/she understands them and the basis for their professional Opinion. This will involve the formation of a hypothesis, the testing of that hypothesis using a reliable methodology, the examination of the results and the drawing of a conclusion.

Summary and Conclusions

This chapter discusses some issues related to a Structural Engineer's involvement in cases of heave due to pyritic infill placed beneath ground-bearing floor slabs and/or pavements.

Examples are given of the effect of the expansion of the fill in different situations and the factors which influence this.

The ways of determining whether the distress is due to pyritic heave are considered as, particularly in the early stages, the problems may easily (and perhaps rightly) be attributed to other causes.

To date, remediation has been based on the removal of all the deleterious material. Attention is drawn to the importance of sequencing the work and to the influence of adjacent buildings while the remediation is being undertaken.

The role of the Structural Engineer in both the remediation and subsequent certification is explained.

Acknowledgments I would like to thank my colleagues Paddy Darling and Martin Bennett for their invaluable and essential technical assistance. Also, Leonie Lawler, Lisa Drohan and Anna Viti for all their work in preparing the presentation and paper. Lastly, but certainly not least, many thanks to my wife Ann for all her encouragement and support.

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The Canadian Pyrite Experience and Comparisons with the Irish Problems

Michael L. J. Maher

Introduction

The phenomenon of swelling shale bedrock affecting building performance was first recognized in Canada in the late 1960s. The therapy treatment building at the Rideau Health and Occupation Centre (later known as the Rideau Veteran's Home) on Smyth Street in Ottawa experienced heave in one section of the building (Quigley and Vogan 1969). The portion of the building that developed a problem was a two-storey section with a service tunnel and no basement. This portion of the building was adjacent to a building section that had a basement area and swimming pool (Fig. 1).

The building was founded in the Lorraine Shales that overlie the Billings Shale in the area. Because the service tunnel and basement were at a lower elevation, the ground water was lowered, which allowed the unexcavated shale beneath the ground floor in the two-storey section of the building to drain and facilitated the oxidation of the fine grained pyrite within the shale. The resulting heave occurred in the ground floor slab as well as in the second floor slab which was also supported on column footings within the Lorraine Shale.

Another well-published early case study is the Bell Canada Building on Albert Street in downtown Ottawa. This building, which was originally built in 1929, had an addition constructed in 1961. The first problems were noted in the basement floor (Penner et al. 1970) in the form of two rounded domes. Based on heave monitoring commenced in 1967, it was estimated by Penner et al. that the average rate of heave was 22 mm per year and the maximum total heave recorded was 120 mm. The Bell Canada Building is still functioning today (Fig. 2) after remedial works were undertaken. The Rideau Veteran's Home was demolished in 1999.

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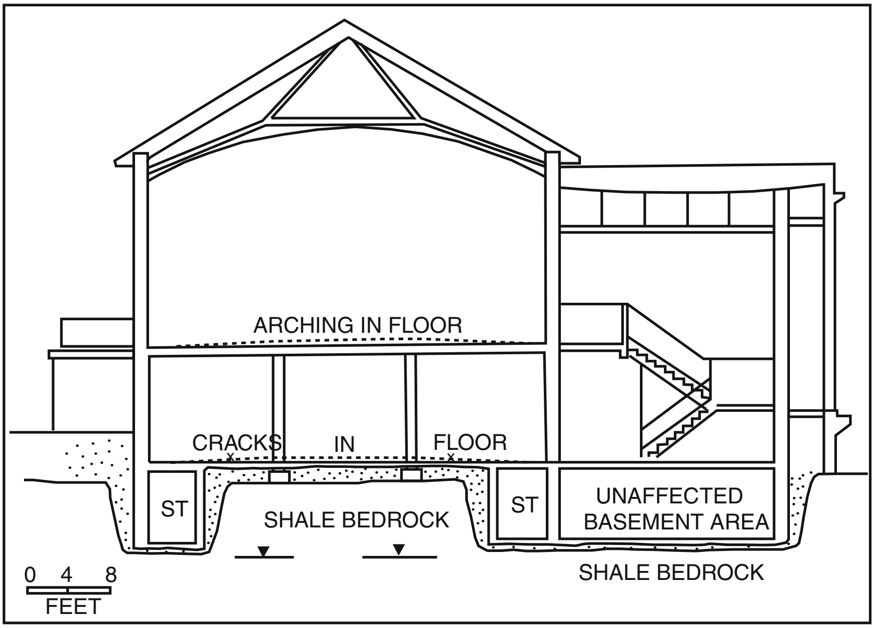

Fig. 1 Cross-section of Rideau Veteran's Home illustrating heave in the ground and second floor slabs (from Quigley and Vogan 1969)

The first case of suspected pyrite-induced floor heave identified in Ireland was in late 2006. The second recorded case was a house in a housing estate in north Dublin which began construction in 2003 (Fig. 3). In March 2007 it was confirmed that the cause of the cracked and heaved floors and cracked partition walls reported in the house was swelling of the underlying crushed rock fill beneath the floor slabs. The damage was confined to the floors and internal partition walls with no visible damage on the exterior of the house. Testing on the fill material confirmed it to be a crushed calcareous mudstone (Fig. 4), with estimated original pyrite concentrations of about 2.6 %. The Petrographic Number (CSA A23.2-15A, 2004 and ASTM C295, 2011) for a sample of the underfloor aggregate was found to be 250, confirming very low physical–mechanical quality.

Geological Setting

Canada

The first identification of pyrite-related problems in buildings in Canada was in the Ottawa area in the 1960s. Subsequently, in the 1970s similar problems were recorded in Sainte-Foy near Québec (Bérubé et al. 1986). By the mid-1980s,

Fig. 2 Bell Canada Building, Albert Street, Ottawa

widespread pyrite-related problems, on the scale of an epidemic, were reported in the Montréal area. As can be seen from Fig. 5, these areas trend in a northeasterly direction parallel to the St. Lawrence River.

When the geological mapping for these areas is examined (Fig. 6), it is seen that the affected areas are characterized by shale deposits. This is consistent with the published literature on pyrite-related problems around the world where they are associated with areas of shale and mudstone, i.e., fine grained sedimentary rocks with significant clay contents.

It should be noted that pyrite-related problems in buildings have come about in two different ways. The first is due to heave of building foundations and floor slabs supported on shale bedrock, and the second is where crushed shale or mudstone has been used as compacted underfloor fill or backfill against foundation walls.

In the Ottawa area, the heave-related problems have been mainly associated with the Billings Formation of Ordovician age. As seen from the schematic in Fig. 7, the Billings Formation is associated with the Carlsbad and Queenston Formations which are also shales.

Fig. 3 The second reported house in Ireland with pyrite-induced floor heave, Dublin

Fig. 4 Trial pit through kitchen floor exposing problematic underfloor fill

Fig. 5 Key plan showing Ottawa, Montréal and Québec City

The Billings Shales are typically described as dark grey, black and brown shales, interbedded with calcareous siltstone and silty limestone of the Carlsbad Formation. They are also frequently interbedded with the red to greenish grey siltstone and shale of the Queenston Formation. These shales were formed in an anoxic marine environment some 450 million years ago. Typical of these rocks originating from fine marine muds, they generally contain widely disseminated fine grained pyrite.

Along the St. Lawrence River, between Montréal and Québec City, are a series of shale deposits comprising Utica Shales and Nicolet and Pontgrave Formation

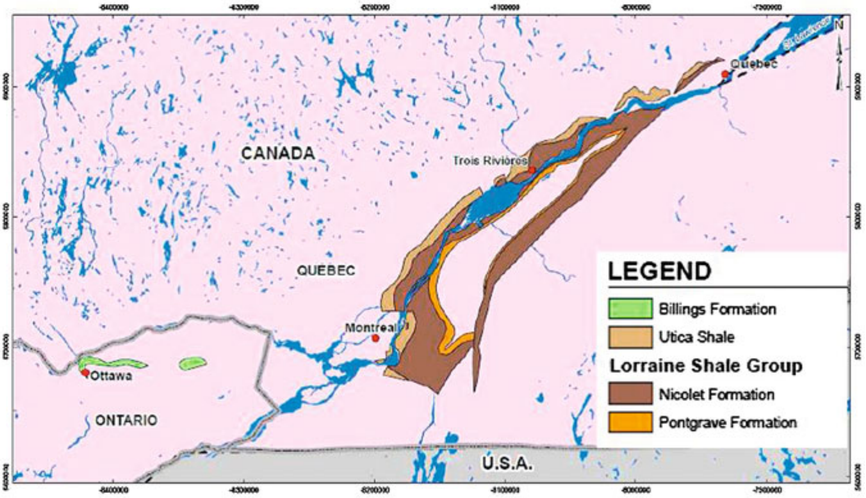

Fig. 6 Areas of shale bedrock in areas reporting pyrite-related problems (from MNR NRVIS, 2004, CANMAP 2006 & Ontario Ministry of Natural Resources, 2008)

Fig. 7 Ordovician sequence in the Ottawa area

PERIOD	GROUP	FORMATION
ORDOVICIAN	QUEENSTON	QUEENSTON
	CARLSBAD	CARLSBAD
	BILLINGS	BILLINGS
	OTTAWA	Lindsay
		Verulam
		Bobcaygeon
		Gull River
		Shadow Lake
	ROCKLIFFE	ROCKLIFFE
	BEEKMANTOWN	Oxford
		March
	POTSDAM	Nepean
CAMBRIAN		
PRECAMBRIAN		

shales of the Lorraine Shale Group. The relationship between these shales in terms of depositional history is shown in Fig. 8.

The Utica Shales are 50–300 m thick and were deposited during a period of rapid sea level rise in a poorly oxygenated environment. They comprise siliciclastic and carbonate muds with moderate to high calcite contents. Because of this calcite content, many of these rocks could be classified as silty limestones and so were frequently used in the 1970s, 1980s and 1990s as processed crushed rock in residential and commercial construction.

The overlying Lorraine Shales are more argillaceous and with lower calcite contents, and comprise mudstones and siltstones as well as true shales. The Lorraine Group shales also have high concentrations of disseminated pyrite.

Ireland

At least four quarries have been identified as supplying aggregate that has given rise to pyrite-induced heave when used as crushed aggregate beneath floor slabs in

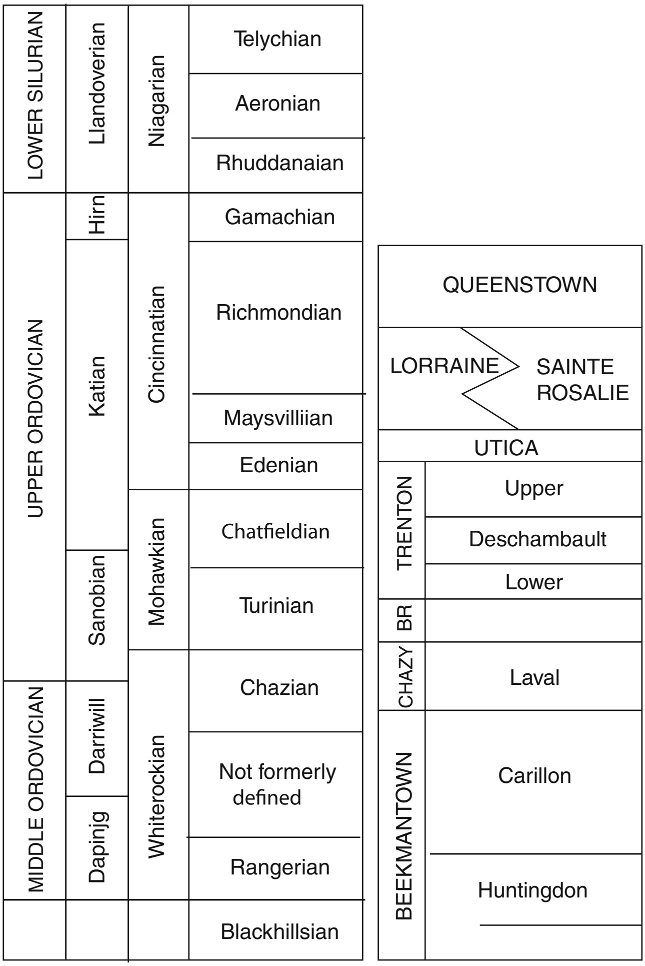

Fig. 8 Geological sequence of the shale formations of Upper Ordovician age along the St. Lawrence River (from Lavoie et al. 2011)

Ireland. Because of ongoing legal actions, these quarries are identified as Quarry B (North Dublin), Quarry M (North Dublin), Quarry R (Co. Meath) and Quarry T (Co. Meath).

The quarry that supplied the largest quantity of crushed rock to the booming development market between 2003 and 2008 was Quarry B. This quarry, located just west of Dublin Airport, obtained planning permission to operate a commercial quarry in early 2003. For the five year period between 2003 and 2008, this quarry produced just over 2 million tonnes of crushed aggregate that was sold as unbound material for residential and commercial construction, generally in the northern part of Dublin. While it was assumed that the quarry could supply aggregate conforming to Clause 804 (NRA 2000), i.e., the National Roads Authority granular road base material, no contemporary independent sampling and test results have been identified that verify this conformance.

Extensive testing carried out on samples of the material recovered from buildings during remedial works demonstrate that the aggregate from Quarry B failed to meet the Liquid Limit, Coarse Aggregate Water Absorption, Magnesium Sulphate Soundness and Ten Percent Fines Value for Clause 804. This is not surprising when it is considered that the quarry is located within the Tober Colleen Formation that is described as dark grey, calcareous, commonly biorturbated mudstones and subordinate thin micritic limestones (GSI 2001). The Tober Colleen Formation is of Lower Carboniferous age and is the lowest unit within the Calp Limestone. Quarry M, located further north of Quarry B, is within the Loughshinny Formation. This rock is described as argillaceous, pyritic, locally cherty micrites and graded calcarenites, interbedded with dark grey to black shale (GSI 2001).

The two Co. Meath quarries that have supplied problematic pyritic aggregates are from the Lucan Formation and are described as dark grey, well bedded, cherty, graded limestones and calcareous shales. The geological succession of these various formations is illustrated in Fig. 9 and examples of some of the materials are shown in Figs. 10 and 11.

Thus the questionable quality of these rock formations for the production of construction aggregates was documented; however, this information was either not consulted or ignored when these quarries were developed. It is worth noting that these quarries did not supply aggregates to major road construction projects and hence no comprehensive independent testing of aggregate was undertaken.

Case Studies

Case Study 1, Commercial Warehouse, Ottawa

This case study relates to a two-storey warehouse building in the City of Ottawa. The building was constructed in the 1960s and damage in the form of floor cracking and unevenness was first noted in the 1980s. There was a relatively high water table at the site so a sump and pump had been installed some 3.6 m below the floor slab. In addition, there was an elevator shaft that extended approximately 2 m below the floor slab. Damage was first noted in the area of the building near the sump (refer to Figs. 12 and 13). Over the intervening years, the floor heave continued to progress and was estimated to be approaching 100 mm in total heave displacement. Some temporary repairs were undertaken but eventually more extensive rehabilitation was deemed necessary as the operations of the fork lift trucks were being affected.

Golder Associates were retained to undertake an investigation of the extent of the problem and to advise on remedial measures. The scope of the investigation comprised a desk top study, one floor cut-out and one corehole to a depth of 3 m.

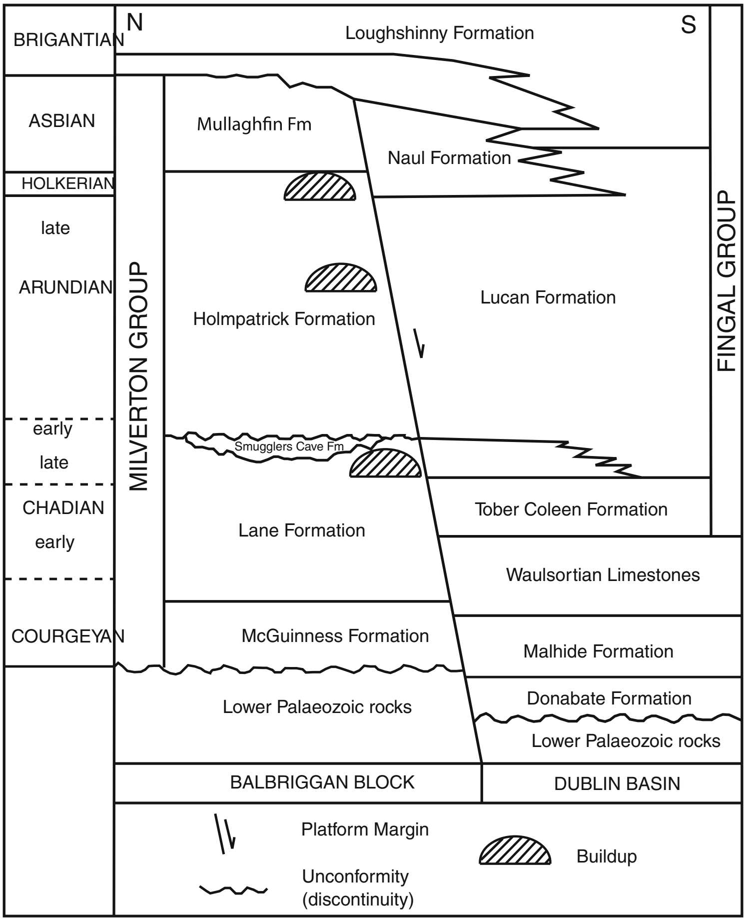

Fig. 9 The Dinantian successions in north Co. Dublin (from GSI 2001)

The investigation confirmed (Figs. 14 and 15) that only a thin layer (<100 mm) of compacted granular base separated the underside of the floor slab from the underlying bedrock surface. The lowering of the local water table in the vicinity of the sump had allowed the pyrite in the upper portions of the shale bedrock to oxidize and for gypsum to develop between laminations (Fig. 16). It could be clearly seen from visual examination that the laminations within the shale were being prised apart by the growth of gypsum.

The remedial options involve removal of affected areas of the floor slab, excavation to remove the upper weathered areas of shale and sealing the surface, typically using shotcrete. New granular fill is then installed and the floor slab reinstated.

Fig. 10 Particle from Quarry B opened on a lamination reveals gypsum clusters

Fig. 11 Aggregate particle from Quarry T with laminations propped open with gypsum

Fig. 12 Intersecting floor cracks indicative of upward heave of the slab

Fig. 13 Cracking in internal block wall supported on floor slab

Fig. 14 Cut-out through floor slab

Case Study 2, Extension to the Light Rail Transit, Ottawa

The City of Ottawa has a well established public transit system but it needs to be upgraded to cater for growing ridership. The upgrade will involve the construction of Ottawa's Light Rail Transit (OLRT) system. This will require converting a portion of the existing Bus Rapid Transit (BRT) system into an LRT system. In addition to upgrades at some existing stations and construction of new stations, the project will

Fig. 15 Chunks of shale bedrock extracted from beneath floor slab

Fig. 16 Close-up views of chunk of brown Billings Shale with clusters of gypsum crystals on lamination surface

also include a Downtown Area Underground Section. The Downtown Area Underground Section will be approximately 2.5 km long and will include three new stations (Fig. 17). Construction of the OLRT is scheduled to commence in 2013.

A geotechnical investigation was carried out to characterize the subsurface (overburden and rock) conditions along the proposed alignment (Golder 2011). Shale of the Billings Formation was encountered at a number of locations, including at the Downtown East Station and at the Maintenance Yard. The Billings Shale comprised fresh, thinly laminated to laminated, dark brown to black, and weak to medium strong shale with grey limestone seams. Testing on samples of the recovered rock core (Golder 2011) yielded results for the Billings Shale as summarized in Table 1.

Shale formations in Southern Ontario and in other areas are known to exhibit swelling behaviour upon stress relief and when in contact with fresh water (Lo and Micic 2010). Since very limited data on the swelling potential of the Billings Shale is available, a preliminary laboratory testing program was undertaken to determine the potential swelling characteristics of this rock formation.

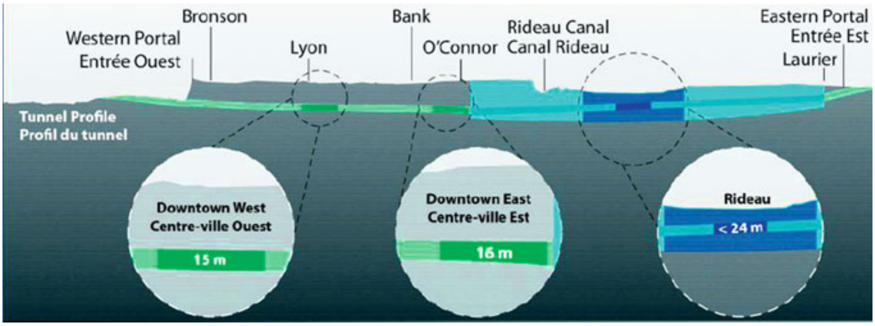

Fig. 17 Proposed tunnel section of extension to OLRT (from OLR 2012)

Table 1 Test results on recovered core from Billings Shale (from Golder 2011)

Test	Test standard	Average	Range
Unconfined compressive strength (MPa)	D 2938	22	17–26
Density (Mg/m^3)		2.62	2.50–2.78
Point load index—axial (MPa)	D 5731	5	2–11
Point load index -diametral (MPa)	D 5731	2	0–4
Mohs hardness		2.5	2.5–2.5
Slake durability index	D 4644	98.8	98.0–99.2
Calcite content		2.6	2.0–3.5

The swell testing was carried out at the University of Western Ontario by K.Y. Lo Inc. The core tested came from about 20 m deep and was subjected to three different test procedures. These specialized tests had been developed by Prof. K.Y. Lo, University of Western Ontario, London (Lo et al. 1978). The tests are the Free Swell Test (FST), the Semi-Confined Swell Test (SCST) and the Null Swell Test (NST); Fig. 18. Each of these tests is run for 100 days and during the tests the samples are immersed in fresh water.

During the course of the tests the following parameters are checked; water content, calcite content, salinity and pore water salinity. In general, the salinity of the rock samples tested was fairly uniform, ranging from 1.67 to 2.55 mg/g. The water content was generally low, ranging from 1.6 to 3.0 %. The calcite content of the test samples was also generally low, ranging from 2.0 to 3.5 %. The salinity of the pore water was generally high, ranging from about 69 to 120 g/L (note: salinity of sea water is around 35 g/L). The high salinity of the pore water is consistent with the marine depositional environment of the Shale and is also consistent with the range of pore water salinity of other shales that exhibit swelling behaviour.

The data obtained from the FSTs and the SCSTs are analysed by plotting the swelling strain versus the logarithm (to the base of 10) of elapsed time (in days). After the initial stabilization period, the swelling strain versus logarithm of time plot approximates a linear relationship. Following the method used by Lo et al. (1978), the average slope of such a plot (taking the approximately linear portion of

Fig. 18 Null swell test apparatus at the University of Western Ontario

the graph) gives an indication of the tendency of the rock to swell. The amount of swelling strain measured within one log cycle of time (generally between 10 and 100 days or extrapolated for such period) is taken as an index of the "swelling potential" of the rock being tested. The swelling potential for the samples of Billings Shale tested (based on the FSTs) ranges from 0.31 to 0.35 % in the vertical direction (z direction), and is higher than those in the horizontal directions (x and y directions) which range from 0.18 to 0.23 %.

Figure 19 shows the relationship between the swelling potential and calcite content of various shale formations in Canada (Lo and Micic 2010). Data from the Billings Shale are also included in the same plot, for comparison. The swelling potential of the shales increases with decreasing calcite contents. It may be noted that the calcite contents of the Billings Shale are within the range of calcite contents in other shales which exhibit swelling behaviour. The swelling potentials of Billings Shale are also consistent with those of other shales with comparable calcite contents.

The stabilized pressure achieved during the NSTs is termed as the "suppression pressure" at which the swelling of the test sample is fully suppressed. The "suppression pressure" in the horizontal direction was between 0.22 and 0.28 MPa, which was much lower than that in the vertical direction which ranged from 0.96 to 1.08 MPa.

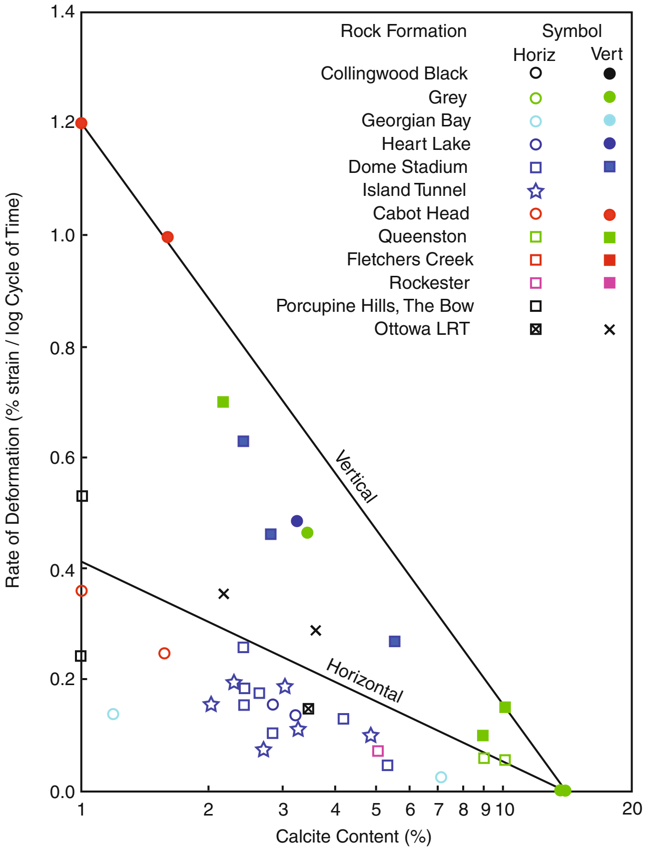

Fig. 19 Relationship between swelling potential and calcite content of various shale formations in Canada (from Lo and Micic 2010)

The swelling tests on Billings Shale confirmed that all the test samples underwent swelling when immersed in fresh water and that this form of swelling could be suppressed under an applied “suppression pressure”. Based on the results of swelling tests on various shales in Southern Ontario and North America, Lo and Micic (2010) postulated that the mechanism of this form of swelling is a result of the dilution of pore water salt concentrations which causes the space between the clay particles to expand. The osmosis and diffusion processes constitute the mechanism for the dilution of the salt concentration in the pore fluid if the rock is surrounded by an ambient fluid of lower salt concentration.

In practice, the conditions for swelling to occur are (a) accessibility to fresh water (b) an outward gradient of salt concentration in the pore fluid to the ambient fluid of lower salt concentration, and (c) the relief of in situ stresses which serves as the initiating mechanism. Swelling is also affected by the interparticle bonding. If the bond strength is higher than the osmotic pressure, no swelling will occur and vice versa. The bond strength is dependent on the calcite content which acts as a cementing agent between the clay particles.

Based on the field conditions pertinent to the OLRT, the rock surrounding the underground structures, including the access and ventilation shafts, will have accessibility to fresh water as the structures will be located below the ground water table. The high salinity of the pore water fluid in the rock will generate a high outward gradient of salt concentration in the pore fluid to the ambient ground water that has a much lower salt concentration. In addition, in situ stress measurements carried out at the OLRT site indicate that high initial in situ stresses exist in the rock formations. As a result, stress relief in the rock formation will occur upon excavation. The low calcite content of the rock also constitutes weak bonding strength between the clay particles. Therefore, these field conditions provide the attributes for swelling to occur in the Billings Shale.

A study of the heaving of black shale in the Ottawa area by Quigley and Vogan (1969) indicated that the black shale (Billings Shale) in the Ottawa area comprises an abundance of illite and mica and minor pyrite (iron sulphide of between 0.7 and 3.9 %) in thin laminae and disseminated form. No significant amount of swelling clay minerals was noted. Heaving of these black shales will occur in areas above the water table where an oxidizing environment (drained, warm and humid) for the pyrite is present. As the proposed underground structures for the OLRT will be located permanently below the groundwater table during its operation and measures could be undertaken to seal the rock formation from oxidation during construction, heaving of the black shale due to the oxidation of the pyrite in the shale will not likely impact the design of the underground structures.

The swelling characteristics of the Billings Shale due to dilution of the salt concentration, as determined from the laboratory swell tests, will need to be taken into consideration in the design of the underground structures located within this rock formation. If an underground structure is constructed directly in contact with the rock, the time-dependent deformation (swelling) of the rock will cause pressure to build up with time at the rock-structure interface. The magnitude of the pressure will depend on the rigidity of the structure, the time schedule of construction, the swelling characteristics of the rock and the initial in situ stresses in the rock formation. These swelling pressures will be allowed for in design.

Case Study 3, Pyrrhotite/Pyrite in Concrete Aggregates, Trois-Rivières, Québec

In the early 2000s, 30 owners of relatively new homes in the Trois-Rivières area, 140 km east of Montréal (Fig. 5), began experiencing problems with cracking and deterioration of the exposed concrete in their basement walls (Roy 2011). Following investigation, it was established that the coarse aggregate used in the making of the concrete was an anorthositic gabbro that contained typically

Fig. 20 Typical damage in exposed house concrete, Trois-Rivières, Québec

between 5 and 10 % pyrrhotite, pyrite and chalcopyrite, all sulphides of iron. Domestic house construction typically uses concrete with compressive strengths of 20–25 MPa for foundation and basement wall construction. The source quarry for the coarse aggregate was a small local quarry that only operated for a few years.

Subsequently, in 2009, several new cases of early deterioration of concrete in houses were reported, also in the Trois-Rivières region (Fig. 20). The aggregate used was predominantly an anorthositic gabbro or norite containing calcic plagioclase feldspars, biotite, and pyroxene with various proportions of pyrite, chalcopyrite and pyrrhotite (Duchesne and Fournier 2011). The pyrite and pyrrhotite contents vary significantly and are reported to be as high as 5–7 %. The houses were generally 4–6 years old at the time damage occurred.

By 2011, the Garantie des Maisons Neuves (GMN), a government sponsored mandatory home warranty programme in the province of Québec, had received over 600 claims, with potential repair costs estimated at $65 million (Nantel 2011).

Internal sulphate attack on concrete has been well documented in the literature, although mainly relating to the oxidation of pyrite in aggregates of sedimentary origin. The 'mundic' problem in Cornwall, England is a well documented example of early deterioration of concrete blocks due to the presence of pyrite in the aggregate (Bromley 2000). In that region it became common to process local mine waste rock for use as aggregate in the production of concrete and concrete blocks used in residential and commercial construction (Lugg and Probert 1996).

The rocks in question were fine grained sedimentary rocks containing high levels of reactive sulphide minerals primarily in the form of pyrite (FeS_2), but also including chalcopyrite ($CuFeS$), arsenopyrite ($FeAsS$) and sphalerite (ZnS). The reactions generated from the presence of these minerals in the mine waste aggregate resulted in deterioration and cracking of concrete. The resulting damage to the houses was attributed to the oxidation of the sulphides in the presence of moisture and oxygen. The production of limonite, or more commonly goethite, and the formation of gypsum result in an expansion in solid volume with an associated

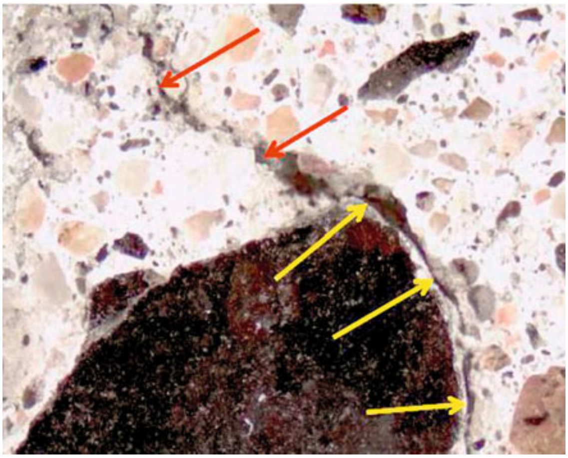

Fig. 21 Photomicrograph showing crack in concrete at coarse aggregate and paste interface

breaking of the bond between the aggregate and the cement paste and the propagation of cracks to accommodate the expansive products.

A paper published in 2005 (Lee et al. 2005) studied the premature deterioration of ten highway bridges in the State of Iowa due to secondary ettringite formation as a result of pyrite oxidation in the aggregates. Concrete degradation problems related to pyrrhotite were identified in Sweden in the 1940s (Hagerman and Roosaar 1955). Concrete damage was noted at the Norrforsen hydroelectric plant. Investigation attributed the damage to the presence of pyrrhotite in the crushed gneiss and granite aggregate. In the recent problems in Trois-Rivières, which came to light in 2009, the suspect aggregate is from a different (although nearby) source quarry from that which gave rise to similar problems in 2000. The aggregate in question was of extremely high quality in terms of physical properties. The oxidation of the pyrrhotite resulted in the formation of ettringite and thaumasite and the development, over time of extensive internal cracking in exposed concrete (Fig. 21). For example, Micro-Deval loss values were about 7 %. However, the Canadian Standards (CSA A23.1 and .2 1994) for concrete aggregate do not provide a limit for sulphur in aggregate for concrete. Since 1994, the Standard contained a warning that the use of aggregates that produce excessive expansion in concrete through cement-aggregate reaction other than alkali reactivity shall not be used for concrete unless preventive measures acceptable to the Owner are applied. In contrast, the European Standard (EN 12620 2002) suggests a limit on the total sulphur content of concrete aggregates to 0.1 % where the sulphide is in the form of pyrrhotite.

Some Characteristics of Problematic Shales and Mudstones

Shales and mudstones, in general, have always been acknowledged as not suited for the production of good quality construction aggregates. Due to their high clay contents, low strength and laminated structure, they tend to have high water

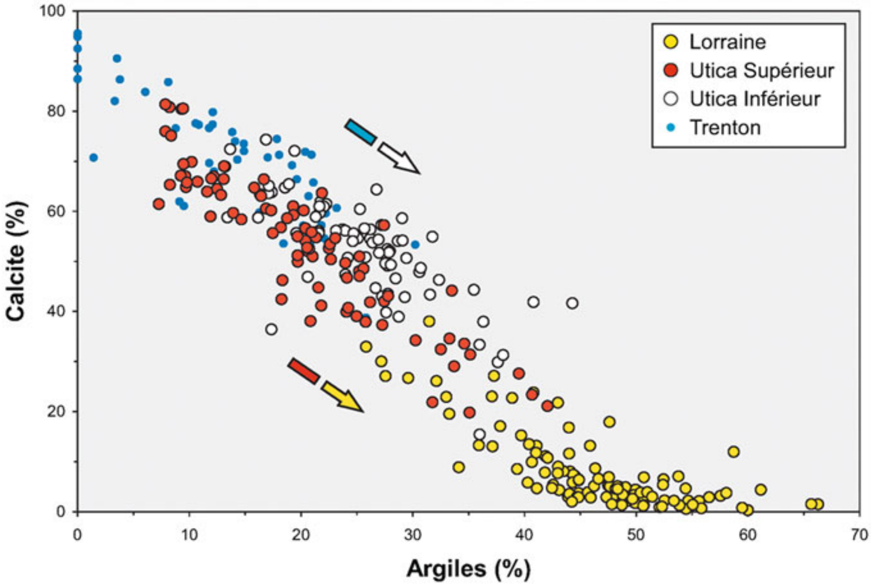

Fig. 22 Diagram showing calcite and clay (argiles) contents for Québec shales (from Thériault 2012)

absorption characteristics and low resistance to abrasion and impact. With these characteristics, these rock types are very vulnerable to chemical weathering. The easy access to moisture and the low internal bonds between laminations allow the very fine disseminated pyrite to readily oxidize. Since many of these shales may also contain small amounts of calcite, all the ingredients for the formation of calcium sulphate dihydrate, or gypsum, are present. It is generally accepted that the higher the clay contents in shales and mudstones, the poorer the quality of the rock in terms of durability and mechanical properties. It is for these reasons that the test standard developed in Québec (BNQ 2560-500 2003) to assess susceptibility of an aggregate to pyrite-induced heave, is the Swelling Index Test which is based on establishing the clay content of the sample.

A recent study of the shales of the St. Lawrence Lowlands of Québec (Thériault 2012) has compiled extensive mineralogical and other data on these materials. Figure 22 shows the relative calcite and clay (argiles) contents in Québec shales. It can be seen that the Lorraine Shales have very high clay contents and very low calcite contents. These shales are highly prone to pyrite-induced heave but because of their extremely poor quality were generally not used in construction.

On the other hand, the Utica Shales were used extensively as crushed rock fill throughout the 1970s and 1980s. These results span quite a range extending into lithologies with over 60 % calcite and less than 10 % clay. Generally rocks comprised of greater than 50 % calcite can be described as limestones, sometimes

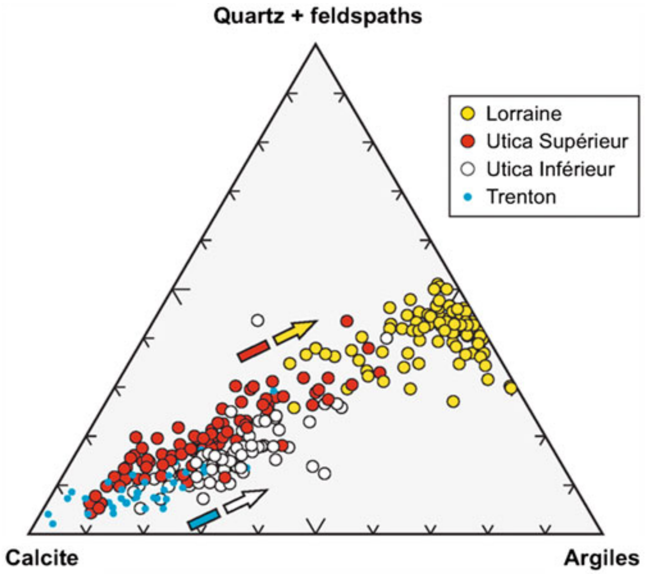

Fig. 23 Trilinear diagram showing composition of Québec shales in terms of quartz and feldspars (feldspaths) calcite and clay (from Thériault 2012)

with description modifiers of "muddy" or "silty". As reported in Table 1, the Billings Shale tested for the OLRT project had up to 3.5 % calcite content.

To allow comparisons with the Irish problematic mudstones, the data for the Utica and Lorraine Shales (Fig. 23) have been re-plotted with similar mineralogical data for the Irish mudstones. The combined results are shown on Fig. 24. It can be seen that Quarry B plots close to the centre of the triangle and with close to 30 % calcite in some instances. However, it also has generally greater than 20 % clay content and about 2.5 % pyrite content.

Figure 25 compares the estimated pyrite contents in some problematic mudstones and shales. However, as an indicator of the potential for pyrite-induced heave, clay content is likely better than pyrite content. This is the approach taken in Québec which is discussed later in this chapter.

In our experience with these problematic shales and mudstones, the pyrite content is not the controlling factor since there is typically more than sufficient sulphides available to sustain the reactions if the other enabling conditions are present.

The low quality of the aggregates prone to pyrite-induced heave can be confirmed from conventional aggregate suitability testing. The most indicative tests are coarse aggregate absorption/water absorption, Micro-Deval and Magnesium Sulphate Soundness. Figure 26 shows typical test results for these problematic aggregates with the red line indicating the test limits generally exceeded by these

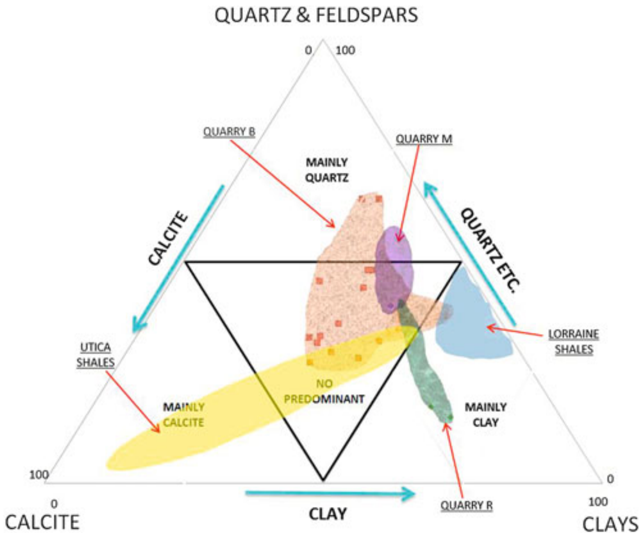

Fig. 24 Comparison between Utica and Lorraine Shales and Irish mudstones that cause pyrite-induced heave

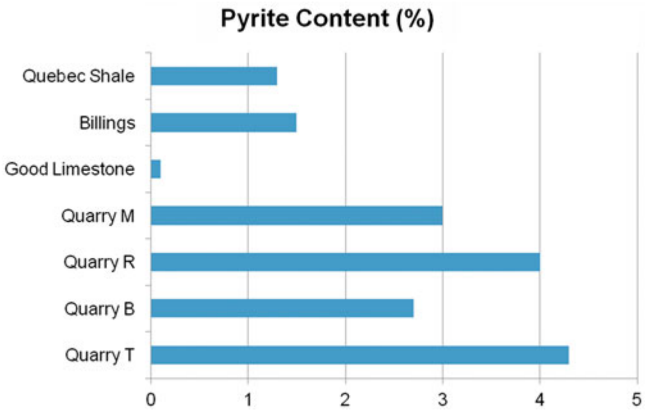

Fig. 25 Comparison of estimated pyrite contents in problematic mudstones and shales

materials. Physical testing undertaken as part of a research study for the Canada Mortgage and Housing Corporation (Bellaloui et al 2003) obtained Micro-Deval results for Québec shales ranging from 90 to 97 % and coarse aggregate water absorption ranging from 2.8 to 3.7 %.

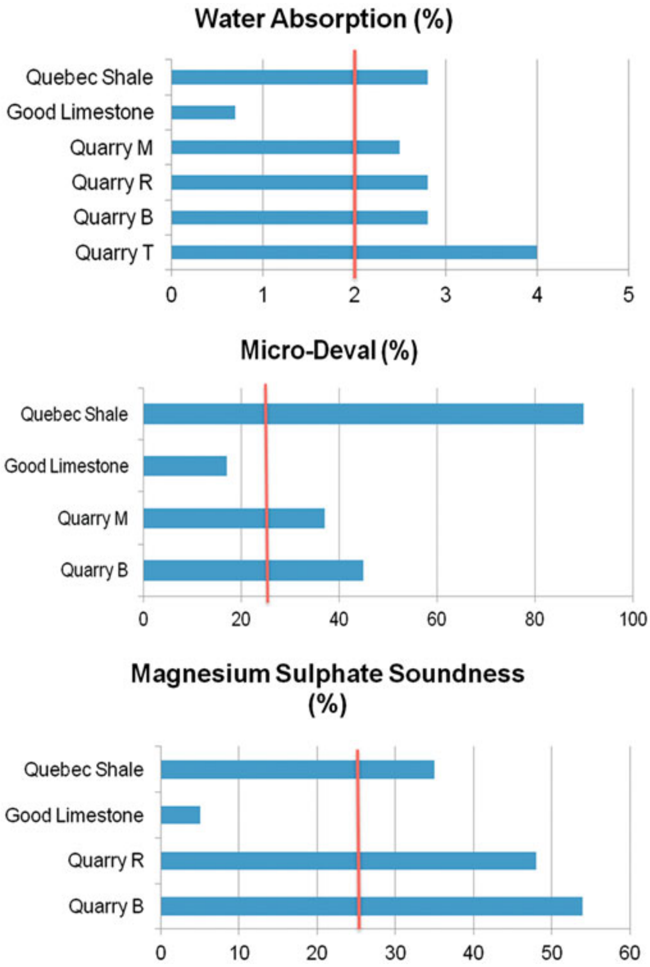

Fig. 26 Typical results for water absorption, micro-deval and magnesium sulphate soundness for problematic shales and mudstones. *Red line* indicates the values generally exceeded with these materials

Rates of Expansion

The rates of pyrite-induced expansion within buildings will vary significantly depending on a wide range of influence factors. Among others, these will include the following:

- Whether it is a foundation on shale bedrock or a floor slab placed on a compacted shale or mudstone fill;
- Quality of the source rock and proportion of mudstone/shale versus limestone;
- Distribution and form of pyrite within the aggregate;

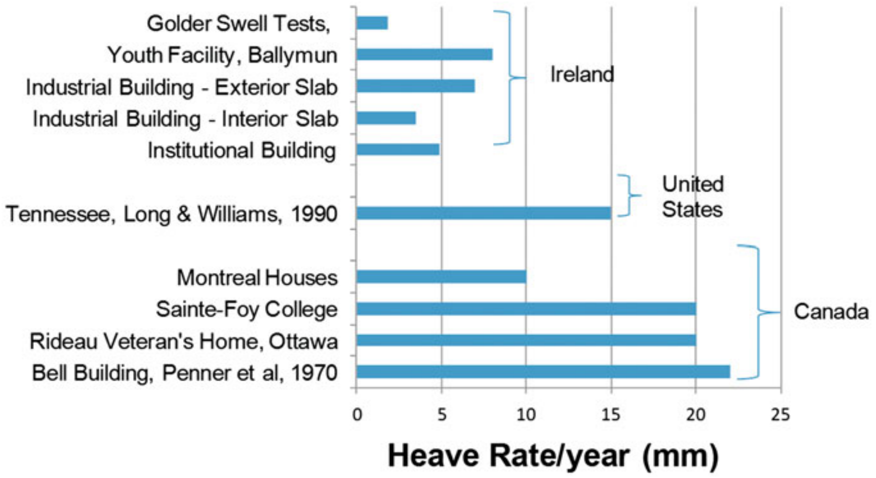

Fig. 27 Recorded heave rates in buildings due to pyrite-induced heave

- The in situ density of the infill (based on the degree of compaction and applied loads);
- The extent of moisture within the infill and access to capillary water;
- Ambient temperature and pH;
- The particle size distribution of the infill (the fine fraction will oxidize faster than the coarse fraction);
- Trace element concentrations;
- The thickness of the fill; and
- The presence of bacteria.

A study of houses undergoing pyritic heave in the Montréal area demonstrated that the total heave in garages was significantly larger than in the adjoining basement and this was attributed to the fact that the garages are underlain by one meter or more of compacted fill while the basement slabs typically have less than 200 mm (Pépin 2000).

Despite these variables, some orders of magnitude for rates of heave can be established from a review of monitoring in buildings that has been reported in the literature and from the results of forensic engineering investigations. Some recorded heave data is plotted in Fig. 27. For North America the reported heave ranges are from 10 to 22 mm per year.

From a number of buildings in the Dublin area where monitoring has been undertaken for periods of up to three years, the heave rates are lower and generally in the range of 4–8 mm per year. From laboratory swell tests undertaken using crushed mudstone from the Dublin area, heave rates were measured at about 2 mm per year in a 300 mm thick layer of compacted fill (Maher et al. 2011).

Laboratory swell testing has shown that compacted mudstone can attain a relatively uniform rate of heave in a controlled laboratory environment. In

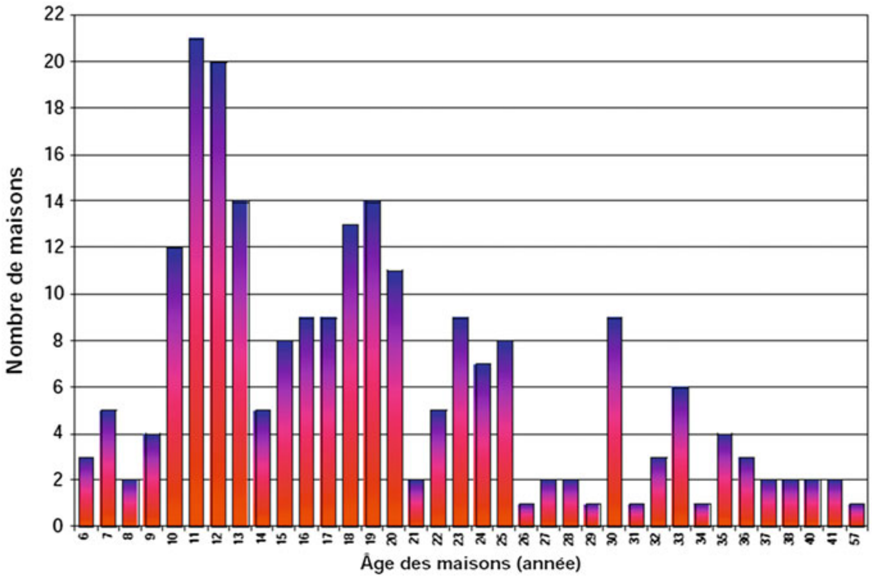

Fig. 28 Age distribution of houses with pyrite-induced damage from the Montréal area study (from Pépin 2000)

practice, the length of time from placement of compacted fill to the development of damage in a building is extremely variable. The main variables will relate to the nature of the compacted fill as listed above, the climatic conditions and local groundwater and temperature regime in the building, and most importantly, the nature of the structure, its rigidity and the fill confinement conditions. Anecdotal evidence suggests that in Québec, damage in houses related to pyrite took typically 10 years to occur. This is corroborated by a study of 224 houses in the Montréal area (Pépin 2000). Figure 28 shows the distribution of houses by age from that study which indicates that houses in the 10–13 year old category were the most frequent.

Over the past six years and based on investigations of thousands of houses and other buildings experiencing pyrite-induced heave in Ireland, the typical time span for initial damage to manifest itself is in the range of 2–6 years. Even after the swelling of the infill starts, the rate is quite small, in the order of 3 or 4 mm per year.

Most buildings can tolerate a certain amount of minor swelling of infill before damage will occur in the structure. The initial heave will be 'absorbed' within the building (e.g., within the insulation layer below the floor slab) and will take time to lead to cracking. The underlying subgrade soils can also compress when load is applied to it. This would reduce the upward pressure on the floor slabs until such time as consolidation of the underlying soil had occurred and then the pressure would be applied upward.

The generally faster times to building damage in Ireland can be attributed mainly to differences in climatic conditions and building design practices.

Expansion Pressures

In connection with legal proceedings in Ireland, Golder Associates developed a large scale laboratory swell test to study pyrite-induced heave in a controlled laboratory environment. The initial experiment with a large scale laboratory swell test began in December 2007 (Maher et al. 2011). The test was performed in a 1.2 m internal diameter concrete manhole ring with a compacted sample height of 1.02 m. The concrete pipe section was placed vertically within a heavy duty steel trough and the aggregate (removed from a house being remediated), with a maximum particle size of 75 mm, was compacted within the cylinder (Fig. 29).

There was no base installed in the pipe as it was assumed that the mass of the concrete pipe and fill would be adequate to force the heave to occur at the top of the fill. This assumption proved wrong. Within seven weeks of commencement of the test it was noted that the entire test cylinder had tilted slightly on the base, due to the expansion of the fill and the friction acting on the inside of the concrete pipe. After 17 weeks, a vertical hairline crack developed in the side of the concrete pipe. After 50 weeks, the vertical crack had expanded to 12 mm (Fig. 30).

Using analytical and numerical techniques, the pressure produced inside the pipe at rupture was back-calculated and established to be about 600 kPa. Figure 31 illustrates various estimates of pressures generated from pyrite expansion. It can be seen that the back analyzed value from the Golder swell test of 600 kPa is in line with estimates made by Spanovich (1969).

Fig. 29 Initial large scale laboratory swell test

21 weeks 25 weeks 50 weeks

Fig. 30 Progression of vertical crack in concrete manhole ring in 21, 25 and 50 weeks. At 33 weeks it was 12 mm wide

Solution Developed for Pyrite-Induced Heave Problems in Québec

As a result of the extent of the problem in the Québec area, a technical committee (*Comité Technique Québécois D'étude Des Problèmes De Gonflement Associés à La Pyrite*) was created in 1997 to examine the problems caused by the swelling of granular backfill under concrete floor slabs. It was established that the swelling occurs as a result of chemical reactions involving some of the minerals present in the aggregates used in that area of Québec. Due to the extent of the problem, the committee developed standard procedures for investigating and evaluating the problem. These procedures are known as Procedure CTQ-M200, and entitled, "Appraisal procedure for existing residential buildings" (Comité Technique 2001).

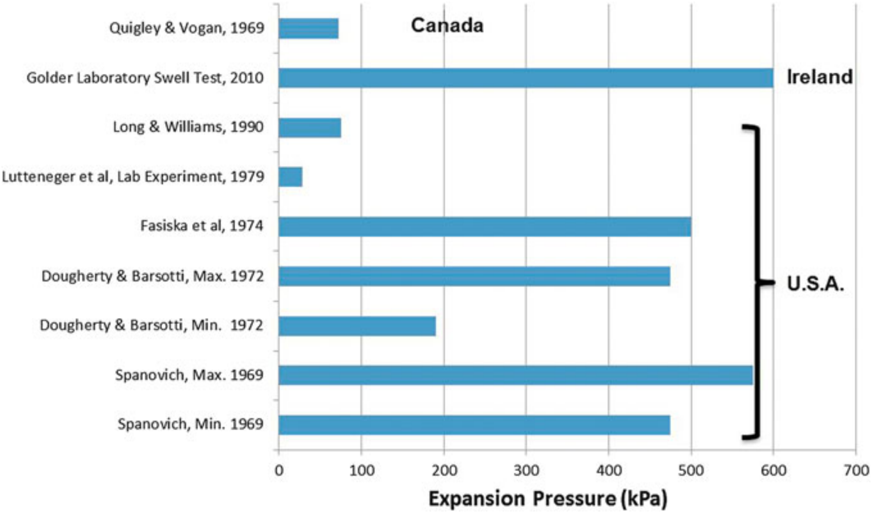

Fig. 31 Comparison of estimated pyrite heave pressures from a literature review

One of the key aspects of CTQ-M200 is the performance of a Swelling Index Test. This petrographically-based test procedure was developed in 1999 by the Québec Technical Committee and was referred to as CTQ-M100/2000. This was subsequently adopted as a Québec Standard (BNQ 2003) and designated as BNQ 2560-500. The laboratory test procedures are divided into two stages.

Stage 1 comprises:

- Sieve analysis
- IPPG (indice pétrographique du potential de gonflement)—Swelling Index Test
- Absorption test
- Micro-Deval testing

Essentially, the Stage 1 evaluation focuses on establishing the clay content of the crushed rock material (i.e., Swelling Index Test) and two key physical quality parameters. What is interesting is that it does not involve the determination of pyrite contents. In the Swelling Index Test, also referred to as the SPPI test (Swelling Potential Petrographic Index), the sample is divided into 20, 14, 10 and 5 mm size fractions. These are then examined by the petrographer who evaluates the clay content within each of the sample particles. Depending on the clay content, a weighting factor ranging from 0 to 1 is applied. If no clay is present in the particle, a granite or basalt, for example, it is scored as 0. If it is a pure shale it is scored as a 1. On this scale a clayey limestone would be assigned a score of 0.5 and a limestone with some clay veneer would be assigned 0.1. A final weighted score is then determined, taking into account the original grading of the sample. This final score, or Swelling Index, will fall between 0 and 100.

An Index of 0 would indicate a crushed rock product containing no clay and thus with no likelihood of causing pyrite-induced heave. Crushed rock products with Swelling Index values of 10 or less are considered suitable for use in construction.

Stage 2 of the BNQ testing protocol is generally undertaken when the results of the Stage 1 testing are not conclusive. Stage 2 involves:

- Total sulphur content (S)
- Sulphate content (SO_4)
- Alumina content (clay content)
- Carbon dioxide content (carbonate content)

BNQ 2560-500 has been adopted as the basis for certifying aggregates for use in building construction. Since 1999, most of the aggregate producers observed this certification requirement and purchasers look for it. The process is referred to as “DB” (dalle de béton or concrete slab) certification. The process for certification requires the sampling and testing to be performed by an approved laboratory and must be performed for every 10,000 tonnes of material for which the Swelling Index must be 10 or less. Each approved stockpile is then assigned a certification number to ensure future traceability.

The École Polytechnique de Montréal undertook a statistical analysis of reports prepared according to the CTQ-M200 protocol for crushed rock fill from 1,700 houses in 26 towns and cities in Québec in 1999. The results were reported by Cormier in 2000 (Cormier 2000). This study concluded that the Swelling Index protocol was a very good predictor of damage. In only 3 % of cases where an index of 10 or less was obtained was damage detected in a house. For Swelling Index values greater than 20, there was a one in three chance of the house having damage. It should be noted that non-representativeness of the sample taken could also account for some of the 3 % of inaccurate assessments.

The vital role played by petrography in identifying the problematic aggregates in Ireland was confirmed in a recent paper by Shrimer and Bromley (2012). The paper concluded that,

> Petrography provided the proof positive that the aggregates were of substandard quality in the sense that they were demonstrably not chemically inert, and that gypsum and other secondary minerals had developed both within the aggregate particles as well as on their surfaces.

In Situ Treatments

Grouting Solutions

While crushed rock products are relatively inexpensive, the costs associated with their removal and replacement after they have been incorporated into a building are huge. In Québec, the problems affected both the basement floor as well as the garage floor. In general, the heave in the garage floor was the most severe, since the underlying fill was quite thick, usually greater than one meter, and a lower grade fill with high fines content was used. The basement slab was typically underlain by a clean stone and was usually less than 200 mm thick. Nevertheless, the repair work generally did not require the residents to vacate their homes. In Ireland, where houses do not have basements, the remedial works are more costly and much more disruptive with the residents having to vacate their homes for up to 12 weeks. In addition, the exterior backfill against rising walls and under footpaths and driveways also needs to be replaced. The typical remedial costs, even for a small house, are at least €30,000.

Clearly, the development of an effective in situ remedial technology would represent a major advance in the treatment of pyrite-induced heave problems in buildings. Over the years, in situ treatments have been considered. They have generally focused on various grouting options. An experimental study to evaluate grouting options was commissioned by the Canada Mortgage and Housing Corporation (Bellaloui et al. 2003). The approach followed in this research was to cut off the supply of oxygen and humidity to the aggregates. Therefore, to be successful, the process needed to completely coat the aggregates with cement grout. The tests showed that with well compacted, graded aggregates (i.e., 0–20 mm), grout penetration could not be achieved, regardless of the type of grout applied. It was concluded that a grouting solution could only work in the case of thin layers of clean stone without fines.

It is our view that grouting solutions are inherently the wrong approach for an in situ treatment for this problem. The basic principle for grouting solutions is that every particle needs to be encapsulated so as to seal it from access to oxygen and moisture—in essence, this process attempts to recreate the condition that the rock had, prior to being quarried, for millions of years. This is extremely difficult to achieve in a well compacted crushed rock, frequently with up to 15 % fines content. The documented cases of concrete undergoing internal sulphate attack suggests that incorporating reactive aggregates into concrete mixes is not a permanent solution.

Grout requires injection under some pressure to achieve penetration. Even modest pressures applied under a floor slab would have a tendency to lift the slab. Encapsulation requires a coating of grout around every particle which necessitates a volume increase. Further, the compatibility and durability of cement-based grout in conjunction with highly reactive pyritic mudstone is an overriding concern with these treatments. A further complication is the solidification of the compacted fill. Thus, if the treatment was unsuccessful, the costs to remove the cemented fill would be significantly increased.

"pHoam" Solution

Modern mining activities, both coal and hard rock, generate acid rock drainage (or "ARD"). The formation of ARD is a natural process. In the presence of air, water, and bacteria, sulfide minerals such as pyrite oxidize and produce sulphuric acid. To have ARD, one needs air, water, and a metallic sulphide mineral source and the bacteria to speed reactions that would otherwise occur slowly.

Based on this, Gusek el al (2008) have proposed a new approach to in situ remediation for problems caused by pyrite oxidation. We can visualize each requirement for ARD generation being positioned at a corner of a tetrahedron (Fig. 32). If any of these primary ingredients are missing, isolated, or chemically

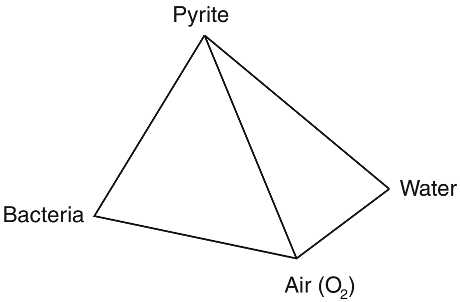

Fig. 32 The ARD tetrahedron (from Gusek 1994)

neutralized, ARD will not occur. The active ingredients to disrupt the tetrahedron and thereby prevent ARD, include liquids, solid particles, gases, and living microbes.

Pyrite-induced heave in buildings requires the same key ingredients as ARD. Current research efforts are underway to apply these principles as the basis for in situ treatment to stop the oxidation process and thereby stop the heave.

By fully understanding the chemical processes that lead to the production of gypsum in compacted shale and mudstone fills, we can devise chemical treatments that prevent the oxidation from occurring. These treatments can comprise liquids as well as solids, as described by Gusek et al. (2012).

These treatments directly control one or more of the four essential elements in pyrite-induced heave, in a similar approach to the use of pharmaceuticals in treating disease. Some examples are provided below:

- Air: Treatments that consume or displace air such as carbon dioxide or sawdust or vegetable protein.
- Water: Coat reactive surfaces with chemical treatments such as potassium permanganate solutions, bentonite clay etc.
- Sulphides: Neutralize acid such as with lime solutions or flyash.
- Bacteria: Bactericides such as sodium lauryl sulphate or phosphate solution.

While a cocktail of chemical treatments could be delivered by way of a liquid solution, in the case of compacted fills within buildings, this is impractical. The solution would drain to the bottom and escape through joints in walls. The solution devised is to utilize foam technology. Foam is a two-phase fluid consisting of a gas component surrounded by a thin fluid phase that is developed with a soluble surfactant or soap (Gusek et al. 2012). The pyrite oxidation-suppressing active ingredients can be entrained in, or are a part of, the foam structure. In addition, solid phase ingredients such as limestone, lime, biosolids, or cement kiln dust can be entrained and suspended in the foam structure. Such mixtures comprised of ARD-suppressing or pyrite oxidation-suppressing components are hereafter referred to as pHoam$^{\text{TM}}$ to distinguish it from common foams used in other industrial applications, including fire-fighting.

The proposed pHoam$^{\text{TM}}$ method solves the active ingredient delivery problem by increasing the mobility and surface area of solutions or mixtures of active ingredients without sacrificing hydrologic control. Active ingredients suspended or contained in a pHoam$^{\text{TM}}$ of predetermined "stability", can flow omni-directionally or bi-directionally from a single injection point as an advancing front. It is also considered possible to introduce agents to dissolve gypsum by way of pHoam$^{\text{TM}}$.

Laboratory experiments are currently underway to develop the optimum treatments for suppressing the oxidation of pyrite in shales and mudstones and to confirm the effectiveness of pHoam$^{\text{TM}}$ as the delivery mechanism. The basis of the testing program is to utilize a series of Golder laboratory swell tests. Once the steady state condition of pyrite-generated heave is attained, these test cells can be injected with pHoam$^{\text{TM}}$ containing different ingredients either singly or in combinations.

Fig. 33 Series of six Golder swell tests, five containing compacted swelling mudstone and one containing inert limestone

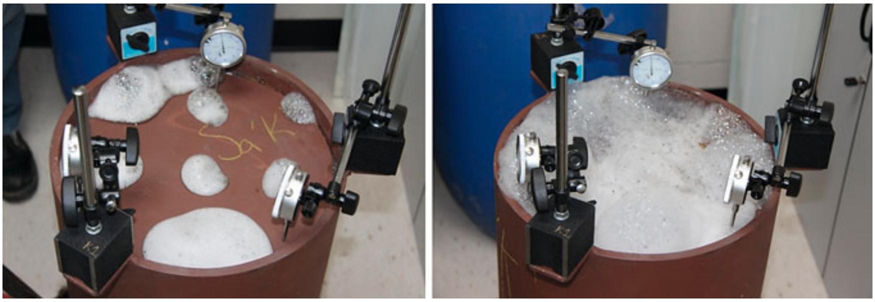

Fig. 34 Foaming trial showing foam injected from the *bottom* of the sample escaping through and around the *top* plate

The test cylinders contain samples that are 336 mm in diameter and 302 mm high (Fig. 33). The bases of the cylinders are perforated to allow moisture to enter the sample from the water trough in which it stands.

The first foaming trial included a bactericide. This was introduced into Test Cell K by way of a foam injection from the bottom of the test cylinder (Fig. 34). The injection was performed at Week 15 and the results at Week 20 demonstrate that the introduction of the bactericide interrupted the steady state pyrite-induced heave (Fig. 35).

While this testing program is ongoing, the early results are very encouraging. We have confirmed that the Golder swell tests develop a steady state rate of heave within 5–10 weeks in compacted mudstone. We have also demonstrated that pHoam^{TM} is effective in permeating compacted crushed mudstone with dry densities as high as 1.90 Mg/m^3 and fines contents (passing 75 μm) of 11 %. We have

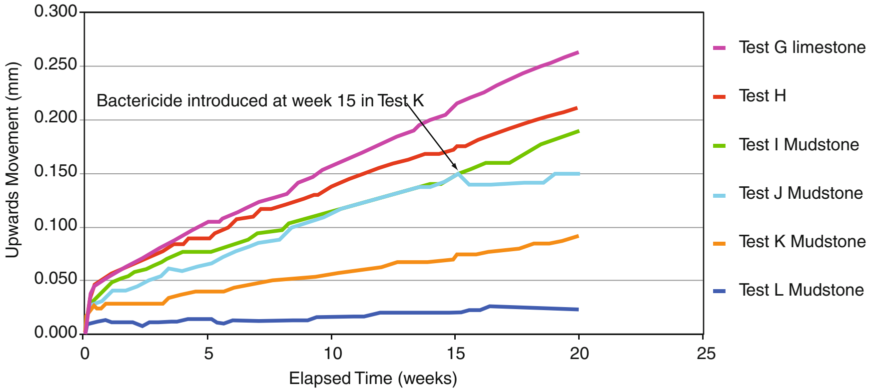

Fig. 35 Results of swell tests showing effect of introducing bactericide into swelling mudstone

also demonstrated that the introduction of a bactericide suppresses pyrite-induced heave for at least a period of five weeks. This indicates the importance of bacteria in supporting the reactions.

Conclusions

This chapter presents an overview of problems associated with sulphide minerals in rocks used in construction in Canada and compares them to similar problems experienced in Ireland, which were first identified in 2006. The first problems with pyrite-induced heave in shales in Canada were identified in the Ottawa area in the 1960s. These related to foundations supported on Billings Shale. The problems were appropriately investigated and the causes identified. These early investigators were accurate in the mechanisms they ascribed to the problem and they recognized the key characteristics of these problematic fine grained sedimentary rocks.

Despite this clear identification of problems associated with shales containing disseminated pyrite, a widespread ‘epidemic’ of pyrite-induced problems developed in the Montréal area in the mid 1980s. In this case, the problems came about from the use of pyritic shales as compacted fills beneath floor slabs in residential and commercial construction. While it could be argued that the Utica Formation shales of the Montréal area were generally of better quality than the shales of the Billings Formation, it points to an overall lack of quality and testing standards for construction aggregates used in residential construction.

It is worth noting that these problematic aggregates do not appear to have made their way into municipal infrastructure works, which suggests that the industry applies different quality standards to aggregates used in low rise building construction. It is observed that tests for total sulphur have not been historically performed in Canada for construction aggregates. These problematic aggregates could have been identified as being of extremely poor quality and low durability by simply performing the standard aggregate source acceptance testing protocols.

This chapter also presents three contemporary pyrite-related problems in relation to building and infrastructure developments. The first case deals with an industrial building partly supported on Billings Shale where the water table was lowered, triggering oxidation of the underlying shales. These are legacy problems from a time when this problem was not fully understood and the appropriate mitigative measures were not instituted. The case of the Ottawa Light Rail Transit system demonstrates that potential problems with pyritic shales can be avoided when they are identified by investigation at the pre-design stage of a project. It also demonstrates that shales are not just problematic because they contain reactive pyrite. They also contain high clay contents and are subject to swelling when exposed to fresh water. Pioneering work undertaken at the University of Western Ontario has developed test procedures to quantify these expansive pressures so that they can be fully accommodated in construction works in shales.

The third case study describes a current problem with aggregates used in concrete mixes mainly in residential construction in Québec within the last eight years. These aggregates were of extremely high quality from a mechanical-physical perspective, but contained reactive pyrrhotite, pyrite and chalcopyrite. There was a failure to appreciate at the time the risks associated with the incorporation of aggregates containing pyrrhotite into concrete mixes, even in cases where the aggregates were very dense and of low permeability.

In the light of the Canadian experience, which has been well documented in the scientific and engineering literature since the 1960s, it is difficult to understand how such widespread problems could have arisen in Ireland in the early part of the 2000s. Although much of the Canadian literature on the topic refers to shales while in the Irish cases the problematic aggregates are generally classified as mudstones, the similarities are quite stark—fine grained sedimentary rocks deposited in a marine environment and containing disseminated very fine grained and framboidal pyrite.

This chapter also presents some mineralogical data on the problematic Lorraine and Utica Shales. While the Lorraine Shales contain extremely high clay contents and very low calcite contents, the Utica Shales are quite variable and many have relatively high calcite contents. Nevertheless, due to their high porosity they are prone to ingress of humidity and oxygen and allow the growth of gypsum with consequential damage to buildings in which they are used. From Fig. 24 it is clear that some of the Utica Shales are of similar mineralogical composition to the problematic Irish mudstones.

Since the introduction of the DB aggregate certification program in Québec in 2003, it is our understanding that no buildings using certified fills have experienced pyrite-induced heave. This confirms the effectiveness of the protocols developed which are based primarily on petrographic examination rather than simply quantifying the pyrite content. However, the concrete problems in Trois-Rivières demonstrate that each aggregate application must be assessed separately, as the problematic aggregates that have given rise to extensive concrete deterioration would have had a Swelling Index of 0.

This chapter also reviews some current research work aimed at developing in situ remedial treatments for compacted fills undergoing pyrite-induced heave. Given the history of this problem, it is reasonable to assume that related problems will continue to occur in the future in other parts of the world. Whilst any in situ treatment of this nature has inherent complications, not least of which is confirming that it will provide long term relief from future damage, nevertheless, we need to continue to progress our understanding of this problem which has devastating impacts on both people's lives and on commercial enterprises.

Acknowledgments The assistance of the following Golder Associates colleagues in the preparation of this chapter is acknowledged: Bernadette Azzie, Barry Balding, Mario Gervais, Jim Gusek, Terry Nicholas, Fred Shrimer, Troy Skinner, and Mark Telesnicki.

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Pyrite Oxidation and Structural Problems in the Chattanooga (Ohio) Shale, East Central Kentucky

Warren H. Anderson

Introduction

The Chattanooga Shale, also called the Ohio and New Albany Shale, extends over a large section of the east-central United States and is a thick black organic shale composed of various clay minerals and up to 5 % pyrite. In east-central Kentucky (Fig. 1), the pyrite in the Shale can be both lenticular and disseminated and occurs throughout the Shale stratigraphic section. In an aerated environment, pyrite can oxidize and form secondary sulphate minerals in the soil residuum, which creates the subsequent expansive or heaving problems for any structures built on Shale foundations. It also creates an acidic soil environment and results in the formation of a mild sulphuric acid. This formation of sulphates and creation of sulphuric acid causes the Shale to weather very rapidly and degrade into unstable clay and sulphate minerals. The Shale can also have expanding clay minerals such as montmorillonite, but most of the problems presented in this chapter are from pyrite oxidation and sulphate formation.

Several case studies were examined to study this problem in east central Kentucky (Fig. 1). The Estill County Middle School, Carhartt Factory, Marcum and Wallace Hospital auxiliary buildings and the Clay City Water Treatment Plant (Beech Fork) (Figs. 2, 3) have all had foundation problems as well as cracked and heaving floors, cracked walls, ceilings and sidewalks, and broken subsurface utility lines Anderson (2008).

The Middle School was built in 1996 and has had extensive foundation problems and numerous stages of remediation to correct the problems. The Carhartt Factory was built in 1994 and had severe foundation problems since it was constructed. The Hospital was built in 1959 and has had minor repairs to correct foundation- and plumbing-related problems at the time this report was completed.

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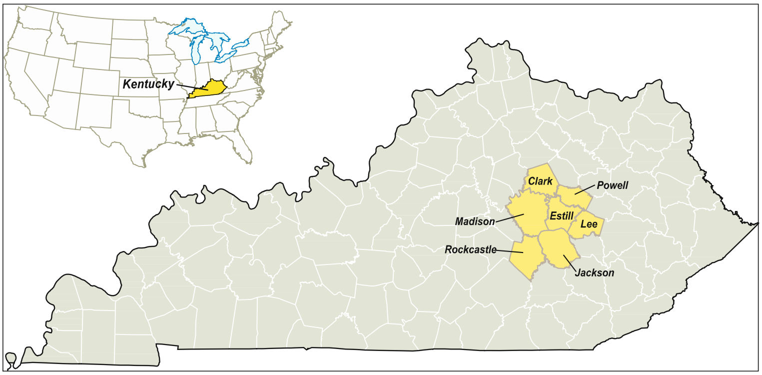


Fig. 1 Location map of Kentucky showing area of study

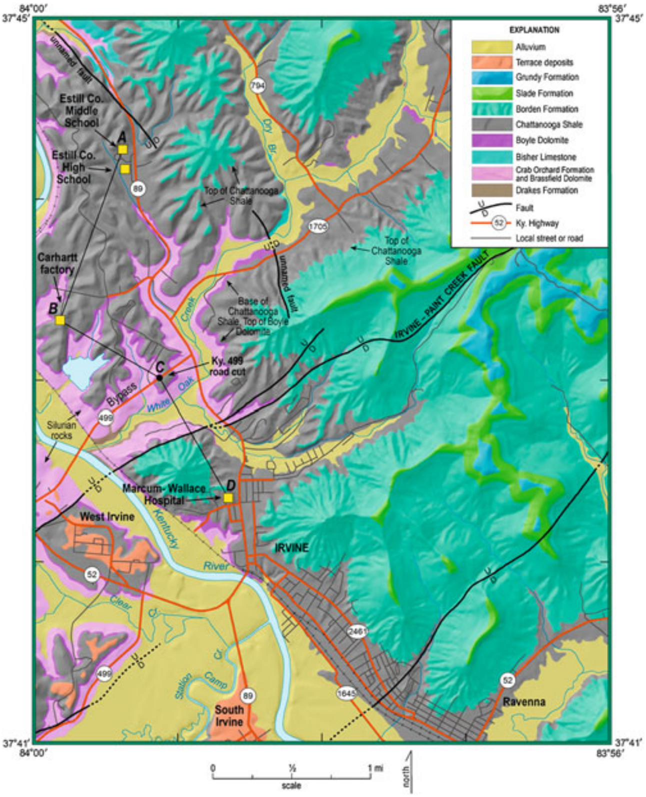


Fig. 2 Geologic map showing Black Shale outcrop, faults, pipe-lines, roads, drainage, study areas

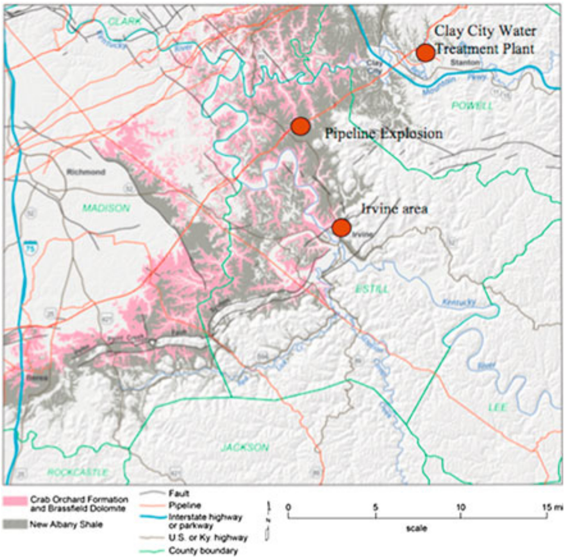


Fig. 3 Detailed geologic map of the Irvine area showing schools, factory and hospital locations

The Clay City Water Treatment Plant has had similar foundation problems that are starting to affect the pump and pipeline facilities at the Plant.

Numerous natural gas pipelines occur in the study area and the pyrite oxidation problem could be responsible for accelerated corrosion of steel pipelines and natural gas explosions. In January, 2012, a major gas transmission line explosion occurred in Estill County and although the exact cause has not been determined, it appears that the pipeline is sited in the black Shale.

Analysis of the chemistry and mineralogy was performed to determine the source(s) of the foundation problems associated with the Shale. This study will suggest steps that are necessary to assist in preventing future foundation problems or remediate existing construction problems related to pyrite oxidation within the Chattanooga (Ohio) Shale.

Location and Geologic Setting

East central Kentucky is located along the eastern flank of the Cincinnati Arch and in the west central portion of the Rome Trough in eastern Kentucky in Estill, Powell, Madison, Montgomery, Jackson, Rockcastle and Bath Counties. The Irvine Paint Creek Fault System (Figs. 2, 3) is a northeasterly trending basement fault system that occurs in the area. Several additional unnamed faults exist in the area and there are several northwest and northeast trending cleats (discontinuities) in the Shale outcrops near the structures referred to in this study.

The Irvine 1:24,000 scale geologic map (Hoge et al. 1976) and the Irvine digital geologic map Morris and Curl (2000) show that the Chattanooga Shale is exposed

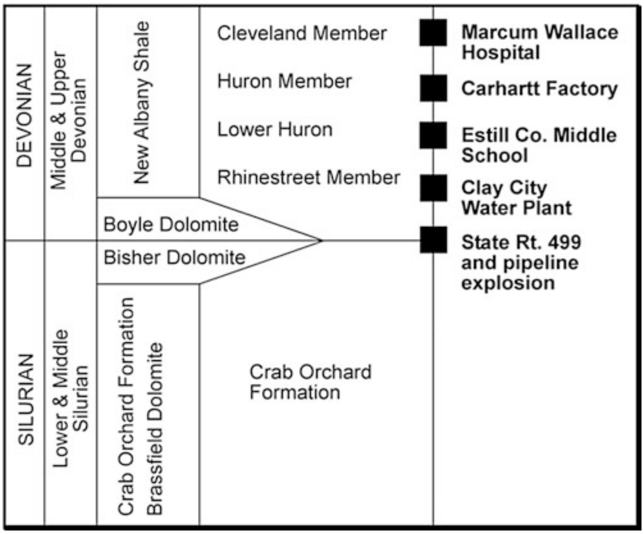


Fig. 4 Stratigraphic column showing pyrite zones within the Cleveland or Huron Member of the New Albany (Chattanooga and Ohio) Shale, which are a common factor in the foundation problems

Fig. 5 Shale outcrop showing cleat fractures and pyrite nodule zone

and gently dipping over the Estill and Powell County area (Figs. 2, 3). The Shale contains abundant pyrite nodules and quartz silt in this area and several tributaries drain the Shale near White Oak Creek (Hoge et al. 1976). Pyrite lenses and nodular zones are common in the outcrops adjacent to several of the buildings (Figs. 5, 6, 7, 8, and 9).

Several fractures or faults are mapped in the vicinity of the buildings, and numerous cleats (Figs. 10, 11) appear to be parallel to the northwest trending fault. These cleats may facilitate the flow of groundwater toward the school and remediation contractors working at the school noted moisture in some of the sub crop cleats during repair work. No springs were observed on the surface outcrop or sub crops, but the location of Masters Creek and other tributaries of White Oak

Fig. 6 Weathered Shale outcrop showing yellow secondary sulphate

Fig. 7 Pyrite oxidation, iron oxide, sulphate staining and precipitate in Chatanooga Shale

Fig. 8 Secondary sulphate, white coating of melanterite in Chatanooga Shale

Creek lie near the schools, factory and hospital at the base of several sloping hills. This water and runoff would accelerate weathering and dissolution in the Shale in the zone of pyrite nodules, react with the pyrite and create a mild sulphuric acid in the creek.

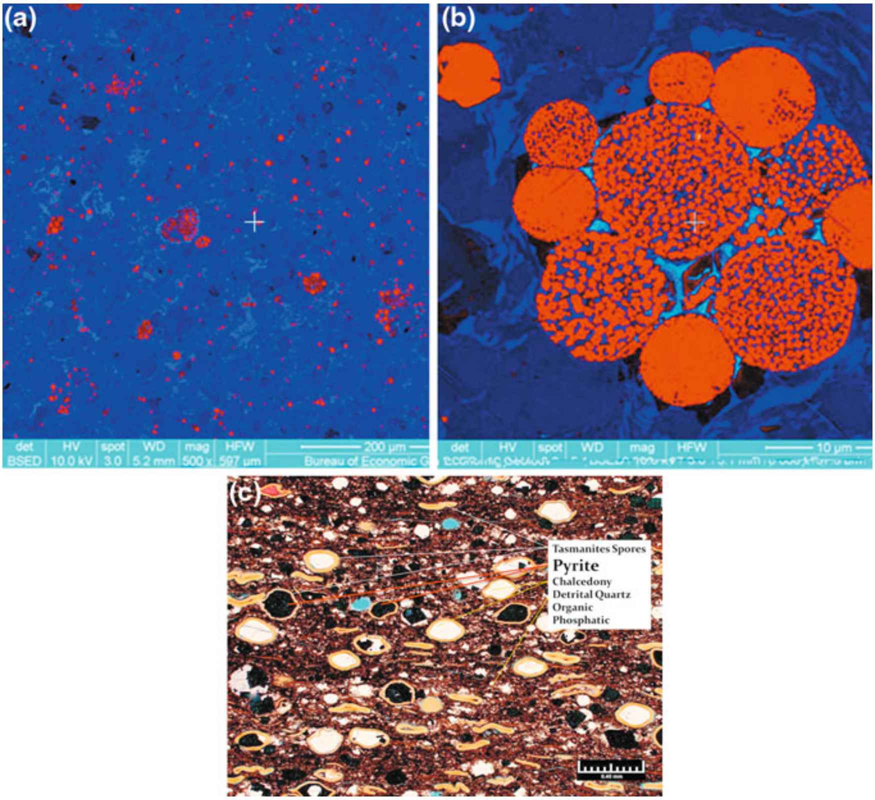


Fig. 9 Framboidal pyrite in black Shale, scanning electron microscope images, argon milled polished thin section, (**a**, **b**) and (**c**) thin section showing tasmanites spores, pyrite, phosphate and detrital quartz; Blan No. 1 Stratigraphic Test Well, Hancock County, Ky, Kentucky Geological Survey, Operator, courtesy Bureau of Economic Geology, University of Texas and Weatherford International

Fig. 10 Chattanooga Shale outcrop behind the Middle School, looking north. *Note* retaining wall

Stratigraphy/Mineralogy

The Chattanooga Shale (also called the Ohio and New Albany Shale) in the study area is between 100 and 160 feet (30–50 m) thick and is composed of fissile, silty, brownish black shale with abundant carbonaceous material, limonite and pyrite nodules (Figs. 7, 8). Limestone beds occur in the Shale and exhibit a cone-in-cone structure. Generally, the unit is called the Ohio Shale in the northeastern part of Kentucky, the Chattanooga in the southeastern part of Kentucky and the New Albany in western Kentucky.

The coloration of the carbon-rich Shale relfects organic content and depositional oxygen saturation. The Black Shales are more organic containing tasmanites algal spores and phosphate (Fig. 9c)

Slow deposition, the abundance of organic material and the lack of oxygen during diagenesis of the Shale allowed sulphide minerals, primarily pyrite, to precipitate between organic matter and along bedding planes. The Huron Member may have been more susceptible to dysoxic or low oxygen conditions, contributing to increasing framboidal pyrite size (Rimmer et al. 2001; Hawkins et al. 2002).

The organic matter was derived primarily from marine material (Cortland Eble, 2012, personal communication) with variable amounts of terrestrial material (Rimmer and Hawkins 2006). The Shale also contains minor amounts of iron, uranium, phosphate, vanadium, chromium, and nickel as discussed by Tuttle et al. (2003), and is also slightly radioactive.

The clay mineralogy of the Cleveland Member consists of illite (60 %), illite/smectite (30 %), chlorite (10 %) and a trace of kaolinite. The Huron Member primarily contains an illitic clay (60 %), mixed layer clay of illite/smectite (20 %), chlorite (10 %) (Hosterman 1983) and the remainder is kaolinite. There is a possibility that the mixed illitic smectite layer could contain some expanding clays. Examples of this weathered Shale lie in the outcrop drainage near each of the building sites examined where it is evident that it has a semi-plastic property with little or no shear strength.

The Chattanooga Shale in this area of the State has a high pyritic content, which oxidizes into various iron or powder like, (efflorescent) sulphate minerals (Figs. 7 and 8). Commonly called pyrite swelling, it is actually a chemical oxidation reaction between groundwater and pyrite (Fig. 9a, b, c). There are many sulphates formed from this chemical reaction, but two of the most common are jarosite and copiapite. Jarosite, an iron sulphate, is a mineral salt and a product of pyrite oxidation. Copiapite is a calcium-iron sulphate that has a distinctive yellow color.

Underlying the Chattanooga (Ohio) Shale is the Devonian Boyle Dolomite, Silurian Bisher Limestone/Dolomite and Crab Orchard Group. The Boyle Dolomite is very thin (<20 ft/6 m thick). An erosional unconformity at the top of the Silurian may truncate the Bisher Limestone such that the overlying Devonian Boyle may reside on top of the Crab Orchard. The Crab Orchard Group is primarily Shale that also contains expandable clays and pyrite (McDowell 1983).

Geochemical trend maps by Wys (1981) in Pike, Floyd, Martin, Johnson and Knott Counties in eastern Kentucky suggest that pyrite content in the Chattanooga Shale may concentrate or occur in specific trends related to original deposition, structure and/or stratigraphy. The pyrite concentration could be as high as 8 % in eastern Kentucky. Although his maps are outside the current study area, it would be expected that this idea of concentration of minerals and metals would exist in many areas of the Shale, particularly eastern Kentucky. One of these areas of concentration could be occurring in Estill County and account for the high pyrite content.

Stratigraphic Context of the Building Sites

The Estill County Middle School structure was built near pyrite zones in the Lower Huron Member of the Devonian Chattanooga (Ohio) Shale (Figs. 5, 6, 10, 11) (Hoge et al. 1976) and on construction fill derived from the Shale. The Estill County High School is also built in the Lower Shale nearer the contact with the underlying Devonian Boyle Dolomite, but was not founded on fill material (Christopher, personal communication, 2005) and apparently not on a pyrite zone, since no problems were noted at the High School.

The Carhartt Factory is located at a higher stratigraphic position than the Middle School in the upper Chattanooga (Ohio) Shale, either the Cleveland or Upper Huron Member. Parts of the Factory were built on fill, whereas the parking lot was not. The factory parking lot pavement was recently finished (in 2007) and had not experienced any heaving problems at that time. The Marcum and Wallace Hospital auxiliary office building is situated in the Cleveland Member of the Chattanooga (Ohio) Shale, slightly above the stratigraphic position of the Carhartt Factory. The Clay City (Beech Fork) Water Treatment Plant is located in the Beech Fork tributary of the Red River in Powell County and built in the middle

Fig. 11 Outcrop and road behind Middle School showing Shale outcrop sloping toward rear of school

part of the Chattanooga Shale, probably in the Lower Huron Member. Geologic map evidence suggests that at the location of the catastrophic failure the pipeline is built in the lower portion of the Black Shale.

The Middle School, factory, and water treatment plant are located on the north side of the Irvine Paint Creek Fault System where the Shale is between 120 and 160 feet (36–49 m) thick. The hospital lies south of the northernmost fault of the Irvine Paint Creek System, where the Shale is 100 feet (30 m) thick, i.e. thinner than at the school location. The factory and hospital are located in the upper parts of the Shale whereas the Middle School is located in the middle to lower section of the Shale. The thickness variability of the Shale is related to its original deposition and to the Devonian unconformity.

Methods

Site Inspections

Beginning in 2000, the Middle School and factory were both examined for foundation-related failures in interior floors, walls and ceiling and exterior sidewalks, roadways, parking lots and retaining walls. In 2006, the hospital and State Route 499 were also examined. In 2011, the Clay City Water Treatment Plant was examined and in 2012, the pipeline explosion site was investigated. The geology of each site foundation was examined in maps, core and outcrop samples when possible to determine lithologic and mineralogic characteristics of the Shale bedrock supporting the foundation and any important associated hydrologic characteristics. Each of these items could provide useful geologic information and help determine the probable cause of the foundation failures.

Site Descriptions

As early as the opening of the Estill County Middle School (Fig. 12), problems were noted with the floors, walls and doors and exterior sidewalks. There have been several cosmetic repairs to masonry cracks in the walls, concrete floors and along door frames, including cracks around the frame for the only elevator in the building. Many sections of exterior walkways have had the concrete replaced because of the severity of heaving and cracking. The Middle School had gaps in the tile floors, cracks in the ceramic floor and one inch (c.25 mm) offsets in brick or concrete block walls (Fig. 13). The Middle School gymnasium floor has also heaved considerably and the raised relief of the gym floor was impeding the opening and closing of the bleacher seats in 2000 (Fig. 14). In the 2000 inspection, the gymnasium floor and foundation had heaved and would not allow the bleacher

Fig. 12 Estill County Middle School

Fig. 13 Repaired masonry block cracks

Fig. 14 Bright spots highlight heave of gymnasium floor (2000)

seating to retract to a storage position. All of these foundation problems threatened the functional and structural integrity of the school. In 2005, gymnasium foundation material was removed and the sub crop bedrock was sealed with a resin to prevent further foundation and structural damage. Additional repair work in 2006 and 2007 involved removal and repair of concrete flooring in hallways, classrooms and offices and replacement of utility lines.

The Estill County High School is located several hundred feet (100 m or so) south of the Middle School and is approximately 30–40 feet (10–12 m) lower in elevation. The High School has had no apparent foundation problems. The Master Creek tributary that lies behind the High School that drains the landscape of both schools and is a "red" creek, implying it is iron rich and sulphurous, containing acidic water.

The Carhartt Clothing Factory is located in an industrial park located about 1 mile southwest of the Middle School and north of Kentucky Route 499. It has also had significant wall and foundation problems including cracks and floor heaving. The Factory remains functional and current remediation has been to cut the bottoms off of the doors for accessibility and implementation of steel ramps for forklift maneuverability. The factory is currently evaluating more significant remediation possibilities.

The Marcum and Wallace Hospital auxiliary offices building in Irvine has foundation problems such as heaving floors and cracked plaster. The basement portion of the hospital had a few basement floor cracks. The basement is adjacent to the floor slabs that are heaving. Basement flooring has iron stains and water marks in the tiles, implying sub-surface moisture seeping into the hospital flooring. The main hospital, which is adjacent to the office complex, does not have any apparent foundation problems, but the slab flooring in the auxiliary offices building does.

The Clay City (Beech Fork) Water Treatment Plant was examined to assess the heaving in the plant slab flooring and in concrete block walls. Cracks in the walls were threatening the electrical conduits and power supplies, and heaved flooring threatened the water filtration, pumping and pipe integrity. Several inches of heave were noted from the edges of the load bearing walls to the slab flooring in the middle of the building.

In 2012, a natural gas pipeline explosion occurred in Clark County, Kentucky, and although site inspection was not granted by the owners of the pipeline, a geologic map review would suggest that the pipeline is sited near the base of the black shale and may have the same heaving tendencies.

Excavations of the black shale in the vicinity of the pipeline and all of the buildings are numerous; ball fields or practice fields are located west of the schools, Shale outcrops were adjacent to where buildings and foundations were excavated and some Shale material was used as aggregate fill material.

Analytical Methods

Five cores were collected at the Middle School, one was collected in an interior hallway and four were collected on the exterior perimeter of the school foundation. Marshall Miller and Associates provided locations and obtained the core. Detailed core descriptions were compiled to identify lithological and mineralogical characteristics of the Shale. Additional outcrops were examined and descriptions were conducted on the samples collected along the western outcrop of the school. Additional outcrops near the factory, hospital, treatment plant and bypass were also examined to determine the stratigraphic position and other geologic or physical characteristics of the Shale.

Preliminary visual mineral identification was conducted on sample sets of core and outcrop, which was confirmed by X-ray diffraction (XRD) and fluorescence (XRF) analysis. Both Shale and clay mineral analyses were conducted.

Shale analysis was conducted by X-ray fluorescence to determine whole rock chemistry, and clay mineral analysis was determined by X-ray diffraction to identify the types of clays within the Shale. Both of these analyses were conducted to determine the percentage of the elements: calcium, iron, silica, aluminum, potassium, magnesium, sodium, and sulphur. These are principal elements in sulphate minerals.

Sulphate analysis was conducted by XRD to determine mineralogical composition. Mossbauer Spectroscopy Analysis was conducted on pyrite samples to determine the variations in iron and sulphur composition of pyrite. Induced Coupled Plasma Spectroscopy (ICP) analysis was conducted on major elements in the core and water samples to determine overall major and minor element composition.

Variance in percentage composition in each component mineral is important to determine areas of chemical reactions involving the Shale, pyrite and sulphates.

Results

Site Conditions and Remediation

Estill County Middle School

Construction to repair the interior rooms and hallways and gym floor in 2005, involved excavation and removal of all flooring and foundation material and sealing the sub-crop bedrock foundation with an asphaltic, fiber resin to prevent further oxidation and subsequent heaving. Subsequent remediation in 2006 in other parts of the school (Figs. 15, 16, 17, 18) involved removal of additional concrete floors and utility lines and replacement with concrete columns, steel beams and joists to create a sub floor above the Shale. It appears that the damage has not penetrated to the second floor of the Middle School as only minor damage was noted there. As can be seen in Fig. 16, in 2008 the load bearing walls on the right side of the photograph and in the background do not show any signs of failure.

A 10 inch (c.250 mm) poured concrete retaining wall in the parking lot shows signs of bulging, confirmed by tension fractures along the face (Fig. 19). Mineral

Fig. 15 Interior of Middle School showing Bobcat loader removing existing concrete slab flooring (2006)

Fig. 16 Shale beneath School and new trench construction for column footers, new and old sewer PVC pipe, cleats with the sulphate mineral

Fig. 17 Multidirectional cleat fractures with sulphate precipitates below walls. *Note* green re-bar

Fig. 18 Cleats with sulphate precipitate in Shale beneath Middle School; note new concrete columns

Fig. 19 Tension fractures in retaining wall; note iron stained drain holes (2000)

precipitates in the tension cracks and drain holes along the wall (Fig. 20) confirmed the presence of sulphate minerals.

An outcrop behind the school exhibits some of the physical characteristics of the Shale including sulphates, pyrite nodules and pyrite lenses (Figs. 5, 8, 9). The sulphate formation is visible in the sub crop foundation of the school (Figs. 17, 18), and outcrop behind the school (Figs. 10 and 11). Massive pyrite oxidation occurring in the Shale leaches minerals, including sulphates, sulphur and iron into the Master's Creek Tributary, resulting in low pH, high sulphate and significant iron staining in the "red" creek. The outcrop behind the school is red stained with iron oxide precipitates.

The south east corner of the school has some exterior masonry cracks on the brick veneer and there is a report of a teacher's desk drawer that will not remain closed, but will slide open by gravitational forces, implying subsidence on the southeast corner of the school. Shale fill was used in this portion of the school.

Fig. 20 Sulphate precipitates around drain pipe (2000)

Carhartt Factory

The Carhartt Factory (Fig. 21) had similar foundation problems. The factory is sited higher in the stratigraphic column, in the Cleveland Member of the Chattanooga Shale.

There were cracks near doorways, ceilings, and in floors (Figs. 22, 23, 24, 25). Doorways have been cut to allow functionality. As seen in Fig. 24, floor heaving was considerable; the top of the cell phone near the I-beam indicates about 4 inch (c.100 mm) of upward heaving of the main floor. In the truck loading area, steel inclines had to be deployed to accommodate factory forklifts navigation over heaved flooring. Although no major remediation had been conducted during 2006, the factory is currently evaluating its options for repair.

Fig. 21 Carhartt Industries Plant and Chattanooga (Ohio) Shale outcrop, Irvine

Fig. 22 Substantial floor cracks in Carhartt break room; rise of walls has caused the window to be inoperable

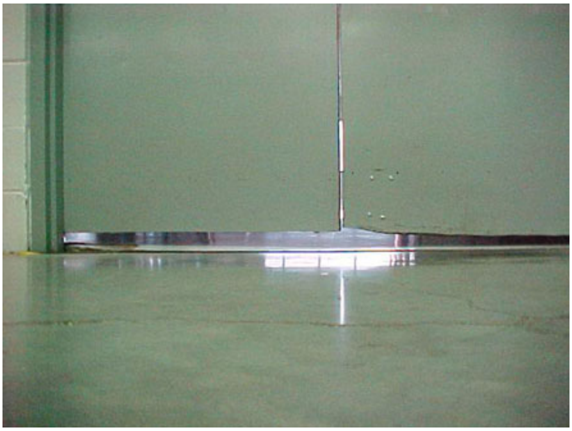


Fig. 23 Doors have been cut to allow functionality for opening and closing

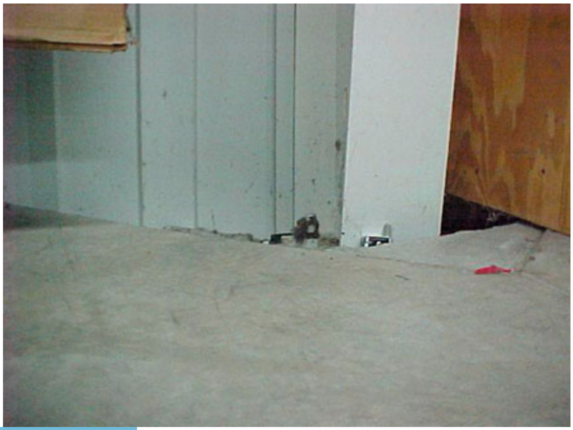


Fig. 24 Heaved floor adjacent to load-bearing wall on main floor of the Carhartt Factory. Note the cell phone resting on steel column for scale

Fig. 25 Large cracks (1 inch) in concrete block adjacent to doorway. Note the attempt to bracket the wall cracks

Marcum and Wallace Hospital

The hospital's location in the Upper Chattanooga Shale contributed to some of its foundation problems (Fig. 26). Interior floors and non-load bearing concrete block walls have cracked and heaved considerably, bending and breaking copper water lines and radiators and breaking ceiling plaster. External load bearing walls did not have any major cracks or fractures in the exterior brickwork.

Fig. 26 Exterior of the Marcum and Wallace Hospital office wing and an adjacent outcrop of the Cleveland Member of the Chattanooga (Ohio) Shale. Note the absence of cracks or offsets in the load bearing walls and exterior brickwork of rooms with heaved floor slabs

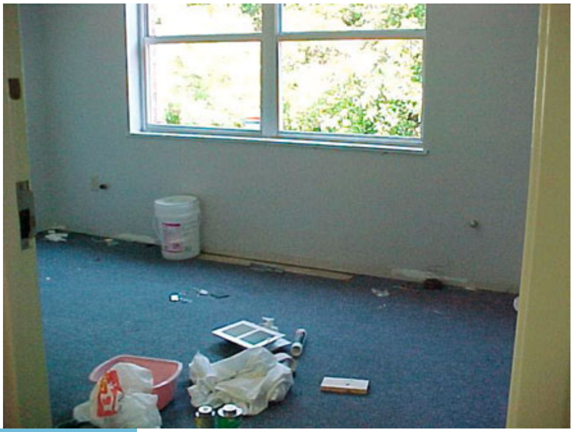
Fig. 27 Displacement of ceiling wall-board along non-load bearing walls due to floor heaving

Water run-off from the Shale outcrop at the rear of the Hospital and a roof drainage system which channeled water run-off into an area within 15 feet (5 m) of the foundation, could be the reason many of the rooms were having floor heaving. Based on cleat directions, iron stains and water marks, sulphate rich run-off waters are seeping into the hospital foundation bedrock from these drains, aiding the oxidation of the pyrite and decomposition of the Shale. These precipitates form iron stains and other mineral residues such as sulphates in the basement flooring and are evidence that sulphates could be the cause of floor heaving and foundation problems.

The primary foundation problems were repaired by re-installation of water lines, replacement of drywall or ceiling tiles (Fig. 27) and patching cracked concrete block walls. One radiator located beneath a window was lifted by some 2–3 inches (c.50-75 mm) and had to be removed.

Unless the drainage system is modified, it is possible that heaving problems in floor slabs could continue. Damage appeared to be restricted to non-load bearing walls, since damage to exterior load bearing walls was not observed (Figs. 26, 27, 28).

Fig. 28 Repair of floor, walls and copper water lines damaged by office floor heave



Clay City (Beech Fork) Water Treatment Plant

The Clay City Water Treatment Plant (Fig. 29) has been in operation for about 20 years and serves a community of approximately 3,000 residents in Powell County, Kentucky.

Foundation problems at the plant were noted by plant operators in 2010 and the site was examined by engineers and geologists during a field examination in 2011. Concrete block walls were cracked, and heaved flooring was placing stress on large diameter water pipes and chlorine tank connections. The electrical room had similar cracked concrete block walls which threatened the electrical wiring and conduits systems.

Figure 30 shows typical building foundation structural components, which demonstrate floor heaving due to sulphate formation and apparent stability of load bearing walls while non-load bearing walls will heave with slab flooring. Heaving of flooring and walls will result in broken utility lines including water, gas, sewer, and electricity.

Pipelines in the Chattonooga Shale (Acidic Soil Horizons)

Kentucky is located in the central part of the United States and has numerous high pressure interstate natural gas transmission pipelines that cross the State. In the last 30 years approximately 10 major pipeline explosions have occurred in the State, most recently in January, 2012 (Fig. 31).

Approximately 30 % of those pipeline failures have occurred when the pipeline is constructed in the black Shale (Fig. 32). Since these pyritic Shales are known to cause heaving, and since they are an acidic soil horizon, it is possible that the pipelines built in these pyritic Shales experience failure. Most pipeline failures are classified as corrosion or seam failure, but the type of corrosion or type of ground conditions which caused the failure is not recorded. Some pipelines have liners to

Fig. 29 Clay City (Beech Fork) Water Treatment Plant

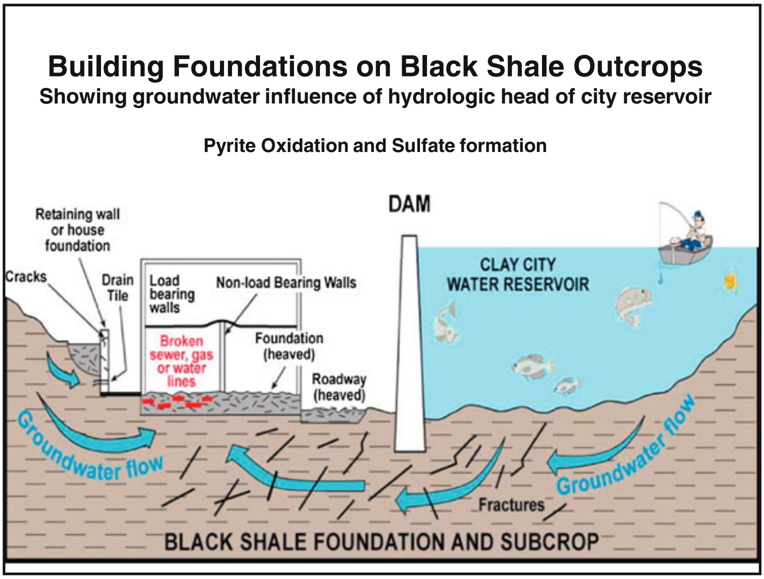


Fig. 30 Schematic diagram of building foundation in Chattanooga Shale showing water reservoir and groundwater infiltration

correct for galvanic corrosion, or pillows to protect from heaving, both of which help with prevention of pipeline incidents. Planning and proper geochemical and engineering personnel should be knowledgable about the heaving and acidic soil conditions when routing pipelines in pyritic Shales.

Fig. 31 Estill County Natural Gas Pipeline Explosion, January, 2012, taken approximately 15 miles from site by Melissa Kingsley, Richmond, Kentucky, used with permission

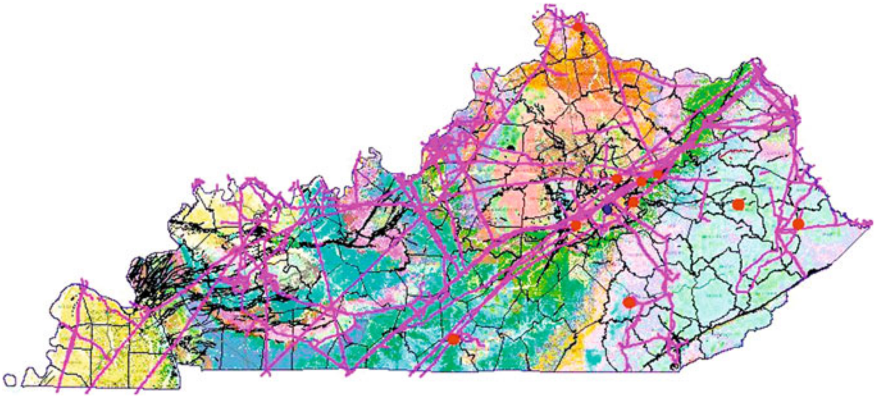


Fig. 32 Explosive incidents in pipelines in Kentucky (*red dots*) in the past 30 years

State Route 499 (Irvine Bypass)

The Irvine Bypass (State Route 499) was constructed between 1998 and 2000. It began heaving during construction and was milled and rebuilt during the initial construction period (Fig. 33) (Bechham and Hopkins, 2005).

During the field investigation and in discussions with Hopkins (2006, personnal communication), it was determined that heaving at the eastern-most location in SR 499 is caused by expanding clays in the Crab Orchard Shale and that pyrite oxidation from the Chattanooga Shale has only a minor impact on the road base at this location. Although the actual road base is in the Crab Orchard, the cut banks adjacent to the highway are Lower Chattanooga Shale. This means that water derived from the Chattanooga Shale could have a low pH and that any pyrite in the outcrop could oxidize and contribute to the swelling problems.

Fig. 33 State Highway Route 499, the Irvine Bypass is sited in the Crab Orchard Shale with Chattanooga (Ohio) Shale cut banks adjacent to the road

Analytical Results

The Kentucky Transportation Center conducted testing of swelling properties in the Crab Orchard at this location. The analytical results are discussed under three categories:

1. shale chemistry and clay mineralogy
2. pyrite chemistry and sulphate mineralogy and
3. hydrochemistry

The clay mineralogy of the Shale will distinguish the expandable clays from the non-expandable while pyrite/sulphate analysis is used to analyze the relationship between pyrite chemistry/oxidation and the formation of various sulphate minerals. In order to understand the foundation problems, the relationship of complex chemical reactions between the Shale, groundwater and pyrite must be understood. These complex chemical reactions form various minerals, which create the foundation problems in Estill County. The mineralogic and chemical relationships explain the swelling or heaving component of the foundation materials.

Shale Chemistry and Clay Mineralogy Analyses

Shale Analysis

The mineral composition of the Shale foundation material was analyzed by X-ray diffraction and fluorescence for the Estill County Middle School and the analyses indicated that the Shale is composed of clay (60 %), quartz silt (30 %), pyrite nodules (5 %) and some calcite (<5 %). The most important aspect of the analysis is that the Shale is composed of 60 % clay minerals and 5 % pyrite. Raw sulphur values in the Shale ranged from 2.95 to 5.47 weight percent but sulphur can be bound as either a sulphate or sulphide. The high pyrite and sulphur content contribute to the formation of sulphates such as jarosite and copiapite. Numerous secondary sulphates and a minor amount of phosphate were also noted in the core descriptions and analysis.

Chemical analyses for major oxides in the Shale were determined by XRF. Elemental concentrations were calculated which indicate cores B-1 and B-2 (Fig. 34) had variable levels of calcium and iron. This implies that major oxidation has started at these locations. Chemical and mineralogical analyses of core B-3 indicated lower values of calcium in the Shale, suggesting that the chemical and mineralogical transition to sulphates had begun. Iron (Fe) values were constant in B-3. Chemical and mineralogical analyses of core B-4, located in the southeast portion of the site, indicated low values of calcium and iron in the Shale. It is, however, high in iron and sulphur in the sulphate minerals (jarosite and copiapite), which suggests accelerated weathering and decomposition of the Shale, oxidation

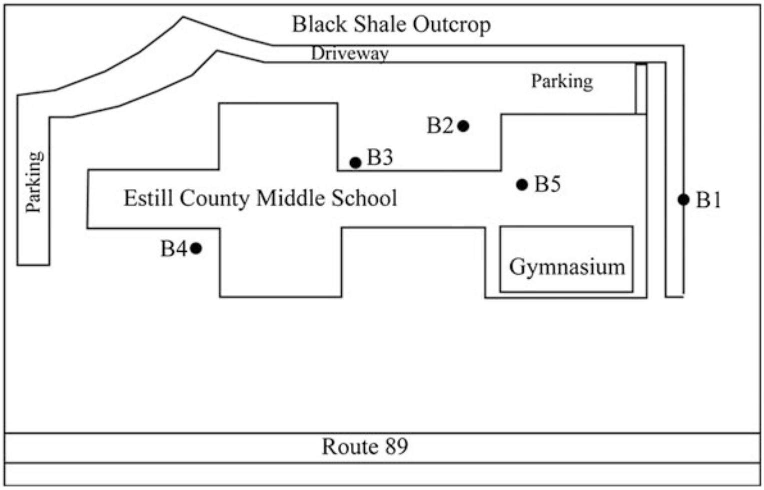


Fig. 34 Plan view of the Estill County Middle School showing core locations

of pyrite, and formation of sulphate. Jarosite and other sulphates are forming at the expense of pyrite (Figs. 35 and 36).

All of the bedding planes in this core had visible oxidizing efflorescent sulphate minerals. All of the bedding planes and cleats in the subcrop of the School also contained efflorescent sulphate minerals (Figs. 17, 18, 35, 36). Analysis of core B-5 showed that the uppermost section of the core contained extremely high values of calcium, which is also suggestive of the formation of calcium sulphate minerals such as jarosite or copiapite.

Fig. 35 Secondary sulphates jarosite, copiapite and melanterite derived from drain tiles at rear of school

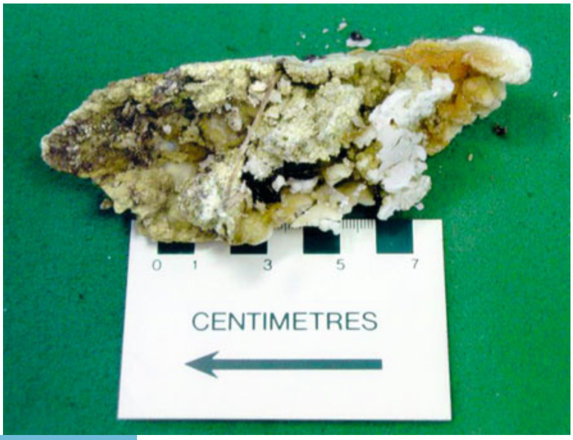


Fig. 36 Chattanooga Shale showing evidence of heave due to growth of copiapite

Clay Analysis

The clay mineralogy of the Huron Member of the Chattanooga Shale is primarily illitic clay (65 %), mixed layer clay of illite/montmorillonite/muscovite (20 %), minor chlorite and kaolinite (<10 %) and undetermined (5 %). Illite is a non-expanding clay mineral, but it does weather rapidly into soft, pliable clay. The mixed layer clay contains approximately 20 % expanding clays, based on XRD and XRF, which swell when in contact with water. All five cores analyzed in this report had a similar clay mineral composition at the time of analysis, September 7, 2000 and July 6, 2006.

The samples were stored in a controlled, room temperature, standard humidity environment. X-ray diffractograms (Fig. 37) for each of the 5 core samples looked similar showing the zone of both illite and smectite clays. Cores B-1, B-3, and B-4 also showed evidence of illite, chlorite, kaolinite, montmorillonite, and smectite (Fig. 34).

Pyrite Analysis

Mossbauer Spectroscopy pyrite analysis indicates all pyrite in the core samples tested had similar chemistry. Pyrite had greater than 85 % (weight percent) iron except as noted, which is high for normal pyrite, but represents high sulphur dissociation in an high oxidation environment. Other iron sulphides such as marcasite or pyrrhotite were not detected in large quantities in the analyses (Table 1). Within the pyrite, the weight percent pyritic sulphur was also analyzed on several core samples and suggested that pyritic sulphur content changed in the cores. Most pyritic sulphur averages about 5.26 weight percent in the core samples analyzed although in Core B-4 it is equal to 3.69 %, which is low compared to the other samples. Analysis for percent iron in the mineral jarosite in core B-4

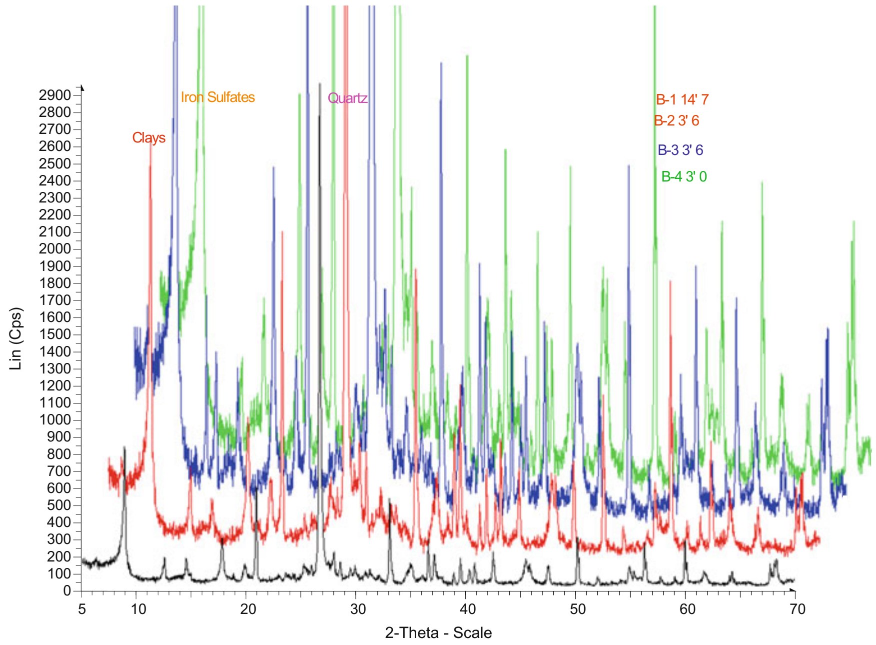


Fig. 37 Diffractograms of cores in the study area showing regions of clay minerals and of sulphate activity between 10 and 20 2-theta. Data projected in a 3-D view

Table 1 Mossbauer spectroscopy compositional variance in samples B-11 and B-42 showing a decrease in total pyritic iron (from 89% to 85.5%) and a corresponding increase in the iron content of secondary sulfate mineralogy (Jarosite). Pyritic sulfur also shows a decrease in percent sulfur (5.29-3.69) because of pyrite oxidation

Sample	Mineral	Total iron %	Pyritic sulphur Wt %
B-11	Pyrite	89	5.11
	Fe^{2+}/clay	11	
B-12	Pyrite	90	5.29
	Fe^{2+}/clay	10	
B-13	Pyrite	87	4.9
	Fe^{2+}/clay	11	
	Jarosite	2	
B-14	Pyrite	86.5	5.74
	Fe^{2+}/clay	11	
	Jarosite	2.5	
B-41	Pyrite	86.5	3.7
	Fe^{2+}/clay	8	
	Jarosite	5.5	
B-42	Pyrite	85.5	3.69
	Fe^{2+}/clay	9	
	Jarosite	5.5	

indicated about 5.5 % which was high compared to the other samples (∼2 %), suggesting pyrite is oxidizing more rapidly in core B-4. This is confirmed in the diffractogram in Fig. 37, while jarosite forms at the expense of pyrite. This process is a critical chemical reaction and the oxidation of pyrite and subsequent growth of secondary sulphates in the Shale causes crystal growth and resultant volume increase (heaving/expansion) in foundation bedrocks.

Additional information on pyrite and trace elements in pyrite in east central Kentucky is available in Tuttle et al. (2003). They discuss availability and mobility of many trace elements in addition to iron, calcium and sulphur.

Sulphate Analysis

The following sulphates are oxidation products of pyrite that were detected visually and in the XRD mineralogical analysis: jarosite, melanterite, copiapite, gypsum, alunite, kalinite, pickeringite and epsonite (Figs. 35, 36). Other minerals may exist, Tuttle et al. (2003) determined that melanterite, haliotrichite, and szomolnokite occurred in the Middle Huron at a sample site located 7 miles north and east, near Clay City, Kentucky in Powell County. They completed additional chemical analysis of the sulphates, iron and other metal variability among the Shale samples in this region. The abundance of trace elements in the Shale and pyrite produces many elements for the formation of various secondary sulphates. These sulphates are humidity or water sensitive and can change chemistry within an hour or so. As a consequence, existing sulphates may change and/or new crystals grow following rainfall or a change in humidity conditions.

Cores B-1, B-3, and B-4 showed a marked difference in the sulphate content at the 15 degrees, 2-theta zone of the XRD of sulphates. The comparative diffractograms (Fig. 37) of the intervals within cores B-1, B-2, B-3, and B-4 show a variable activity in the sulphate region within each core, implying sulphate formation in the various sampled intervals.

ICP analysis of the sulphate precipitate sample indicated 200 ppm each of Fe, Mg, Ca, and sulphate, all common elements in secondary sulphates. Cleat joints in the outcrop, sub-crop and bedding planes in the core samples also show visual evidence of rapid oxidation to sulphates, suggesting that the pyrite occurs along these surfaces and is easily weathered (Figs. 5, 6, 17, 18).

Oxidation of pyrite results in the formation of new minerals, the crystal structure of the sulphates is larger than that of the initial constituents; the increase in volume can be substantial, resulting in heaving and other movement of structures. The expansion exerts pressure and is the major cause of floor heaving in all the structures described here.

These sulphates will grow where the Shale containing pyrite has been exposed to weathering. The drains in the retaining wall of the Middle School show these sulphate mineral precipitate (Figs. 20, 35). Other drains that are buried around the school are likely to be partially filled or filled with these minerals, and are not functioning as designed. There is evidence that excavated Shale was used in the south east portion of the building as foundation fill. Material used as fill will have become aerated and hence can weather extremely rapidly, resulting in significant heaving or subsidence.

Hydrogeochemistry

Sulphides are easily oxidized when exposed to the atmosphere as occurred in the study area. High sulphate values in the White Oak Creek and a low pH suggest chemical reactions with the pyrite have taken place. As the surface water reaches the exposed pyrite, sulphuric acid is formed and hence the pH of the water is reduced. Progressively, as sulphates are developed, the pH drops such that in the tributary of White Oak Creek it was approximately 1.5, i.e. very acidic. Oxidation is fastest when the pH is low, partly because of the action of acidophilic bacteria. Analysis of a water sample in a creek behind the High School confirms high levels of sulphate (800 ppm) in the water system. Tuttle et al. (2003) describe other streams in their study area near Clay City as having a pH of 7–8, considered a normal pH. It is likely that the low pH in White Oak Creek is the result of the release of sulphuric acid during the oxidation of the Shales exposed during the extensive excavation for the school, playgrounds and ball fields.

Summary

All of the structures examined in this investigation were founded in the pyrite zones of the Chattanooga (Ohio) Black Shale and because of pyrite oxidation and sulphate heaving, they had extreme foundation problems. Pipelines could also be subjected to the same heaving or acidic corrosion and should be monitored. The swelling in the pavement in SR 499 is related to expanding clays in the Crab Orchard and it appears that any effects from the Black Shale are minor at this location.

A contributing factor is that many of the structures were built on Chattanooga Shale fill, which weathers rapidly such that the pyrite oxidizes and sulphates are formed. As a consequence of the increase in volume when the sulphates develop, the structures suffered floor heaving, wall and flooring cracking, and structural instability. In addition to the expansion, the sulphates can penetrate into the concrete causing crystal growth that can crack the concrete and lift foundations. The sulphates will naturally grow in the area of least pressure and hence although they will lift the floors slabs, they are less likely to affect the rising walls.

The stratigraphic column in Fig. 4 shows the elevation, location and approximate stratigraphic position of the buildings, roads and pipelines inspected during this investigation. The column shows that the entire Chattanooga Shale unit can and does contain pyrite and can be prone to heaving. Caution should therefore be used when building in the east central Kentucky area.

Geochemical trend examples (Wys 1981) demonstrated that high pyrite in the Shale can occur in other areas of the State and suggest that Estill County may have some of these anomalous concentrations of pyrite.

The weathering of excavated pyrite-bearing shale makes it unsuitable for fill material or as a foundation for load-bearing structures or highway construction. Water draining towards the construction sites results in wetting and drying, which may contribute to pyrite oxidation and the formation of sulphuric acid and sulphates.

Sulphates are prone to erosion at outcrop but under confined conditions, oxidation would result in continued crystal growth, a large increase in volume and the subsequent heaving of floors.

Another minor contributing factor to the structural problems is the presence of expanding lattice clay minerals in both the Cleveland and Huron Members, which could enhance any floor heaving if exposed to water.

The release of acid from the pyrite oxidation process may affect limestone aggregate causing dissolution and the creation of large voids and subsidence in the outcrop and beneath the foundation.

Causes of Foundation Failure

1. Oxidation of pyrite and growth of secondary sulphates in the Shale is the primary cause of foundation problems in part of Estill and the surrounding counties. Pyrite oxidation causes crystal growth and the resultant volume change creates expansion of the foundation material beneath the concrete slabs resulting in a rise in the slabs and lateral pressure on the retaining walls. The oxidation of pyrite and formation of sulphates also releases a mild sulphuric acid into the creeks and tributaries. This acidic creek water is a contributing factor to the foundation problems.
2. On weathering the Shale degrades into various clay and sulphate minerals and has a lack of shear strength when subjected to load. The behavior of the weathered clay minerals in the Shale makes the Shale very unstable. The Shale will move through compression and expansion, which may be the major problem with structural stability in the school. There is the possibility of a lens of smectite or expanding clays in the Shale. When this clay comes into contact with water it will also expand and heave the foundation. When the Shale dries out, the site will settle. This could be a perpetual problem, but based on analysis of the clay minerals in the Shale, the smectite problem is minor compared to the sulphates.
3. Parts of the school building, factory and water plant discussed appear to be constructed on Shale fill, which will weather more rapidly than Shale bedrock.

Pipelines sited in the black Shale normally use a limestone aggregate base which would neutralize the pH and mitigate the effects of ongoing pyrite oxidation. The floors of the factory, the water plant and parts of the school structure, however, have a considerable potential for heaving. The factory, school, hospital, and water plant locations are down dip from surface drainage run-off which involves the ground experiencing wetting and drying conditions which enhance the oxidation process.

Recommendations

Pre-Construction Prevention

1. Avoid construction and excavation in the pyrite zone of the Lower Chattanooga Shale. Avoid using Chattanooga Shale aggregate as construction fill. Conduct minimal excavation into the Shale to reduce pyrite oxidation.
2. Keep water away from the school foundations, preferably through the barrier method. However, ditches or drains can still accumulate sulphates from weathered Shale material such that they become inefficient. Drainage did not solve the Middle School problem.
3. If possible, build structures in areas where both surface and groundwater do not drain or flow toward the building foundations. Construction on hilltops away from water sources is preferred.
4. Encapsulate the area by means of non-permeable geo-textiles, geo-membranes or other chemically inert products such as bentonites and lime products to neutralize acidic fluids and balance the pH, then cover with an appropriate neutral soil horizon. This process is similar to the creation of landfills.

Remediation Solutions

1. Remove foundation material and fill, and replace with an impermeable, water/moisture barrier. Create new sub-floor using bearing walls or piers, and refill with non-Shale (inert) aggregate leaving space for residual sulphate growth.
2. Take micro-piles and/or special grout to the Boyle Dolomite or deeper hard rock formation, underlying the Shale (probably <60 ft (20 m) deep in this area). This would stabilize the foundation by transferring loads to formations with a higher bearing capacity.
3. Another remedy would be the treatment of the foundational materials under distress, eg the injection of a suite of balanced stabilizing grout slurry designed to remove sulphates and "tighten" the formation to residual permeability and shear strength values. Maher (2012) discusses the work being undertaken to

reduce the chemical reactions in fill containing pyrite by the use of special chemicals/grouts.

4. Placing lime would reduce the acidity of the ground and hence, if acidophilic bacteria are active, the rate of oxidation. However, the application of lime where sulphuric acid is present can result in the formation of calcium sulphates and hence can exacerbate the potential heave problem (Bryant et al. 2003).

A comprehensive geochemical and geotechnical investigation of the Shale should be conducted at planning stage as well as prior to any remedial works.

Future Work

Although the foundation problems analyzed were locally reported in parts of east central Kentucky, the Shale outcrops over a wide area of Kentucky where pyrite zones occur and could induce foundation failures. Where the Chattanooga (Ohio) Black Shale outcrops, construction should be avoided if possible. Where construction is to take place, appropriate investigates are strongly advocated. In view of the expense of remediation, every effort should be made to establish the problems and how they can be mitigated during the construction process.

Where pipelines are to be placed through the pyrite-rich Shales, consideration should be given to both the potential for combustion and for the corrosion of concrete or steel pipes.

Additional State-wide detailed mineral and litho-stratigraphic investigations of the Chattanooga Shale would assist in understanding the larger geographic extent and potential for this type of problem. This would assist in planning where construction takes place and sound engineering of the development in order to reduce the need for costly repairs and maintenance.

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Iron Sulphides and Surface Heating: Further Engineering Considerations for the Dublin Area

A. Brian Hawkins and Thomas W. St John

Introduction

In comparison with other documented cases of sulphate-related heave, notably in the UK and Canada, the onset of heave following construction has been particularly quick in Ireland. Hawkins (2012) presented a model to explain this rapid onset of heave, considering the development of ferrous sulphates around oxidising iron sulphides as well as the probable role of pyrrhotite. The Pyrite Panel Report (2012) also noted this rapidity, suggesting that Ireland's mild climate and the stockpiling of pyritic aggregates were influential factors.

This chapter discusses recent research which indicates that there are a number of characteristics of the iron sulphides within the Carboniferous rocks of the Dublin area which have not been fully appreciated. The importance of temperature during deep burial in the formation and the occurrence of pyrrhotite (a less stable form of iron sulphide) are reviewed. Case histories from a number of countries are presented to illustrate the involvement of pyrrhotite in sulphate-related heave and attack on concrete.

The chapter highlights the significance of the near-surface temperatures in the Dublin region where heat emanates from the Leinster Granites to the south and thermal springs issue from the Carboniferous strata. Localised rising groundwaters at temperatures of up to 25 °C are an important consideration when assessing the rate of oxidation of iron sulphides and hence sulphate-related heave. In addition, raised temperatures are also likely to be present in the overlying Dublin Boulder Clay, particularly where there is only a limited cover over rocks containing faults/

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master joints. New evidence for a variety of textures/structures in pyrite/pyrrhotite from the Dublin area is presented and the implications of this for the rate of oxidation are considered.

The Nature and Identification of Pyrrhotite

Cases of sulphate heave and sulphate attack due to the oxidation of pyrite in fill or natural ground are well documented and discussed further elsewhere in this volume. However, the role of pyrrhotite, a highly reactive iron mono-sulphide, is under-appreciated and remains poorly understood, although there are published accounts of the involvement of pyrrhotite oxidation in damage to buildings and civil structures from as long ago as 1919 (Fiskaa et al. 1971).

Pyrrhotite has been described as "one of the most hazardous" inclusions in concrete aggregate (Chinchón et al. 1990). Some engineering Standards have recognised these problems and recommended special precautions in the form of very low total sulphur acceptance criteria when pyrrhotite is identified. However, bearing in mind the speed of reactions with pyrrhotite, current standardised methods of assessment and tolerance criteria may be inappropriate.

Mineralogical Background and Identification

Pyrrhotite, an iron mono-sulphide with the general formula $Fe_{(1-x)}S$ (x between 0 and 0.125), is the second most abundant iron sulphide. When observed in hand specimen it appears bronze to dark brown in colour, often with a metallic lustre (Fig. 1).

Fig. 1 Hand specimen fragment with coarse pyrrhotite grains from Canada

High temperature phases typically crystallise in the hexagonal system whilst low temperature phases are typically monoclinic. Habits include tabular forms as well as anhedral “chunks”. Pyrrhotite will decompose in HCl and has a hardness of 3.5–4. In thin section, it is weakly pleochroic and strongly anisotropic (Vaughan 2011). Some polytypes exhibit weak magnetism.

Chemical Testing

Routine testing for sulphur species in aggregate/fill material is undertaken according to EN 1744-1:2009 (BSI 2010). The tests described include those for total sulphur, acid soluble sulphides, acid soluble sulphates and water soluble sulphates. As the total sulphur test involves the addition of HCl to the sample, pyrrhotite will be dissolved, although its composition will be accounted for in the final percentage sulphur value.

The EN 1744-1:2009 test for acid soluble sulphides involves decomposition of the sample by HCl and conversion of the dissolved sulphides to hydrogen sulphide. The gaseous hydrogen sulphide reacts with an ammonium-bearing zinc sulphate solution, causing the precipitation of the zinc sulphide. The sulphide content in zinc sulphide is then calculated and expressed in percent sulphur.

The use of acidified chromium results in the digestion of pyrite and marcasite in the test described above (Czerewko et al. 2003; BSI 2010). As pyrite is not soluble in HCl, whereas pyrrhotite is, by omitting the chromium the pyrrhotite would be dissolved in the HCl, leaving the pyrite. It is therefore possible this method could be modified to determine the mono-sulphide content (i.e., pyrrhotite). Potential problems could arise from the dissolution of pyrite due to other reagents, the dissolution of other acid soluble sulphides (such as greigite and mackinawite) or only partial dissolution of the mono-sulphides (Czerewko et al. 2003; Reid et al. 2005).

A simpler procedure for identifying mono-sulphides was proposed by Tuttle et al. (1986) whereby the H_2S gas produced during dissolution of the sample by HCl is analysed directly (rather than further reacted as in the BSI 2010 method). The gas is analysed quantitatively by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

No standardised test exists to determine the pyrrhotite content of a sample. However, further research is being undertaken into a method which can simply and reliably quantify the amount of pyrrhotite within a test sample. Although attempts have been made to estimate the “equivalent pyrite” content of a sample based on various test results, for example in the Canadian assessment procedure CTQ-M200 (Comité Technique 2001), to date no similar calculation exists to estimate the “equivalent pyrrhotite”. However, as discussed in Hawkins (2013 this book), there are problems with the reliability of such estimations, which involve a number of assumptions.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) is a technique which allows identification based on morphology (Fig. 2) and elemental analysis. Careful sample preparation and appropriate coating is essential for quantitative analysis. An electron microprobe can also be used for quantitative identification.

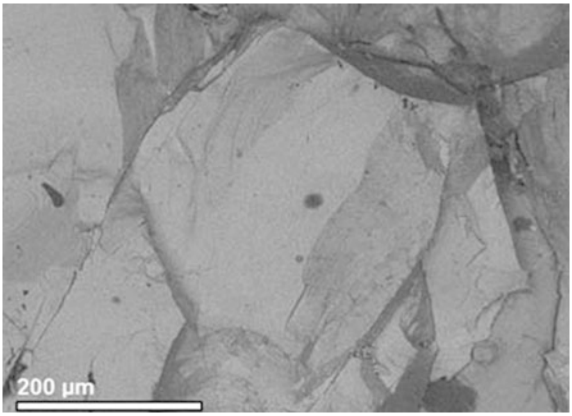


Fig. 2 SEM image of hexagonal pyrrhotite from Sudbury, Canada

However, as pyrite and pyrrhotite comprise only iron and sulphur, distinguishing one grain from another can be difficult. For confirmation, the Fe/S ratio (by weight) is required. For idealised pyrite, the ratio is 0.87. Pyrrhotite exhibits a range of compositions based on the $Fe_{1-x}S$ formula. Assuming x values between 0 and 0.125, the calculated end-member compositions are given in Table 1. It can be seen that weight percent Fe/S ratios for pyrrhotite range from 1.52 to 1.74, which can be used as guidance for identification using EDS results.

Table 1 Pyrrhotite compositions and Fe/S ratios for end-member values of x

Value of x	Ideal compound	Atomic Fe:S	Wt % Fe/S ratio
0	FeS	1:1	1.74
0.125	Fe_7S_8	0.875:1	1.52

X-ray Diffraction

X-ray diffraction (XRD) is another long-established technique used to identify pyrrhotite, as reported by Tagnit-Hamou et al. (2005) for aggregate analysis. However, Hammarstrom and Smith (2002) note the failure of XRD to identify pyrrhotite despite its observation in thin section. Indeed, these authors have recorded that alteration to pyrite and goethite may give rise to major XRD peaks which mask the presence of pyrrhotite. Alternatively the XRD preparation processes may destroy pyrrhotite such that its presence is undetectable. Ideally, samples should be prepared with minimal disturbance and tested immediately after recovery to reduce the extent of pyrrhotite oxidation.

Occurrence and Formation of Pyrrhotite

Pyrrhotite is found in a wide range of igneous rocks including gabbro (Duchesne and Fournier 2011), diorite (Kelly and Zumberge 1961), basalt (Xie et al. 2010) and granite (Gottesmann and Wirth 1997). It is ubiquitous in low-grade metamorphosed shales (Aubourg et al. 2004). Occurrences in slates and meta-shales include the Welsh Cambrian slates (Fuller 1964), Scottish Dalradian Ballachulish slates (Hall 1982) and Norwegian Cambrian Alum Shale (Abreham 2007). Up to 15 wt % pyrrhotite is present in the Cambro-Ordovician Halifax Formation shales of Nova Scotia (Fox et al. 1997).

Although pyrrhotite has been less reported in sedimentary rocks in the UK it has been found in the Pleistocene swamp deposits of the Lea Valley, England (Davies 1912), the Carboniferous Coal Measures of Wales (Simpson and Stuart 1934) and the Brownstones of the Devonian Old Red Sandstone sequence in the Merthyr Tydfil area of South Wales (Barclay et al. 1988). Pyrrhotite is also found within hydrothermal vein deposits in sedimentary/meta-sedimentary sequences, such as in the Exmoor region in south west England (see later).

Formation

Pyrrhotite formation in igneous rocks occurs via crystallisation from magma which is rich in both iron and sulphur; it is not considered here.

Although uncommon as an authigenic phase in sediments, pyrrhotite can form in abundance at the expense of pyrite during low grade metamorphism (including burial) of pyritic strata. As discussed below, pyrrhotite formed in this manner has caused numerous engineering problems. The main formation mechanisms for pyrrhotite in sedimentary and meta-sedimentary rocks include:

1. Detrital
2. Authigenic
3. Metamorphic desulfidation of pyrite
4. Precipitation from sulphidic ore fluids

Detrital pyrrhotite has been reported by Shi et al. (2001) who observed large and irregular shaped grains in a loess section at Znojmo (Czech Republic), in association with galena. Horng and Roberts (2006) argued that pyrrhotite in a section of Pleistocene sediments in Tsailiao-Chi (Taiwan) originated from metamorphic rocks. These reports are quite surprising considering the chemically unstable nature of pyrrhotite, which would make it unlikely to survive erosion and transportation.

In sedimentary rocks, iron sulphides are generally believed to form authigenically in anoxic subaqueous conditions. Preservation of pyrrhotite may be aided by the consumption of H_2S in low permeability sediments (Roberts and Turner 1993).

Bastiansen et al. (1957) observed the formation of pyrrhotite when pyritic shale was heated to c. 300 °C. The conversion was later described as a thermal decomposition effect and found to occur at temperatures as low as 200 °C (Lambert 1973; Butcher and Rowson 1995). This process represents a loss of sulphur and was termed “desulfidation” by Ferry (1981). It is thought to be aided by the presence of carbon-bearing phases (Lambert 1973). Ferry (1981) proposed reaction (1):

$$2FeS_2 + 2H_2O + C_{(graphite)} \rightarrow 2FeS + 2H_2S + CO_2 \quad (1)$$

The transformation has been confirmed by Pitcairn et al. (2010), who studied the conversion of pyrite in New Zealand schists of various grades and demonstrated that as temperature increases, pyrrhotite abundance increases at the expense of pyrite.

Pyrrhotite may also be precipitated from sulphidic fluids during ore concentration. In massive sulphide deposits, chalcopyrite and pentlandite are also typically present, while in veins/bedding plane coatings it can be found with marcasite, chalcopyrite, sphalerite and other metal-sulphides. Major deposits of this type exist in Sudbury, Canada, where pentlandite is mined for nickel and pyrrhotite is discarded to waste tailings (Becker, Bradshaw and de Villiers 2011). At the Phoenix Mine in Botswana, pyrrhotite is mined for nickel hosted within pentlandite intergrowths (Becker et al. 2011).

Elsewhere, pyrrhotite from massive sulphide deposits has been mined for use in the production of sulphuric acid, such as at the now abandoned Kettara Mine in Morocco. More than 5 million tons of Carboniferous-hosted pyrrhotite ore was mined here between 1964 and 1981 (Hakkou et al. 2008). The mining left vast areas of tailings which have contributed to a major acid drainage problem. The mine was ultimately closed due to acid corrosion of the plant equipment.

Oxidation and Reactivity

Pyrrhotite is unstable under atmospheric conditions, making it prone to oxidation. Cai et al. (2005) suggest that oxidation occurs as early as the blasting stage during aggregate sourcing. Like pyrite, pyrrhotite can oxidise when exposed to oxygen and moisture (2):

$$Fe_{1-x}S + \left(2 - \frac{x}{2}\right)O_2 + xH_2O \rightarrow (1 - x)Fe^{2+} + SO_4^{2-} + 2xH^+ \quad (2)$$

The oxidation of pyrrhotite can produce ferrous iron, sulphate ions and hydrogen ions, which may combine to form ferrous sulphates and sulphuric acid (Seal and Hammarstrom 2003). From a study of mine tailings, Georgopoulou et al. (1995) report that up to 1.1 tonnes of sulphuric acid can be produced by a single tonne of pyrrhotite. Equation (2) shows that where the value of x in the pyrrhotite composition is at a maximum (i.e., 0.125 or the monoclinic form), there is a greater amount of H^+ ions released, and hence the acidity generated is at a maximum.

The sulphuric acid generated can react with any remaining pyrrhotite to produce $FeSO_4$ (Fiskaa et al. 1971). If hydrated ferrous sulphate is formed instead, Casanova et al. (1996) have shown that a volume increase of over 180 cm^3 per mol of pyrrhotite ($x = 0.125$) is possible. Recent work has shown that the formation of ferric hydroxide from pyrrhotite may involve an expansion of up to 34 %, compared to only 13 % for pyrite (Oliveira et al. 2013). Where calcite exists in the host rock, it may react with the released sulphuric acid to produce gypsum, with additional expansion (Bérard et al. 1975).

In addition to oxygen-bearing products, Hammarstrom and Smith (2002) report that pyrrhotite oxidation can yield pyrite. It is possible that pyrite may replace pyrrhotite, leaving a pseudomorph which has the hexagonal habit (e.g., Fig. 2) of pyrrhotite.

The $Fe_{(1-x)}S$ structure is a “defect structure” with less iron than the ideal FeS stoichiometry. Iron vacancies are thought to give rise to instability and influence oxidation (Nicholson and Scharer 1993). In terms of crystallography, the majority of workers suggest that monoclinic pyrrhotite is more reactive than hexagonal forms (e.g., Becker 2009). This implies that the form likely to be encountered in low grade metamorphosed rocks may be more prone to oxidation.

There are many published accounts of factors believed to influence pyrrhotite oxidation. As with pyrite, oxygen, moisture, Fe^{3+}, temperature, presence of bacteria and surface area all aid oxidation (Janzen et al. 2000; Belzile et al. 2004; Oliveira et al. 2011). Many workers suggest that alkaline conditions favour faster oxidation (e.g., Truche et al. 2010) although the build-up of oxidation products may limit reactivity while *Thiobacilli* bacteria aid oxidation at a low pH (Bhatti et al. 1993).

Pyrrhotite can oxidise up to 100 times faster than pyrite under atmospheric conditions (Nicholson and Scharer 1993). It will also oxidise faster than pyrite in the presence of *Thiobacilli* bacteria (Bhatti et al. 1993). In addition, recent laboratory work by Chinchón-Paya et al. (2012) has shown that pyrrhotite can generate more sulphates than pyrite. The presence and oxidation of pyrrhotite in rock may also catalyse the oxidation of pyrite (Bastiansen et al. 1957; Moum and Rosenqvist 1959).

Case Studies

A review of the literature highlights a number of accounts of structural distress which involved pyrrhotite.

Oslo and the Alum Shale

Numerous problems have occurred in Oslo where concrete has come into contact with the Norwegian Alum Shale, a low grade Cambro-Ordovician carbonaceous black shale containing pyrrhotite (Hagelia 2011). Problems were noticed as early as 1919 and became so severe that the "Alum Shale Committee" was established in 1943 (Fiskaa et al. 1971). The most renowned example is the sulphate attack on an underground concrete shelter founded in Alum Shale (Moum and Rosenqvist 1959). It is reported that within only nine months, acidic water associated with weathered pyrite and pyrrhotite had degraded the concrete to "mush". Similar problems were reported where aggregate containing pyrrhotite was used. Damage was noted where pyrrhotite mineral and pyrrhotite sulphur contents in the aggregate were as low as 0.01 % and 0.071 wt % respectively (Bastiansen et al. 1957; Hagelia 2011). The Alum Shale Committee concluded that aggregates with pyrrhotite sulphur contents below 0.001 % were safe (reported in Hagelia and Sibbick 2009).

Spanish Experiences

As early as 1962, the potential for problems arising from pyrrhotite in aggregate were published in the Spanish literature (Vidal 1962). Between 1970 and 1972, severe and rapid degradation of concrete used in buildings in the Maresme region of Barcelona was attributed to the oxidation of sulphides (Vazquez and Toral 1984). Low grade dark Silurian shale had been included in the aggregate, which was confirmed by SEM to contain pyrrhotite. Samples from the source quarry were described as having undergone contact metamorphism, producing graphite (Chinchón et al. 1995). Pyrrhotite was identified in layers and disseminations within the shale while gypsum was observed on discontinuities (Chinchón et al. 1995). During the 2000s the concrete in several dams in the Spanish Pyrenees was observed to have cracked and deteriorated. In all cases, the aggregate used in the concrete was sourced from local quarries. Araujo et al. (2008) used optical microscopy, SEM, XRD and XRF to investigate the materials. Needle-like ettringite was found within the cracked concrete and pyrrhotite, pyrite, gypsum and jarosite were all observed within the quarry material. Araujo et al. (2008) concluded that the oxidation of pyrrhotite had produced sulphates which resulted in expansion of the concrete.

Swedish Experiences

During the 1960s many buildings in the Östersund area suffered damage and deterioration (Martna 1970; Jangdal 1971). The cause was not appreciated at first, but was later attributed to the swelling of pyrrhotite-bearing shale.

A number of Swedish dams also experienced cracking during the 1960s (Fristrom and Sallstrom 1967). In one case, up to 10 % "magnetic pyrite" (pyrrhotite) was found within the concrete aggregate. The oxidation of both pyrrhotite and pyrite led to major swelling and cracking of the dam concrete, as well as the formation of calcium alumino-sulphates. Ultimately the damaged zones of the dam required replacement.

Martna (1970) reported sulphate attack on the concrete of a hydro-electric station in Stornorrfors. Part of the power station extended some 100 m below ground, within pyrrhotitic gneiss. Sulphuric acid produced during the oxidation of the pyrrhotite severely degraded the concrete lining.

Canadian Experiences

Many pyrite and pyrrhotite problems have been reported from Canada in the last 40 years. The earliest distress which involved pyrrhotite oxidation was recognised by Bérard et al. (1975), who discussed the deterioration of concrete house foundations within only two years after construction. In the areas of distress, it was found that black Utica Shales had been used as concrete aggregate. Analysis by XRD, traditional microscopy, electron microprobe and chemical methods identified around 4.5 % pyrrhotite within the aggregate. Pyrrhotite was observed both as very fine grains and as clusters and veinlets (Bérard et al. 1975). Oxidation of pyrrhotite in the presence of carbon and the formation of gypsum were considered to be the causes of the distress.

In February 2012, Robert Aubin (QC) referred to a new "pyrrhotite crisis" in the Trois Rivières area of Québec, stating that over 1,000 homes had "disintegrating foundations" due to the use of aggregate containing pyrrhotite. Damage was manifested as concrete degradation and cracking as well as floor slab heaving (PCC 2012). Repair costs are estimated at around $200,000 per home. However, some 10 years ago around 40 homes in this area also suffered pyrrhotite problems in the form of degradation of basement concrete (Coalition Proprio-Béton 2012). In these cases, locally sourced pyrrhotite-bearing gabbro had been used as concrete aggregate.

Investigations into damaged foundations in Trois Rivières were also published by Tagnit-Hamou et al. (2005) and later by Duchesne and Fournier (2011). Visible damage was observed as early as two years post-construction. Petrographic analysis indicated that the aggregate was again gabbro with up to 7 % pyrrhotite and pyrite—the pyrrhotite being more oxidised than the pyrite. Oxidation of the iron sulphides and the development of gypsum and ettringite were identified as the causes of the deterioration. Remediation involved complete foundation replacement.

The “Mundic” Problem

The term “Mundic” derives from a Cornish word for pyrite and the problem refers to a legacy of concrete degradation in Devon and Cornwall due to the presence of sulphides within the concrete aggregate (Bromley and Pettifer 1997). Whilst much of the deleterious aggregate was sedimentary or sulphidic mine waste, igneous rock was also quarried. Pyrrhotite was identified in quarried slate from Delabole and gabbro from Porthoustock, S W England.

The meta-dolerite quarry at Penlee (Newlyn, Cornwall) was used to source aggregate for concrete blocks and foundations. Detailed petrography of the dolerite identified pyrrhotite among other sulphides (Bromley and Pettifer 1997). Deteriorated concrete blocks were often found to contain the oxidation products of these sulphides, including gypsum within voids. The Penlee Quarry eventually closed due to the excessive sulphide levels.

Switzerland

Schmidt et al. (2011) reported on a Swiss dam with cracked and deteriorated cement due to the use of concrete containing schist aggregate. Analysis with SEM and EDS confirmed the presence of pyrrhotite with an oxidised exterior. The iron sulphide content in the aggregate was reported to be 0.28 %, of which 80 % was pyrrhotite. It was suggested that only 30 % of the iron sulphides in the aggregate had reacted within 40 years. Pyrrhotite was found to be more extensively oxidised than pyrite.

Central Himalayas

In 1978, red-brown water was observed to have seeped from cracks in the Pandoh Dam in the Central Himalayas (Dubey et al. 2004). Petrographic analysis of the local bedrock revealed pyrrhotite both as disseminated grains and infilling fractures, as well as iron hydroxides in the low to medium grade schist. Gypsum and ettringite were identified by XRD in a precipitate of the red-brown water. The workers concluded that the damage resulted from sulphide oxidation and the formation of gypsum and ettringite.

Scotland

Concrete degradation in a Scottish bridge in Strathclyde was reported by Macleod et al. (1990). Pitting and discolouration of the concrete was observed, in addition to a coating of mineral precipitates. Petrographic assessment of the concrete by stereo microscopy identified both pyrrhotite and pyrite within the dolerite aggregate. XRD analysis also revealed ettringite needles and gypsum within the concrete cavities. It was concluded that expansion had occurred due to the formation of sulphates and iron hydroxides from the oxidation of sulphides in the concrete aggregate.

South Africa

Damage to houses in South Africa in the form of external wall cracking and heaving of the ground-bearing floor slabs was reported by Oberholster et al. (1983). Petrographic examination and XRD analysis of defective concrete blocks confirmed the aggregate used contained both pyrrhotite-bearing black shale and gold mine spoil. Gypsum developed as a consequence of the oxidation of the iron sulphides and ultimately thaumasite formed due to the reaction of gypsum with cement components. The aggregate was found to have a total sulphur content of 1.44 % S corresponding to a total potential sulphate content of 4.3 % SO_4 (Hobbs 2003).

Similar problems in Windhoek, Namibia were later noted by Davies and Oberholster (1988). Iron staining and pop-outs were observed on ash–cement brick walls in houses less than a year old. Petrographic analysis revealed the presence of black sulphurous nodules within the bricks, which had been sourced from the burnt-coal waste of a nearby power station. The use of SEM and XRD confirmed that the nodules were rich in iron sulphides, including pyrrhotite.

Samples of the damaged brick were later stored above water inside sealed containers. The storage room environment was maintained at around 38 °C with a relative humidity of approximately 100 %. Over the course of 93 days the samples were seen to expand, in one case fracturing the brick. XRD analysis of the broken sample identified pyrrhotite, which when tested again two weeks later had oxidised to melanterite, a hydrated ferrous sulphate. Davies and Oberholster (1988) suggest that the main damage had resulted from iron sulphide oxidation, triggered by a recent wet season which allowed water to enter the bricks and oxidise the pyrrhotite.

Aggregate/Concrete Standards and Pyrrhotite

In the light of the problems caused by the presence of pyrrhotite in aggregate and fill, various Standards have set specific criteria for total sulphur (% S) when pyrrhotite is identified (Table 2). The tolerance is often considerably less than when pyrrhotite is believed to be absent, reflecting the highly reactive nature of this mineral. As seen from Table 2, the allowable total sulphur within aggregate where pyrrhotite is identified is between 2.5 and 10 times lower than if pyrrhotite were absent.

Early work by Hagerman and Roosaar (1955) suggested that an upper limit of 1 % pyrrhotite was acceptable in coarse aggregates but Bastiansen et al. (1957) reported damage for pyrrhotite contents in aggregate as low as 0.01 %. The Alum Shale Committee was even more cautious, suggesting that if pyrrhotite was

Table 2 Total sulphur criteria for pyrrhotite-bearing aggregates (compared to those devoid of pyrrhotite), for various Standards across Europe

Standard	Pyrrhotite present (% S)	Pyrrhotite absent (% S)
EN 13242:2002 + Al:2007 (BSI 2008a) (Aggregates for civil engineering and road construction)	≤0.4	≤1
SR 21 (2004; 2007) (Irish guidance on the use of EN 13242)	≤0.4	≤1
EN 12620:2002 + Al:2008 (BSI 2008b) (Aggregates for use in concrete)	≤0.1	≤1
EHE-08 (2008) (Spanish use of concrete aggregates)	≤0.1	≤1

present, only aggregates with sulphur contents below 0.001 % were safe. In view of this, it is not surprising that some Standards have stipulated very low total sulphur criteria where pyrrhotite has been identified. However, EN 12620:2000 + Al 2008 and EHE-08 have been criticised for the low sulphur tolerance. It has been suggested that the upper limit of 0.1 % S is unnecessarily low and could rule out suitable aggregates (Chinchón-Paya et al. 2012).

Pyrrhotite in South West England

As noted above, the report on the Mundic problem (Anon 1997) implicated pyrrhotite as a contributor to the concrete degradation and indicated its presence within igneous and metamorphic rocks. A review of the literature has highlighted that pyrrhotite in south west England is more abundant and widespread than originally appreciated (Fig. 3).

The geology of the region comprises a predominantly Devonian and Carboniferous succession of siliciclastic-argillaceous rocks into which five major granite bosses intruded during the Permian (Edmonds et al. 1969). These granites are connected at depth to form the Cornubian Batholith and their emplacement was associated with alteration and metamorphism of the country rock (typically extending 5 km from the granite outcrop).

In Devon and Cornwall pyrrhotite was formed in four main situations. In the groups discussed below the numbers refer to Fig. 3:

1. Within igneous rock (7, 12, 19, 20)
2. Within massive veins and ore mineralisation (6, 9, 10, 13–18)
3. Within aureoles, not associated with mineralisation (3, 4, 5)
4. Outside aureoles, not associated with mineralisation (1, 2, 8, 11)

Pyrrhotite is a common accessory phase in igneous rocks hence the localities in group one are expected. The majority of occurrences are associated with mineral veining (group two). Mineral ores and veins in south west England are generally

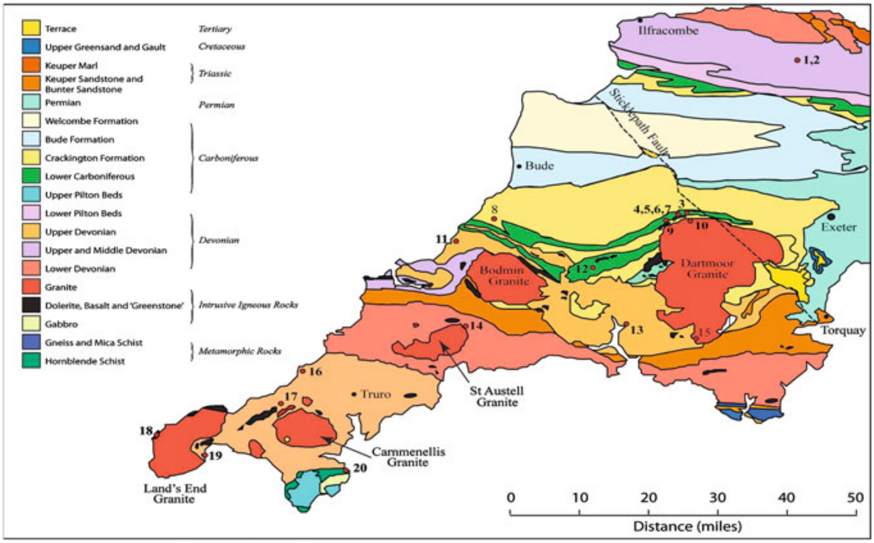


Fig. 3 Approximate locations of pyrrhotite in Devon and Cornwall (numbered 1–20). Map adapted from Edmonds et al. (1969)

accepted as having formed from fluids associated with the cooling of the granites. The flow of metal-rich fluids along faults and fractures produced veins known as lodes (Edmonds et al. 1969).

The localities in group three include contact metamorphosed rocks and those within the granite aureoles. Here pyrrhotite is found within hornfels and meta-chert formations, in disseminated granular form, generally below 0.1 mm in size (Edmonds et al. 1968). Localities 3 and 5 are sited within the Carboniferous Teign Chert Formation which includes numerous bands of (probably pyritic) black meta-shale. Pyrrhotite formation in these rocks may have occurred by conversion of pyrite during metamorphism, as has been proposed for the Exmoor area.

Group four localities are outside any metamorphic aureole. Pyrrhotite was observed within slates at each of these localities and granite has been discounted as the source for localities 1 and 2 (Bott et al. 1958). Instead, Jones et al. (1987) favour fault-facilitated mineralisation. More probably, the pyrrhotite was formed at these locations by the metamorphic transformation of pyrite (Leveridge et al. 2002).

Pyrrhotite and the Irish Problems

The rapidity with which distress has occurred in Dublin where ground-bearing floor slabs have been founded on aggregate containing iron sulphides was discussed by Hawkins (2012) who noted that the development of a ferrous sulphate rim around oxidising iron sulphides results in a previously unappreciated initial expansion. Hawkins also postulated that pyrrhotite may in some way contribute to the speed at which the expansion has occurred in the Dublin area. Subsequently, the report of the Pyrite Panel (2012) suggested a number of other factors which may have accelerated heave including:

1. The relatively mild climate of Dublin (compared to Québec for example)
2. The exposure of fill to poor weather prior to use, triggering oxidation

Distribution of Pyrrhotite in Ireland

The Pyrite Panel Report (2012) states that "Pyrrhotite is present only in specific geologic environments in Ireland of which there are relatively few." The Geological Survey of Ireland (GSI) database of Irish mineral occurrences was consulted for the preparation of the Pyrite Panel Report. This database identifies only nine localities for pyrrhotite—around 0.1 % of all the mineral occurrences recorded. However, a review of the literature and other mineral databases highlighted a further 15 localities, giving a total of 24 for Ireland (Fig. 4). In addition to these mapped localities, it has been proposed that pyrrhotite in black shale is responsible for high conductivity anomalies in central Ireland (Rao et al. 2007). Furthermore, the Navan ore body is also suspected to contain pyrrhotite.

The pyrrhotite occurrences noted in Fig. 4 can be grouped as follows:

1. Within igneous rock (2, 4, 6, 7 and 10)
2. Within sulphide deposits, veins, lodes or ores (5, 8, 9, 11–15 and 17–24)
3. Within metamorphic aureoles, not associated with mineralisation (1, 3 and 16)

Of these 24 localities, seven are within Carboniferous rocks and in general these appear to be located towards the edges of the Carboniferous outcrop, i.e., at the margins of the original depositional basin. The majority of these seven localities are shale or carbonate-hosted ore bodies, including those at 18, 20 and 21 in the Silvermines District where mineralisation is associated with the Silvermines Fault system.

Contact metamorphism of Carboniferous rocks in Ireland is not as extensive as that observed in the south west of England, as the major igneous intrusions of Ireland pre-date the Carboniferous period. Minor, localised metamorphism has occurred at locality 3 where Tertiary dykes intruded into calcareous shales. Whilst there are no available reports of pyrrhotite within the Irish Carboniferous rocks in modes other than vein type or contact metamorphic phases, it could also have been incorporated as detrital grains during deposition or formed by regional/heating/burial of pyrite.

Heating of pyritic mudrocks to in excess of 200–250 °C has been shown to produce pyrrhotite, particularly when carbon-bearing phases are present. A

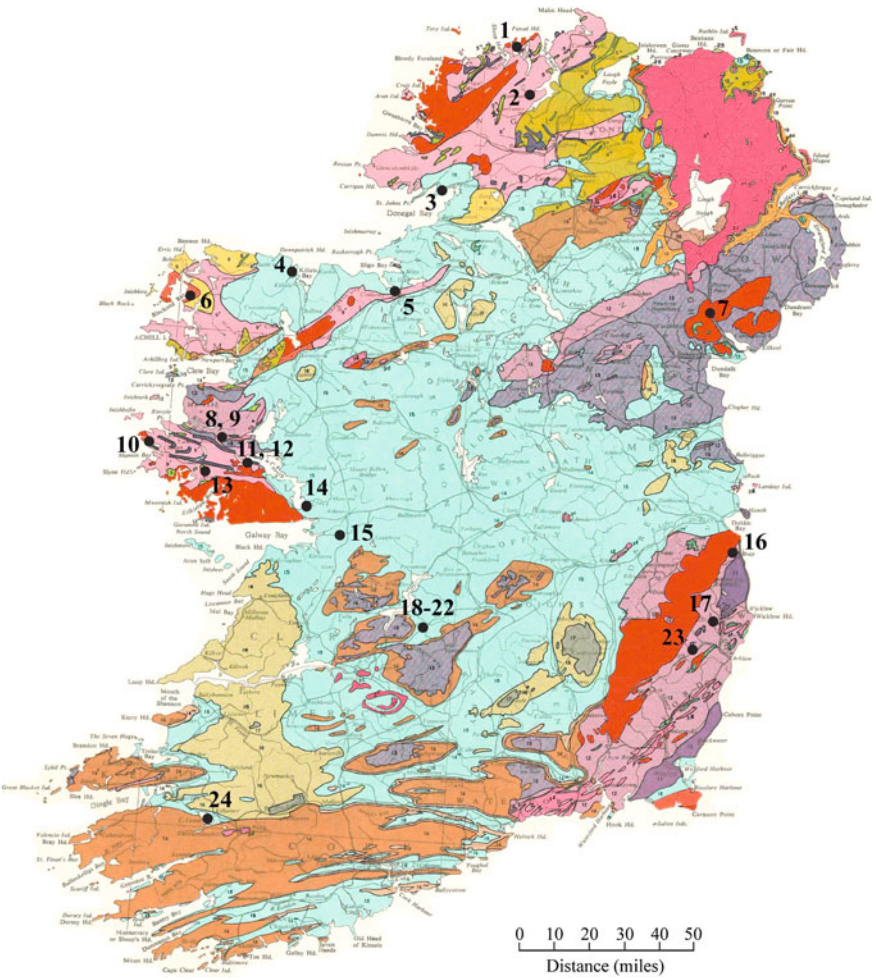


Fig. 4 Approximate locations of pyrrhotite in Ireland; map after Dunham (1969)

number of studies, including those on Irish conodont alteration, suggest that temperatures exceeded 250 °C in the Carboniferous rocks, due to burial alone (Jones 1992; Clayton et al. 1989). Recent work by Goodhue and Clayton (2010) on thermal maturity indicators has even suggested that burial geothermal gradients in Carboniferous strata offshore of Dublin may have reached 115 °C/km. Clearly only a few kilometres of burial would be required to reach conditions where pyrrhotite could form.

Pyrrhotite within Carboniferous Calcareous Mudrock in the Dublin Area

When petrographic analysis was undertaken on fill which had been removed from beneath a damaged structure in north Dublin, in addition to pyrite, pyrrhotite was identified by SEM and EDS. Iron-sulphur (wt %) ratios were in the approximate range of 1.5–1.7, confirming a pyrrhotitic composition. Unusually, however, the morphological form of this pyrrhotite was framboidal. Framboidal habits are typical of pyrite. Pyrrhotite with a framboidal texture is rare, but has been observed in Texan lignite deposits (Aleksandrov and Kamneva 1976). As the central core of the mineral often remains pyritic, it is possible that framboidal pyrrhotite is associated with the conversion of pyrite to pyrrhotite.

Pyrrhotite displaying a characteristic habit was also identified by SEM–EDS within samples of the Carboniferous Tober Colleen Formation (TCF) from the Baytown area, Fingal (Fig. 5). Several sub-hexagonal grains less than 30 μm in size were identified within a calcite vein, particularly at calcite grain boundaries. On first examination, the grain shown in Fig. 5 had an iron-sulphur ratio of 1.6. After only three weeks of exposure to the atmosphere the composition was checked and confirmed to be pyritic, i.e., the pyrrhotite had converted back to the more stable iron sulphide.

Sub-hexagonal grains with pyritic compositions are common within the TCF samples (Fig. 6). These are believed to be pseudomorphs after pyrrhotite and may have formed through oxidation of pyrrhotite, as recently as during SEM preparation. In addition to burial heating, the Carboniferous rocks of Dublin underwent deformation during the Variscan Orogeny. Rotation of fault-bound blocks in the Dublin Basin produced upright to tight folding in the Chadian-Brigantian rocks (Hitzman 1999).

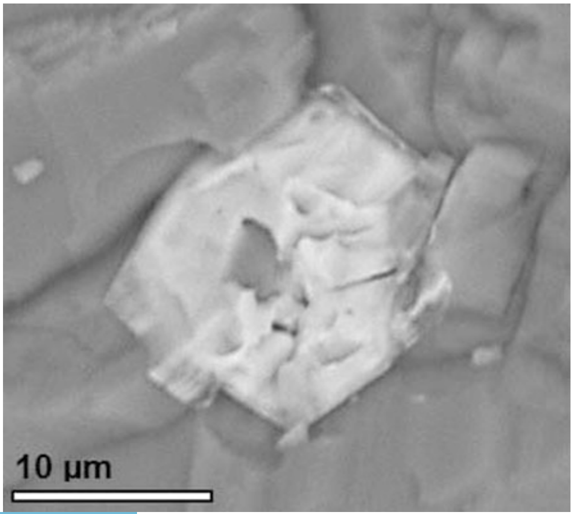


Fig. 5 SEM image of a sub-hexagonal iron sulphide with a pyrrhotite composition from a borehole core, N. Dublin

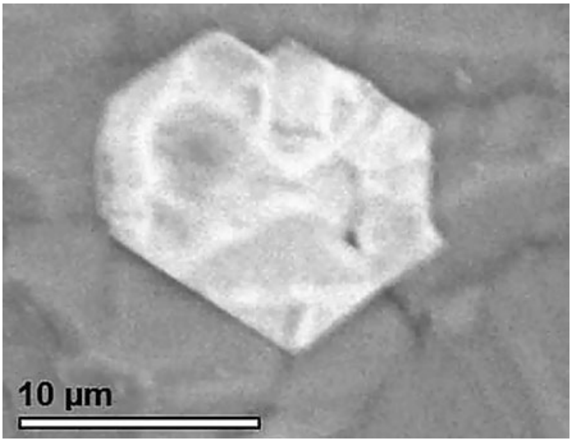


Fig. 6 SEM image of sub-hexagonal pyrite—probable pseudomorph after pyrrhotite from a borehole core, N. Dublin

The TCF in general comprises dark, sometimes black, pyritic calcareous mudstones and minor limestones (McConnell et al. 2001; Strogen et al. 1990). The TCF itself is known to have experienced deformation which is manifest as open folding and pressure solution cleavage (McConnell et al. 2001). As it is likely the TCF experienced burial temperatures in excess of 250–300 °C, it is not unreasonable to suggest that pyrrhotite may have formed at the expense of pyrite, especially as the dark shales probably contain carbon, which would aid the conversion.

Vein-type pyrrhotite may be the more common mode of occurrence in these rocks, particularly considering the abundance of shale-hosted sulphides in the Irish Carboniferous strata. Most of the Irish Carboniferous zinc deposits comprise abundant massive sulphide lenses associated with major faults (Hitzman 1999). It is likely that faulting played an important role in the distribution of the sulphides. Unfortunately, the identification of pyrrhotite and estimation of its abundance in these rocks is problematic as it appears to oxidise quickly.

Framboidal Pyrite from the Dublin Region: Implications for Oxidation

The framboidal form of pyrite is particularly common within the Carboniferous mudrocks of the Dublin area. Framboids and their formation have been the subject of much study and debate, but they are frequently described as sub-spherical clusters of uniformly sized and shaped pyrite microcrystals. They are typically less than 50 μm in diameter with individual microcrystals as small as 0.2–0.5 μm in diameter.

Pyrite Framboids from the Baytown Area

Samples of Carboniferous calcareous mudrock were obtained from core recovered from a 20 m deep borehole at Baytown, north of Dublin. Small (<10 mm) fragments were selected at regular depth intervals and resin-mounted into thin walled sample rings. Each sample was polished to <1 µm using an oil-based lubricant to minimise exposure to moisture. Samples were then coated with approximately 20 nm of carbon to provide a conductive surface for examination. A Hitachi S-3500 N SEM equipped with an EDS detector and a JEOL JXA 8530F electron microprobe, both based at the University of Bristol, were used for imagery and quantification.

In addition to the sub-cubic, octahedral and vein-type morphologies, pyrite framboids were abundant in all the samples. The framboids were typically found disseminated within the rock but were also common on fracture surfaces. It was observed that the framboids showed a wide variation in each of the following properties:

1. Size (diameter)
2. Large-scale morphology
3. Number of microcrystals and ordering
4. Microcrystal morphology and habit

Framboids in the Baytown samples ranged from <5 µm up to about 40 µm. Other aggregations of octahedra in non-framboidal morphologies were present at larger sizes, up to 60–100 µm across. A common observation was the co-existence of pyrite framboids of various sizes within 10 µm of each other (Fig. 7).

In most cases the pyrite framboids display a near-spherical form, sometimes producing a "poly-framboidal" appearance (Fig. 8). However, there are some instances where the large-scale structure is non-framboidal but still comprises pyrite microcrystals. In these instances, forms include rods (Fig. 9), cubes, octahedra (Fig. 10) and anhedral scattered masses (Fig. 11). Non-spherical types

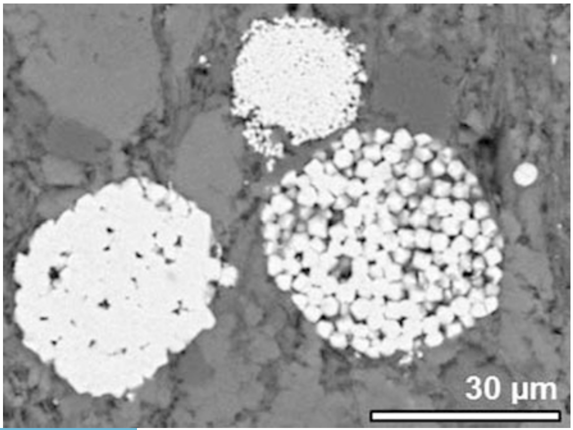


Fig. 7 Various pyrite framboid sizes, from <1 µm (far right) to >30 µm. Microcrystals are arranged in a disordered manner with varied orientation

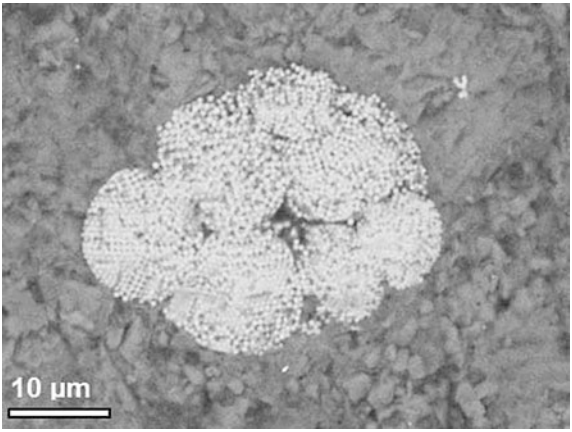


Fig. 8 Variations in framboid macro-structure and ordering/packing; sub-spherical framboids clustered together producing a "poly-framboidal" appearance

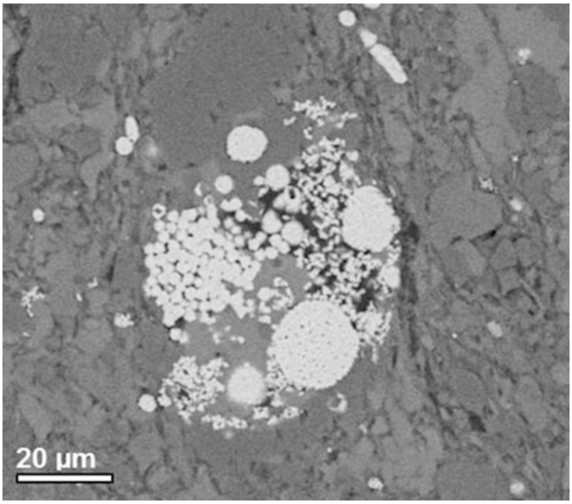


Fig. 9 Variations in framboid large-scale morphology—spherical clusters (*centre*) and elongate rods (*top-centre*). Dispersed masses of microcrystals are also present

would more appropriately be termed "aggregations" or "clusters" of pyrite microcrystals.

Ohfuji et al. (2005) identified two internal structures for framboids which can be generalised as ordered and disordered. Although examples of both types are seen within the Baytown samples, the disordered form appears to be dominant (e.g., Fig. 7). The Baytown samples also exhibit a wide range of packing densities, which appears to be a function of the orientation, size and habit of the individual microcrystals. In some cases microcrystals appeared aligned into rows whilst in others the microcrystals are scattered widely (Fig. 11).

Variations in microcrystal size directly influence the number of microcrystals possible within a framboid. There are several occurrences of equal-diameter

Fig. 10 Variations in framboid large-scale morphology—spherical clusters and sub-octahedral aggregations

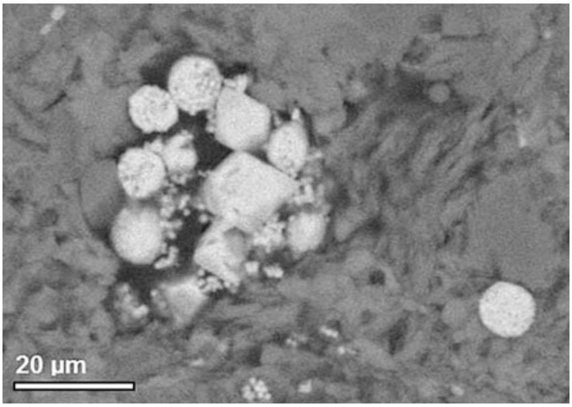
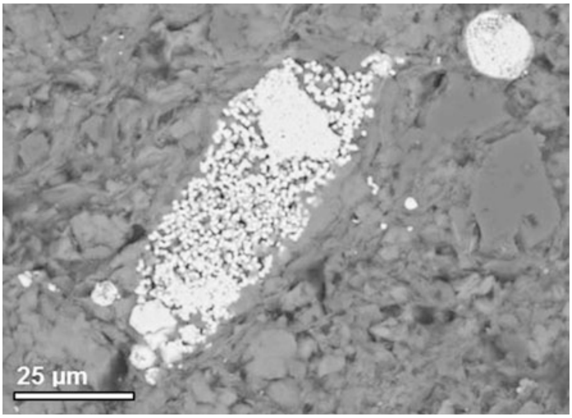


Fig. 11 Variations in framboid large-scale morphology—anhedral mass of dispersed/scattered pyrite microcrystals. Note cracking in pyrite cube (*bottom-left*)



framboids adjacent to one another but with stark differences in microcrystal size and quantity (e.g., Fig. 7).

Two major types of microcrystal habit were observed within the pyrite framboids. Octahedral microcrystals are by far the most common (Fig. 12), but pyritohedra (irregular dodecahedra) were also observed. In some cases high magnification of the microcrystals revealed that they had a very tightly packed framboidal structure, containing many smaller microcrystals, although the individual habits could not be identified (Fig. 12).

A common texture observed within the samples from Baytown is the fracturing or cracking of microcrystals within framboids (Fig. 13). This microcrystal appearance is not known to have been previously reported in the literature, although several authors have published SEM images of fractured microcrystals without addressing this aspect (e.g., Ohfuji et al. 2005). Cracks vary considerably in their appearance but in general they are observed as irregular or undulating dislocations (Fig. 14). In some cases the fractures traverse an entire microcrystal and may cause it to break into two (Fig. 15).

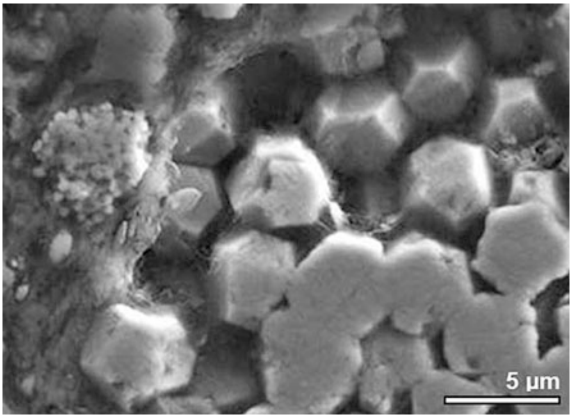


Fig. 12 Variations in pyrite microcrystal habit—equant octahedra (*top-right*) and “micro-framboid” or framboidal microcrystal (*left*)

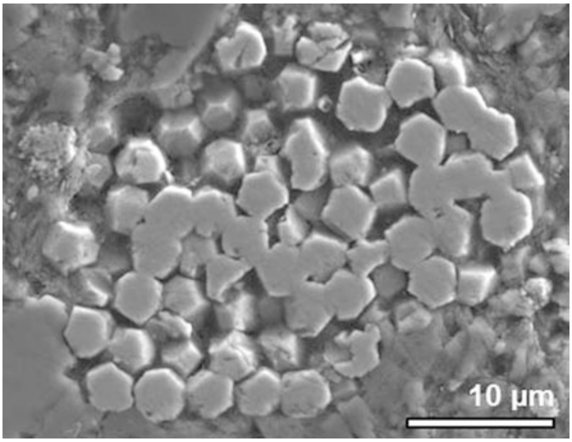


Fig. 13 Pyrite framboid with microcrystals displaying irregular fractures

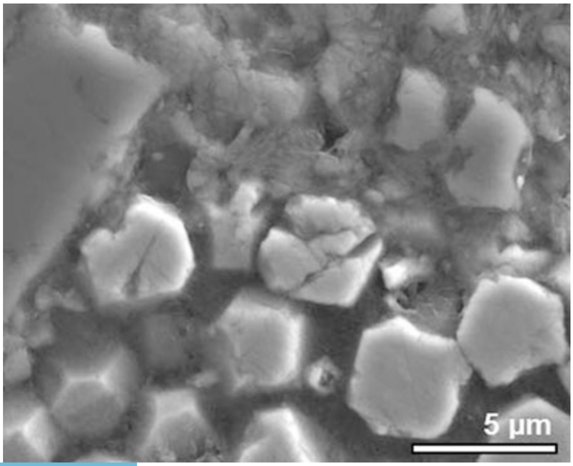


Fig. 14 High-magnification image of fractured microcrystals

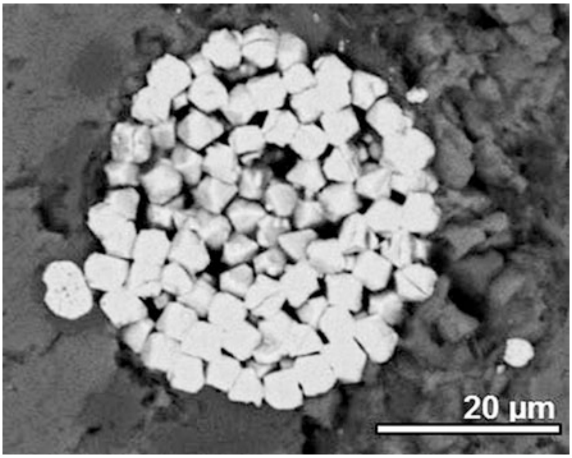


Fig. 15 Pyrite framboid showing fracturing of over half the microcrystals, many of which are completely divided into two

The cause of the microcrystal cracking is not known at present, but could be related to tectonic shearing or faulting. They are unlikely to be the result of sample preparation as although fine (<0.1 μm) polishing scratches can be seen on some samples, the fractures are typically wider and show a distinctly different, irregular orientation to the scratches. The cause of the cracking is the subject of ongoing research.

Implications of Framboid Geometry for Oxidation

Framboidal pyrite is widely believed to oxidise faster than pyrite in “chunks” or cubes of equal size (e.g., Pugh et al. 1981). The porous nature of the structure, a result of the spacing between individual microcrystals, provides a large exposed surface area on which oxidation reactions can occur.

The differences in framboid morphology and texture observed in the Baytown samples will give rise to a range of available surface-area-to-volume ratios (specific surface). In particular, the fracturing of a single octahedral microcrystal into two identical halves would expose two relatively large new faces, both square in shape. In this scenario, the theoretical surface area for the entire microcrystal would be increased by some 160 %.

Consequently, these varied framboid morphologies and textures will influence the rate of oxidation and thus the release of sulphuric acid/formation of sulphates. In general, framboid characteristics which are likely to promote fast oxidation rates are:

1. Large numbers of microcrystals
2. Small microcrystal sizes
3. Large microcrystal surface areas

4. Low density and high void space
5. Fractured microcrystals

Observations made on the samples of Carboniferous calcareous mudrock from Baytown suggest that whilst the presence of framboidal pyrite can be detrimental to civil engineering, the texture and structure of the framboids will have a significant influence on the rate and severity of any adverse effects.

Effects of Surface Heating

Ireland is not well known for geothermal energy and has a relatively limited number of such resources (Lund et al. 2011). Despite this, there are at least 42 warm springs recorded in Ireland, with temperatures ranging from 13 to 24.7 °C (Aldwell and Burdon 1980). The potential for geothermal development has been noted in the past (e.g., Aldwell and Burdon 1978) but it was not until 2004 when the Sustainable Energy Authority of Ireland commissioned a study into the nature of ground-sourced heat that it was fully appreciated.

The final report of the CSA Group study (2004) includes a number of geothermal maps based on measured and modelled temperatures at a variety of depths. It also includes a compilation of data and discussion of the Irish thermal springs, which are suggested as possible resources for geothermal exploitation. The findings of the CSA Group report are discussed below with reference to the implications for the sulphate-induced heave process.

Irish Thermal Springs

Warm springs in Ireland can be broadly divided into the Leinster and Munster springs. The Leinster springs are the closest to the Dublin area and hence the Munster springs are not considered here. Thermal springs, wells and boreholes listed by the CSA Group within 50 km of Dublin are plotted in Fig. 16. The temperature of the springs typically ranges from 12 to 25 °C, with temperatures tending to increase with discharge and flow rate. In general, both temperature and discharge peak in the spring and summer months (e.g., Fahy 1975).

It can be seen that all 18 of the springs plotted in Fig. 16 issue from rocks of Carboniferous age, which are typically overlain by a layer of glacial deposits or boulder clay in the east of Ireland. Figure 16 also shows that the North Leinster springs are located sub-parallel to and north of the Blackrock-Rathcoole Fault, an observation discussed by the CSA Group (2004). This fault separates the Carboniferous rocks from older rocks to the south (including the Leinster Granites) and has been postulated as the heat source for the springs. A number of other faults are also recorded on the 1:100,000 geological map apparently radiating from the

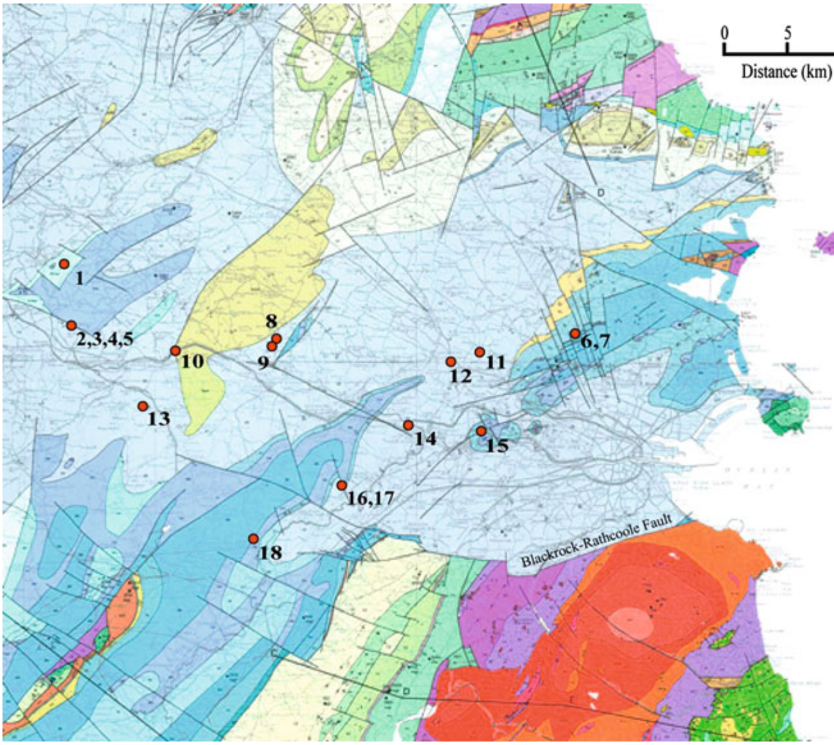


Fig. 16 Approximate locations (Nos 1–18) of thermal springs, wells and boreholes in the Dublin region. Geological map adapted from GSI (1995; 1999)

Leinster Granites. Undoubtedly there are many less significant faults which are not included on this small scale map. Examination of Fig. 16 reveals that all the springs are close to a mapped fault (i.e., within a few kilometres) and many appear to issue directly on the fault trace.

The spring water itself has been shown to have a meteoric origin, with the exception of locality 14 in Leixlip (CSA Group 2004). It is believed that this meteoric water is circulated within deep fault structures related to the Blackrock-Rathcoole Fault where it becomes heated and later rises to the surface through fracture systems (CSA Group 2004; McConnell et al. 2001).

Shallow Heat-Flow in the Dublin Area

Typical soil temperatures in Ireland range from 9.5 to 12 °C in the uppermost 1.5 m (CSA Group 2004) whilst typical shallow groundwater temperatures are in the range of 10–12 °C (Aldwell 1997). Local temperature anomalies have been identified and were elucidated on a map of contoured heat-flow density for the depth range of 0–100 m which was produced as part of the CSA Report. The map indicates that whilst Northern Ireland hosts warmer sub-surface material than the south, there are several areas which display an above average heat flow density, including the Dublin area.

Surface heat-flow density in the Dublin area modelled by the CSA Group (2004) exceeds 75 mW/m, with heat-flow decreasing away from Dublin (Fig. 17). A local maximum coincides with the area underlain by Caledonian granite in Co. Wicklow. Other Caledonian granites in the east of Ireland include the Kentstown Granite (c. 40 km north west of Dublin) and the Drogheda Granite (c. 45 km north of Dublin). The former is buried at some 500–600 m depth and overlain by Carboniferous strata while the latter was encountered in a shallow excavation (McConnell and Kennan 2002). Jones et al. (2011) report that the Irish granites continue to generate heat despite their Caledonian age and may contribute to the surface heat flow.

Both the thermal springs and the granites locally increase the ground temperature (CSA Group 2004). As a consequence of the warm ground, several buildings in the Dublin area operate ground-source heat pumps, including one installed in 1994 at Temple Bar which utilises a borehole in the Carboniferous strata (O'Connell and Cassidy 2003).

Implications for Iron Sulphide Oxidation

It is well established that elevated temperatures increase both the extent and rate of iron sulphide oxidation (e.g., Quigley and Vogan 1970; Hawkins and Pinches 1987; Hawkins (2013 this book). Lehmann et al. (2000) report the rate of oxidation of pyrrhotite increases by up to four times with a temperature rise from 25 to 40 °C.

Figure 16 indicates extensive faulting in the Dublin Basin, including both a WSW-ENE fault set (sub-parallel to the Blackrock-Rathcoole Fault) and a NW–SE set. Faults play an important role in the movement of groundwater and it is likely that the NW–SE orientated faults provide a pathway for transmission of heat away from the Leinster Granites and across the basin. In view of the difficulty of mapping faults in argillaceous rock, thermal waters may also occur associated with unrecognised fault zones in this area.

Much of the Dublin area is overlain by the Dublin Boulder Clay (DBC), a geologically recent glacial till. The DBC is a stiff, fissured till with a permeability between 10^{-9} and 10^{-11} m/s, although higher values may be present in granular zones. Long and Menkiti (2007) have shown that where lodgement till is present, it is highly fissured but the discontinuities are tight/closed. Considering the low permeability and closed nature of the fissures, the DBC may act as an insulating "cap" for upwelling thermal fluids in the Dublin area. Particularly to the north of Dublin where the superficial cover is relatively thin, engineering works for foundation construction may remove (or reduce the thickness of) the DBC and expose locally warm sub-surface conditions.

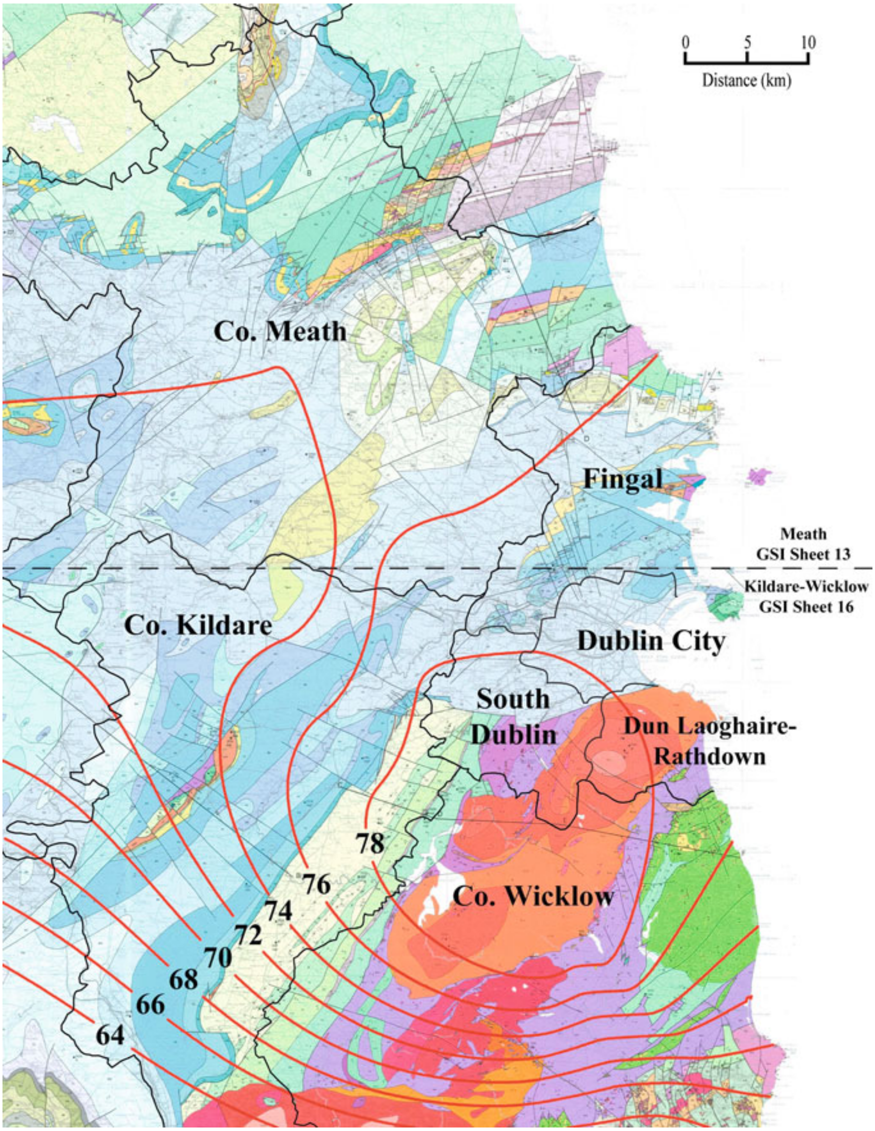


Fig. 17 Heat-flow density (*units* milliwatts/metre) map of the Dublin area (CSA Group 2004) for depths of 0–100 m, superimposed upon the 1:100,000 regional geology, adapted from GSI maps (1995; 1999)

In cases where sulphide-bearing aggregate or fill has been placed in areas of locally warmer ground conditions, oxidation will occur more rapidly. As a result, the rate of sulphate-induced heave and hence the manifestation of damage in affected structures may be accelerated. The higher temperatures during the spring/summer months may also exacerbate oxidation effects in already naturally warmer ground.

As noted above, soil temperatures in Ireland typically range from 9.5 to 12 °C in the uppermost 1.5 m. Soil temperature data from the Canadian National Climate Data and Information Archive for a weather station in Montréal gives an annual range of 5–7.5 °C for the same depth interval over a 15 year period. These conditions go some way to explaining why damage has typically been manifested in two to three years in Dublin compared with around five to ten years in many Canadian case histories (e.g., Maher 2013).

Conclusions

This chapter draws attention to some of the ongoing research work being undertaken to better understand the processes of sulphate heave and concrete deterioration in the Dublin area of Ireland. In order to provide a background, examples of problems related to iron sulphide oxidation from other parts of the world are also discussed.

The chapter considers four main topics:

1. The origin and significance of pyrrhotite, which can oxidise some 100 times faster than pyrite. It is considered that to date the presence and significance of this form of iron sulphide has not been adequately appreciated in Ireland.
2. The variable size of the iron sulphide microcrystals (typically between 0.25 and 5 µm); the differing size of the framboids into which they cluster; and the variable degree of packing (from tightly packed/ordered to more open porous disordered structures), all of which have an effect on the speed of oxidation.
3. The fact that microcrystals <5 µm across may be fractured. The examples studied from a specifically drilled rotary-cored borehole indicate that such fractures are not induced during the quarrying process but probably relate to tectonic stresses, hence may be more commonly found in the vicinity of faults. The presence of these fractures greatly increases the available surface area of the microcrystals hence increasing the potential speed of oxidation of pyrite and/or pyrrhotite. It is also noted that cubes/lumps of pyrite are frequently fractured during the quarrying processes hence this form of pyrite should not be considered "non-reactive".
4. The near surface ground temperatures beneath Dublin are higher than would occur over much of Ireland. In addition to the locations where thermal springs are recorded, undoubtedly heat will also rise to the surface via the linear faults and master joints which radiate from the Leinster Granite. The presence of unmapped springs, concealed by developed land, is also possible. Where the overlying Dublin Boulder Clay is thin, engineering works may reduce the thickness of the impermeable cover such that individual house plots on a single estate may have different temperatures at foundation level or in the fill. For this reason the rate of oxidation of iron sulphides and the associated ferrous sulphate-produced heave as well as the growth of gypsum, ettringite and thaumasite may vary widely across a site.

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