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The distribution and evaluation of sulfur species in geological materials and manmade fills

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Abstract

Groundwaters containing acidity and/or dissolved sulfate species are a primary factor in the attack on concrete and other construction materials. In the case of concrete, attack may be prevented by the use of suitably resistant concrete, eliminating sources of acidity and/or sulfate ions or by protecting the concrete structure from the offending solutions. Official guidelines, which have recently been modified to take account of the possible formation of sulfate and acidity after construction, are provided for the design of concrete structures to be placed in potentially aggressive situations. Limiting values for sulfates and other chemical species are also given for highway, road and bridge structures, but recent problems involving buried galvanised steel structures have highlighted the need for revised procedures to be put in place. Potential sources of aggressive solutions include the ground surrounding the structure and the construction materials, including fills, situated proximally to the structure.

Unfortunately the current British Standard testing procedures are unsuitable for the purpose of assessing the potential aggressive nature of the ground and construction materials, hence risk assessments prove inadequate. This paper considers potential sources of ground acidity and sulfate rich solutions. Attention is given to suitable testing procedures for the evaluation of sulfur species in geological and construction materials. Particular attention is given to limiting values appropriate to the use of buried steel that forms part of highway, road and bridge structures.

Keywords: Sulfur species evaluation; Pyrite; Sulfate; Assessment for structural backfills

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1. Introduction

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 sulfate ions and/or acidity in groundwater. As indicated in Table 1, sulfur may occur in geological and natural construction materials in a wide variety of forms of which gypsum, pyrrhotite, pyrite, marcasite, barytes and organic sulfur are commonly encountered in the UK.

Not all the sulfur minerals are troublesome in engineering situations, although this does depend upon the particular environmental conditions. Mineral sulfates such as barytes are uncommon in most geological materials, occurring mostly in areas of mineralisation. Also, unless groundwater conditions are unusual they pose little risk to engineering works. Similarly, organic sulfur is relatively stable in weathering environments and therefore would not be expected to contribute to the sulfur present in groundwaters.Recently problems with deterioration of buried concrete structures, 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 during the initial site investigation in 1964–1965 indicated that both weathered and unweathered Lower Lias Clay used as fill material adjacent to the concrete had low sulfate levels. However bridge strengthening work undertaken in 1998 identified serious deterioration of buried concrete foundation members due to the formation of thaumasite. Among the predisposing factors, this was attributed to the presence of soluble sulfates apparently resulting from the oxidation of pyrite present in Lower Lias clay fill.

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Table 1
Various sulfur mineral species found in the UK

Form and [Valency]	Mineral	Formula	Occurrence	Diagnostic features
Monosulfide—S^{2-} [−2]	Greigite	Fe_3S_4	Black finely divided phase found in modern sediments, unstable under sedimentary conditions	Soluble in HCl
	Mackinawite (collective name)	$Fe_{1.05}S$		
	Hydrotilite	FeS		
	Pyrrhotite	FeS	Occasionally found in sediments and rocks. Soluble in HCl.	
Disulfides—S_2^{2-} [−1]	Pyrite	FeS_2	Common constituent of rock and sediments	Insoluble in HCl, digest using acidified Cr(II)
	Marcasite	FeS_2	Found as nodules in chalk and limestone	Insoluble in HCl, digest using acidified Cr(II)
Sulfates—SO_4^{2-} [+6]	Gypsum	$CaSO_4 \cdot 2H_2O$	Widespread occurrence in rock and sediments	Slightly soluble in water, HCl soluble (solubility 1.4 g/l as SO_4)
	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 (solubility 216 g/l as SO_4)
	Mirabilite (Glaubers salt)	$Na_2SO_4 \cdot 10H_2O$	Common in evaporite sequences	Water-soluble (solubility 288 g/l as SO_4)
	Jarosite	$KFe_3(OH)_6(SO_4)_2$	Common weathering product of pyrite	HCl soluble
	Alunite	$KAl_3(OH)_6(SO_4)_2$	Common weathering product of pyrite and clay	Insoluble in HCl. Determined as total S
	Alum	$KAl(SO_4)_2 \cdot 12H_2O$	Common weathering product of pyritic mudstones	Water-soluble
	Alunogen	$Al_2(SO_4)_8 \cdot 18H_2O$	Forms in ore and coal piles associated with pyrite and melanterite	Water-soluble
	Melanterite	$FeSO_4 \cdot 7H_2O$	Oxidation product of pyrite and pyrrhotite	Water-soluble
	Rozenite	$FeSO_4 \cdot 4H_2O$	Oxidation product of pyrite and pyrrhotite	Water-soluble
	Szomolnokite	$FeSO_4 \cdot H_2O$	Oxidation product of pyrite and pyrrhotite	Water-soluble
	Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	Oxidation product of pyrite found in coal	Water-soluble
	Barytes	$BaSO_4$	Common in mining areas, also found in limestone and marl	Insoluble in HCl. Determined as total S
	Celestine	$SrSO_4$	Rare mineral, occasionally associated with marl	Insoluble in HCl. Determined as total S
Elemental sulfur—S [0]		S	Rare, found at volcanic sites and in evaporites	Insoluble in HCl, digest using acidified Cr(II)
Organic sulfur—S [0]		(CHO–S)	Covalently bound, common constituent of organic matter	Insoluble in HCl. Determined as total S

This was not tested for but was confirmed subsequently in tests on Lower Lias clay fill from adjacent locations [2].

Problems have also occurred recently with the extensive corrosion of buried galvanised steel structures on the new A564 Hatton–Hilton–Foston by-pass near Derby [3]. The problem was attributed to the oxidation of pyrite present in the River Trent alluvium used as backfill. The process produced sulfuric acid that was responsible for the extensive corrosion. As a result of this problem the Highways Agency commissioned an investigation of sulfur speciation in structural backfills. The project was led by TRL Limited and included the development of a new testing protocol for characterising sulfur bearing materials and made new recommendations for limiting values for acceptability of material as fill in highway road and bridge structures.

2. Formation and occurrence of sulfur minerals

Sulfur is the ninth most abundant element in the earth's crust. It may occur in various forms, as a gas, such as sulfur dioxide, in aqueous form such as the sulfate ion or as a solid. As Table 1 shows, in solid form sulfur tends to occur as native sulfur, sulfate minerals, of which gypsum is the most common, and as sulfide minerals of which pyrite is the most common and widespread.

Sulfates occur mainly as gypsum and anhydrite associated with marine sedimentary limestone and mudstone deposits. In seawater there is on average 3.5% dissolved material, of which the bulk is sodium chloride and about 4% is calcium sulfate [4]. Gypsum is the stable hydrated form of calcium sulfate under near surface conditions. If gypsum undergoes deep burial to depths exceeding 900 m it dehydrates to anhydrite. With subsequent uplift, it re-hydrates in the presence of water to form gypsum at around a depth of about 100 m [5].

Primary sulfates are also formed by the evaporation of salt rich waters in coastal settings and inland lakes under arid conditions, in which rates of evaporation greatly exceeded rainfall. Besides gypsum and anhydrite, epsomite, which is a very soluble sulfate (see Table 1) may also occur in evaporite deposits, although it is more common in present-day arid conditions [6]. Non-marine saline lakes commonly have initial compositions that differ from seawater and these deposits may contain exotic sulfates such as borax and mirabilite [6]. Secondary sulfate minerals including gypsum, jarosite and melanterite may form as a weathering product of sulfide minerals such as pyrite.

Reduced sulfur species, in particular pyrite, may form under either low- or high-temperature conditions. High temperature forms occur in, or are associated with igneous and metamorphic rocks. Pyrite may also be formed at low temperatures in sediments, including Recent deposits. It is particularly associated with anaerobic conditions that occur within stagnant water-courses, 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 below the water–sediment interface. Under these conditions sulfate reducing bacteria convert dissolved sulfates into hydrogen sulfide gas that reacts with the ferric iron present in solution forming metastable iron sulfides, which transform to pyrite as an authigenic mineral in these sediments. Such conditions gave rise to framboidal pyrite. As shown in Fig. 1, this consists of many individual octahedral crystallites, <1–5 μm in size that form into an ordered spherical mass between 20 and 50 μm across. Due to their great collective surface area such pyrite framboids are very reactive in oxygenated and humid weathering environments.

Deep burial and geothermal heating of pyrite bearing sediments 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 sediment to a metasediment. 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.

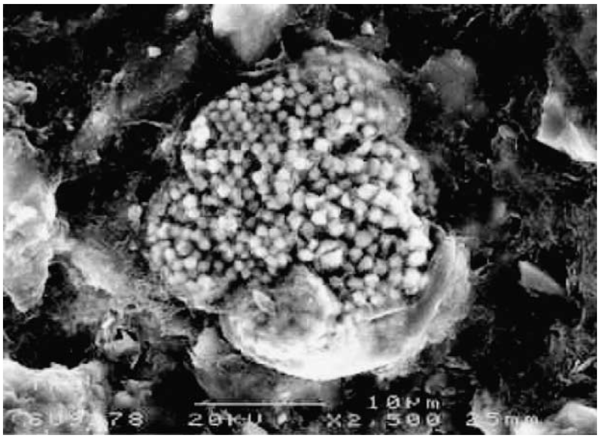

Fig. 1. Pyrite polyframboid (Lower Lias Clay).

Pyrite may also occur in sediments, for example sand and gravel deposits derived from rocks containing pyrite. Therefore, as well as the occurrences noted above, sulfides might be present in Recent lacustrine, bog, alluvial and estuarine sediments. An example of pyrite distribution within British sedimentary formations is presented in Table 2.

3. Sources of soil and groundwater sulfate

Sulfate in groundwater may be derived by dissolution of sulfate minerals or the oxidation of sulfide minerals. The British Standard for the testing of soils for civil engineering purposes [7] states that a pessimistic indication of the danger due to sulfate is presented by the acid-soluble sulfate (AS) determination if only calcium sulfate (gypsum) is present. This may be the case in a static environment but groundwater movement can produce long-term aggressive ground conditions. However, much higher concentrations of sulfate, and hence more aggressive conditions, can occur under acidic conditions. Such conditions can arise as a consequence of the infiltration of rainwater or as a consequence of the oxidation of sulfide minerals, especially pyrite. If only gypsum is present the concentration of sulfate in solution will be limited by the solubility of gypsum (see Table 1) but much higher sulfate concentrations are possible if high solubility sulfate minerals such as epsomite or mirabilite are also present. Gypsum solubility is also increased by the presence of calcium carbonate or halite [4].

Pyrite is a common, although minor constituent of many geological deposits, especially of those of an argillaceous nature (see Table 2), such as clays, mudrocks and metamudrocks. It can also occur in recent and ancient sand deposits [3]. When exposed to an oxidising,

Table 2
The distribution of pyrite in formations of sedimentary origin within the UK

Geological age	Formation or rock type	Sample localities	Pyrite (%)	References
Holocene	River alluvium and terrace gravel	Hampshire	0.4–0.9	[24]
	River alluvium and terrace gravel	Derbyshire and S. Lancs	0–1.08	[3]
Palaeogene	London Clay	London Basin and Hants	2.6–3.7	[17,23]
	London Clay	Kent	0–4	[17]
	Harwich formation—sand	N. Kent	0	[3]
	Lambeth formation—sand	London	0.33–2.41	[16]
	Lambeth formation—mottled clay	Hampshire	<0.1	[3]
	Lambeth formation—shelly clay	N. Kent	2.03–12.94	[3]
	Lambeth formation—clayey lignite	N. Kent	19.2	[3]
Cretaceous	Gault Clay	S. England	0.7–1.0	[17]
	Sandgate Beds	SE England	0.5–0.9	[21]
	Fullers Earth	Surrey	0.5	[17]
Jurassic	Kimmeridge Clay	Dorset	4	[17]
	Kimmeridge Clay	Oxfordshire	0.4–0.8	[3]
	Oxford Clay	Oxon Cambs Wilts	3–5	[3,17]
	Oxford Clay	E. and S. England	5–15	[17]
	Fullers Earth	Somerset	3	[17]
	Whitby Shale	Teesside	3–17	[3,17]
	Upper Lias Clay	Northants	3–5	[17]
	Lower Lias Clay	Gloucs, Lincs	1–8	[3,21]
Triassic	Westbury formation	S. Glamorgan	4–6	[17]
	Mercia mudstone	Nottinghamshire	0–0.78	[3]
Permian	Marl slate	Durham	<4	[17]
	Magnesium limestone	S. Yorks	0.1	[3]
Carboniferous	Namurian mudstone	Derbyshire and Lancs	0–6	[3,17,22]
	Culm Measures	Devon	2.4	[20]
	Limestone mudrock	Yorkshire and Derbyshire	0.2–10	[3,17]
	Coal Measures mudrock	England	0.7–1.4	[17]
	Coal Measures—claystone	UK	0.1–6.9	[22]
	Coal Measures—mudstone	UK	0.2–8.4	[22]
	Coal Measures—siltstone	UK	0.9–2.3	[22]
	Colliery Spoil	UK	0–12	[17–19]
Devonian	Metamudrock and slate	Devon and Cornwall	0–4.3	[22]
Silurian	Mudrock and metamudrock	Mid and SW Wales	0.1–3.3	[22]
Ordovician	Metamudrock and slate	N. and E. Wales	0.4–7.1	[22]
Cambrian	Slate	N. Wales	0.5–5.4	[22]

humid environment, it rapidly oxidises to intermediate ferric sulfosalts and end products consisting of ferric oxyhydroxide with aqueous sulfate anions. Due to the liberation of protons, acidic conditions are produced. The reactions are illustrated in Fig. 2.

As explained in [2] the process may proceed either abiotically or biotically. The involvement of microbial catalysts can increase the rate of oxidation by many orders of magnitude. In either case the acidity may be neutralised by reaction with ground or construction materials. If calcite is present, this will be taken into solution and gypsum may be precipitated. In the case of mudrocks in which the amount of carbonate is insufficient to neutralise the acid, reactions take place with illite to produce jarosite. If neutralisation of the acid is incomplete, the concentration of sulfate ions in the groundwater can become very high. The attack of construction materials and structures depends on the acidity and sulfate anions being transported to these locations away from the source where pyrite oxidation is taking place. Rapid movement of the reaction products may give insufficient opportunity for neutralisation to take place even if suitable minerals are present in the flow path. Thus an assessment of the risk of attack of concrete or steel buried structures should also include an appraisal of the effects of the movement of groundwater.

4. Quantitative determination of sulfur species

Although it is feasible to undertake the quantitative determination of sulfur species by mineralogical methods such as X-ray diffraction, chemical techniques are liable to be simpler and more accurate to carry out.

Reaction		
	Saturated conditions:	
1	$\underset{\text{Pyrite}}{\mathbf{2FeS_{2(s)}}} \mathbf{+ 2H_2O + 7O_2 \rightarrow} \underset{\text{Ferrous iron}}{\mathbf{2Fe^{2+}}} \mathbf{+ 4SO_4^{2-} + 4H^+_{(aq)}}$	-Initial oxidation of pyrite proceeds by purely chemical means, producing ferrous iron.
	$\underset{\text{Ferrous iron}}{\mathbf{4Fe^{2+}}} \mathbf{+ 4H^+_{(aq)} + O_2 \rightarrow} \underset{\text{Ferric iron}}{\mathbf{4Fe^{3+}}} \mathbf{+ 2H_2O}$	-Ferrous iron is oxidised to ferric iron by bacterial mediation.
	$\underset{\text{Pyrite}}{\mathbf{FeS_2}} \mathbf{+} \underset{\text{Ferric iron}}{\mathbf{14Fe^{3+}}} \mathbf{+ 8H_2O \rightarrow} \underset{\text{Ferrous iron}}{\mathbf{15Fe^{2+}}} \mathbf{+ 2SO_4^{2-} + 16H^+_{(aq)}}$	-Ferric iron is a strong oxidising agent, acts as an electron acceptor in further oxidation of pyrite.
1-b	$\mathbf{4Fe^{2+} + 10H_2O + O_2 \rightarrow} \underset{\text{Ochre}}{\mathbf{4Fe(OH)_{3\,(S)}}} \mathbf{+8H^+_{(aq)}}$	-If conditions of pH ≥ 4, i.e. flushing of the system & atmospheric exposure, results in hydrolysis and precipitation of orange ochre.
	Humid conditions:	
2	$\underset{\text{Pyrite}}{\mathbf{2FeS_{2(s)}}} \mathbf{+ 7O_2 + x.H_2O \rightarrow} \underset{\text{Ferrous sulfate salt}}{\mathbf{2FeSO_4.nH_2O_{(s)}}} \mathbf{+} \underset{\text{Sulfuric acid}}{\mathbf{H_2SO_{4\,(l)}}}$ (x ≥2, when x = 2, n = 0)	-Ferrous sulfate salts seen as efflorescent deposits, such as yellow, blue-green melantorite ($FeSO_4.7H_2O$).
3	$\underset{\text{Sulfuric acid}}{\mathbf{H_2SO_{4(l)}}} + \underset{\text{Calcite}}{CaCO_{3(s)}} + H_2O_{(l)} \rightarrow CO_{2(g)} + \underset{\text{Gypsum}}{CaSO_4.2H_20_{(s)}}$	-Calcite and limestones react with sulfuric acid forming gypsum
4	$\underset{\text{Ferrous sulfate}}{\mathbf{12FeSO_4}} + 4\underset{\text{Illite}}{(KAl_2Si_3O_8(OH)_2)} + 48H_2O + 4O_2$ $\rightarrow 4\underset{\text{Jarosite}}{(KFe_3(SO_4)_2(OH)_6)} + 8Al(OH)_3 + 12Si(OH)_4 + \underset{\text{Sulfuric acid}}{4H_2SO_4}$	-In clay rich deposits under acidic conditions generated during pyrite weathering the oxidation products react with illite forming Jarosite.

Fig. 2. Simplified equations showing the natural weathering reactions of pyrite and the formation of various reaction products.

However, because sulfur compounds may occur in a variety of natural materials where different combinations of species may be present, the use of a multi-staged approach is required. Existing well established test methods for water-soluble, acid-soluble and total sulfur are presented in British Standards [7–9]. Recent research [3] has highlighted a number of practical limitations with these procedures. In addition there is no existing standard procedure for the direct determination of reduced sulfur species such as the monosulfide pyrrhotite and disulfide pyrite. As the potential for the generation of acidic and high sulfate conditions can arise due to the oxidation of sulfides, it is important that a method be specified for sulfide.

Discussions with personnel in chemical testing houses and experience of commissioning the chemical characterisation of geological materials by Halcrow Ltd (Mike Floyd, personal communication) revealed considerable confusion in the industry concerning the chemical determination of sulfide minerals. In addition to this the British Standards methods for the determination of water and acid soluble sulfate specify the use of barium chloride and gravimetry for the determination of the amount of sulfate in solution. Although, these methods do provide a means of analysis, there are a number of sources of error. Recent advances in the analysis of elements in solution by the use of inductive coupled plasma–atomic emission spectrometry (ICP–AES) provides a more convenient and more accurate means of quantifying the sulfate in solution. Discussions with personnel in a number of chemical testing houses revealed the general use of such equipment for the end point determination in the analysis of sulfate rather than use of the methods specified in British Standards, it being argued that such ‘in house’ methods provides equivalent results. It was also revealed that the ‘in house’ methods differ from each other giving rise to the possibility that different results will be obtained from different testing houses. Therefore, the methods described below were validated by carrying out parallel tests on a range of materials using the British Standard specified methods [3]. It is argued here that all determinations of sulfur compounds in soils, rocks and construction materials should be carried out using the following methods. They are simpler and more accurate than the British Standard methods and universal adoption of the same methods will eliminate any variation caused by differences in approach by different testing houses.

In view of the forms of sulfur potentially present in geological material it is suggested that a five-stage analytical procedure should be used for full characterisation of the material. In order to provide a full evaluation of the risk of attack of construction material, the proposed protocol also includes the determination of sample pH, carbonate, organic carbon and chloride ions. Depending upon the natural of the material, it may not be necessary to carry out all the procedures described. For routine analysis to assess the risk of attack on construction materials, the water-soluble, acid-soluble and total sulfur tests should be carried out.

Test no. 1: water-soluble sulfur (WSS) and pH determination. The extraction procedure is as per BS 1377: 1990 where any soluble sulfate and sulfide is taken into solution using a 2:1 water to soil extraction. The soluble sulfur in the extract is determined using ICP–AES. Water-soluble sulfate minerals species are very reactive in engineering situations.

Test no. 2: acid-soluble sulfur (ASS). Rapid reflux digestion of the sample using 5N hydrochloric acid with the determination of the total ASS present in the extract using ICP–AES. The procedure determines all sulfate species that are potentially available under environmental conditions. Certain inert sulfate species that pose no threat to construction materials such as celestine and barytes are not determined.

Test no. 3: total reduced sulfur (TRS). Reduced sulfur species including all mono-, disulfides and elemental sulfur are digested using acidified chromium (II) reduction in a reducing atmosphere. The evolved hydrogen sulfide gas generated by their breakdown is trapped and used to quantify the presence of reduced sulfide species by means of ICP–AES or iodometric titration.

Test no. 4: total sulfur (TS). Two procedures are recommended for the determination of TS content.

1. Microwave digestion of the sample using reverse aqua regia in which sulfur containing species are broken down releasing the sulfur into solution which is determined using ICP–AES.
2. The use of new automated high temperature combustion analysers installed with infra-red cells for direct determination of sulfur is also recommended. The instruments must be regularly calibrated using standards with sulfur covering the working range of the samples contained in a similar matrix to that of the samples.

The determination of TS involves relatively inexpensive and rapid procedures and is useful for initial sample characterisation and as a screening procedure.

Test no. 5: monosulfide sulfur (MS). Monosulfide species such as pyrrhotite are relatively uncommon, although if present they are slowly soluble in natural ground water and become more soluble under acidic conditions resulting in very aggressive ground conditions. They may be determined by slightly modifying the experimental procedure for test no. 2 allowing for the collection of evolved hydrogen sulfide gas produced by acid digestion of monosulfides in a reducing atmosphere. Monosulfides are included in the tests for total reduced sulfur and TS.

Full details of the test methods are given in TRL Report 447 [3]. Test nos. 1, 2 and 4 are recommended for routine use by commercial laboratories and for assessment of the potential to attack construction materials. Test no. 3 shows considerable promise, but requires further work to be suitable for use as a routine test. Test No. 5 is appropriate in special circumstances. Test nos. 1, 2 and 4 provide up to date standard methods, which should replace the variety of in-house methods currently in use.

The test results for the various sulfur species are expressed as S percentage, and are converted to a sulfate value using standard factors before use in structural fill or concrete design classification systems. Thus WSS is converted to WS and ASS to AS. The relations between the various sulfur species is summarised in Table 3. The oxidisable sulfides (OS), which are a product of the oxidation of reduced sulfur species such as pyrite, is calculated as the difference between TS minus ASS, expressed as sulfate. To determine the suitability of a material as backfill to concrete, the total potential sulfate (TPS) is also calculated from the TS content [3,10]. Assessment procedures are described below.

5. Distribution of sulfur species within UK geological and fill materials

Table 4 presents the results of quantitative sulfur speciation tests on a variety of geological materials. This testing was carried out as a part of the validation procedure for the sulfur species testing protocol by Reid et al. [3]. It can be seen that the majority of materials

Table 3
Relations between forms of sulfur and symbols used in BRE Special Digest 1 and TRL Report 447

Parameter	Units	Test no.	Conversion factor	Symbol
Water-soluble sulfur	% S	1	–	WSS
Acid-soluble sulfur	% S	2	–	ASS
Total reduced sulfur	% S	3	–	TRS
Total sulfur	% S	4	–	TS
Monosulfide sulfur	% S	5	–	MS
Water-soluble sulfate	g/l SO_4	–	15×WSS	WS
Acid-soluble sulfate	% SO_4	–	3×ASS	AS
Total potential sulfate	% SO_4	–	3×TS	TPS
Oxidisable sulfides	% SO_4	–	TPS – AS	OS

Notes: WS can also be as % SO_4. The conversion factor is then WS (% SO_4) = 3×WSS. OS can also be determined from TRS. The conversion factor is OS = 3×TRS checks that can be employed on sulfur species include the following: TS $\geqslant$ ASS + TRS; ASS $\geqslant$ WSS; TRS $\geqslant$ MS; TPS $\geqslant$ AS.

Table 4
Site survey of sulfur species in fill and potential fill material within the UK

Material	Sample locality	No. tested	WSS (%S)	ASS (%S)	MS (%S)	TRS (%S)	TS (%S)
Potential or intended fill material							
Cambrian slate	Penhryn Quarry, N. Wales	3	0	0–0.02	0–0.32	0.33–2.86	0.34–2.97
Devonian slate	Dolebole Quarry, Devon	1	0	0.07	0.04	0.05	0.14
Coal Measures mudrock	S. Yorkshire	1	0	0.01	0	0.10	0.09
Permian magnesium limestone	S. Yorkshire	1	0	0.02	0	0.05	0.26
Mercia Mudstone	Nottinghamshire	2	0–0.12	0.06–7.42	0–0.13	0.17–0.42	0.17–8.27
Lower Lias Clay—fresh	Gloucestershire	6	0–0.18	0.04–0.31	0–0.26	0.66–2.22	0.73–2.30
Lower Lias Clay—weathered	Gloucestershire	7	0.08–0.18	0.09–0.92	0–0.12	0.02–0.35	0.18–1.35
Whitby Alum shale	Whitby, Teeside	1	0.03	0.05	0.17	2.26	2.35
Oxford Clay	Wiltshire	1	0.14	0.27	0.11	1.14	1.37
Kimmeridge Clay	Oxfordshire	2	0.01–0.19	0.21–1.08	0	0.21–0.41	0.31–1.43
Jurassic Oolitic limestone	Cotswolds	1	0	0.37	0	0	0.37
Lambeth formation—shelly clay and lignite	Kent	3	0.08–0.18	0.14–0.19	0	1.09–10.28	1.29–16.06
Lambeth Formation—mottled clay	Reading, Berkshire	3	0	0.02–0.03	N/D	0–0.05	0.02–0.04
Harwich formation—sand	Kent	1	0	0.02	0	0	0.02
London Clay—weathered	Slough	2	0.08	0.08–0.09	N/D	0.23–0.27	0.36
Alluvial sand and gravel—fresh/(orange)	Derbyshire and Gt. London	5	0–0.01	0.01–0.09	0	0	0.01–0.08
Alluvial sand and gravel—fresh/(grey)	Derbyshire and S. Lancs	4	0.02–0.25	0.04–0.12	0	0.1–0.58	0.19–0.60
Alluvial sand and gravel—weathered (grey)	Derbyshire	6		0.10–0.51	0	0–0.02	0.09–0.52
Glacial Till	Glasgow and S. Lancs	2	0–0.01	0.02–0.04	0	0–0.17	0.11–0.22
Pink Granite	Shap, Cumbria	2	0	0.01–0.03	N/D	0.15–0.17	0.14–0.15
Basic Ironmaking Slag	Workington, Cumbria	3	0.10–0.34	0.53–0.84	0.15–0.31	0.41–2.10	0.95–2.96
Sampled backfills							
Carboniferous Namurian mudrock	Gt. Manchester	1		0.08	0.01	0.03	0.09
Carboniferous Coal Measures mudrock	Swansea, S. Wales	1		0.08	0.03	0.20	0.29
Lower Lias Clay	Gloucestershire	15	0.01–0.18	0.02–0.63	0–0.13	0.06–0.99	0.16–1.17
Chalk, clay and silt	Lincolnshire	3	0–0.01	0.03–0.12	0	0–0.01	0.04–0.18
Glacial Till	S. Lancs	1	0.01	0.05	0	0	0.04
Basic volcanic rock	Bala, Mid Wales	2	0–0.01	0.02	0.01–0.02	0.02–0.12	0.04–0.12
Schist	Achnasheen, Scotland	1	0	0.11	0	0	0.10

analysed contain significant proportions of sulfur, especially in the reduced (pyrite) form.

Primary sulfates are 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 [5,11]. These deposits 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.

Primary sulfates minerals, including gypsum, anhydrite and epsomite and less commonly borax and mirabilite are also present in evaporite deposits of Permian and Triassic age. These were formed in inland drainage basins under arid climatic conditions. Epsomite and other high solubility sulfates tend to be leached out of near-surface natural rocks and soils, although they may be encountered at below the zone affected by surface weathering. Again secondary sulfates such as gypsum may be precipitated in this zone.

As indicated in Table 4 primary sulfide minerals, especially pyrite occurs in both ancient marine and Recent alluvial deposits. As it is also present in metamorphic and igneous rocks, it has a wider geological distribution than primary sulfate deposits. As pyrite is unstable in weathering environments, usually it is present only within fresh or slightly weathered horizons. As construction often involves excavation or lowering of groundwater levels, even if such materials remain in situ, they can be exposed to weathering conditions as a result of engineering works [12]. This potential source of sulfate and acidity needs to given proper attention in site investigations.

Secondary sulfates are liable to be present in the weathered horizons (2–8 m below the ground surface) of formations given in Table 2 that contain primary sulfide minerals. 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 (~2–3 m) and at the base of the weathered zone [5,13]. 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 have developed. Further details of the occurrence of sulfates is given by [1,5,12].

6. Assessment procedures for structural fills

For structural backfill to concrete and metallic elements on highway schemes, TRL Report 447 [3] gives assessment procedures and limiting values for sulfur compounds. 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. The present guidance in the Specification for Highways Works (SHW) [14] only takes account of sulfur present as sulfate. The limiting values are summarised in Table 5. For all other situations relating to concrete in the ground, the procedures in Special Digest 1 [10] should be used.

Water-soluble sulfate. In the SHW, a limiting value of 1.9 g/l SO_3 is given for the water-soluble sulfate content of backfill to concrete, cement-bound material, other cementitious materials or stabilised capping. The same limiting values apply to any fill placed within 500 mm of such materials. This limiting value has been retained, but has been translated to SO_4, which is the correct chemical formula for sulfate and is the form used by BRE [10]. The limiting value becomes 2.3 g/l SO_4. For backfill to metallic elements such as corrugated steel buried culverts, reinforced earth elements and anchored earth elements, or any fill placed within 500 mm of such materials, the limiting values are 0.25 g/l SO_3 for galvanised steel elements and 0.5 g/l SO_3 for stainless steel elements. These have been retained but translated to SO_4 to give limiting values of 0.3 and 0.6 g/l SO_4, respectively.

Oxidisable sulfides. The sulfate that can be generated from reduced sulfur compounds can be estimated by converting the TS content to sulfate. This figure is known as the total potential sulfate (TPS) and is used in BRE Special Digest 1 [10] as a measure of the aggressive potential of pyritic ground. This is a conservative estimate, as it includes unreactive forms of sulfur such as barytes and organic sulfur. A limiting value of 0.6% SO_4 is given for backfill to concrete. A more accurate figure for the sulfate that could be generated is given by the oxidisable sulfides content (OS), which is the difference between TS and AS, expressed as sulfate. The limiting values are 0.46% SO_4 for backfill to concrete and 0.06% and 0.12% SO_4 for backfill to galvanised and stainless steel respectively.

Oxidisable sulfides can also be determined directly from the total reduced sulfur test (test no. 3). This method requires further development to be suitable for routine commercial use, but offers considerable potential for accurate, single step determination of reduced sulfur. The difference method using TS and AS suffers from the problem that any number derived from two other numbers will have a greater error than the individual determinations. However, the accuracy and precision of the new test methods is much better than that of the old British Standards methods [7,8], so the estimate of reduced sulfur is correspondingly much better. The AS and TS methods (test nos. 2 and 4) are also rapid, suitable for automation and relatively cheap.

The limiting values for reduced sulfur compounds have been chosen to ensure that attack on construction materials will not occur. However, the limiting values only take account of the total amount of reduced sulfur and do not allow consideration of factors such as grain size, mineralogy and access to air and water that will determine the actual amount of oxidation in any given situation. As a result, the limiting values for OS and TPS are conservative, and may exclude materials that have performed satisfactorily as structural backfills. Examples would include materials where pyrite is present as large cubic crystals, visible to the naked eye, which

Table 5
Limiting values for structural backfills

Parameter	Units	Within 500 mm of concrete or CBM (Clause 601.13)[1]	Within 500 mm of metallic elements (Clause 601.14)[2]	
			Galvanised	Stainless steel
WS	g/l SO_4	2.3	0.3	0.6
OS	% SO_4	0.46	0.06	0.12
TPS	% SO_4	0.6	N/A	N/A

N/A: Not applicable.

would oxidise very slowly because of their low specific surface area, and materials with unreactive sulfates such as barytes present as cement or vein infill. Where this occurs, enquiries should be made as to whether there is any history of corrosion problems with the material, and detailed chemical and mineralogical testing should be carried out using the new test methods. It is suggested that the use of the material as structural backfill may be permitted if it can be established that:

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

A number of amendments to the SHW and to various sections of the Design Manual for Roads and Bridges [15] are suggested in TRL Report 447 [3] to implement the new assessment procedures. Also, the opportunity has been taken to change all references to sulfate from SO_3 to SO_4.

Corrosion of buried galvanised corrugated steel structures occurred on the A564 Hatton–Hilton–Foston road improvements [3]. Samples of the fresh alluvium that have been tested were found to contain between 0.22 and 0.58% S as TRS (0.41 and 1.08% pyrite). The oxidation of this quantity of pyrite generated sufficiently aggressive ground conditions that buried steel structures were corroded. The values of TRS equate to between 0.66% and 1.74% oxidisable sulfides (OS) as SO_4. These values are well in excess of the proposed limiting values for backfill to corrugated steel buried culverts given in Table 5. The new test procedures would therefore have identified that the materials were unsuitable for structural backfill.

The investigation of thaumasite affected structures on the M5 motorway and the A40 trunk road in Gloucestershire [2] revealed that unweathered Lower Lias Clay contains an average of 1.06% S as TRS (1.97% pyrite) and the backfill clay contained an average of 0.59% S as TRS (1.10% pyrite), compared with 0.09% S as TRS in the weathered clay. Therefore rapid oxidation of around 0.47% S (0.87% pyrite) was sufficient to generate the sulfate involved in the thaumasite reaction. In view of the TS in the fresh Lower Lias Clay, the material would give a total potential sulfate of 3.2% as SO_4, which would exceed the limiting value of 0.6% for TPS given in Table 5 for backfill to concrete.

7. Conclusion

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 but the problem is compounded by the present lack of adequate evaluation procedures. 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, and may also cause corrosion of steel and concrete.

The presently recommended testing procedure for sulfates has been superceded resulting in the use of modified procedures that differ between testing houses. New stardardised procedures are required which address sulfide minerals as well as sulfates. The protocols described in this paper underlie the effective assessment of the suitability of ground materials as fills to concrete and buried steel structures. The new test methods and assessment 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. Further research on topics such as the rate of oxidation of pyrite is ongoing.

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