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Sulfur species in geological materials—sources and quantification

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Abstract

Groundwaters containing dissolved sulfates and sulfuric acid can lead to chemical attack on construction materials such as steel and also concrete and cement stabilized soils forming complex hydrated calcium sulfo-aluminate species such as ettringite and thaumasite. Many factors contribute to aggressive conditions that need to be adequately determined prior to construction. The identification of acid environments is generally tested for, although in some circumstances corrosion may also take place under apparently neutral or alkali conditions. Sulfur reducing bacteria can give rise to such conditions. They thrive under acidic and aerobic conditions within the range of ambient temperatures found in the UK and where there is an availability of reduced sulfur and carbon compounds. As present methods of assessment for aggressive conditions tend to concentrate on sulfate and pH determinations, the problems posed by reduced sulfide species are not fully addressed.

This paper describes research by the TRL Limited and the University of Sheffield for the Highways Agency to develop better test methods for sulfur compounds in structural backfills which may cause problems to buried steel and concrete structures.

Keywords: Sulfur species testing; Sulfur species distribution; Thaumasite attack; Sulfate attack

1. Introduction

Recently problems with deterioration of buried concrete structures, especially road bridge foundations, resulting from the thaumasite form of sulfate attack have come to light on the M5 motorway in Gloucestershire [1]. The limited number of laboratory tests carried out to determine sulfate (SO_4^{2-}) content during the initial site investigation for the proposed motorway in 1964–1965 indicated that both weathered and unweathered Lower Lias clay had low sulfate (SO_4^{2-}) levels. The sulfate test results, presumed to be acid-soluble sulfate values, have an average range between 0.08% and 0.14% SO_4^{2-}, resulting in Class 1 classification using both the then BRS Digest 31 [2] guidelines and the later BRE Digest 363 [3] guidelines. Bridge strengthening work undertaken in 1998 identified serious deterioration of buried concrete foundation members. The thaumasite attack proceeded due to a number of favourable factors including the presence of soluble secondary sulfate minerals apparently resulting from the oxidation of pyrite present in Lower Lias clay [1]. Problems have also occurred recently with the extensive corrosion of buried galvanized steel structures on the new A564 Hatton–Hilton–Foston by-pass near Derby. The problem has arisen from the oxidation of pyrite present in the River Trent alluvium used as backfill. Limited chemical testing during extraction from the borrow pit showed a value of 0.17% acid-soluble sulfate (SO_4^{2-}) and 0.46% total sulfur although the numerous pH determinations carried out on the soils and groundwater gave values ranging between 2.8 and 10.3 with a mean value of 4.4 ($n = 66$). Recent testing [4] of fresh borrow pit material has shown the presence of between 0.41% and 1.08% pyrite. Thus the oxidation of pyrite present in the fill placed around the steel culverts producing sulfuric acid would explain the low pH values of test extracts and groundwater, which has caused the extensive corrosion [4]. As a result of this problem the Highways Agency commissioned an investigation of sulfur speciation in structural backfills led by TRL Limited, including the development of a new testing protocol and new recommendations for

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limiting values for acceptability of material as structural backfill.

Whilst it is recognised that aggressive ground conditions are associated with a wide range of factors encompassing physical, chemical and biological processes, a high proportion of occurrences have been attributed to the presence of sulfur minerals that give rise to high concentrations of (SO_4^{2-}) ions in groundwater. Table 1 shows that sulfur may occur in geological and natural construction materials in a wide variety of forms. Of these gypsum, pyrrhotite, pyrite, marcasite, barite, celestite, and organic sulfur are commonly encountered in the UK [1,4]. Certain industrial wastes such as burnt colliery shale and derived construction materials such as plasterboard, may also contain various sulfur compounds, however, this paper deals only with naturally formed sulfur minerals.

Not all the minerals listed in Table 1 are troublesome in engineering situations, although this does depend upon the particular environmental conditions. Sulfate minerals such as barite and celestite are resistant to weathering processes and they are uncommon in most geological materials, occurring mostly in areas of mineralisation. As they tend to be environmentally inert, unless groundwater conditions are unusual, they pose little threat to engineering works. Similarly, due to its hydrophobic nature organic sulfur is relatively stable in weathering environments and therefore it would not be expected to contribute to the sulfur present in most groundwater encountered, unless the organic matter is decomposed.

2. Occurrence of sulfur minerals in the UK

2.1. Reduced sulfur

Reduced sulfur species in particular are formed during the deposition of dark coloured, organic rich, mainly marine muds. The organic matter deposited within the sediment decomposes through aerobic bacterial reduction resulting in the formation of an anoxic, reducing environment tens of centimeters below the water-sediment interface. In this environment sulfate reducing bacteria convert SO_4^{2-} dissolved in the seawater to dissolved S^{2-}. This reaction also utilizes the Fe^{2+} in pore waters, liberated by bacterial reduction of sesquioxides, clay minerals and organic matter present in the sediment. The evolved H_2S gas reacts with the Fe^{2+} in solution forming metastable iron sulfides, which during diagenesis are transformed to pyrite as an authigenic mineral in these sediments. Such conditions gave rise to deposits of such minerals within the mudrock of Carboniferous age (Coal Measures) as well as various clay formations of Jurassic, Cretaceous and Tertiary age, including the Lower Lias clay, and the Tertiary age

Table 1
Sulfur mineral species that may be encountered in the UK

Mineral	Formula	Occurrence	Diagnostic features
Sulfides			
Pyrite	FeS_2	Common constituent of rock and sediments	Insoluble in non-oxidising acids such as HCl, digested using Cr(II) and conc. HCl
Marcasite	FeS_2	Found as nodules in chalk and limestone	Insoluble in non-oxidising acids such as HCl, digested using Cr(II) and conc. HCl
Pyrrhotite	FeS	Occasionally found in sediments and rocks	Soluble in hot HCl forming H_2S
Greigite[a]	Fe_3S_4	Black finely divided phase found in modern sediments. Unstable under sedimentary conditions and rapidly convert to pyrite unless formation of H_2S ceases	Soluble in hot HCl
Mackinawite[a]	$Fe_{1.05}S$	Black finely divided phase found in modern sediments. Unstable under sedimentary conditions and rapidly convert to pyrite unless H_2S formation ceases	Soluble in hot HCl
Sulfates			
Gypsum	$CaSO_4 \cdot 2H_2O$	Widespread occurrence in rock and sediments	Slightly soluble in water, HCl soluble
Anhydrite	$CaSO_4$	Associated with gypsum, forms at $T > 42$ °C	HCl soluble
Epsomite	$MgSO_4 \cdot 7H_2O$	Common in evaporite sequences	Water soluble
Mirabilite (*Glaubers salt*)	$Na_2SO_4 \cdot 10H_2O$	Common in evaporite sequences	Water soluble
Jarosite	$KFe_3(SO_4)_2(OH)_6$	Common weathering product of pyrite	HCl soluble
Barite	$BaSO_4$	Common in mining areas, also found in limestone and marl	Insoluble in acids. Determine as total S
Celestite	$SrSO_4$	Rare mineral, occasionally associated with marl	Insoluble in acids. Determine as total S
Organic sulfur	Organic(CHO)–S	Common constituent of organic material, especially ancient and recent organic deposits	Insoluble in acids. Determine as total S

[a] These species are collectively known as hydrotilite (FeS).

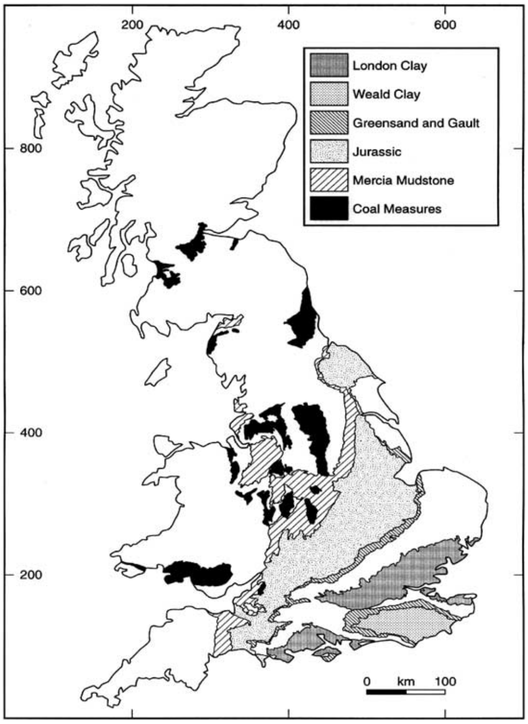

Fig. 1. Geological sedimentary formations within the UK containing dominant clay and mudrock units liable to contain sulfur compounds (excluding alluvial deposits).

London clay deposits [5,6]. The general distribution of these geological sequences in the UK is shown in Fig. 1. They may also contain up to 0.5% S in the organic material present [7].

Typically these reduced sulfur minerals may be very finely crystalline and impure, these being features that result in high reactivity in present-day weathering environments. The presence of sulfide minerals, including pyrite, can be very difficult to determine during the routine description and logging of mudrocks without the use of laboratory procedures such as reflective light microscopy and X-ray diffraction. Pyrite often occurs as framboids in which spherical masses up to tens of microns in diameter are arranged in clusters but in visual assessments of hand specimens these are not discernable as typically they are very finely divided and appear black in colour (see Fig. 2). Pyrite and pyrrhotite may be present in metamorphic rocks, such as slates and hornfelses derived from mudrocks and magmatic rocks such as basalt, granite and gabbro [8]. In this form it is usually easier to recognize these minerals as they usually occur as gold coloured cubic crystals, radiating clusters and flakes in the case of pyrite and irregular gold coloured void infills in the case of pyrrhotite. Sulfide minerals also occur in ore deposits and their derived wastes, in areas such as Wales, northern, mid- and south-western England and Scotland. Sulfates such as barite and celestite may also be present in these ores [9,10].

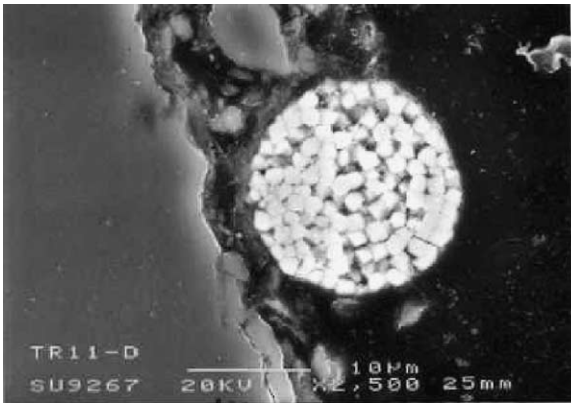

Fig. 2. Pyrite framboid example in alluvial sand (secondary electron image).

Once exposed to weathering environments, pyrite and other sulfide minerals present in the ground, excavated material or mine waste, are liable to undergo oxidation resulting from access of air, water and bacteriological catalysts such as *Thiobacillus* bacteria [11]. Sulfate bearing solutions and secondary minerals may be thus formed. Pyrite, in particular, is subject to chemical oxidation under damp, oxygenated conditions. This reaction is illustrated in Table 2. Oxidation can be greatly accelerated by the activities of acidophilic chemoautotrophic iron oxidising bacteria such as *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, *Leptospirillum ferrooxidans* etc. These autotrophic bacteria derive their carbon for cell generation from carbon dioxide, the absence of which prevents their survival. They thrive under acidic, aerobic conditions and derive their energy from the oxidation of metal ions present in reduced sulfur compounds. The microbes are capable of effectively oxidising Fe^{2+} produced in the initial stage of pyrite oxidation to Fe^{3+} which is a strong oxidising agent that leads to oxidation of further pyrite. This reaction generates more Fe^{2+} and liberates hydrogen ions which raise the acidity of the system. The oxidation reaction is exothermic and the conditions become more acidic. Both of these factors increase bacterial action thus promoting further pyrite oxidation. In calcareous rocks such as the Jurassic mudrocks of central and southern England, the sulfuric acid reacts with calcite, forming gypsum.

2.2. Sulfates

In the UK, sulfates occur mainly in the form of gypsum and anhydrite. As primary minerals these occur in evaporite sequences in deposits of Permian, Triassic (Mercia mudstone), Cretaceous (Greensand and Gault sequences) and Jurassic age [12]. Primary sulfate minerals are usually formed by the evaporation of salt-rich waters under arid conditions where rates of

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

	Saturated conditions:	
1	$\underset{\text{Pyrite}}{2FeS_{2(S)}} + 2H_2O + 7O_2 \rightarrow \underset{\text{Ferrous iron}}{2Fe^{2+}} + 4SO_4^{2-} + 4H^+_{(aq)}$	Initial oxidation of pyrite proceeds by purely chemical means, producing ferrous iron
	$\underset{\text{Ferrous iron}}{4Fe^{2+}} + 4H^+_{(aq)} + O_2 \rightarrow \underset{\text{Ferric iron}}{4Fe^{3+}} + 2H_2O$	Ferrous iron is oxidised to ferric iron by bacterial mediation
	$\underset{\text{Pyrite}}{FeS_2} + \underset{\text{Ferric iron}}{14Fe^{3+}} + 8H_2O \rightarrow \underset{\text{Ferrous iron}}{15Fe^{2+}} + 2SO_4^{2-} + 16H^+_{(aq)}$	Ferric iron is a strong oxidising agent, acts as an electron acceptor in further oxidation of pyrite
1b	$4Fe^{2+} + 10H_2O + O_2 \rightarrow \underset{\text{Ochre}}{4Fe(OH)_{3(S)}} + 8H^+_{(aq)}$	If conditions of pH ⩾ 4, i.e. flushing of the system and atmospheric exposure, results in hydrolysis and precipitation of orange ochre
	Humid conditions:	
2	$\underset{\text{Pyrite}}{2FeS_{2(s)}} + 7O_2 + xH_2O \rightarrow \underset{\text{Ferrous sulfate salt}}{2FeSO_4 \cdot nH_2O_{(s)}} + \underset{\text{Sulfuric acid}}{H_2SO_{4(l)}}$ $(x \geqslant 2,\ \text{when } x = 2,\ n = 0)$	Ferrous sulfate salts seen as efflorescent deposits, such as yellow, blue-green melantorite ($FeSO_4 \cdot 7H_2O$) and rozenite ($FeSO_4 \cdot 4H_2O$)
3	$\underset{\text{Sulfuric acid}}{H_2SO_{4(l)}} + \underset{\text{Calcite}}{CaCO_{3(S)}} + H_2O_{(l)} \rightarrow CO_{2(g)} + \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O_{(s)}}$	Calcite and limestones react with sulfuric acid forming gypsum
4 (i)	$\underset{\text{Cement}}{Ca(OH)_2} + \underset{\text{Groundwater}}{SO_4^{2+}(aq)} + 2H_2O \leftrightarrow \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O_{(s)}} + 2OH^-_{(aq)}$	Ettringite formation requires a source of sulfate, mobile groundwater, calcium hydroxide and hydrated calcium aluminate from the cement matrix. The reaction initially produces gypsum due to calcium hydroxide and sulfate ion interaction. Ettringite is unstable in acidic conditions
(ii)	$\underset{\text{Cement}}{Ca_3Al_2O_6} + \underset{\text{Gypsum}}{3CaSO_4 \cdot 2H_2O} + \underset{\text{Water}}{3OH_2O} \rightarrow \underset{\text{Ettringite}}{[Ca_3Al(OH)_6]2(SO_4)_3 \cdot 26H_2O}$	
5	$\underset{\text{Cement}}{CaSiO_3 \cdot 3H_2O} + \underset{\text{Cement}}{2Ca(OH)_2} + \underset{\text{Groundwater}}{SO_4^{2-}} + \underset{\text{Limestone}}{HCO_3^{2-}} + 8H_2O + 3H^+_{(aq)}$ $\rightarrow \underset{\text{Thaumasite}}{Ca_3[Si(OH)_6](CO_3)(SO_4) \cdot 12H_2O}$	Thaumasite formation requires a source of sulfate, groundwater, hydrated calcium silicate and carbonate phases present in concrete and a low temperature of <15 °C. Thaumasite is unstable in acidic conditions
6	$\underset{\text{Ferrous sulfate}}{12FeSO_4} + \underset{\text{Illite}}{4(KAl_2Si_3O_8(OH)_2)} + 48H_2O + 4O_2$ $\rightarrow \underset{\text{Jarosite}}{4(KFe_3(SO_4)_2(OH)_6)} + 8Al(OH)_3 + 12Si(OH)_4 + \underset{\text{Sulfuric acid}}{4H_2SO_4}$	In clay rich deposits under acidic conditions generated during pyrite weathering the oxidation products react with illite forming Jarosite

evaporation greatly exceed rainfall. Gypsum is the stable hydrated form of calcium sulfate under near surface conditions and is found as crystals (selenite), nodules, veins or fibrous beds (spar). It is a colourless or white mineral, but frequently it is stained red by the presence of iron minerals. It is very soft having a hardness of 2 on the Moh's scale of mineral hardness and therefore it is easily scratched with the fingernail (3 on Moh's scale).

If gypsum undergoes deep burial to depths exceeding 900 m it dehydrates to anhydrite, and if the deposit is subsequently uplifted, it re-hydrates in the presence of water, forming gypsum. This occurs around a depth of about 100 m [12]. Anhydrite is white or clear when pure, but more commonly is found as a pale bluish grey, red or brown rock. Anhydrite may be distinguished from gypsum by its crystal form but also it has greater density and hardness, only just being scratched with the fingernail.

Secondary sulfate minerals including gypsum, jarosite, melanterite and rozenite may form as a weathering product of sulfide minerals in clays, mudrocks and mineral veins. The sulfuric acid solution produced reacts with the calcium in calcite to form gypsum, or the clay mineral illite and K-feldspar to form jarosite. Calcite and illite are both minerals that are commonly present in the host rocks associated with sulfide oxidation.

Thus, depending on the conditions, SO_4^{2-} rich waters may be derived from either sulfate or sulfide mineral deposits. If anaerobic conditions are present, for example in stagnant waters, then contemporary sulfide minerals are liable to be formed. These immature sulfide minerals are extremely reactive in weathering environments. They may also occur in sediments, for example sand and gravel deposits derived from rocks containing such minerals. Therefore, as well as the occurrences noted above, sulfides might be present in Recent lacustrine, bog, alluvial and estuarine sediments.

3. Sulfate forms of concrete attack

The sulfate forms of attack on buried concrete require a source of sulfates dissolved in mobile groundwater. 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. Weathering of pyrite tends to be aided by construction where pyrite-bearing horizons become exposed to atmospheric conditions. In some cases lowering of the water table has been responsible for oxidation.

There are two recognized forms of attack on concrete. The first type is known as the conventional form of sulfate attack and produces gypsum and ettringite $Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 25H_2O$ as seen in Table 2. This has long been recognized and therefore appropriate guidelines are presented in BRE SD1 [13] for preventative procedures during construction. 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. This has a positive effect by increasing the strength and density of the concrete 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 which creates internal stresses within the concrete mass resulting in expansion and deterioration of the structure.

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-eighties and early nineties as identification techniques have improved. The thaumasite form of sulfate attack has been identified in cement mortars and brickwork [14] and more recently in buried concrete structures [1]. Thaumasite formation is a penetrative process that causes buried cement and concrete members, which are quite often load bearing, to loose strength and eventually disintegrate into 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 possibly present in the concrete aggregate. The process is more prevalent where temperatures below 15 °C, as typically occurs in UK ground conditions, are present. It is accepted that high pH (>10.5) conditions are required which is common in cement and concrete due to the alkali nature of their chemistry. A simplified form of the reaction is presented in Table 2 to demonstrate the formation of thaumasite.

The Thaumasite Expert Group [1] identified five factors that increase the likelihood of thaumasite formation in concrete structures. Both conventional and the thaumasite forms of sulfate attack are influenced by the permeability of the concrete and also of the surrounding fill and ground material, and also the position of the water table. Since sulfates come into contact with concrete structures mainly due to transportation by groundwater, structures permanently above the water table will not tend to suffer from sulfate attack, whereas concrete structures below the water table or in contact with groundwater have the potential to be attacked due to the replenishment of sulfate required for the reaction. 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.

4. Determination of sulfur compounds

The quantitative determination of sulfur compounds in a variety of geological materials where different mixes of species may be present within a variety of geological hosts, is a challenge to the applied analytical chemist. As mentioned previously, the recognition of the minerals in hand specimen may not be easy and, in the case of poorly consolidated, non-durable argillaceous deposits, which often contain pyrite, are not readily amenable for determination in microscope thin sections, due to difficulties with sample preparation. Alternative mineralogical and chemical methods are, however, available.

4.1. Mineralogical analysis

It is feasible to undertake semi-quantitative mineralogical analysis of many sulfur minerals in soils and rocks using XRD [15,16]. Also techniques such as scanning electron microscopy using energy dispersive X-ray analysis and backscatter secondary electron analysis [17] are used to identify the types and physical forms of minerals present such as pyrite as seen in Fig. 2. Unfortunately these procedures tend to be less accurate for quantitative determinations whereas chemical techniques are liable to be simpler and provide more accurate data.

4.2. Chemical methods

In view of the well-known problems resulting from the reaction of the hydrated silicate phases of cement with sulfate ions, it is standard practice to determine the sulfate content of soils, bedrock and ground water during civil engineering site investigations. BS 1377 [18] lays down the protocols for soil characterization in connection with civil engineering within the UK but this standard does not provide a scheme for the complete characterization of sulfur compounds. Due to the modes of occurrence of the various forms of sulfur species and their interaction with construction materials, for the purposes of analysis they may be assessed under four main categories:

- Water-soluble sulfates.
- Acid-soluble sulfates ('total' sulfates).
- Total reduced sulfur (includes pyritic sulfur).
- Total sulfur (includes organic sulfur species, especially common in coal samples).

4.2.1. Water-soluble sulfates

Procedures for the determination of water- and acid-soluble sulfates such as those presented in BS 1377 [18] tend to be a universally accepted analytical approach for the determination of these two sulfate forms. BS 1377 [18] states that if calcium sulfate is dominant or the only sulfate present in the soil, as is frequently the case, then due to its low solubility in water, total sulfate values will give a pessimistic indication of the danger due to sulfate. Therefore aqueous extractions should be conducted on samples producing acid-soluble sulfate values greater than 0.5% SO_4^{2-}. Although the solubility of calcium sulfate is relatively low (<1.4 g/L-SO_4^{2-}), in a dynamic environment large quantities can be dissolved due to groundwater replenishment resulting in continual dissolution and long-term aggressive ground conditions. In situations where Na or Mg sulfates are present their dissolution results in very aggressive ground conditions in the short-term, due to their high solubilities (Na sulfate: 240 g/l, Mg sulfate: 180 g/l). Most concrete and metal structures are buried within 5 m of the ground surface. This zone tends to be affected by groundwater flow and water influx from surface runoff and rain, so water replenishment may cause long-term corrosion due to constant dissolution of calcium sulfate. It is therefore prudent to test for both water and acid extracted sulfates.

In BS 1377 [18] sulfur is gravimetrically determined as precipitated barium sulfate that forms on the addition of barium chloride under controlled conditions to the digest solution. This procedure is useful where appreciable quantities of sulfate are present in a sample, otherwise experimental errors may be large due to weighing errors. A soil sample size of around 2 g is advised. However, to produce the recommended amount of barium sulfate from this, the sulfate content of the soil would need to be about 4% SO_4^{2-} (equivalent to almost 7% gypsum) which, for most soil samples, would be considered high. The precipitation of sulfur as a barium salt is also subject to errors and therefore test conditions, including temperature, should be rigorously standardized. Care also needs to be exercised when adding barium chloride to the digest solution to produce barium sulfate, since if it is applied too quickly excess barium chloride may precipitate. Although the solubility of barium sulfate increases when conditions become more acidic, the precipitation must be made under acidic conditions (pH 1–2, optimum, although up to pH 4 is satisfactory) to prevent the co-precipitation of barium carbonate or phosphate. Barium sulfate also tends to co-precipitate with other ions giving erroneous results [19]. In view of the difficulties associated with the gravimetric procedure it was decided to evaluate the potential of inductive coupled plasma-atomic emission spectroscopy (ICP-AES) as a substitute for this method.

4.2.2. Acid-soluble sulfates

The standard procedure for the determination of acid-soluble sulfate presented in BS 1377 [18] indicates that an acid extraction should be prepared by treatment of the sample with dilute hydrochloric acid in an open vessel. This will effectively release sulfates in gypsum, anhydrite, epsomite, mirabilite and jarosite, it also results in the partial loss of monosulfides, but does not dissolve barite and celestite. Since barite and celestite are liable to be non-reactive under most environmental conditions, the threat posed by these sulfates is accurately determined by this procedure. However, monosulfides, which are reactive under environmental conditions, are not determined by this test.

4.2.3. Total reduced sulfur

Currently no suitable procedure exists in any of the solid materials testing standards for the direct quantification of total reduced sulfur. Although BS 1377 [18] states that if the presence of sulfide is suspected then it should be quantified by an indirect method in which total sulfur is determined by a procedure presented in BS 1047 [20] and the sulfide content determined by the difference between this and acid-soluble sulfur values.

Unfortunately BS 1377 [18] is misleading as it states that digestion during acid-soluble sulfate determination destroys any sulfides present and causes H_2S gas which can be detected by smell, to be evolved. Firstly, current laboratory practices necessitates the use of fume cupboards for all digestion work, so routine detection by odour would be precluded and, although H_2S gas detection is possible by the use of lead acetate indicator paper, this would not to be a standard or recommended procedure. Secondly, the only sulfides to be destroyed during HCl digestion are monosulfide species. If monosulfide species are present then the acid-soluble sulfate content may be over-estimated as the H_2S gas tends to be oxidized by atmospheric oxygen present in the dilute hydrochloric acid solution.

An alternative procedure for the determination of pyrite in coal is presented in BS 1016 [21]. The pyritic sulfur is determined by the difference between total iron determined by nitric acid digestion and non-pyritic iron determined by hydrochloric acid digestion.

It is argued in this paper that both these methods of indirect pyrite determination may produce erroneous results, depending on the forms of sulfur present. The difference between total sulfur and acid-soluble sulfates may greatly over-estimate pyrite due to the presence of other sulfur species such as iron monosulfides (pyrrhotite, mackinawite and greigite), acid insoluble metal sulfates (barite, celestite), organic sulfur and elemental sulfur. Furthermore, nitric acid digestion may not necessarily dissolve all the pyrite leading to under-estimation although when organic matter is present a proportion will be oxidized releasing iron and leading to over-estimation of pyrite. As a number of minerals and amorphous substances present in rocks and soils contain iron, over-estimates are common [22].

4.2.4. *Total sulfur*

In the determination of total sulfur BS 1377 [18] advocates the use of the procedure presented in BS 1047 [20]. The procedure involves digestion of the sample using a nitric acid-hydrochloric acid mixture and bromine and the total sulfur is quantified by gravimetric determination of barium sulfate precipitate. As previously mentioned, the gravimetric determination of barium sulfate may be subject to error, and as such should be avoided if possible.

It is clear from the descriptions of the current recommended procedures for determination of sulfur compounds that unreliable results may be obtained. Furthermore, the techniques used are labour intensive, and therefore expensive to carry out. In fact a recent informal survey of commercial laboratories [4] revealed that they tend to employ 'in house' procedures that do not strictly conform to British Standard techniques. Laboratories claim that such practices produce equivalent results, but the different procedures used have not been subjected to published validation trials to confirm this. For a testing protocol to be accepted, not only must it produce accurate results, but it must also be convenient and inexpensive to carry out in the context of commercial testing laboratories. Therefore there is a need for standard and acceptable sulfur species test methods that can be incorporated into a testing scheme that also includes the determination of other relevant causes of corrosion, namely pH, chloride, carbonate and organic carbon contents.

5. Investigation of laboratory procedures for the determination of sulfur species

A thorough and accurate assessment of the sulfur species present in geological materials is necessary for construction purposes. Therefore it is argued that methods of determination need to be capable of distinguishing between water-soluble sulfates, acid-soluble sulfates, monosulfides, disulfides and total sulfur. Unfortunately the existing recommended test procedures may produce inaccurate results. In a study carried out by Reid et al. [4] various standard and non-standard sulfur test procedures were evaluated. The aim was to produce a suitable sulfur species testing protocol for the investigation of potential highways fill materials. Both instrumental and chemical procedures were considered but, in terms of forming the basis of routine testing procedures, chemical methods were found to be more practical and accurate. A total of 18 different test methods, listed in Table 3 were selected for evaluation, these were assessed in terms of convenience, accuracy, time to carry out the determination and requirements for equipment. It was noted that the many different testing methods tended to be based upon a limited number of specific test procedures. Some posed significant hazards in their use.

The procedures for determining water- and acid-soluble sulfate involve long established and quite routine testing procedures. Therefore the general methodology was retained but the procedures were simplified by the introduction of ICP-AES quantitative procedure to replace the traditional gravimetric determination of barium sulfate precipitate.

The procedure for determining acid-soluble sulfur may give over-estimated results if monosulfide species are present, therefore the approach was modified based on a procedure presented by Tuttle et al. [23] so enabling the separate determination of acid-soluble sulfur and monosulfide sulfur in samples.

The chemical procedures used in the determination of total sulfur tend to be quite involved and time consuming while also requiring a high degree of technical proficiency. Therefore new procedures were investigated based on the use of instrumental deterministic procedures which have the potential to improve the accuracy and limit of detection while also making the procedure more rapid and therefore useful as a general screening procedure.

There is no recommended procedure for the direct determination of reduced sulfur species, which is usually deduced indirectly as the difference between total and acid-soluble sulfur. This procedure has been shown to give inaccurate results and therefore a direct and specific procedure for the determination of reduced sulfur species was sought. Several tentative documented methods exist for the determination of pyritic sulfur [24,25] but as

Table 3
Test procedures investigated

Sulfur species	Method ID	Test method
Water-soluble sulfate	1	BS 1377 [18], together with pH determination of the sample
	2	As (1) but using ICP-AES in preference to the recommended gravimetric procedure to determine the sulfur content
Acid-soluble sulfate	3	BS 1377 [18], employing gravimetric determination of sulfur
	4	As (3) but using ICP-AES to determine the sulfur content of the digest solution
	5	BS 1016 [21] but using ICP-AES to determine the sulfur content of the digestion solution
	6	Digestion method of Keattch [38] using phosphoric and hydriodic acids
	7	Digestion method advocated by Kiba et al., [39], Zhabina and Volkov [26] and Purnell and Doolan [40], using Tin (II) and phosphoric acid under non-oxidising conditions
Acid-soluble sulfate and monosulfide	8	Modified digestion method of Tuttle et al. [23] involving reflux digestion with hydrochloric acid and tin (II) chloride under an inert atmosphere
	9	BS:EN196-2 [41] method for sulfide determination in cements
Reduced sulfur	10	Reduced sulfur (sulfide) determination by acidified Cr(II) reduction, and iodometric determination of evolved H_2S gas
	11	As (10), but using ICP-AES for the determination of evolved sulfur
	12	As method 10, but using AAS for the determination of evolved sulfur
Total sulfur	13	Total sulfur and carbon determination using a LECO CS-244 (HTC) elemental analyser
	14	Total sulfur determination using XRF (Spectro X2000) analysis of pressed powder pellets
	15	Total sulfur determination according to BS 1047 [20]. Gravimetric determination using aqua-regia and bromine digestion
	16	As (15) but using ICP-AES for the direct determination of sulfur
	17	Microwave digestion of the sample using aqua-regia in pressurized PTFE reaction vessels and direct sulfur quantification using ICP-AES
	18	Modified version of Eschka fusion based on BS 1016 [42], and ASTM: D2492-90 [43]. Sulfur quantified using ICP-AES

these tend to be difficult procedures or may involve hazardous reagents they are unsuited to a routine testing environment. A procedure was proposed by Zhabina and Volkov [26] for the determination of various sulfur species in marine sediments and rocks, which involves pyrite determination using chromium reduction in a reducing atmosphere. The procedure was rigorously evaluated for use in sulfur isotope investigations [23,27] and proved very successful. In addition it proved to be a reliable procedure for the quantification of pyrite in mudrock samples for engineering classification purposes [28]. The method is specific to reduced sulfur species such as monosulfides, disulfides and elemental sulfur. If elemental sulfur or monosulfide species are present they can be determined separately and a correction applied to obtain a value for pyrite. Although elemental sulfur is very uncommon, monosulfide species may be present and these are determined together with acid-soluble sulfur in the proposed procedure.

6. Evaluation of the testing procedures

The procedures investigated for the determination of various sulfur species were evaluated based on the time taken to perform each analysis, ease of performance, repeatability, accuracy and level of safety. The findings are presented in Table 4. Although the determinations were carried out in batches, the time involved per test is presented to allow for comparison and costing. The ease of performance is scored qualitatively out of 5, where 1/5 is a very difficult procedure and 5/5 is a straightforward procedure, assuming existing familiarity with the method. Most of the procedures involved the prior preparation of test reagents. This tends to be neither time consuming nor very complicated but where it is a comment is presented in Table 4. The results obtained using the methods evaluated in this paper on a range of geological samples are presented in Table 5. The results obtained using the new procedures were compared against results obtained using the existing British Standard [18] procedures in terms of their relative mean deviation, the results are presented in Table 6. For many of the samples where sulfur contents are very low, slight differences in results produced large statistical variations although these differences would not affect categorization for design purposes. The new procedures involved in tests 8 (acid-soluble sulfate), 11 (reduced sulfur) and 17 (total sulfur) were also evaluated for accuracy and repeatability using standards prepared from analytical grade reagents. The results are presented

Table 4
Evaluation of the test procedures selected for the study

Test method	Time per determination	Ease of procedure	Comments
Water-soluble sulfates		(1 hard → 5 easy)	
BS 1377: Gravimetric	$18\frac{1}{2}$ h (2 h technician time)	4/5	Care required with gravimetric analysis. The time involved for testing involves sample agitation, only 2 h of technician time is involved
BS 1377: ICP- AES	$16\frac{3}{4}$ h (2 h technician time)	5/5	Require specialist equipment. The time involved for testing involves sample agitation, only 2 h of technician time is involved
Acid-soluble sulfates			
BS 1377: Grav	$3\frac{1}{2}$ h	3/5	Time consuming, laborious procedure may involve error due to lapse of concentration
BS 1377: ICP-AES	$1\frac{1}{2}$ h	4/5	Requires specialist equipment
BS 1016: ICP-AES	1 h	5/5	Requires specialist equipment
Keattch [38]	$1\frac{1}{2}$ h	2/5	Preparation of test reagents is time consuming, and pre-treatment is required if organic matter is present
Kiba et al. [39]	$1\frac{1}{4}$ h	1/5	Preparation of test reagents is time consuming, and equipment is difficult to assemble
Acid-soluble monosulfides			
Combined SO_4/S^{2-}	1 h	5/5	Requires specialist equipment
BS EN 196-2 [41]	1 h	4/5	Colour change in titration is too gradual
Disulfide determination			
Cr(II): Titration	$2\frac{1}{4}$ h	4/5	No dilution required and sharp titration end point
Cr(II): ICP-AES	$2\frac{1}{4}$ h	4/5	Requires specialist equipment
Cr(II): AAS	$2\frac{1}{4}$ h	4/5	Requires specialist equipment
Total sulfur determination			
LECO analyser	1/2 h	5/5	Require specialist equipment
XRF analysis	1 h	3/5	Require specialist equipment
BS 1047: Gravimetric	8 h	2/5	Time consuming, laborious procedure may involve error due to lapse of concentration and many test stages
BS 1047: ICP-AES	$4\frac{1}{2}$ h	3/5	Requires specialist equipment
Microwave digest	2 h	4/5	Requires specialist equipment
Eschka: ICP-AES	$2\frac{1}{2}$ h	4/5	Requires specialist equipment

in Table 7 along with the calculated (actual) compositions.

6.1. Water-soluble sulfate determination

Since it is recommended in BS 1377 [18] that the quantity of sample to use should generate a precipitate of barium sulfate weighing about 0.2 g, and since the sulfate quantity is not known at the outset repeat tests are sometimes needed to obtain good results and this is time consuming. Comparison of the results in Table 5 for water-soluble sulfate determinations reveals little difference between methods 1 and 2, except in two cases where values appear to be slightly higher for method 2. There is a possible lack of sensitivity with the gravimetric determination of sulfur for these samples in which sulfate contents are low leading to the incomplete precipitation of barium sulfate. On the other hand, with method 2, ICP-AES is capable of accurate detection of sulfur concentrations as low as a few mg/l, the procedure is also less tedious and more rapid to perform, as seen in Table 4.

6.2. Combined acid-soluble sulfate and monosulfide determination

The results in Table 5 indicate that methods 4–7 produce similar results, whereas with method 3, which involves gravimetric determination of sulfur, the results tend to be lower in most cases. Comparing the results between the proposed acid-soluble sulfur procedure (method 5) and the British Standard acid-soluble sulfur procedure (method 3), it is apparent that both procedures have produced similar results although in a few cases the results obtained by method 3 are lower. The differences between the results do not appear to be associated with the presence or absence of other sulfur species, and therefore it seems likely that they are due to a lack of sensitivity of method 3. Confidence in method 8 is provided by data in Table 6, which shows good comparability between the analysis of prepared standard mixtures and their actual sulfur contents. The results in Table 4 show that for method 4 where direct determination using ICP-AES was used, the testing time was drastically reduced. Methods 6 and 7 were both found to

Table 5
Sulfur speciation results for samples using standard (italics), proposed (bold) and other evaluated testing procedure

Determination	Water-soluble sulfate %S		Total/acid-soluble sulfate %S					Monosulfide %S		Pyrite/disulfide %S				Total sulfur %S						Org. S% S
Method	*1*	**2**	*3*	4	**5**	6	7	**8**	9	*Difference* 15 − 3	10	**11**	12	13	14	15	16	**17**	18	Difference 17 − 5 − (11 + 8)
Sample and sample description																				
TR1—Carboniferous mudstone	*0*	**0**	*0.01*	0.01	**0.01**	ND	ND	**0**	0	−0.01	0.10	**0.10**	0.10	0.04	0.03	*0*	0.05	**0.08**	0.09	0
TR2—Permian magnesium limestone	*0*	**0**	*0.05*	0.21	**0.20**	0.20	0.19	**0**	0	−0.01	0	**0.05**	0.08	0.03	0.04	*0.04*	0.26	**0.25**	0.26	0
TR3—Reworked Kimmeridge clay	*0.01*	**0.01**	*0.16*	0.23	**0.21**	0.22	0.21	**0**	ND	−0.11	0.21	**0.21**	ND	0.06	0.05	*0.05*	0.30	**0.31**	0.31	0
TR3B—Reworked Kimmeridge clay	*0.12*	**0.19**	*0.83*	1.24	**1.08**	1.17	1.07	**0**	0	*0.55*	0.41	**0.41**	0.49	1.56	0.76	*1.38*	1.32	**1.39**	1.43	0
TR4—Mercia mudstone	*0*	**0**	*0*	0.08	**0.06**	0.07	0.07	**0.13**	0.10	*0.06*	0.04	**0.04**	ND	0.04	0.03	*0.06*	0.10	**0.17**	0.17	0
TR5—Glacial till, with coal fragments	*0*	**0.01**	*0*	0.02	**0.02**	ND	ND	**0**	ND	*0.32*	0	**0**	0	0.11	0.10	*0.32*	0.45	**0.11**	0.11	0.09
TR6—Lower Lias clay	*0*	**0**	*0.04*	0.05	**0.04**	ND	ND	**0.18**	0	*0.68*	0.52	**0.52**	0.50	0.09	0.54	*0.72*	0.66	**0.73**	0.73	0
TR7—Slate	*0*	**0**	*0.02*	0	**0.01**	ND	ND	**0.15**	0.1	*0.05*	0.18	**0.18**	0.16	0.03	0.01	*0.07*	0.16	**0.31**	0.34	0
TR8—Pyritic slate	*0.01*	**0.01**	*0.03*	0.01	**0.02**	ND	ND	**0.32**	0	*2.47*	2.54	**2.54**	2.52	3.19	0.79	*2.50*	2.01	**2.97**	2.97	0.09
TR9—Jurassic Oolitic limestone	*0*	**0**	*0.03*	0.38	**0.37**	0.37	0.36	**0**	ND	*0.27*	0	**0**	0	0.06	0.04	*0.30*	0.43	**0.37**	0.37	0
TR10—Slate	*0*	**0**	*0.06*	0.06	**0.07**	ND	ND	**0.04**	0	−0.06	0.01	**0.01**	ND	0.10	0.04	*0*	0.09	**0.14**	0.14	0.02
TR11D—Alluvial sand with some gravel	*0.05*	**0.07**	*0.02*	0.07	**0.07**	ND	ND	**0**	0	*0.24*	0.22		ND	ND	ND	*0.26*	0.31	**0.31**	0.31	0.31

ND = not determined.

Table 6
Difference in results between proposed methods ad existing BS methods

Sample	Sulfur speciation	WSS-S% [1:2]	ASS-S% [3:5]	TS-S% [15:17]
		RMD %	RMD %	RMD %
TR1—Carboniferous mudstone		0	0	ND
TR2—Permian Magnesium limestone	Traces of gypsum	0	60	72.4
TR3—Reworked Kimmeridge clay	Traces of gypsum	0	13.5	72.2
TR3B—Reworked Kimmeridge clay	Gypsum, traces of pyrite	22.6	13.1	0.36
TR4—Mercia mudstone	Traces of gypsum	0	ND	47.8
TR5—Glacial till, with coal fragments		ND	ND	48.8
TR6—Lower Lias clay	Gypsum and pyrite	0	0	0.69
TR7—Slate		0	33	63.1
TR8—Slate	Pyrite	0	20	8.6
TR9—Jurassic Oolitic limestone	Traces of gypsum	0	85	10.44
TR10—Slate		0	7.7	ND
TR11D—Alluvial sand with gravel	Pyrite	16.7	55.5	8.77

WSS: water-soluble sulfur, ASS: acid-soluble sulfur, TS: total sulfur, RMD%: relative mean deviation, ND: no relevant sulfur species determined by existing method.

Table 7
Determination of accuracy and repeatability of the proposed test procedures

Method	Form of sulfur	Calculated S%	Three no analyses S%	Average S%	*s* (%)	sr (%)
8	Acid soluble	4.287	4.173/4.162/4.195	4.177	0.136	3.18
		2.536	2.629/2.586/2.561	2.592	0.077	3.02
11	Pyrite	2.39	2.33/2.34/2.35	2.34	0.062	2.60
		0.123	0.112/0.120/0.117	0.116	0.009	7.41
		5.48	5.39/5.43/5.40	5.41	0.092	1.68
		2.56	2.50/2.42/2.46	2.46	0.13	5.03
17	Total	3.73	3.56/3.61/3.67	3.61	0.15	4.10

s: standard deviation, sr: coefficient of variance.

be difficult procedures. A considerable amount of time was spent preparing the required test reagents, therefore they prove not to be suitable as routine testing procedures.

The procedures in BS 1377 [18] (methods 3 and 4), and BS 1016 [21] (method 5) for the analysis of coal and coke involve similar chemical procedures, except that reflux digestion is used for method 5.

Method 5 proved to be an effective technique for determining the acid-soluble sulfate content. The modification producing method 8 enables acid-soluble sulfate with monosulfide determinations to be made. Method 9 proved to be practically unsuitable for monosulfide determination. It proved to be a little more difficult to perform in the preliminary investigation since the colour change during titration proved to be too insensitive to render it suitably accurate.

Determination directly by ICP-AES proved to be much more accurate than the traditional gravimetric procedure involving barium sulfate precipitation. With technological improvements in ICP-AES instrumentation, the technique has become more sensitive for the direct determination of sulfur. This instrumental technique is currently routine in most chemical testing laboratories, and therefore can be utilized for the direct quantification of sulfate in water and acid extractions. Due to its sensitivity the technique is especially suited where concentrations of extracted sulfur are low. However great care has to be exercised over the dilution procedure for samples with higher concentrations of sulfur.

6.3. Reduced sulfur (pyrite) determination

The acidified chromium reduction procedure involved in method 10, proved to be straightforward and very successful. Initially copper sulfate solution was used as the trapping medium for the evolved H_2S gas as recommended by Raiswell et al. [29]. This proved not to be very sensitive and improvement was obtained by the use instead of nitric acid acidified copper nitrate solution for which the iodometric titration proved to be drop sensitive. Iodometric titration and ICP-AES were equally successful for determining the sulfur concentration. However, when compared against the results obtained by difference of total and acid-soluble sulfate agreement tends to be poor. It is thought that this results from the lack of sensitivity of method 15, for total sulfur determination. In the case of sample TR5 it is possible that this is due to the presence of organic sulfur but this does not apply in the case of sample TR8, where monosulfide sulfur was also present. The results presented in Table 7 indicate that a high degree of accuracy was obtained using method 11 on a range of standards, therefore giving confidence in the procedure.

6.4. Total sulfur

In preliminary tests, methods 15 and 16 were found to be insensitive to small quantities of sulfur due to analytical errors. In addition, many procedural stages involved and the determinations also proved time consuming. This is evident from the results presented in Table 5 where it can be seen that most of the values are lower than those obtained using the other methods. This did not apply to sample TR5, which is devoid of pyrite. The procedure used in method 15, which is based on BS 1047 [20] proved to be a lengthy procedure. This was improved upon by the use of ICP-AES for the direct determination of sulfur in the digestion extract as seen in method 16. Method 17, involving microwave digestion, was easy to perform and method 18 involving Eschka fusion was reasonably easy to perform although it involved the use of potentially hazardous chemicals that again may prove to be unsuitable in routine testing procedures. These two procedures are also seen to give extremely comparable results. Table 7 indicates a high degree of agreement between method 17 and the known contents for the standards. Any errors introduced at the gravimetric determination stage of method 18 due to the co-precipitation of sodium salts, were eliminated by the use of ICP-AES, however the methods were not as straightforward as the high-temperature combustion (HTC) procedure involving a LECO CS-244 analyser in method 13. It has been reported by Sparks [30] that the older HTC type of analysers are not quite as accurate as wet chemical methods and this would appear to have been the case here. Subsequent models of automated HTC analysers that use infra red cells for the quantification of total sulfur have been found to be in good agreement with wet chemistry procedures [4,31] and warrant further investigation. Calibration of the equipment needs to be carried out using suitable geological standards over the expected range of sulfur values to validate the accuracy of the analytical results. Although XRF analysis [32], method 14, is a convenient and rapid method it may lack accuracy since standards used for calibration tend to be from rocks lower in sulfur than those commonly analysed and those containing sulfide species are few due to the instability of sulfides under atmospheric conditions.

7. Proposed analytical protocol for sulfur species in geological material

The findings of the research show that the five stage analytical procedure described below and presented in Reid et al. [4] will allow the determination for engineering applications, to a high degree of accuracy and repeatability, of the sulfur compounds common in most geological materials. Sample pH, carbonate, organic carbon and chloride ions should also be determined in a total characterization and evaluation of the risk of chemical attack on construction material. The data in Table 7 for analyses of the standards prepared using analytical grade chemicals provide confidence that the methods advocated produce accurate and repeatable results.

7.1. Test 1: Water-soluble sulfur, method 2

BS 1377: 1990 [18] any water-soluble sulfate and sulfide is taken into solution using a 2:1 water to soil extraction with the determination of soluble sulfur using ICP-AES. Such sulfate is very reactive in engineering situations.

7.2. Test 2: Acid-soluble sulfur, method 8

Reflux digestion using 5 N hydrochloric acid with the determination of acid-soluble sulfur using ICP-AES. The hydrochloric acid solution is prepared as a de-aired solution to avoid any evolved H_2S gas being oxidised to SO_4^{2-} and therefore leading to over-estimation of the acid-soluble sulfate content. This would arise if monosulfide species were present but their determination was not required.

7.3. Test 3: Total reduced sulfur determination, method 11 preferable (method 10 acceptable)

Acidified chromium (II) reduction in a reducing atmosphere with trapping of evolved H_2S gas is used to quantify the presence of reduced sulfide species. The test determines disulfides such as pyrite, monosulfides and elemental sulfur. The use of ICP-AES to indirectly quantify sulfur content is the preferred procedure, but if the required instrumentation is not available, iodometric titration is acceptable. As shown by this investigation, both methods provide reliable results.

7.4. Test 4: Total sulfur, methods 17 and 13

Microwave digestion using reverse aqua-regia in which sulfur containing species are broken down releasing the sulfur, which is determined in solution by ICP-AES.

In addition to the proposed microwave digestion procedure the automated HTC method using equipment fitted with infra-red cells for direct determination of sulfur is also recommended.

The determination of total sulfur is not critical for most engineering applications but it may be useful in knowing the quantity of non-reactive sulfur, since organic sulfur may be gradually released into the environment during natural degradation of the material or more rapidly under acidic conditions. Such a determination may be useful for soils intended to support plant life, such as some fills. However, the determination provides a very useful check on the results for the various forms of sulfur. Furthermore, as these two test procedures are relatively inexpensive and simple to carry out they can be used to form the basis of a screening procedure to identify samples with sulfur contents that would warrant determination of the speciation of sulfur compounds using the proposed methods.

7.5. Test 5: Monosulfide sulfur, method 8

To determine the presence and quantity of suspected monosulfide minerals (i.e. pyrrhotite) the experimental procedure for test 2 is slightly modified to allow for the collection of evolved H_2S gas produced as a result of the acid digestion of monosulfide species under a reducing atmosphere.

These species are slowly oxidisable under atmospheric conditions including natural groundwater and are more rapidly oxidised under acidic conditions with the potential to produce aggressive ground conditions.

8. Practical considerations, comments and conclusions

Analysing the specific sulfur species in samples gives a clearer picture of the distribution of sulfur species and a more accurate assessment of the samples in terms of potential for sulfate production. Table 5 provides a comparison of test results for a suite of samples using the current British Standard procedures and the proposed testing procedures. It is apparent that the total sulfur determination by the standard method lacks sensitivity, which gives rise to negative values for pyrite in some instances. In most cases the standard method for total sulfur determination gives an under-estimate of the total content.

The established British Standard procedures for the determination of total sulfates and total sulfur tend to be slow procedures involving many stages, which may be prone to errors. The main disadvantage of these current procedures is the use of gravimetric determination of precipitated barium sulfate. The quantitative gravimetric determination stage is time consuming and unreliable. Anecdotal evidence indicates that commercial testing laboratories do not employ these methods. Instead a variety of ‘in house’ methods are used but this is apparently without carrying out rigorous cross-testing to ensure an adequate degree of agreement of the results with those of the standard methods.

The use of ICP-AES to quantify directly the sulfur in the water or acid extractions replaces the use of the gravimetric procedure in the suggested test methods. The modified procedures are simple to perform, less time consuming and sensitive to low sulfur concentrations.

Reduced sulfide species such as pyrite, which are commonly found in geological materials, are not directly determined under the British Standard testing procedures but are estimated indirectly by the difference in measured total sulfate and total sulfur. This remains the case with the recently revised version of BRE Special Digest 1 [13]. The presence of monosulfide and organic sulfur are not considered and this may generate inaccurate results.

Total sulfur determinations recommended by the British Standard methods are lengthy procedures prone to operational mistakes and require a high level of laboratory skill. Total sulfur determinations by microwave digestion or using HTC sulfur analysers are recommended, but a strict regime of rigorous calibration of the equipment needs to be maintained. These two procedures involve the use of what are fast becoming routine pieces of laboratory equipment and therefore readily available in most laboratories.

The recommended more sensitive techniques, for example ICP-AES, should be used for the quantitative determination of sulfur in the form of sulfates, mono- and disulfides. It should be noted that it is preferable to use ICP-AES rather than atomic absorption spectrometry (AAS) since ICP-AES has a working range up to an order of magnitude greater than that of AAS, so less sample dilution is required. Older AAS equipment may be incapable of analysing sulfur directly, and may be less sensitive than ICP-AES for many other elements. Since ICP-AES is now one of the most widely used techniques for analytical analysis, its use is preferred and recommended.

The sulfur species content of a sample is unique to when it was determined; therefore sample history including handling, transportation, processing and storage conditions should be carefully controlled and details of it recorded. Notable differences may be detected in sulfur species test results and pH of the samples depending on storage conditions and time between sampling and testing. It is recommended that samples should be stored in air-tight containers, at 0–4 °C to minimize reaction during storage and tested within one month of sampling. Alternatively, and for longer-term storage, samples may be dried and then stored in an oxygen-free environment, under vacuum, or in a desiccator. The effects of storage conditions of samples have also been investigated as gypsum and pyrite may undergo degradation during short-term storage under atmospheric conditions [33–36]. These findings are presented in a separate paper [37].

A valid interpretation of test results depends on a clear understanding of the limitations of the data and the way these can be affected by the sampling procedures and analytical techniques used. The chemical process liable to affect the results obtained must also be appreciated. It is rarely advisable to attempt detailed sulfate and sulfide determinations on samples with very small total sulfur contents, as errors in individual determinations may be larger than the total sulfur content.

Protocols for assessing the results of sulfur speciation tests in terms of potential attack on construction materials are presented in Reid et al. [4] for highways structures and BRE Special Digest 1 [13] for buried concrete structures.

Further work is required to provide a more accurate means of assessing the amounts of sulfate liable to be generated from sulfide bearing rocks and soils in different situations such as backfill, structural fill and in situ ground. The rate of pyrite oxidation is affected by the supply of oxygen and water and by the removal of reaction products. As the reactions tend to be mediated by bacteria, the conditions for microbial growth are also important. Research into the form and occurrence of sulfide minerals and the changes in texture, chemistry and permeability of the host soil or rock would improve the understanding and assist in the design of groundworks. This further research would provide data for assessing the potential for sulfide oxidation and rates under particular environmental conditions that are subject to change during and after construction work.

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