Sulfate and sulfide minerals in the UK and their implications for the built environment

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Abstract: In recent years a number of research projects have been commissioned to investigate the causes of deterioration of concrete and ferrous structures in contact with pyritic ground. It has been concluded that various sulfur species and their response to environmental changes caused by construction have been the cause. Although chemical attack of concrete and other construction materials due to the presence of chloride and sulfate ions is well known, only recently has it been appreciated that guidance on the topic was seriously deficient as the possibility of sulfate formation as a result of pyrite oxidation was not specifically included. Revised guidance on the assessment of aggressive ground conditions and the design of concrete structures has been issued by BRE, while TRL has issued guidance on the design and construction of highways in potentially aggressive conditions. The relevant documents provide engineering geologists and geotechnical engineers with a general awareness of sulfide oxidation and sulfate attack, however there still tends to be a poor understanding and practical appreciation of the processes of, the controls on and the implications of pyrite oxidation. This often results in incorrect diagnosis of problems leading to extensive and costly remediation to engineering schemes.

This paper aims to discuss the occurrence, distribution and assessment of sulfur bearing minerals with respect to the potential sources of sulfate in natural and waste materials often encountered during ground engineering work in the UK. The reactions and processes associated with the environmental changes brought about by typical engineered structures are reviewed. Of importance is the effect the design and construction process can have on the generation of sulfate. Pertinent case studies are considered providing useful background and guidance to practitioners in geotechnics.

Résumé: Ces dernieres annees il y a un certain nombre de projets de recherche pour etudier la deterioration des structures en beton et ferreuses qui ont eu contacte avec la terre pyriteuse. On a conclus que les diverses especes de soufre et leurs reactions aux changements envirenmentaux etaient provoques par la construction. Bienque l'attaque chimique de beton et d'autres materiaux de construction soit bien connu a la presence de chlorure et des ions de sulphate. Il a ete reconnu tout recemment que conseils sur le sujet etaient serieusement deficients et la possibilite de la formation de sulphate en raison d'oxydation de pyrite n'etait pas specifiquement inclus. Conseils revisees sur l'evaluation des conditions au sol aggressive et a la conception des structures en beton a ete publie par BRE, at TRL a publie des conseils sur la conception de routes sous des conditions aggressives. Les documents appropries fournissent aux geologues de technologie et des ingenieurs geotechniques une conception generale d'oxydation de sulfure et attaque sulphate il y a cependant une conception faible, et une appreciation pratique des processus et les implications de l'oxydation de pyrite. Les resultants donnent souvent un diagnostic faible des problemes ce qui menent au remediation bian etendu et couteux.

Cet article va discuter l'occurrence, la distribution et l'evaluation de minerais contenient du soufre quant aux sources potentielles du sulphate at minerais naturelles de rebut, rencontre pendant du travail au sol de technologie de RU. Les reactions et processus associes aux changements envirenmentaux provoques par les structures machines sont passes en revue. Important c'est l'effet que les process de conception et de la construction pouvent avoir sur la generation de. Ces etudes de cas sont considerees utiles aux practicioners en geotechnics.

Keywords: Backfill, expansion, geomaterials, materials, preventive measures, weathering.

INTRODUCTION

Aggressive ground conditions are associated with a wide range of factors encompassing physical, chemical and biological processes although a high proportion of occurrences in the engineering environment have been attributed to the presence of sulfur minerals that give rise to high concentrations of sulfate ions in groundwater. Sulfur minerals occur in geological materials in a variety of forms (Czerewko et al, 2003a) of which the sulfate gypsum and sulfide pyrite are most commonly encountered in the UK. These occur either as primary constituents or, in the case of gypsum as a product of contemporary processes such as weathering. Sulfur species are also commonly found in waste products from industrial and engineering processes including chemical production, demolition waste, as well as colliery spoil. They may also occur in sediments, including river flood plain gravels, where reducing, anoxic conditions exist in stagnant sections. Not all forms of sulfur are troublesome in engineering situations, although this depends upon the particular environmental conditions. Mineral sulfates, such as barytes, and organic sulfur are both relatively stable in weathering environments, and these would not normally be expected to contribute to the sulfur present in groundwaters unless conditions are unusual.

For many decades it has been standard practice to determine the sulfate content and aggressive nature of soils and fills for the design of cement and concrete in buried structures and more recently soil stabilisation using lime and cement according to guidelines presented in BRE Digest 363 (1996). Generally this evaluation and design approach has worked well with few instances reported of sulfate attack on buried concrete structures attributed to chemical attack. However, Hawkins & Pinches (1986) suggest that engineers tend not to appreciate the mineralogical host of the sulfate nor consider the holistic ground model, but simply use the value to design the cement and concrete mixes. Therefore, problems associated with aggressive ground conditions or volume changes due to the presence of sulfur species, particularly pyrite, have been experienced in many areas of civil engineering such as rapid degradation of mudrock fill, reduced permeability of limestone drainage layers and production of carbon dioxide that resulted in fatalities during dam and embankment construction, (Pye & Miller 1990; Cripps et al. 1993; Davies & Reid 1997); ground heave damage to foundations caused by gypsum precipitation (Nixon 1978; Wilson 1987; Hawkins & Pinches 1987); heave problems associated with ground stabilisation for highway construction, (Haviland et al. 1967; Worley 1971; West 1996; Snedker & Temporal, 1990); heave associated with ground stabilisation for foundation construction (BRE, 2002); chemically aggressive conditions encountered during tunnelling (Varley 1990; Bracegirdle et al. 1996); corrosion of buried steel structures due to chemically aggressive conditions (Reid et al. 2001; Czerewko et al, 2003b); and thaumasite form of concrete attack (Thaumasite Expert Group 1999).

These problems have been attributed to the generation of chemically aggressive soluble sulfates and acidity caused by the oxidation of pyrite present in the ground material for which prior to 2001 appropriate guidance was not available. Therefore for an adequate assessment of the potential for ground heave, concrete attack or metal corrosion, merely determining the total sulfate content of a soil or fill is insufficient. The sulfide content must also be determined. Recent recommendations for assessing structural backfills (Reid et al. 2001, 2005) and the design of concrete in aggressive ground (BRE 2001, 2005) involve not only the determination of sulfate content of material but also potential sulfate content, calculated from the sulfide present.

The recognition of sulfur-bearing minerals in hand specimen is not easy and requires an experienced eye, especially in the case of argillaceous deposits, which often contain disseminated pyrite in the form of microscopic framboids up to tens of microns in size (Figure 1). Not only is it difficult to make the thin sections required to carry out optical microscopy, but it requires skill to identify pyrite by this method.

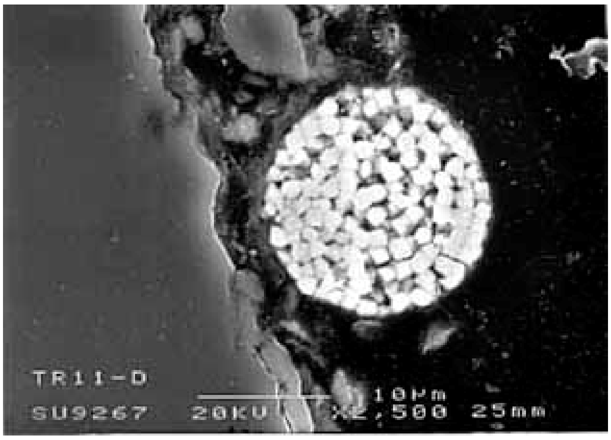

Figure 1. Pyrite framboid from River Trent alluvium. (SEM-Secondary electron imagery).

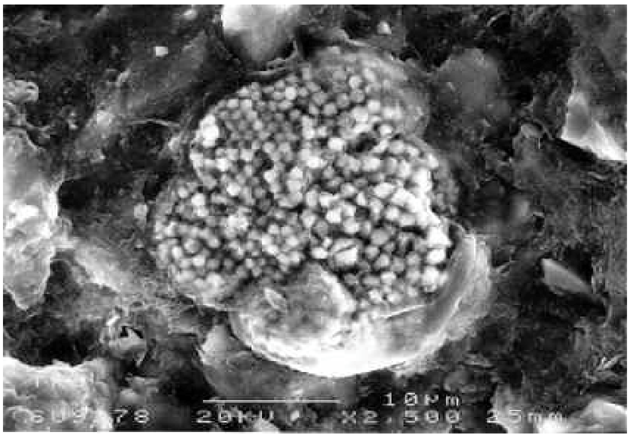

Figure 2. Pyrite polyframboid in Lower Lias Clay.

Alternative mineralogical methods, for instance X-ray diffraction and electron microscopy, and chemical procedures are available although these techniques tend to be beyond the scope of most engineering schemes in terms of cost. Furthermore the mineralogical procedures are not ready available and there is a lack of guidance as to what quantities of pyrite might be acceptable in particular situations. Therefore, in terms of forming the basis of routine commercial testing and evaluation, chemical methods have proved to be more practical. In recent years appropriate test procedures for evaluating geological and man-made materials have been presented by TRL and BRE (TRl, 2001, 2005; BRE 2001, 2005).

FORMATION OF SULFUR MINERAL SPECIES

Sulfur, as the ninth most abundant element in the earth's crust, occurs in various forms including, as a gas, such as sulfur dioxide, in aqueous forms such as the sulfate ion or as a solid. In solid form other than elemental sulfur it occurs in two common forms that also impact on engineering construction namely sulfate minerals, of which gypsum is the most common and as sulfide minerals of which pyrite is the most common and widespread.

Sulfate minerals:

Primary sulfate minerals commonly encountered in the UK comprise gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$) associated with marine sedimentary limestone and mudstone deposits. Gypsum is the stable hydrated form of calcium sulfate under near surface conditions. When gypsum undergoes deep burial it dehydrates to anhydrite. With subsequent uplift, anhydrite re-hydrates in the presence of water to form gypsum. Gypsum resulting from primary deposition is a colourless or white mineral, which tends to occur, in a massive form as a soft fine-grained white or pale coloured rock or in a fibrous habit known as satin spar. Other primary sulfates include the very soluble epsomite ($MgSO_4.7H_2O$) which tends to be found with salt deposits and in the UK is generally encountered only in brines and mineral-rich groundwaters (Foster et al 1995). Glaubers salt ($Na_2SO_4.10H_2O$), is an extremely soluble sulfate mineral that may also occur in evaporite deposits or as a weathering product in mining environments. These primary sulfate deposits are generally formed by the evaporation of hypersaline waters under arid conditions where rates of evaporation greatly exceed any rainfall. Examples in the UK of sulfates formed by such processes are to be found in the Triassic Mercia Mudstone deposits. During the Triassic Period the climate in Britain was hot with alternating wet and dry seasons, which produced deposits comprising conglomerates, sandstones, and red brown mudstones and dolomitic mudstones formed under aeolian and lacustrine conditions. Marine incursions occurred during the Mid-Triassic forming arenaceous and rudaceous deposits, which was superseded during the mid to late Triassic with formation of hypersaline lagoons producing the thick intermittent evaporite deposits containing gypsum and the other sulfate minerals mentioned above.

Primary sulfates such as barytes ($BaSO_4$) and celestine ($SrSO_4$) also occur as the gangue minerals in ore deposits. As such they are often encountered in the waste materials generated in the course of mining for lead, copper, zinc, iron and other ore minerals, or as a result of the processing and refining of ores. Such materials may be encountered in engineering projects and may have been used as fills. They occur mainly in the Pennine area (including the Peak District), Lake District, Wales, Cornwall and Shropshire.

Secondary sulfates form as the weathering products of sulfide minerals that are commonly present in clays, mudrocks and mineral veins. If calcium carbonate (calcite), commonly found in marine deposits is present, the sulfuric acid solution produced by the oxidation of pyrite reacts with the calcium in calcite forming gypsum. Under the suitably acidic conditions the sulfuric acid will also react with clay minerals such as illite and smectite, and the sodium feldspar mineral albite forming alunite group sulfates, particularly jarosite and alunite, and liberating exchangeable cations such as K^+, Na^+ and Mg^+. Secondary gypsum tends to form as euhedral transparent crystals known as selenite. Selenite crystals tend to adopt a flat tabular habit, which also grow as elongated prismatic crystals due to contact twins joining at the end faces and this form it is commonly referred to as swallowtail or arrowhead crystals.

Sulfide Minerals:

Reduced sulfur species, in particular pyrite, may form under low- or high-temperature conditions. High temperature forms occur in, or are associated with, igneous and metamorphic rocks and mineral veins. Pyrite may also be formed at low temperatures in organic rich sediments, including Recent and contemporary deposits. It is particularly associated with anaerobic conditions that occur within stagnant watercourses, estuaries and marine basins in which dark coloured, organic rich, muds are deposited. Aerobic bacterial decomposition of the organic matter produces an anoxic, reducing environment tens of centimetres below the water-sediment interface. Under these conditions sulfate reducing bacteria convert the dissolved sulphate anion dissolved in the water to sulfide anion by replacement of the oxygen component of the molecule by hydrogen thus forming hydrogen sulfide gas. This then reacts with the ferric iron present in solution forming metastable iron sulfide, which subsequently transforms to the chemically more stable pyrite commonly found as an authigenic mineral in these sediments. Such conditions give rise to framboidal pyrite. As shown in Figure 1, this consists of many individual octahedral crystallites, <1 to 5 microns in size that form into an ordered spherical mass between 20 and 50 microns across. Due to their great collective surface area such pyrite framboids are very reactive in oxygenated and humid weathering environments. In the UK, pyrite commonly occurs in this form in Carboniferous, Jurassic, Cretaceous and Tertiary mudrocks and clays. These deposits account for a large part of the near surface stratigraphy of England. These deposits may also contain relatively large (up to approximately 0.5%) quantities of sulfur in the organic material present (Rowell, 1994).

Deep burial and geothermal heating of pyrite bearing sediments produce polyframboid aggregates as seen in Figure 2, and deeper burial and associated diagenetic processes cause the recrystallisation and cementation of framboids into octahedral or cubic crystals that are hundreds or thousands of microns in size. Such changes operate in parallel with the conversion of the original muddy sediment to a hard clay and with further lithification to claystone or mudrock and ultimately to a metasediment such as slate, phyllite or schist.

Larger octahedra and cubes of pyrite, ranging from millimetres to centimetres in size, may also form in hydrothermal deposits and from magmatic melts. Due to the smaller collective surface area, large individual crystals of pyrite are much less reactive than framboids. Pyrite and pyrrhotite (FeS) present as visible crystals, infill strata such as lenses or coating along discontinuities in diagenetically mature mudrocks, metamorphic rocks, such as slates, phyllite, hornfels schist and gneiss derived from mudrocks and most magmatic rocks. In this form it is usually easier to recognise these minerals as they usually occur as gold coloured cubes, radiating clusters and flakes. As mentioned above, sulfide minerals also occur as metallic ores, and with their derived wastes they are common in former mining areas.

UK DISTRIBUTION OF SULFUR MINERAL SPECIES

In the UK, sulfur minerals occur in most sedimentary deposits found at or near to ground level in which construction interacts and takes place particularly in water formed argillaceous deposits. As mentioned above, sulfur may also occur in geological materials as a product of contemporary processes such as weathering. Sulfur species are also commonly found in waste products arising from gas, oil and chemical production. They are common in spoil heaps resulting from metalliferous-, coal- and oil-shale mining and mineral processing. However, not all forms of sulfur are troublesome in engineering situations, although this does depend upon the particular environmental conditions. As mineral sulfates, such as barytes, and organic sulfur are relatively stable in surface weathering environments, they would not normally be expected to contribute to the sulfur present in groundwater.

Primary sulfates minerals, including gypsum, are present in evaporite deposits of Permian and Triassic age. Primary sulfates may also be present in minor amounts in several marine Mesozoic and Cenozoic sedimentary clay deposits, including Lower Lias Clay, Kimmeridge Clay, Oxford Clay, Gault Clay, Weald Clay, Lambeth Beds and London Clay. These deposits alone occupy about 25% of the land surface of England, and small areas of Wales and Scotland. Secondary gypsum derived by the dissolution of primary gypsum by percolating groundwaters may also be precipitated within the ground profile in these areas (see Cripps and Edwards, 1997).

Secondary sulfates are liable to be present in the weathered horizons (2-8m below the ground surface) of formations that contain primary sulfide minerals. It may take many thousands of years for weathering to progress a few metres into clay deposits (Chandler, 1972). The distribution varies within the weathered zone with the top few metres having negligible sulfate contents due to rain leaching but elevated levels may be present at the base of the root zone (~2-3m) and at the base of the weathered zone (Cripps & Edwards, 1997). Significant quantities may be encountered in weathered Carboniferous Coal Measures deposits and also in ancient and more recent sand and alluvial deposits. These strata are of significance as they form large areas of outcrop on which a majority of British urban centres are located. Figure 3 shows an example of natural pyrite weathering processes resulting in the formation of gypsum (selenite) crystals.

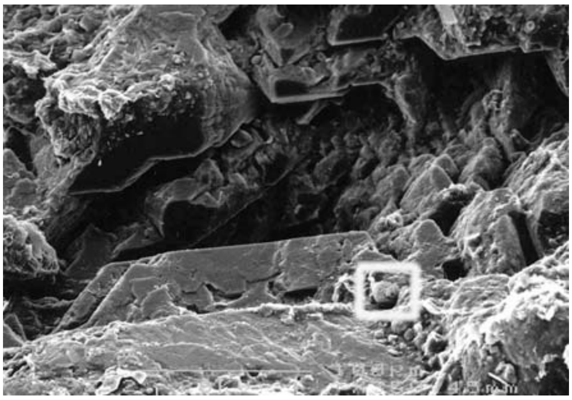

Figure 3. Oxidation of pyrite framboid (within frame) euhedral gypsum crystals.

Figure 4. Insitu gypsum crystal growth in stockpiled producing Ancholme Clay.

Of the sulfides, pyrite is by far the most widespread and commonly occurring variety. It forms under less acidic or alkaline conditions than its polymorph marcasite. It therefore tends to be marginally more stable in weathering environments and is more widespread in occurrence. Marcasite tends to be confined to calcareous sedimentary rocks of Carboniferous and Cretaceous ages, where is occurs as nodules, particularly in Chalk and it may also occur as a late-formed mineral in low-temperature mineral veins. Pyrite may be found in almost all types of geological environments from ancient rocks of igneous, metamorphic and sedimentary origin particularly lower and upper Carboniferous (Namurian and Westphalian) mudrocks and marine Mesozoic and Cenozoic sedimentary clay deposits, including Jurassic Lower to Upper Lias Clay, Kimmeridge and Ancholme Clay, Oxford Clay, Gault Clay, Weald Clay, Lambeth Beds and London Clay. It is also present in recent sediments forming under anaerobic conditions such as lakes, bogs, stagnant watercourses and estuaries.

DEGRADATION AND WEATHERING OF PYRITE

The characteristic black colour of sediments that frequently contain pyrite is due to the presence of the iron sulfides themselves associated with organic matter formed, and stable, under reducing anoxic conditions. Although pyrite is chemically stable in these conditions, it is metastable in a damp, oxidising environment. The chemical weathering of pyrite and other sulfide minerals is an oxidation reaction mechanism. that requires oxygen and water to be present It results in the formation of sulfates and eventually of iron hydroxides and their hydrates. Acid waters rich in leached environmentally toxic heavy metals are also produced. Together with sulfate rich solutions these are liable have deleterious effects on engineering materials such as concrete and steel. The acidic waters can also lead to the dissolution of associated mineral species present in the host rock, sediment or engineering structure, producing voids. The subsequent precipitation of new mineral species may produce ground heave resulting in serious damage to engineering structures. The oxidation reaction may be accelerated by bacteriological catalysts such as Thiobacillus bacteria (Temple and Delchamps, 1953). In addition, the acidic conditions generated by the oxidation provide environmental conditions that favoured the growth of sulfate reducing bacteria, the activities of which increase the rate of pyrite oxidation (Hawkins & Pinches, 1987). In the reaction sequence described below, one mole of pyrite produces one mole of iron hydroxide and two moles of sulfuric acid demonstrating generation of highly aggressive conditions.

Although pyrite oxidation may proceed both abiotically or involve biotic catalysis, natural pyrite oxidation will only occur in the presence of both water and oxygen (Silverman, 1967, Edwards et al., 1998). The free oxygen in air is necessary to oxidise the pyrite whereas the water is believed to act as a catalyst, speeding up the rate of the reaction and serving as a solvent for the products and constituent of the hydrates that tend to be formed.

The basic form of the chemical oxidation of pyrite consists of three steps. The first step involves the oxidation of pyrite by molecular oxygen producing ferrous iron and is a purely chemical reaction, under saturated conditions this can be represented as follows: $2FeS_{2\,(s)}$ (pyrite) + $2H_2O + 7O_2 \rightarrow 2Fe^{2+}$ (ferrous iron) + $4SO_4^{2-} + 4H^+_{(aq)}$.

The second step involves the oxidation of ferrous iron by molecular oxygen to ferric iron which is a strong oxidising agent as follows: $4Fe^{2+}$ (ferrous iron) + $4H^+_{(aq)} + O_2 \rightarrow 4Fe^{3+}$ (ferric iron) + $2H_2O$.

The third step consisting of further oxidation of pyrite by ferric iron which acts as an electron acceptor producing ferrous iron, sulfate anion and protons as follows: FeS_2 (pyrite) + $14Fe^{3+}$ (ferric iron) + $8H_2O \rightarrow 15Fe^{2+}$ (ferrous iron) + $2SO_4^{2-} + 16H^+_{(aq)}$.

The second step involving oxidation of ferrous iron is the rate-governing step in the process. Chemically the reaction is extremely slow particularly under acidic conditions such as those generated by the first step of the reaction, and therefore under purely chemical conditions complete pyrite oxidation will proceed at a slow rate. This accounts for the partial oxidation of pyrite evident in many museum specimens, in which the sulfuric acid produced is the main cause of damage to specimen, packaging and labels (Newman, 1998). Since museum samples are treated with bactericides, the reaction is known to be abiotic. Bacterial activity may also be inhibited in ancient marine deposits in which circulating connate waters may contain chlorine rich pore-waters that are detrimental to the survival of most microbes. Changes to these environmental conditions resulting from engineering works such as exposure, changes in groundwater conditions and flushing by rainfall or groundwater, may well result in rapid oxidation. As, generally speaking the oxidation process pyrite in damp surface environmental conditions is rapid it can be inferred that microbially catalysation is taking place.

The initial stage in the reaction is considered to be abiotic and involves oxygen as the oxidant but produces acidic conditions, and under these increasing acidic conditions (pH <4), oxidation by O_2 becomes so slow, as to be almost non-existent. Under such acidic conditions pyrite tends to be oxidised by ferric iron, which is a strong oxidising agent. The ferric iron is produced by the activities of acidophilic sulfate reducing bacteria including *Thiobacillus ferro-oxidans, Leptospirillum ferrooxidans* and *Thiobacillus thio-oxidans* (Schlegel & Jonnasch, 1986, Nordstrom & Southam, 1997 and Edwards et al., 1998). These autotrophic bacteria derive their carbon for cell generation from carbon dioxide, the absence of which prevents their survival, and therefore they tend to be found in environments exposed to surface conditions. The microbes derive energy for their metabolic process and reproduction by mediating chemical redox reactions of simple inorganic compounds such as the oxidation of ferrous to ferric iron. As well as greatly increasing the rate of pyrite oxidation the processes also contribute ferrous iron and liberates protons that raise the acidity of the solution (Andrews et al., 1997). Ferric iron is soluble only under acidic conditions (pH <4), under less acidic oxidising conditions it precipitates as insoluble ferric oxihydroxide. The oxidation reaction is also exothermic due to its positive oxidation potential and the conditions become more acidic. The increase in temperature and the rise in acidity both favour bacterial action, thus promoting further pyrite oxidation, which therefore proceeds at a rapid rate.

Although pyrite is oxidised by ferric iron in the absence of oxygen (Moses et al., 1987 and Luther, 1991), oxygen generally forms the rate determining step as it is required by the microbes as an electron acceptor in the oxidation of ferrous to ferric iron. Therefore the whole pyrite oxidation reaction is catalysed by microbial action largely by the regeneration of ferric iron. Oxidation of pyrite by ferric iron is found to be between 3-100 times faster than by oxygen (Edwards et al., 1998). Abiotic oxidation of ferrous to ferric iron is rapid in soils and rocks under pH >5 conditions, but when the pH drops to <4 it is extremely slow. Therefore, under acidic conditions the oxidation requires mediation by acidophilic chemoautotrophic iron oxidising bacteria which speed up the reaction by 5-6 orders of magnitude (Sasaki et al., 1998).

PRODUCTS OF PYRITE OXIDATION

During weathering where humidity, rather than free water, is the only source of water, pyrite is decomposed and the reaction becomes arrested with the formation of hydrated iron sulfate generally observed as efflorescent deposits ranging from rozenite ($FeSO_4$) to the more commonly found yellow, blue-green melantorite ($FeSO_4.7H_2O$), and generation of sulfuric acid, as follows: [$2FeS_{2(s)}$ (pyrite) + $7O_2 + nH_2O \rightarrow 2FeSO_4.nH_2O_{(s)}$ (ferrous sulfate salt) + $H_2SO_{4(l)}$ (sulfuric acid). These products are often seen as a green to blue green efflorescent coatings on pyrite in museum samples stored under humid conditions (Wiese et al., 1987; Newman, 1998). Such minerals are stable under the new acidic conditions and are occasionally found as pyrite pseudomorphs. Subsequent saturation or flushing of the rock or soil mass by flowing water removes these soluble minerals in solution, which may also become acidic. Such solutions may well be highly aggressive and are typified by the highly polluting discharges from flooded mines (Banks & Banks, 2001).

Under saturated conditions where pyrite is exposed to air, water and microbial agents, such as in mines, spoil heaps and engineering earthworks, the oxidation of pyrite produces an acidic environment due to production of sulfuric acid, which maintains the products as aqueous ions in solution. The acidity of the environment is a crucial factor, since the oxidation states of iron depend on pH and Eh. Ferric iron is stable under oxidising conditions, which are mildly acidic, neutral and alkali, whereas ferrous iron is stable under more reducing, acidic conditions. Generally speaking, under natural environmental pH-Eh conditions such as on exposure to the atmosphere, ferrous iron is oxidised to ferric iron accompanied by hydrolysis and precipitation out of solution as orange iron oxyhydroxide as follows: $4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_{3(S)}$ (ochre) $+8H^+_{(aq)}$ and is commonly observed as the highly insoluble orange ochre. The detrimental component of this reaction is the production of sulfuric acid, which is bio-toxic, highly corrosive to metals, concrete and rocks, and also is a strong leachant removing potentially harmful elements, including heavy metals, and releasing them into the environment.

This corrosive effect of these solutions may be eliminated or 'buffered' in the presence of certain mineral species. In the presence of carbonates particularly calcium carbonate often present in argillaceous pyrite host deposits as shell debris or limestone nodules and concretions or limestone rock deposits, neutralisation of the excess acidity occurs as the following acid-base reaction producing gypsum: $CaCO_3(s) + 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow CaSO_4.2H_2O_{(s)} + C0_{2(g)}$.

In acid mine drainage, due to the presence of ferric iron (FeIII), the reduction in acidity results in precipitation of ochre which covers any carbonate species with a relatively impervious layer preventing further acid neutralisation. But in soils and rocks exposed in engineering works where the environment provides for excessive flushing by ground- or rainwater, the discrete disseminated nature of framboidal pyrite species and distribution of calcite as shell debris tends to result in production of gypsum as shown in the previous equation.

A volume expansion results on conversion of sulfides to sulfate species during weathering. In the pyrite structure the sulfide ions are arranged in tightly packed hexagonal sheets with iron ions fixed between the sulfide sheets and the packing density is controlled by the size of the sulfide ion. In a sulfate anion, each sulfur atom is surrounded by atoms of oxygen in a tetrahedral formation and here the packing density is related to the size of the sulfate anion representing a volume increase per unit of 35% (Forster et al, 1995). Hydration of the products cases a further volume increase.

The buffering reaction with calcium carbonate produces a volume increase of around 107% over the original minerals involved and the precipitation of gypsum can exert pressures of up to 500kPa resulting in ground heave. In mass terms, the sulfuric acid produced by the oxidation of 1 mole (120g) of pyrite, will react with 2 moles of calcite (200g) producing 2 moles of calcium sulfate (272g) more commonly as the calcium sulfate dehydrate gypsum (308g). This reaction may occur at some distance from the site of hydration and oxidation resulting in a net transport of sulfur from the original location. A high content of calcium carbonate may neutralise the acid produced therefore rendering the environment unsuitable to microbes thus slowing down the rate of pyrite oxidation. From personal experience this tends to happen if $CaCO_3$ is in the range of 0.5 to 8% $CaCO_3$, although higher concentrations of calcium carbonated may be tolerated in situations where high through-flow of groundwater exist, such as in stockpiles or spoil heaps, where an acidic environment is maintained and the buffering reaction contact time is reduced by high water flow. Gypsum crystals will commonly develop in capillary zones and grow in areas of least stress such as voids, discontinuities or at groundwater discharge zones at the ground surface (see Figure 4). However, the expansive growth of gypsum crystals occurs due to the continued growth of large crystals, as surface energy requirements are lower, even if there is space for the precipitation of smaller crystals in existing void space. Once gypsum crystallises it is not easily redissolved by groundwater unless an acidic environment ensues.

In clay rich deposits, two widely formed minerals which form because of bacterial oxidation and reaction of sulfuric acid with illite are potassium jarosite ($KFe_3(SO_4)_2(OH)_6$) or its analogues, ammoniojarosite and natrojarosite and native sulfur (Pye & Miller, 1990; Bromley & Pettifer, 1997). The precipitation of jarosite involvesr a net volume increase of 114% over the volume occupied by the original mineral species.

Reaction between sulfuric acid and kaolinite may also occur forming halotrichite (Wiese et al, 1987). $Al_2Si_2O_5(OH)_4 + 2FeS_2 + 19H_2O + 7O_2 +2H^+ \rightarrow FeAl_2(SO_4)_4.22H_2O + 2SiO_2 + Fe^{2+}$.

GEOTECHNICAL AND ENGINEERING IMPLICATIONS OF SULFATE REACTIONS AND PYRITE OXIDATION

As it is recognised that sulfur minerals can give rise to acidic ground conditions, high concentrations of sulfate ions in groundwater and associated problems of degenerative attack on engineering materials and the heave of structures, a number of recommendations and guidelines for avoiding problems are available. Unfortunately, for various reasons, using the guidance does not always result in an avoidance of difficulties.

The British Standard for the testing of soils for civil engineering purposes [BS 1377, 1990] states that a pessimistic indication of the danger due to sulfate is presented by the acid-soluble sulfate determination if only calcium sulfate (gypsum) is present. This may be the case in a dry or static groundwater conditions but groundwater movement can produce long-term aggressive ground conditions. Also, much higher concentrations of sulfate, and hence more aggressive conditions, can occur under acidic conditions such as those resulting from unbuffered pyrite oxidation, CO_2, NO_2, SO_2 dissolution in rain and groundwater and areas of high organic activity. If only gypsum is present the concentration of sulfate in solution will be limited by the solubility of gypsum (1400 mg/l as SO_4 under neutral conditions) but much higher sulfate concentrations are possible under the acidic conditions or if high solubility sulfate minerals such as epsomite or mirabilite are also present. Gypsum solubility also increases in the presence of calcium carbonate or halite.

As discussed above, the oxidation of pyrite is a common cause of deterioration of the ground or construction materials hosting the pyrite. The resulting sulfate rich, acidic conditions give rise to deleterious chemical attack of construction materials, the precipitation of expansive minerals and the pollution of ground- and surface waters. If, due to the absence of buffering minerals or a high rate of groundwater flow, neutralisation of the acid is incomplete, the concentration of sulfate ions in the groundwater can become very high. Since the sulfate ions and acidity are transported away from the site of pyrite oxidation, the aggressivity is not limited by the amount of pyrite and other minerals in the materials concerned.

Thus an assessment of the risk of attack of concrete, lime/cement stabilised ground or steel buried structures and the potential for heave should also include an appraisal of the potential sources of sulfur, opportunities for buffering of acid conditions, the effects of the transport of reaction products by groundwater and the possibilities for deleterious reactions with construction materials and of the expansive precipitation of minerals. Particular cases encountered in UK geotechnical engineering are briefly discussed below, where the chemistry, in terms of the water soluble, acid soluble, and oxidisable sulfur, the carbonate carbon (as CO_2) contents, and the BRE ground aggressivity classes are as shown in Table 1.

Aggressive Acidic Environment:

The oxidation of pyrite is unlike other geochemical reactions in that it actually generates protons in the form of sulfuric acid resulting in a net acidity increase. The sulfuric acid produced is a strong corrosive agent that is commonly responsible for causing accelerated rusting and corrosion of iron and steel used in construction. Galvanised steel is particularly vulnerable to such attack, because although the zinc coating is resistant to attack, any imperfections in the coating, or exposed steel in edges cut or holes drilled after the galvanising process give rise to serious damage to the underlying steel. In the case cited by Bracegirdle et al, (1996) and Reid et al, (2001) the oxidation of pyrite in alluvial sands used as fill for embankments led to severe damage to the corrugated steel linings of culverts installed in the fill. The material was tested only for pH during construction and found to be acceptable. However subsequent tests and one test during construction indicated total potential sulfur and oxidisable sulfur contents well above the guideline values for this application. As can be seen from the low CO_2 content reported in Table 1 the buffering capacity of the material was low. Thus pyrite oxidised rapidly giving rise to sulfate rich, highly acid conditions.

Weathering of pyrite when unbuffered produces an acidic environment, which can affect the chemistry of the pore water, which was ascribed to reductions in the residual shear strength of fissile mudrocks implemented in the continued sporadic movements of the landslip at Mam Tor, near Castleton, Derbyshire, UK (Stewart & Cripps, 1983). In this case Vear and Curtis (1981) calculated that buffering of 99% of the protons produced by pyrite oxidation and hydrolysis could be attributed to dissolution of dolomite ($CaMg(CO_3)_2$) and reactions with clay minerals.

It was a significant feature of the failure in 1984 of the Carsington Dam, Derbyshire (Pye and Miller, 1990) where the engineering properties of the engineered Namurian mudstone fill were seriously compromised by rapid breakdown and concerns were raised that the oxidation would reduce the strength of the fill. Weathering of the pyritic mudrock generated sulfuric acid that resulted in the loss of up to 10% of the fill material that probably generated strains within the dam structure. Secondary sulfates were formed including jarosite and gypsum. Since the Namurian mudrocks are low in calcium carbonate content (see Table 1), the formation of jarosite suggests that buffering would have involved clay minerals, but extensive gypsum and limonite (FeO) precipitation in the limestone aggregate forming the drainage layers was considered to be impairing their function. Buried concrete structures showed evidence of acid attack, especially where they were adjacent to the limestone drainage layers. One very tragic result of pyrite oxidation was the asphyxiation of workmen probably due to the presence of carbon dioxide produced as a result of reaction between the acid and calcium carbonate. Reid et al (2005) note that the run-off from the site was highly acidic and needed to be treated before being discharged to the local watercourse.

Ground Heave:

As noted above neutralisation of acidic water by reaction with buffering minerals such as calcite and clays results in the expansive precipitation of gypsum and other minerals. Usually this will occur some distance away from areas of dissolution, particularly in areas of least stress such as bedding planes, joints or construction interfaces. It is often prevalent beneath ground supported slabs and basements of buildings, where capillary rise of water occurs in response to ground heating. Theoretically, under controlled conditions the formation of jarosite involves a 115% volume increase compared with the original volume occupied by pyrite; the formation of melanterite results in a 536% volume increase; and the formation of gypsum from the products of pyrite oxidation and calcite results in a 103% volume increase (Taylor, 1988). However, as the products are not replacing pyrite and buffering minerals in situ, precipitation of the products can result in expansion many times this value. Such reactions in mudrocks have caused heave in excess of 100mm (Penner et al, 1970; BRE 2002) for structural foundations, and heave in the order of 150mm in stabilised ground associated with highway construction (Snedker & Temporal, 1990).

Examination of an ongoing earthworks scheme in the Ancholme Clay Group, in Humberside by Czerewko & Cross (2006) revealed rapid generation of selenite crystals in stockpiled clay. Within 6 weeks of excavation, which was during a dry period with occasional seasonal downpours commencing in July 2005, surface efflorescence was observed, after 12 weeks selenite crystals up to 18mm in size were recovered. A further site visit conducted 22 weeks after stockpiling revealed selenite crystals of up to 130mm in length, both as tabular and elongate crystals found within zones of least stress (see Figure 4). Chemical testing revealed that the environment comprised a self buffering system due to the modest calcium carbonate content of the clay present as shell debris (see Table 1) and the crystals were seen to form at exposure interfaces as seen in Figure 4, the water percolating through the material tested at neutral pH. The design approach at site included for robust drainage construction including the use of limestone aggregate as drainage channel fill since dissolution was discounted. The selected drains were constructed in flexible HDPE to allow for lateral movement in the event of heave caused by selenite precipitation. Highway construction allowed for exposure and natural reaction to occur prior to final compaction and construction.

Attack on lime / cement stabilised ground and concrete materials:

In recent years pyrite oxidation has been implicated in numerous cases of chemical attack and resultant compromise in strength and serviceability of cementitious materials. Attack on ground bearing and buried concrete and stabilised ground requires a source of transient sulfates. This criterion is readily met by sulfate anion dissolution in mobile groundwater in areas of near surface pyrite oxidation often caused by exposure and changes to the groundwater conditions resulting from construction. The sulfate source is usually in the surrounding rock, soil, fill or groundwater and may occur as soluble sulfate minerals or more commonly sulfate generated by pyrite oxidation.

In the last few decades improvement of the workability and bearing characteristics of clay soils for road and building construction has seen an increase in the use of in situ stabilisation techniques avoiding the high costs of imported aggregates. The technique includes the addition of lime as slaked lime [$Ca(OH)_2$] or [CaO] or cement. Addition of lime has the effect of altering the moisture condition of the soil improving handleability and strength characteristics. Further enhancement may be made by the addition of GGBS (Granulated Ground Blastfurnace Slag) or PFA (Pulverised Fuel Ash) and cement. These additives have a rapid pozzalonic effect on the soil producing a cementitious product known as HBM (Hydraulically Bound Material) or CBM (Cement Bound Material). Since this procedure has become a more commonly used method to form capping layers in highway construction in the UK, there have been a number of cases of adverse affects caused by sulfate attack resulting from pyrite oxidation resulting in heave of the highway pavement due to formation of secondary sulfates. Documented cases include M40 near Banbury where adverse conditions were caused by pyrite oxidation of the stabilised Lower Lias Clay (Snedker & Temporal, 1990) producing 150mm of heave from a 250mm thick stabilised layer over a few months. More recently construction of the A10 Wadesmill bypass in Hertfordshire has been temporarily affected by heave caused by sulfate attack of lime stabilised capping (Parker, 2004). Cases have also been documented of foundations affected by the heave of stabilised pyritic soils (BRE, 2002).

It would appear that in the case of lime stabilised ground, treatment of the ground when it is in a dry condition can lead to subsequent heave by sulfate attack caused by post-construction increases in the availability of water, by which means pyrite oxidation reactions can be sustained.

There are two recognized forms of attack on concrete and lime / cement stabilised soils. The first type is known as the conventional form of sulfate attack and produces gypsum and ettringite. This reaction requires the presence of sulfate anions or sulfuric acid, which reacts with calcium hydroxide and hydrated tricalcium-aluminate present in the cement matrix. Initially the formation of gypsum occurs as a result of the reaction between sulfate with calcium hydroxide as follows: $Ca(OH)_2$ (cement, clay or lime) + $SO_4{}^{2+}{}_{(aq)}$ (pyrite oxidation, groundwater) + $2H_2O \leftrightarrow$ $CaSO_4.2H_2O$ (gypsum) + $2OH^-{}_{(aq)}$. This has a positive effect by increasing the strength and density of the concrete or stabilised soil as the gypsum precipitates in pore space. Once all the pore space is occupied further reaction of gypsum with hydrated calcium aluminate forms calcium sulfo-aluminate or ettringite as follows: $Ca_3Al_2O_6$ (cement or high pH degraded clay) + $3CaSO_4.2H_2O$ (gypsum) + $30H_2O_{(aq)}$ (groundwater) $\rightarrow$ $Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$ (ettringite). Ettringite is an expansive mineral containing a large amount of water in the crystal lattice. It tends to form in clumps of acicular crystals that push the soil fabric apart. This creates internal stresses within the concrete or stabilised soil mass resulting in expansion and deterioration of the structure. This has long been recognized and therefore appropriate guidelines are presented (BRE SD1, 2005) for preventative procedures during construction.

The second form of sulfate attack, referred to as the thaumasite form of sulfate attack, has been occasionally documented since the 1960s but it received more attention during the mid 80s and early 90s as identification techniques have improved (Crammond, 1985). Problems due to excessive deterioration of the buried concrete foundations of 30 year old concrete bridge structures on the M5 motorway in Gloucestershire, led to extensive investigation of this form of concrete deterioration and of the Lower Lias Clays of the area, that was used as backfill to the foundation excavations. The degradation of concrete and cement and conversion to thaumasite is a penetrative process. It causes durable cement and concrete to loose strength and eventually decompose producing a residual soft paste. The reaction requires the presence of sulfate anions in mobile groundwater and sources of hydrated calcium silicate and calcite. The latter are respectively present in cement and occasionally present as concrete aggregate it may also be present in the groundwater as the bicarbonate anion from dissolution of calcite typically present in most argillaceous deposits. The process is more prevalent where temperatures are below 15°C, as typically occurs in UK ground conditions and at the ground surface at certain seasons. It is accepted that high pH (>10.5) conditions are required for thaumasite formation, which is common in cement and concrete due to the alkali nature of their chemistry. A simplified form of the reaction to demonstrate the formation of thaumasite is as follows: $CaSiO_3.3H_2O$ (cement or unstable clay minerals at high pH) + $2Ca(OH)_2$ (cement, clay or lime) + SO_4^{2-} (pyrite oxidation, groundwater) + HCO_3^{2-} (calcite aggregate, in soil, groundwater, carbonate concrete or atmosphere) + $8H_2O$ + $3H^+{}_{(aq)} \rightarrow$ $Ca_3[Si(OH)_6](CO_3)(SO_4).12H_2O$ (thaumasite). Thaumasite contains less sulfate in its crystal structure than gypsum does, so as long as the reactants are in plentiful supply, a greater volume of thaumasite is produced.

In the case of the deterioration of the M5 bridges, the fresh Lower Lias Clay contains 1.05% total reduced sulfur, which compares with about 0.53% in the weathered fill. It is clear that the relatively high calcium carbonate content contributed to the buffering of the acid, since neutral pH measurements were recorded for the groundwater present in the fill. However only part of the sulfur present so reacted and it was concluded that only about 15% of the sulfur present reacted to form thaumasite. Thus pyrite oxidation continued even though there was a high buffering capacity for the acid, presumably because much of the calcite was contained in the clods of clay and was therefore unavailable for reaction. Similarly it is possible that the residual pyrite may not be subject to rapid oxidation for the same reason. In view of the experience with Ancholme Clay mentioned above, it seems likely that much gypsum was present in the clay by the time it was used as fill. With the oxidation of pyrite and generation of acid following backfilling, this would give rise to the sulfate rich conditions conducive to thaumasite formation.

Since sulfates come into contact with concrete and stabilised ground mainly due to transportation by groundwater, structures permanently above the water table will not tend to suffer from sulfate attack. Whereas concrete structures and stabilised ground below the water table or in contact with ground water have the potential to be attacked due to the replenishment of sulfate required for the reaction and conditions conducive for the oxidation of pyrite in stabilised ground. In conditions where due to the low permeability of soil or bedrock the groundwater flow is extremely slow, the potential for sulfate attack will be low, or at least very slow, even where sulfate contents may be high.

Where ground improvement is undertaken using lime and cement stabilisers particularly when conditions are dry it is prudent to allow chemical reaction to take place at an early stage of the process, particularly over a winter period so that ettringite or thaumasite form and any volume increase occurs prior to final ground compaction. This situation for road and foundation construction may be further improved by the provision of appropriate drainage to maintain the groundwater level below the stabilised horizon.

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Thermodynamic modelling shows at high pH conditions such as in cemetitious products, pyrite becomes unstable under oxidising conditions (Figure 5). Bromley & Pettifer, 1997 have documented observations of abiotic pyrite oxidation in concrete blocks containing pyritic aggregates, resulting in severe degradation. This was prevalent particularly when carbonation of portlandite had occurred due to interaction with atmos-pheric carbon dioxide producing calcium carbonate, as follows: $Ca(OH)_{2\ (Portlandite)} + CO_2 \rightarrow CaCO_3 + H_2O$. When carbonation of concrete occurs the pH of the pore fluids in the concrete generally drops from >12 to about 8. This mechanism may also be prevalent in lime and cement stabilised soils where pyrite is present.

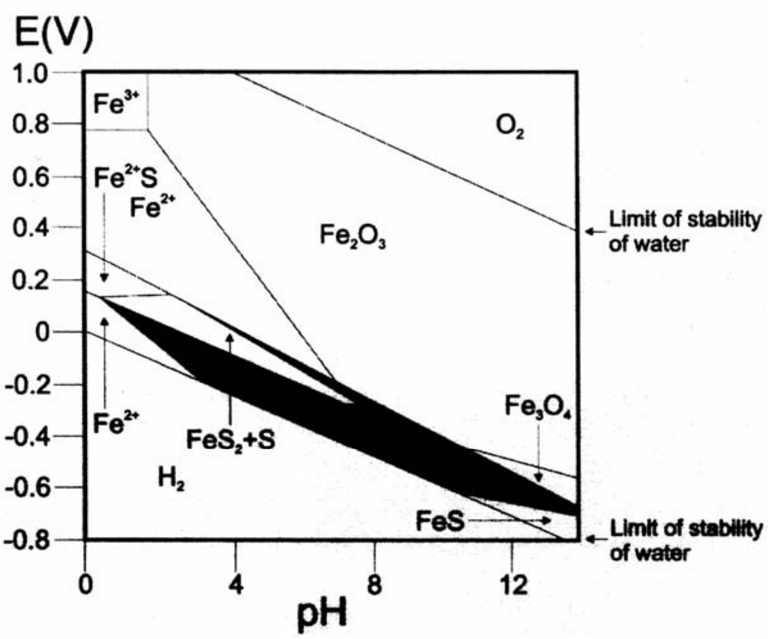

Figure 5. Stability of pyrite at 20ºC & atmospheric pressure (from Bromley & Pettifer, 1997).

ASSESSMENT PROCEDURES FOR SULFUR AGGRESSIVE GROUND

Dissolved sulfate ions in groundwater are a prime factor in chemical attack on construction material including steel, concrete and engineered ground particularly where lime or cement stabilisation techniques and selected fill have been used. Therefore appropriate characterisation of material to determine the potential for creation of an environment aggressive to engineering materials or one with a potential for ground heave, should include tests for sulfates, both water-soluble sulfate (for concrete design purposes), total sulfate as acid-soluble sulfate, total sulfur and carbonate content. Awareness of the deleterious effects of sulfates has long been recognised, which was addressed by various standards including BS 1377 (1990) and BRE SD1 (2005), which has superseded BRE Digest 363 (1996). This latter guidance proved inadequate as only sulfate test procedures were included so the potential for generation of aggressive ground conditions and the problems posed by further sulfate generation by sulfide oxidation were not considered. During the late 1990s problems with deterioration of buried concrete structures, resulting from the thaumasite form of sulfate attack, came to light on the M5 motorway in Gloucestershire [Thaumasite Expert Group, 1999] and gave rise to extensive investigations and increased awareness or the deficiencies in the guidance then in use. The laboratory tests carried out during the initial site investigation in 1964-1965 in line with the then current standards indicated that both weathered and unweathered Lower Lias Clay used as fill material adjacent to the concrete had low sulfate levels and therefore did not pose any apparent cause for concern. However, bridge strengthening work undertaken in 1998 identified serious deterioration of buried concrete foundation members due to the formation of thaumasite. This was attributed to the presence of soluble sulfates apparently resulting from the oxidation of pyrite present in Lower Lias clay fill. This was not tested for but was confirmed subsequently in tests on Lower Lias clay fill from adjacent locations [Reid et al, 2001]. At around the same time, the problems mentioned above entailing severe corrosion of buried galvanised corrugated steel culverts on the A546 road improvement scheme in Derbyshire led to a programme of investigation and research. Here local river alluvium containing pyrite was found to be the cause (Reid, 2001, 2005). The normal practice at the time involved pH determination to ascertain the suitability of material, and results indicated that the alluvium was acceptable, In addition, water-soluble sulfate content of the material was determined and proved to be low. Subsequently it was recognised that oxidation of pyrite present in the alluvium had taken place and was the cause of the aggressive ground conditions experienced. As a result, these cases were investigation by TRL and BRE and new guidance published on the assessment of aggressive ground conditions.

For structural backfill to concrete and metallic elements on highway schemes, TRL Report 447 (Reid *et al.* 2001, 2005) presents assessment procedures and limiting values for sulfur compounds including new and improved analytical procedures, and includes methods the determination of carbonate and pyrite contents. The procedures take account of sulfur present as sulfate in the material and the potential sulfate that could be generated by oxidation of reduced sulfur compounds. For all other situations relating to concrete in the ground, new guidance similar to TRL Report 447 was published in Special Digest 1 (BRE 2001, 2005).

The results of chemical analysis should be presented in terms of %S as this has the advantage of enabling comparison between the amount of sulfur present in its various forms within the material. It also allows for easier checking of suspicious values. However, in order to interpret the results in terms of potential for attack on construction materials, it is necessary to transform the sulfur content into; sulfate, either as (mg/litre SO_4) for water-soluble sulfate; (%SO_4) for acid-soluble sulfate; or (%SO_4) for TPS (see Table 8.1 in Reid *et al.* 2001, 2005). Proposed symbols, several of which are already used by BRE Special Digest 1 (BRE 2005) are used to define the design sulfate (DS) class, these include WS for water-soluble sulfate, AS for acid-soluble sulfate and TPS for total potential sulfate. Examples are presented in Table 1 of a number of the lithologies discussed in this paper also providing a comparison of inappropriate assessment of material using previous procedures based on sulfate content and current procedures, which consider the total potential sulphate content of the material, including for sulfide oxidation availability. It is also prudent to determine the carbonate content of material if ground heave is considered to pose a threat, and also to assess the potential for buffering reactions. The chemical characterisation of the ground alone does not necessarily provide sufficient information for appropriate design. Consideration of the ground model including groundwater conditions, and the effects of the proposed construction procedure and final design should also be included to allow for appropriate mitigating ground remedial measures. Appropriate advice on ground and site assessment is now provided in BRE Special Digest 1 (2005) and TRL Report 447 (2005).

Table 1. Sulfur speciation and classification of select UK lithologies implicated in producing aggressive chemical environments for engineering materials.

Material Location	**Weathering grade No tested**	**WS (%S)**	**AS (%S)**	**TS (%S)**	**OS (%S)**	**CO_2 (%)**	**SD1 WSS class**	**SD1 TPS class**
Cretaceous Weald Clay Kent	UW-SlW (n=3) W (n=3)	0.01-0.02 0.5-0.71	0.03-0.04 0.07-0.11	0.14-0.16 0.01-0.11	0.10-0.13 0-0.06	2.6 nd	DS1 DS5	DS2 DS2
Jurassic Ancholme Clay Humberside	UW (n=4) W (n=5)	0.03-0.13 0.01-0.12	0.06-0.37 0.13-0.44	0.11-1.22 0.01-0.37	0.12-1.08 0-0.08	0.32-1.25 0.04-1.11	DS1-DS3 DS1-DS3	DS2-DS5 DS1-DS3
Kimmeridge Clay Oxfordshire	UW (n=2) W (n=2)	0.01-0.03 0.17-0.19	0.05-0.21 0.98-1.08	0.31-2.35 1.16-1.43	0.21-2.26 0.18-0.41	18.7-22.5 10.2-10.5	DS1 DS3	DS3-DS5 DS5
Oxford Clay SE Midlands	UW (n=11) W (n=9)	0.01-0.06 0.03-0.22	0-0.43 0.05-1.37	0.31-1.43 0.30-1.37	0.41-1.37 0.21-0.40	11.2-15.1 3.9-16.9	DS1-DS2 DS1-DS4	DS3-DS5 DS3-DS5
Lower Lias Clay Gloucs, Wilts,	UW (n=6) W (n=5) W Fill (n=8)	0-0.18 0.08-0.18 0.01-0.17	0.04-0.31 0.11-0.92 0.02-0.63	0.73-2.30 0.2-1.50 0.16-1.17	0.63-1.99 0.09-0.63 0.11-1.11	4.8-21.6 1.6-18.6 0.9-18.8	DS1-DS3 DS2-DS3 DS1-DS3	DS4-DS5 DS2-DS5 DS2-DS5
Triassic Mercia Mudstone E. Midlands	UW (n=12) W (n=8)	0-0.38 0.12-0.44	0.03-8.5 0.02-7.4	0.02-8.5 0.02-7.4	0 0	0-6.7 0-5.8	DS1-DS4 DS3-DS5	DS1-DS5 DS1-DS5
Carboniferous Coal Msrs mudrock Yorks & Lancs	UW-SlW n=18) W-spoil (n=10) W-tailing (n=5)	0-0.02 0.02-1.2 0.02-0.18	0.01-0.04 0.03-0.32 0.03-0.20	0.48-4.35 0.25-1.35 0.08-1.22	0.44-4.33 0.22-1.04 0.05-1.02	0-5.02* 0-4.88* 0.5-2.0	DS1 DS1-DS5 DS1-DS3	DS4-DS5 DS3-DS5 DS2-DS5
Namurian Mudstone Lancashire	UW (n=7)	0-0.08	0.08-0.72	0.2-3.70	0.4-2.98	0-0.2	DS1-DS2	DS2-DS5
Recent Grey Trent Alluvium Derbyshire	UW (n=3) W (n=6)	0.05-0.18 0.07-0.45	0.04-0.19 0.10-0.51	0.31-0.93 0.09-0.52	0.24-0.74 0-0.02	0.10-0.12 0-0.26	DS2-DS3 DS2-DS5	DS3-DS5 DS2-DS4
Ferruginous Slag								
Cumbria	(n=3)	0.1-0.60	0.53-0.84	0.95-2.96	0.44-2.10	nd	DS2-DS5	DS5
Teeside	(n=9)	0.05-0.17	0.1-0.60	0.11-0.63	0.03-0.51	nd	DS2-DS3	DS2-DS4
S Yorks	(n=10)	0.01-0.04	0.02-0.4	0.39-1.35	0.28-0.95	nd	DS1-DS2	DS3-DS5
W Midlands	(n=5)	0.02-0.09	0.25-0.43	0.16-0.53	0.06-0.26	nd	DS1-DS2	DS2-DS4

*Siderite ($FeCO_3$) occurs in these deposits and the content of which has not been included.

UW – Unweathered (fresh) material; SlW – Slightly weathered; W - Weathered

CONCLUSIONS

Sulfur mineral species, especially sulfates such as gypsum and reduced sulfides such as pyrite, have been found to be widely distributed within British sediment, rock and fill materials. As such they are commonly encountered during engineering works. Although sulfate contents tend to be determined, sulfides are often ignored. In part this is due to a lack of appreciation of their importance although adequate evaluation procedures have now been made available in an attempt to remedy this situation. Sulfide minerals, in particular pyrite may rapidly oxidise once exposed to atmospheric conditions. They generate the chemical conditions necessary for the ettringite and thaumasite forms of sulfate attack, may also cause corrosion of steel and concrete and can also give rise to the expansive precipitation of minerals and the pollution of ground and surface waters.

The new procedures in TRL Report 447, together with BRE Special Digest 1, present a comprehensive framework for the testing and assessment of sulfur compounds in soils, rocks and fill materials for civil engineering purposes. The aggressivity of the materials is based on the premise that all the reduced sulfur will be oxidised, which, in most cases, is a conservative or worst case position. It is known that coarser grained pyrite is much less reactive than fine grained and amorphous forms. Further research is required to determine what controls the proportion of, and at what rate, pyrite is oxidised. The permeability of the ground and the presence of buffering minerals are obviously important considerations. For a complete avoidance of problems due to sulfur minerals, in addition to information about the amount and reactivity of pyrite, cognisance needs also to be taken of the groundwater conditions and environmental changes to be caused by the construction processes and the design itself. This requires an understanding of the processes leading to problematic situations coupled with an appreciation for the effects of construction on the materials involved. In other words a more holistic approach is required, rather than a strict adherence to published guidelines. This is particularly relevant in the case of the design of stabilised soils (CBM and HBM) and cast in situ (CFA) piles, where work is required to establish the appropriateness of the guidance in BRE SD1 (2005), which is for buried concrete, and TRL447 (2005), which is targeted at backfill for roads, to this application.

Now that procedures exist for appropriate determination of mineralogy actual published case studies are required to enable sound engineering judgement to be reached since mechanisms of reaction and deleterious results are not easily predictable or a subsequent result. Further research is required to determine the extent to which sulfur minerals weather under different environments.

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