Sulfate specification for structural backfills

Prepared for Quality Services, Highways Agency

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TRL Report TRL447 (Updated)

First Published as TRL447 2001
Updated as TRL447 (Updated) 2005
ISSN 0968-4107
ISBN 1-84608-436-9

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Executive Summary

Problems have been experienced on recent highway schemes with corrosion of galvanised, corrugated steel buried structures (CSBS) due to chemical reactions from structural backfill. The corrosion has been attributed to the presence of sulfates and sulfides in the selected fill, which were not detected under current testing requirements. More recently, problems have arisen due to the thaumasite form of sulfate attack on buried concrete in bridge foundations. A review by TRL (Unpublished Project Report PR/CE/169/96) indicated that improvements could be made in the identification and assessment of sulfur compounds in the current Specification for Highway Works (MCHW1) and related documents. The present project was undertaken to develop appropriate test methods for sulfur compounds in structural backfills, to determine appropriate limiting values for the various sulfur compounds and to prepare modifications to MCHW1 and related documents.

This is the final project report and contains the proposed test methods, limiting values for sulfate generated by oxidation of reduced sulfur and modifications to the relevant sections of the MCHW and DMRB.

The existing MCHW and DMRB require improvement in respect of testing for sulfur compounds in structural backfills. They only consider water-soluble sulfate and do not allow for oxidation of reduced sulfur compounds such as pyrite. Recent examples have shown how oxidation of pyrite can lead to corrosion of corrugated steel buried culverts and the thaumasite form of sulfate attack on buried concrete.

Existing test methods for sulfate and total sulfur suffer from a number of limitations, and there is no existing standard for reduced sulfur species such as pyrite. New test methods have been developed building on the existing methodology and using advances in analytical techniques, to allow better characterisation of sulfur compounds in rocks, soils and fill materials. Five tests have been developed:

Test No. 1: Water-soluble sulfur (WSS)

Test No. 2: Acid-soluble sulfur (ASS)

Test No. 3: Total reduced sulfur (TRS)

Test No. 4: Total sulfur (TS)

Test No. 5: Monosulfide sulfur (MS)

Full details of the test methods are given in Appendix C. 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 requires further work and Test No. 5 is appropriate in special circumstances.

The relative abundance of sulfur compounds in samples can change considerably during storage if conditions are not correct, due to oxidation of reduced sulfur species. Experiments with storage of samples under different conditions indicate that samples taken in airtight containers and stored in a refrigerator at 0 - 4°C should not undergo significant change. This method is recommended for all samples to be tested for sulfur compounds. Samples should be tested as soon as possible, and if they are to be stored for longer than one week, they should be dried at 60°C, placed in an air-tight container and stored at 0 - 4°C.

Sufficient tests should be carried out to give a representative picture of the material. A minimum of 5 tests for each material proposed for use as structural backfill is recommended. The test results are given as % S, and are converted to sulfate using standard factors before use in classification systems. Existing limiting values for water-soluble sulfate (WS) should be used. The oxidisable sulfides (OS), which could develop from oxidation of reduced sulfur, should be calculated from the total sulfur minus acid-soluble sulfate. If this is greater than the limiting values given in the document, the material should not be used for structural backfill. For backfill to concrete, the total potential sulfate (TPS), calculated from the total sulfur content, also has to be considered, and a limiting value is given in the report.

If a material is unacceptable because of the OS or TPS values, but has been used satisfactorily in the past, expert advice should be taken. The history of the material should be established and detailed testing to establish its mineralogy and chemistry using the full suite of new test methods should be carried out. The use of the material may be permitted as structural backfill if it can be established to the satisfaction of the Overseeing Organisation that:

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

The oxidisable sulfides can also be estimated directly from the total reduced sulfur (TRS) value. However, the test method requires further work to be suitable for routine commercial use. It is anticipated that the total reduced sulfur test will eventually become the standard method for determining oxidisable sulfides.

BRE Digest 363 has been revised to incorporate the findings of the thaumasite expert group, and has been issued as SD1: 'Concrete in aggressive ground' 2001. For classifying ground conditions for sulfate level in respect of design of buried concrete, the recommendations of SD1 should be followed. The test methods and assessment procedures in this report are compatible with SD1. The new test methods will give more accurate values for the sulfur compounds than the existing methods in BS 1377: Part 3 and BR 279.

Experience from embankment dam and highway construction projects indicates that oxidation of even a small proportion of the pyrite present in fill materials can lead to the production of polluted drainage water, which requires treatment prior to discharge to watercourses. This is in addition to attack on construction materials. The

environmental effects should be given equal consideration with potential attack on construction materials when assessing potential materials for structural backfill and for bulk fill.

Changes in 2005 revision

This updated version of TRL447 has been produced in response to the revised version of BRE SD1, ‘Concrete in aggressive ground’ published in June 2005. The changes to SD1 include revisions to the limits of Design Sulfate Classes based on 2:1 water/soil extracts; the limits have been revised downwards as a result of studies following the discovery of the thaumasite form of sulfate attack in the concrete foundations of highway structures. The limits for WS and OS in this report are based on those in SD1, hence it has been necessary to update the report to incorporate the revised values.

The units for sulfate in solution in SD1 have changed from g/l to mg/l. The units for limiting values in Chapters 8 and 9 of the report have also been changed to mg/l. Appendix D has been omitted, as the proposed changes were incorporated into the MCHW in November 2003 and the revised limits will be incorporated in November 2005.

Apart from these changes, the text has not been significantly altered, other than to give more prominence to the number of tests that are required and how the results should be interpreted. This follows the recommendations given in SD1. The methods in Appendix C have not been altered, apart from changing the units for reporting water soluable sulfate (WS) from g/l to mg/l.

1 Introduction

It is known that sulfur compounds can lead to corrosion of construction materials in civil engineering works (Paul, 1994; Building Research Establishment, 1996). Standard tests for a number of forms of sulfur are available (e.g. British Standards Institution, 1977; 1983; 1990; Building Research Establishment, 1995). Limiting values for sulfates and other chemical species in structural backfills are given in the Specification for Highway Works (Manual of Contract Documents for Highway Works Volume 1 (MCHW1)), the Design Manual for Roads and Bridges (DMRB), BS 8006 (British Standards Institution, 1995) and for concrete in BRE Digest 363 (Building Research Establishment, 1996). In spite of these procedures, problems still arise from time to time on highway schemes and other civil engineering works due to corrosion caused by sulfur compounds.

On a recent highway scheme in England, severe corrosion was found in corrugated steel buried structures (CSBS) soon after construction. The backfill to the structures was local river gravel, which was found to contain pyrite. This was not revealed by the standard tests, which identified the pH and water-soluble sulfate content only. On being excavated and placed in a free-draining situation as backfill to the CSBS, the pyrite in the gravel had oxidised, producing sulfuric acid which subsequently attacked the steel. This prompted the Highways Agency (HA) to instigate a review of the current procedures in the MCHW and DMRB for identifying and assessing sulfur compounds in structural backfills.

The review was carried out by the Transport Research Laboratory (Reid and Perry, 1996). It revealed inadequacies both in the procedures and in the analytical methods used to determine the various sulfur compounds. The main gap was the lack of any assessment of the sulfides content; all the current procedures are based on sulfate content and pH. The sulfate and acidity which could be produced if the sulfides oxidise subsequent to being placed as structural backfill is therefore not included in the assessment of corrosion potential.

The sulfides content can be estimated by determining the total sulfur content according to BS 1047 and subtracting the acid-soluble sulfate content determined according to BS 1377. This approach is recommended in BS 1377 if sulfides are thought to be present (British Standards Institution, 1990). However, this gives a very imprecise estimate of the sulfides content, as both these test methods are liable to significant errors and interferences and have poor reproducibility. The review found that problems may arise in situations not anticipated by BS1377: 1990 and so there is a need for more accurate and precise methods of determination and screening for all forms of sulfur in backfill materials.

The present project was devised to address these two issues: suitable test methods for all forms of sulfur in backfill materials; and procedures for assessing the corrosion potential of the various sulfur compounds. The project was carried out by a team from TRL and the Department of Civil and Structural Engineering at the University of Sheffield. Although the focus of the project was structural backfill to metallic elements, such as culverts, reinforcing strips and anchors, the findings are relevant in other engineering situations. The results are presented in this report.

When the present project was at an early stage, the thaumasite form of sulfate attack was discovered by the Halcrow Group in a number of bridge piers and foundations on the M5 motorway. Halcrow were then commissioned by the Highways Agency to undertake an investigation of thaumasite at bridge piers and foundations in Gloucestershire. The problem was subsequently identified at a national scale and the Thaumasite Expert Group was set up by the Department of the Environment, Transport and the Regions (DETR) to produce interim advice and guidance. There was liaison with the Gloucestershire thaumasite investigation project and the Thaumasite Expert Group, though each retained its own programme. The scope of the present project was widened to include the testing of a number of samples from the thaumasite investigations using the new methods.

The report of the Thaumasite Expert Group was published in January 1999 (Thaumasite Expert Group, 1999). From the investigations carried out following the discovery of thaumasite attack, it became clear that oxidation of pyrite in the Lias Clay backfill was the main source of the sulfate which had attacked the foundation concrete. This had resulted in a sulfate class of 4 or 5 in the backfill adjacent to the foundations, whereas tests for sulfate at the time of construction had indicated sulfate class 2 conditions. This is clearly a similar problem to that which had affected the CSBS in the example above. The report contained revised guidance on procedures to assess the risk of sulfate attack on concrete, including the use of total sulfur determination to assess the total potential sulfate content. This procedure is acknowledged to be conservative, since it includes inert forms of sulfur such as organic sulfur and barytes as well as reactive minerals such as pyrite. The Thaumasite Expert Group included recommendations for future research topics in their report. Among these were:

- Development of a standard laboratory test protocol to take account of sulfides (particularly pyrite) in clay soils which may be oxidised leading to enhanced sulfate levels
- Revised procedure for assessment of sulfate class of ground taking account of this new test for oxidation of sulfide-bearing clays. This is needed for revision of Digest 363 and BS 5328: Part 1.

Further to the publication of the Thaumasite Expert Group Report, BRE has been engaged in revision of Digest 363 to include the results of the report. Liaison has continued to ensure that the present document and the revision of Digest 363 are compatible. The revised document was published as BRE Special Digest 1 in 2001 (Building Research Establishment, 2001). A revised version of Special Digest 1 was published in 2005 (Building Research Establishment, 2005).

2 Occurence of sulfur compounds in nature and incidence of corrosion problems

Sulfur compounds occur in a number of different forms in natural and artificial materials, as shown in Table 2.1. In the reduced form they occur as sulfides such as pyrite in a wide range of rocks and soils, and less commonly as mineral ores of lead (galena), zinc (sphalerite), and other metals. These minerals generally have very low solubility, and are not in themselves a hazard to construction materials. However, weathering of reduced sulfur species leads to the production of soluble sulfate minerals, which may cause attack of construction materials. Weathering also often leads to an increase in acidity, which besides increasing the solubility of sulfates may also be involved in the corrosion of construction materials. The main weathering reactions of pyrite are shown in Figure 2.1.

Sulfates also occur naturally in evaporite sequences as minerals such as gypsum and epsomite (Table 2.1). Some sulfates such as barytes have very low solubility and are relatively inert; others such as epsomite are highly soluble, and as a result, in the UK, have often been leached out of natural rocks and soils in the near surface zone where most civil engineering works are carried out. Gypsum, with a sulfate (SO_4) solubility of 1.4 g/l, is the most common naturally occurring sulfate mineral. However, much higher concentrations of sulfate can occur under acid conditions, or where unweathered materials with sulfides or soluble sulfate minerals are excavated and placed in spoil tips (as with mining waste) or used as structural backfills in civil engineering works. In both cases, the free access of air and water to the materials allows rapid oxidation of sulfide minerals and leaching of sulfates. This can lead to corrosion of construction materials and the production of leachate, which can pollute surface waters and groundwater (Cripps *et al.*, 1993; Davies and Reid, 1997).

Problems attributed to sulfur compounds in ground conditions have been documented in many areas of civil engineering. These include embankment dam construction (Pye and Miller, 1990; Cripps *et al.*, 1993; Davies and Reid, 1997, etc), building foundations (Hawkins and Pinches, 1987; Wilson, 1987; Cripps and Edwards, 1997 etc), highway and associated schemes, (Haviland *et al.*, 1967; Worley, 1971, etc) and tunnelling (Bracegirdle *et al.*, 1996). A literature review was carried out to assess the extent to which corrosion due to sulfur compounds had been recorded in corrugated steel buried culverts.

Brady and McMahon (1994) report details of two UK surveys consisting of a total of forty-six corrugated steel buried structures. Sulfur compounds were not found to be a major factor in the corrosion of the culverts. Corrosion was promoted principally by the action of acidic and chloride-ion rich water. In some cases it appeared that acidic water had drained from the natural soil into the backfill adjacent to the structure. The general absence of corrosion on buried surfaces was mainly due to the excellent protection provided by the bituminous coatings in all but the most aggressive environments.

Cases of rapid corrosion of galvanised steel culverts due to oxidation of pyrite in the surrounding backfill have been reported from France (Le Bris and Chevassu, 1978). A considerable database of culvert performance is available from the USA, in particular for Michigan, Ohio, Kansas and Maine (Haviland *et al.*, 1967; Worley, 1971). Corrosion was found in mining areas where sulfur bearing shales and coals were used as backfill, and was ascribed to oxidation of pyrite. However, cases were also reported where corrosion occurred in heavy textured soils such as clays with a high water table and high sulfate content (Noyce and Ritchie, 1979). The deterioration was attributed to the activity of sulfate reducing bacteria.

Table 2.1 Sulfur mineral species that may be encountered during UK site investigations

Mineral	*Formula*	*Occurrence*	*Diagnostic features*
Pyrite	FeS_2	Common constituent of rock and sediments.	Insoluble in non-oxidising acids such as HCl, digested using Cr(II) and c(HCl)[1].
Marcasite	FeS_2	Found as nodules in chalk and limestone.	Insoluble in non-oxidising acids such as HCl, digested using Cr(II) and c(HCl).
Gypsum	$CaSO_4.2H_2O$	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.
Jarosite	$KFe_3(OH)_6(SO_4)_2$	Common weathering product of pyrite.	HCl soluble.
Pyrrhotite	FeS	Occasionally found in sediments and rocks.	HCl soluble forming H_2S.
Barytes	$BaSO_4$	Common in mining areas, also found in limestone and marl.	Insoluble in acids. Determine as total S.
Celestine	$SrSO_4$	Rare mineral, occasionally associated with marl.	Insoluble in acids. Determine as total S.
Epsomite	$MgSO_4.7H_2O$	Common in evaporite sequences.	Water-soluble.
Mirabilite (Glaubers salt)	$Na_2SO_4.10H_2O$	Common in evaporite sequences.	Water-soluble.
Organic sulfur	Organic(CHO)-S	Common constituent of organic material.	Insoluble in acids. Determine as total S.

[1] *c(HCI): concentrated hydrochloric acid*

(1) $FeS_2 + H_20 + 7\ O \rightarrow FeSO_4 + H_2SO_4$ – This stage of the reaction is purely chemical involving oxidation of pyrite to ferrous sulfate.

(2) $2\ FeSO_4 + O + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$ – This stage involves further reaction aided by the catalytic action of thiobacilli bacteria, especially Th. ferro-oxidans and Th. Thio-oxidans.

(3) $Fe_2(SO_4)_3 + FeS_2 \rightarrow 3\ FeSO_4 + 2\ S$ – Ferric sulfate, which is a strong oxidising agent, reacts with pyrite.

(4) $S + 3\ O + H_2O$ ® H_2SO_4 – In the presence of free oxygen and water and catalytically assisted by Thiobacilli, the sulfur is converted to sulfuric acid.

(5) $FeS_2 + 7.5\ O + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4$ – In the presence of abundant oxygen and water, oxidation of pyrite forms ferric hydroxide (ochre).

(6) $CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2$ – The sulfuric acid formed is generally consumed by calcite, when present, forming gypsum.

Figure 2.1 The natural weathering reaction of pyrite and formation of gypsum

Overall, the number of published examples of sulfur compounds in backfill that contribute to soil-side corrosion of buried steel structures is limited. Where concern regarding the contribution of sulfur compounds to soil-side corrosion has been expressed, it is usually with regard to the oxidation of pyrite or the activity of sulfate reducing bacteria. These mechanisms occur in markedly different environments. Sulfate reducing bacteria require anaerobic conditions usually associated with heavy clay soils, whereas pyrite oxidation requires an aerobic environment such as can be found in granular fills above the water table.

A recent example of corrosion of stainless steel reinforcing elements behind a 26-year-old retaining wall in Edinburgh is described by Winter and Butler (1999). The corrosion was ascribed to sulfates in the backfill, which was a burnt oil shale. This material is known to have high sulfate content and is not permitted as backfill to reinforced soil, anchored earth or corrugated steel buried structures in the current Specification for Highway Works (MCHW1).

3 Present limiting values and test methods for sulfur compounds

3.1 Existing specification

For highway works in the UK, limitations on the materials permitted for structural backfill and the concentrations of various chemical species to prevent corrosion of construction materials are given in the Specification for Highway Works (Manual of Contract Documents for Highway Works Volume 1) and in Departmental Standards BD70 and BD12 (Design Manual for Roads and Bridges). Structural backfill includes all fills which may be used below, around or above: structures and structural concrete foundations (Clauses 610 and 611); reinforced earth (RE) and anchored earth (AE) structures (Clause 622); and corrugated steel buried structures (CSBS) (Clause 623). It thus covers Classes 6N, 6P, 7A and 7B fill (Clause 610 and 611), Classes 6H, 6I, 6J, 7B, 7C and 7D fill (Clause 622) and Classes 6K, 6L, 6M, 6Q and 7H fill (Clause 623). Both granular (Class 6) and cohesive (Class 7) materials may be involved.

The permitted constituents of the fills are given in Table 3.1, which summarises Tables 6/1 and 6/3 and other Clauses of MCHW1. The wording is intended to exclude argillaceous rock from all structural backfills. Argillaceous is a generic term for fine-grained sedimentary rocks such as mudstones, clays and shales. This follows work by West and O'Reilly (1986) which showed that argillaceous rocks could give rise to problems in reinforced earth structures due to sulfates, chloride, acidity and other undesirable properties. Clays, however, are not excluded so long as they comply with the requirements of the specification.

The notes to MCHW1 Table 6/3 state that the methods of test (except for Microbial Activity Index) are given in BS 1377:Part 3 (British Standards Institution, 1990). They also state that 'the corrosion potential of frictional fill shall be assessed from resistivity, pH, chloride and soluble sulfate tests. For cohesive soil it will be necessary to test additionally for organic matter. Should either organic content or sulfate be in excess of the specified levels, then tests shall also be included for Redox Potential and Microbial Activity Index.' Sulfate is thus only one of the parameters that have to be considered when assessing corrosion potential.

Test methods for soluble sulfate, sulfides and hydrogen sulfide are given in Table 6 of BD 12. The use of BS 1377:Part 3 is specified for soluble sulfate, but no mandatory method is given for sulfides and hydrogen sulfide. Reference is made to 'Standard textbook of qualitative inorganic analysis', but other methods may be used provided they lead to a points ranking, and Table 5 of BD 12 suggests the use of lead acetate paper to detect evolved hydrogen sulfide gas.

In BS 8006: Code of practice for strengthened/reinforced soils and other fills (British Standards Institution, 1995), it is stated that the fill used for permanent works should be frictional or cohesive frictional material Classes 6I, 6J, 7C and 7D as described in the MCHW1. Colliery spoil and argillaceous materials are permitted subject to specific testing and assessment. Limits on a range of electrochemical properties are given in Table 4 of BS 8006, and are reproduced in Table 3.2 of this report. Separate values are given for galvanised steel and stainless steel and for structures in or out of water.

The test for sulfate is the water-soluble sulfate SO_3 test, Test 5 in BS 1377: Part 3: (British Standards Institution, 1990). The limits quoted in Table 4 in BS 8006 are as a percentage, whereas the water-soluble

Table 3.1 MCHW1 corrosivity limits for selected fills for structures, reinforced earth (RE), anchored earth (AE) and corrugated steel buried structures (CSBS)

		Acceptable corrosivity limits on material properties													
		Max. water-soluble sulfate (g/l SO_3)		*Min. pH*		*Max. pH*		*Max. chloride ion content (% Cl)*	*Min. resistivity (ohm.cm)*		*Max. organic content (%)*	*Min. redox potential (volts)*		*Microbial activity index*
Class	*Slag permit-ted*	*Gal.*	*Stain.*	*Gal.*	*Stain.*	*Gal.*	*Stain.*		*Gal.*	*Stain.*		*Gal.*	*Stain.*	
Fill to RE and AE structures														
6H	✕	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
6I	✔	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
6J	✔	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
Fill to RE only														
7B	✕	Selected conditioned pulverised fuel ash – within chemical limits on delivery												
7C	✕	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
7D	✕	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
Fill to CSBS														
6K	✕	0.25		6		9		0.025	2000					
6L	✕	0.25		6		9		0.025	2000					
6M	✕	0.25		6		9		0.025	2000					
6Q	✕	0.25		6		9		0.025	2000					
7H	✕	0.25		6		9		0.025	2000					
Fill to structures														
6N	✔	1.9 if within 500mm of cement bound or cementitious materials												
6P	✔													
7A	✕													
7B	✕													

1 Argillaceous rock is excluded from all Classes.

2 Slag is not specified as either steel slag or blastfurnace slag.

3 Well-burnt colliery spoil is permitted for all Classes.

4 Class 6 = granular materials, Class 7 = cohesive materials.

5 Gal. = Galvanised steel, Stain. = Stainless steel.

sulfate is as grams/litre (g/l) in BD 12 and MCHW1. According to BS 1377, the results for water-soluble sulfate may be expressed in either unit. As the water:soil ratio for the test is fixed at 2:1, the results can be converted from percentage to grams/litre by multiplying by 5; this gives limits of 0.5 g/l (SO_3) for structures out of water and 0.25 g/l (SO_3) for structures in water. The limits are presented using these units in Table 3.2. The values are similar to those given for other structural fills, but a distinction is made as to whether the fill is in or out of water.

The limits for most electrochemical properties in Table 4 of BS 8006 are similar to those given in MCHW1 (see Table 3.2). However, BS 8006 also contains limits for maximum sulfides content, which are not included in MCHW1. No further guidance is given in the text as to which fills are liable to contain sulfides. The limiting S values given are 0.03% for structures out of water and 0.01% for structures in water.

The notes to Table 4 of BS 8006 state that 'the measurement should be carried out …. Using a method such as that given in the Encyclopaedia of Industrial Chemical Analysis by Snell and Hilton (1974)'. The notes state that 'the measurement of sulfide content should be carried out if the origin of the fill raises the possibility of its presence', i.e. judgement has to be exercised before specifying whether a test is required.

3.2 Forms of sulfur

Sulfur can occur in a number of different forms in nature. There are also a variety of ways in which it is expressed in the scientific literature. As a result, confusion can easily arise regarding the forms, amounts and units of sulfur compounds, and in comparing results from different sources.

The forms in which sulfur occurs in nature are summarised in Table 3.3.

Reduced forms of sulfur, and 'total' sulfur, are generally reported in units of sulfur, either as % or mg/kg. Pyrite is sometimes quoted as FeS_2. This usually involves assumptions as to the form of the sulfur compounds, as what is actually determined is not pyrite directly but an indirect measure such as [total sulfur minus sulfate-sulfur] or [total iron minus non-pyritic iron]. It is best to quote results in terms of the parameter determined, especially where assessing the potential oxidation of the reduced sulfur compounds. Where results are quoted as FeS_2, they may be converted to S as follows:

$$\% \text{ S} = 0.53 \text{ x } \% \text{ FeS}_2$$

$$\% \text{ FeS}_2 = 1.87 \text{ x } \% \text{ S}$$

Confusion may also arise in the reporting of sulfate, either as a solid (%, mg/kg) or in solution (usually as g/l).

Table 3.2 Comparison between MCHW1 and BS 8006 corrosivity limits for reinforced earth (RE) and anchored earth (AE) structures

		Acceptable corrosivity limits on material properties														
Class	*Slag permit-ted*	*Max. sulfides content (% S)*		*Max. water-soluble sulfate (g/l SO_3)*		*Min. pH*		*Max. pH*		*Max. chloride ion content (% Cl)*	*Min. resistivity (ohm.cm)*		*Max. organic content (%)*	*Min. redox potential (volts)*		*Microbial activity index*
		Gal.	*Stain.*	*Gal.*	*Stain.*	*Gal.*	*Stain.*	*Gal.*	*Stain.*		*Gal.*	*Stain.*		*Gal.*	*Stain.*	
MCHW1: Fill to RE and AE structures																
6H	×	–	–	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
6I	✔	–	–	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
6J	✔	–	–	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
MCHW1: Fill to RE only																
7B	×	–	–	Selected conditioned pulverised fuel ash – within chemical limits on delivery												
7C	×	–	–	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
7D	×	–	–	0.25	0.5	6	5	9	10	0.025	5000	3000	0.2	0.43	0.35	< 5
BS 8006: Fill to RE and AE structures 'Out of water'																
6I	✔	0.03	0.03	0.5	0.5	5	5	10	10	0.02	1000	1000	0.2	0.4	0.35	< 5
6J	✔	0.03	0.03	0.5	0.5	5	5	10	10	0.02	1000	1000	0.2	0.4	0.35	< 5
7C	×	0.03	0.03	0.5	0.5	5	5	10	10	0.02	1000	1000	0.2	0.4	0.35	< 5
7D	×	0.03	0.03	0.5	0.5	5	5	10	10	0.02	1000	1000	0.2	0.4	0.35	< 5
BS 8006: Fill to RE and AE structures 'In water'																
6I	✔	0.01	0.01	0.25	0.25	5	5	10	10	0.01	3000	3000	0.2	0.4	0.35	< 5
6J	✔	0.01	0.01	0.25	0.25	5	5	10	10	0.01	3000	3000	0.2	0.4	0.35	< 5
7C	×	0.01	0.01	0.25	0.25	5	5	10	10	0.01	3000	3000	0.2	0.4	0.35	< 5
7D	×	0.01	0.01	0.25	0.25	5	5	10	10	0.01	3000	3000	0.2	0.4	0.35	< 5

1 Argillaceous rock is excluded from all Classes in MCHW1 but is allowed in BS 8006 provided a specific study is undertaken and client approval is obtained.

2 Slag is not specified as either steel slag or blastfurnace slag

3 Well-burnt colliery spoil is permitted for all Classes

4 Class 6 = granular materials, Class 7 = cohesive materials

5 Gal. = Galvanised steel, Stain. = Stainless steel

Table 3.3 Forms of sulfur

Form	*Chemical formula*	*Valence state*	*Examples and comments*
Hydrogen Sulfide	S^{2-}	-2	H_2S (gas) toxic and corrosive.
Monosulfide	S^{2-}	-2	Pyrrhotite (FeS); Galena (PbS). The most reduced form of sulfur. Found in reducing groundwater as the sulfide ion.
Disulfide	S_2^{2-}	-1	Pyrite and Marcasite (FeS_2). The most common forms of reduced sulfur.
Elemental	S	0	Rare; found around volcanic springs and fumaroles.
Organic	S	0	Covalently bound, hard to oxidise common constituent of organic matter.
Sulfur Dioxide	SO_2	+4	Gas, constituent of acid rain, produced by volcanoes, power station emissions and vehicle exhausts.
Sulfur Trioxide	SO_3	+6	Toxic gas, does not exist in nature, intermediate product in the industrial production of sulfuric acid.
Sulfite	SO_3^{2-}	+4	Anion found only in reducing waters, does not occur as a solid.
Sulfate	SO_4^{2-}	+6	Gypsum ($CaSO_4.2H_2O$); Barytes ($BaSO_4$); Epsomite ($MgSO_4$). May be soluble (Epsomite) or insoluble (Barytes). The sulfate ion is common in groundwater.

Traditionally, sulfate has been reported as SO_3, although the correct chemical form is SO_4. SO_3 is a gas, which does not exist in nature, and the sulfite ion (SO_3^{2-}) is rare and only occurs in waters where reducing conditions are present (Table 3.3). The reasons for this probably relate to the traditional geochemical habit of expressing chemical analysis of rocks and soils in terms of oxides, e.g. SiO_2, Al_2O_3, TiO_2, MnO, NaO, P_2O_5, SO_3, etc. This allowed the analyses to be summed to 100%, and thus any mistakes could be identified if the sum came to more or less than 100%. There was no implication that the constituents were present as oxides – it was known that most of them were combined in silicate minerals, and various algorithms were developed to reconstruct the mineral compositions from the elemental analyses. However, expressing the results of analyses as oxides has become the standard way of reporting them. The current BS1377: Part 3: (British Standards Institution, 1990) and BS812: Part 118: (British Standards Institution, 1988) tests for sulfate still specify the results to be reported as SO_3.

The early guidance notes on sulfate attack on buried concrete by the BRE followed this convention, and expressed the limiting values in terms of SO_3. The MCHW and DMRB also followed this convention. However, while using SO_3 was appropriate when dealing with a complete chemical analysis, it was not sensible when only sulfate and a few other minor components, such as chloride, organic matter and pH, were being determined. This is particularly so when dealing with sulfate in solution. If it is desired to check the ionic balance of a water sample, the sulfate must be as SO_4^{2-}.

The BRE recognised this when they published Digest 363, Sulfate and Acid Resistance of Concrete in the Ground (Building Research Establishment, 1991). This gave limiting values for sulfate in terms of SO_4 for soil samples, soil-water extracts and groundwater samples. Subsequent BRE publications (e.g. Bowley, 1995) and the revision of Digest 363 in 1996 have followed this format, as have the Thaumasite Expert Group (1999). This is the correct chemical form for sulfate. However, subsequent editions of the MCHW and DMRB have continued to use SO_3, justifying this on the basis that this is the format specified in BS1377: Part 3 (British Standards Institution, 1990). The values in Tables 3.1 and 3.2 are therefore in this format.

It is simple to convert values from SO_3 to SO_4 and vice-versa: the conversion factors are given below. However, it is very important to state clearly which units are used when quoting results of sulfate tests, so that proper comparisons can be made. Sadly, this is not always done, with the result that figures can often be quoted incorrectly. This may result in the misclassification of materials.

$$SO_4\ (\%,\ g/l) = 1.2 \times SO_3\ (\%,\ g/l)$$

$$SO_3\ (\%,\ g/l) = 0.83 \times SO_4\ (\%,\ g/l)$$

Finally, in scientific investigations of the different sulfur compounds present in a sample, it is useful to quote the results in terms of sulfur, so that the amounts in different forms can be directly compared. Thus sulfur in the form of sulfate (as S), or sulfate-sulfur as it often known, can be directly compared to reduced sulfur (as S), and the sum can be checked to ensure it does not exceed the total sulfur (as S). This provides a useful internal check on the analyses, as illustrated by the following example.

A sample of Lower Lias Clay (TR14-6, Appendix B2) gave the following analytical results:

- Total sulfur 1.17 % (as S).
- Sulfides 0.99 % (as S).
- Sulfate 0.48% (as SO_4).
- Sulfate-sulfur 0.16 % (as S).

At first sight, the sum of sulfate and sulfides appears greater than the value for total sulfur. But when the sulfate is expressed as sulfur in the form of sulfate, it is clear that the total amount of sulfur in the sulfate and sulfides almost exactly matches the measured total sulfur content.

In geochemical literature, sulfur in the form of sulfate is often quoted as SO_4-S or SO_3-S. Sulfur in the form of sulfate can be converted to sulfate by the following equations. The factors are different depending on whether the sulfate is expressed as SO_3 or SO_4.

$$SO_4\ (\%,\ mg/kg) = 3.0 \times SO_4\text{-S}\ (\%,\ mg/kg)$$

$$SO_4\text{-S}\ (\%,\ mg/kg) = 0.33 \times SO_4\ (\%,\ mg/kg)$$

$$SO_3\ (\%,\ mg/kg) = 2.5 \times SO_3\text{-S}\ (\%,\ mg/kg)$$

$$SO_3\text{-S}\ (\%,\ mg/kg) = 0.40 \times SO_3\ (\%,\ mg/kg)$$

Where water-soluble sulfate is determined, using 2:1 water to soil ratio, results as SO_3, SO_4, SO_3-S or SO_4-S as % may be converted to g/l:

$$SO_4\ (g/l) = 5.0 \times SO_4\ (\%)$$

$$SO_3\ (g/l) = 5.0 \times SO_3\ (\%)$$

$$SO_4\ (g/l) = 15 \times SO_4\text{-S}\ (\%)$$

$$SO_3\ (g/l) = 12.5 \times SO_3\text{-S}\ (\%)$$

For this project, it was decided that the results of the new test methods should be expressed in terms of sulfur, to allow direct comparison between the different forms. The results for sulfate-sulfur therefore have to be converted to sulfate, using the conversion factors above, before they can be compared with limiting values. These aspects are dealt with in detail in the following chapters and in Appendix C. In order to help the reader get a feel for the different forms, a conversion table containing many commonly used values for the different species is given in Table 3.4.

4 Test methods for sulfur compounds

4.1 Forms of sulfur and existing test methods

Sulfur exists in nature as a component of modern and ancient marine and freshwater sediments, igneous and metamorphic rocks. In spite of wide occurrence quantitative determination of the forms of sulfur present in

Table 3.4 Conversion between different forms of sulfate

% SO_3	% SO_4	% SO_3-S	% SO_4-S	SO_3 (g/l)	SO_4 (g/l)
0.05	0.06	0.02	0.02	0.25	0.30
0.10	0.12	0.04	0.04	0.50	0.60
0.20	0.24	0.08	0.08	1.0	1.2
0.38	0.46	0.152	0.152	1.9	2.28
0.50	0.60	0.20	0.20	2.5	3.0
0.62	0.74	0.25	0.25	3.08	3.7
1.0	1.20	0.40	0.40	5.0	6.0

The table is based on the following equivalences:

1. % SO_4 = 1.2 x %SO_3
2. % SO_4-S = % SO_4/ 3.0
3. % SO_4-S = % SO_3-S
4. SO_3 (g/l) = 5.0 x % SO_3 *(in water-soluble sulfate test at 2:1 water to soil ratio only)*
5. SO_4 (g/l) = 1.2 x SO_3 (g/l)
6. SO_4 (g/l) = 5.0 x %SO_4 *(in water-soluble sulfate test at 2:1 water to soil ratio only)*
7. SO_3 (g/l) = 12.5 x %SO_3-S
8. SO_4 (g/l) = 15 x %SO_4-S

potential fills has proved to be inadequate. Having considered the modes of occurrence of sulfur compounds and their interaction with construction materials, for the purposes of analysis, they may be grouped under 5 main categories: -

1. Water-soluble sulfur (mainly sulfates, e.g. epsomite, mirabilite). Extremely reactive in engineering situations.
2. Acid-soluble sulfur (total sulfates including gypsum, anhydrite, jarosite). Slowly soluble in natural ground water and become more soluble under acidic conditions resulting in very aggressive ground conditions.
3. Total reduced sulfur (disulfides such as pyrite and marcasite, monosulfides and elemental sulfur). Oxidise during exposure to atmospheric conditions which, assisted by bacteriological attack, leads to the formation of very aggressive ground conditions.
4. Total sulfur (all the above as well as organic sulfur, barytes and celestine). The determination of total sulfur is not critical for most engineering applications. It may be useful to know 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. It is also very useful to be able to check the results for the sulfur speciation mentioned above.
5. Monosulfide sulfur (pyrrhotite and other minerals associated with reducing conditions such as mangrove swamps and contaminated land). Oxidise during exposure to atmospheric conditions which, assisted by bacteriological attack, leads to the formation of very aggressive ground conditions. Included in total reduced sulfur. Pyrite can be estimated from total reduced sulfur minus monosulfide sulfur.

Current testing procedures for sulfur species determination for engineering works are presented in BS 1377: Part 3 (British Standards Institution, 1990) and consist of the determination of water and acid-soluble sulfates. It suggests that where calcium sulfate is the dominant or only sulfate present in the soil, as is normally the case, then due to its low solubility in water the total sulfate values give a pessimistic indication of the danger due to sulfate. It therefore suggests that aqueous extractions should be conducted on values greater than 0.5% SO_4. Although the solubility of calcium sulfate is low (1.4 g/l SO_4) in a dynamic environment, large quantities can be dissolved due to ground water replenishment resulting in continual dissolution, producing 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 SO_4, Mg sulfate- 180 g/l SO_4).

Most concrete and metal structures tend to be buried within 5 metres 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.

BS 1377:1990 indicates that an acid extraction should be prepared by treatment of the sample with dilute hydrochloric acid in an open reaction vessel. This procedure effectively releases sulfates such as gypsum, anhydrite, epsomite, mirabilite and jarosite; it also results in the loss of monosulfide species, but it does not dissolve sulfates such as barytes and celestine. Since barytes and celestine are liable to be unreactive in most environmental conditions, the threat posed by sulfates is accurately determined by this procedure.

Although not common, monosulfide compounds are reactive under environmental conditions. BS 1377: 1990 states that soils containing sulfides may require special attention. It adds that acid extraction for sulfate determination destroys the sulfides present but in fact this is the case only for monosulfides and their dissolution may not be totally effective. Disulfides such as pyrite are not affected by this dissolution. The standard also advocates the use of the procedure in BS 1047 (1983) for the determination of total sulfur. This technique involves aqua regia (HNO_3/HCl) and bromine digestion of the sample and the gravimetric determination of total sulfur by barium sulfate precipitation. Total reduced sulfur is determined by the difference between the total sulfur and the acid-soluble sulfate-sulfur results. An alternative method, specifically for pyrite determination is given in BS 1016: Part 11 (1977) where pyritic sulfur is determined by the difference between total iron determined by nitric acid digestion and non-pyritic iron determined by hydrochloric acid digestion.

Both these methods of indirect reduced sulfur determination may produce erroneous results depending on the forms of sulfur present:

- The difference between total sulfur and acid-soluble sulfates may over-estimate reduced sulfur due to the presence of other sulfur species such as iron monosulfides, acid insoluble metal sulfates and organic sulfur. The latter may account for up to 0.5% of the organic content (Rowell, 1994).

- Not all pyrite is dissolved by nitric acid digestion, and as the acid tends to oxidise a proportion of the organic matter, non-pyritic iron is released.
- Hydrochloric acid digestion also suffers from interference from other compounds, which may be present.
- In addition, the estimate of reduced sulfur is based on the difference between the results of two test methods, both of which are relatively insensitive and have fairly high standard errors. There is therefore bound to be an even higher error associated with the difference.

All the British Standard test procedures for the determination of sulfur species employ the gravimetric method of barium sulfate precipitation for quantifying the sulfur content in solution. Care needs to be exercised with this method, as the results obtained are sensitive to operator techniques and interference from a number of other compounds. It also has low precision, potentially leading to large errors. New test methods are available, such as direct determination of S by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy). This method is also referred to as ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy).

4.2 Determination of sulfur compounds

The quantitative determination of sulfur compounds in a variety of geological materials, where different mixes of species may be present, is a challenge to the applied analytical chemist. The recognition of the minerals in hand specimens may not be easy and very fine-grained deposits, which often contain pyrite, are not suitable for determination either by this method or optical microscopy. Alternative mineralogical methods such as X-ray diffraction and electron microscopy, and chemical methods are, however, available. In terms of forming the basis of routine testing procedures, chemical methods are more practical and are considered further below.

There are many possible test methods for sulfur species, but these are based upon a limited number of test procedures. However, in terms of the sulfur species present in natural deposits being considered as potential engineering fills, five tests will provide suitable guidance:

1 Water-soluble sulfur **WSS.**

2 Acid-soluble sulfur **ASS.**

3 Total reduced sulfur (disulfides, monosulfides and elemental sulfur) **TRS.**

4 Total sulfur **TS.**

5 Monosulfide sulfur **MS.**

The results of all five tests are given in terms of %S, which allows easy comparison between the different forms of sulfur in each material. In order to evaluate potential testing procedures, parallel analyses by 18 different test methods, including both standard and non-standard ones, were carried out on a suite of 11 selected soils and rocks with differing sulfur mineralogies (see Appendix B). The methods were rated in terms of accuracy, convenience, time to carry out the determination and requirements for equipment. Consideration was given to the use of certain tests other than those described below, but these were excluded from the investigation for reasons of safety, general availability of specialised equipment and convenience in an industrial context. Work was also carried out to determine the accuracy and repeatability of selected methods using testing standards made up from mixtures of analytical grade chemicals.

References to the products of particular manufacturers should not be taken as endorsement of the equipment concerned. The details are given so that the testing is fully described.

4.2.1 Water-soluble sulfur (WSS)

The various tests given in different standards for the determination of water-soluble sulfates consist of preparing a mixture of deionised water and powdered sample, of recommended ratio (generally 2:1 water to sample). This is then mixed for a standard period of time (16 hours or overnight) after which the sulfate content of the filtrate is determined. These tests determine soluble sulfates and in addition any soluble sulfides that may be present when ICP-AES is used.

1 Water-soluble sulfates determined according to BS1377: Part 3: 1990, together with pH determination of the sample, using gravimetric determination of precipitated barium sulfate.

2 As above but with ICP (Inductively Coupled Plasma) – AES (Atomic Emission Spectroscopy) to determine the sulfur content.

4.2.2 Acid-soluble sulfur (ASS) and monosulfide (MS)

The sulfate or ‘total sulfate’ content of rocks and sediments is determined by means of acid extractions, which effectively breaks down gypsum, anhydrite, epsomite, mirabilite and jarosite. Recalcitrant sulfates such as barytes ($BaSO_4$) are not dissolved by the acid used for these tests. The addition of acid to the sample results in the partial loss of monosulfides, which are driven off as hydrogen sulfide and are not therefore analysed. Monosulfides are extremely reactive, though, if present, they are generally in very small amounts in most natural materials. Five methods were investigated:

3 Total sulfate determination according to BS1377: Part 3: 1990, using dilute hydrochloric acid digestion and the gravimetric determination of precipitated barium sulfate.

4 As above but with ICP-AES to determine the sulfur content.

5 Total sulfate determination according to BS1016: Part 11: 1977, but using ICP-AES to determine the sulfur content.

6 Total sulfate determination based on the use of phosphoric and hydroiodic acids as described by Keattch (1964).

7 Total sulfate determination procedure using tin (II) and phosphoric acid under a non-oxidising N_2 atmosphere as advocated by Kiba *et al.* (1955), Zhabina & Volkov (1978) and Purnell & Doolan (1983).

Tuttle *et al.* (1986) presented a method for the combined determination of acid-soluble sulfur and monosulfides. A slightly modified version of this technique was investigated in this study:

8 Reflux digestion with hydrochloric acid and tin (II) chloride under an inert (nitrogen or argon) atmosphere. Sulfur is liberated into solution by the acid extraction as acid-soluble sulfate and also evolved as H_2S gas from any monosulfide species which may be present. The gas is trapped in acidified copper nitrate solution and quantified by ICP-AES.

9 Sulfides determination according to the method of BS: EN196-2: 1994. This method, for cement testing, does not state which sulfide species are being detected. It is grouped with the monosulfide determinations, as the method is incapable of completely digesting pyrite.

4.2.3 Total reduced sulfur (TRS)

This includes disulfides, monosulfides and elemental sulfur, species that can be oxidised to form sulfates. By far the most significant mineral in this group is pyrite. In spite of pyrite being a widely occurring sulfur species, there is no standard direct quantitative method for its determination in geological and engineering materials. BS1377: 1990 advocates its determination as the difference between total [method 15] and acid-soluble sulfur [method 3].

Zhabina and Volkov (1978) proposed a technique for the determination of various sulfur compounds in marine sediments and rocks that involves chromium reduction in a reducing atmosphere. Tuttle *et al.* (1986) and Canfield *et al.* (1986) have rigorously evaluated the method. When applied by Czerewko (1997) for determining the pyrite content of a suite of varying mudrocks it proved very promising as it is specific to pyrite, monosulfides and elemental sulfur if present. If elemental sulfur or monosulfide species are present they can be determined separately (see above) and a correction applied to obtain the value for pyrite.

10 Total reduced sulfur determination by acidified Cr (II) reduction. The evolved hydrogen sulfide gas is trapped in acidified copper nitrate. The decrease in copper is determined by iodometric titration, from which the amount of reduced sulfur is calculated.

11 As method 10, but using ICP-AES for the determination of copper and evaluation of reduced sulfur.

12 As method 10, but using AAS (Atomic Absorption Spectroscopy) for the determination of copper and evaluation of reduced sulfur.

4.2.4 Total sulfur (TS)

The total sulfur content of the test samples was determined by means of six different methods involving combustion, wet chemistry, X-ray and fusion procedures. Combustion techniques involve the rapid heating of the sample using an induction furnace in an oxidising atmosphere at high temperature with the assistance of a combustion catalyst and the determination of the evolved sulfur dioxide gas. This forms the basis of the LECO automatic total carbon and sulfur analysers. Wet chemical methods involve the dissolution of the sample in aqua regia (concentrated nitric and hydrochloric acid mixture) and then determination of sulfate. Fusion techniques, for example Eschka fusion, tend to be preferred where samples are insoluble in aqua regia. After high temperature fusion the sulfur is present as sodium sulfate and this is then determined.

13 Total sulfur and carbon determination using a LECO CS-244 elemental analyser.

14 Total sulfur determination using XRF (X-ray Fluorescence) (Spectro X2000) analysis of pressed powder pellets.

15 Total sulfur determination according to BS1047: 1983, using standard wet chemistry, which includes the gravimetric determination of sulfate.

16 As method 15 but using ICP-AES for the direct determination of sulfur.

17 Total sulfur determination by microwave digestion of the sample using aqua regia and direct total sulfur quantification using ICP-AES.

18 Total sulfur determination using a slightly modified version of Eschka fusion from BS1016: 1993 Subsection 106.4, and ASTM: D2492.90: 1993 for the analysis of coal samples but with sulfur quantification using ICP-AES.

4.3 Evaluation of the testing procedures

To enable the 18 test procedures for the determination of various sulfur species to be evaluated the time taken to perform each analysis, ease of performing each method and any additional comments such as safety features are presented in Table 4.1. Although the determinations were carried out in batches, the time involved per test is presented to allow comparison and costing. The ease of performance is scored out of 5, where 1/5 is a very difficult procedure and 5/5 is a very simple procedure based on prior familiarity with the method. A number of the procedures involved the prior preparation of test reagents. This was normally neither time consuming nor very complicated but where it was, a note is made in the comments section. The analyses obtained for a range of geological samples by the standard methods and those advocated and evaluated in this report are presented in Table 4.2. The results are presented as %S, to allow easier comparison between the different results.

4.3.1 Water-soluble sulfur (WSS)

Comparison in Table 4.2 of the results obtained by methods 1 (gravimetric) and 2 (ICP-AES) reveals little difference, except that in two cases the values are slightly higher for the latter method. There is a possible lack of sensitivity with the gravimetric determination of sulfur. On the other hand, with method 2, ICP-AES is capable of accurate detection of sulfur down to a few mg/l and it is also less tedious and more rapid to perform, as seen in Table 4.1.

Table 4.1 Evaluation of the test procedures selected for the study

Test method	*Time per determination*	*Ease of procedure*[1]	*Comments*
Water-soluble sulfates			
1. BS 1377: Grav	18½ hours	4/5	Care required with gravimetric analysis. The time involved for testing involves sample agitation, only 2 hours of technician time is involved.
2. BS 1377: ICP- AES	16¾ hours	5/5	Requires specialised equipment. The time involved for testing involves sample agitation, only 2 hours of technician time is involved.
Acid-soluble sulfates			
3. BS 1377: Grav	3½ hours	3/5	Time consuming, laborious procedure may involve error due to lapse of concentration.
4. BS 1377: ICP-AES	1½ hours	4/5	Requires specialised equipment.
5. BS 1016: ICP-AES	1 hour	5/5	Requires specialised equipment.
6. Keattch (1964)	1½ hours	2/5	Preparation of test reagents is time consuming, and pre-treatment is required if organic matter is present.
7. Kiba et al. (1955)	1¼ hours	1/5	Preparation of test reagents is time consuming, and equipment is difficult to assemble.
Acid-soluble monosulfide			
8. Combined SO_4/S^-	1 hour	5/5	Requires specialised equipment.
9. BS:EN 196-2	1 hour	4/5	Colour change in titration is too gradual.
Total reduced sulfur determination			
10. Cr(II): Titration	2¼ hour	4/5	No dilution required and sharp titration end point.
11. Cr(II): ICP-AES	2¼ hour	4/5	Requires specialised equipment.
12. Cr(II): AAS	2¼ hour	4/5	Requires specialised equipment.
Total sulfur determination			
13. LECO analyser	½ hour	5/5	Requires specialised equipment.
14. XRF analysis	1 hour	3/5	Requires specialised equipment.
15. BS 1047: Grav	8 hours	2/5	Time consuming, laborious procedure may involve error due to lapse of concentration and many test stages.
16. BS 1047: ICP-AES	4½ hours	3/5	Requires specialised equipment.
17. Microwave digest	2 hours	4/5	Requires specialised equipment.
18. Eschka: ICP-AES	2½ hours	4/5	Requires specialised equipment.

[1] *Ease ranges from 1/5 very difficult to 5/5 very simple.*

4.3.2 Acid-soluble sulfur (ASS) and monosulfide (MS)

The values shown in Table 4.2 indicate that methods 4, 5, 6 and 7 produced similar results, whereas for method 3, the BS 1377: Part 3 method in which the sulfur determination was gravimetric, results are low in most cases. As seen in Table 4.1, for methods 4 and 5, where direct determination using ICP-AES was used, the testing time was drastically reduced compared with method 3. Methods 6 and 7 were both found to be difficult to apply with considerable time being spent preparing the reagents, therefore they are not recommended as standard procedures.

Method 5 was further modified, without detriment, to include monosulfide determination in method 8. The results presented in Table 4.2 indicate that the threats posed by this reactive form of acid-soluble sulfur would not be detected using method 3. Method 9 for monosulfide determination proved to be a little more difficult to carry out in preliminary tests as the colour change for the titration was too gradual for accurate determination.

Comparing the total sulfate (method 8) values with total acid-soluble sulfate (method 3) values, it is apparent that the methods have either produced quite similar results or the latter has under-estimated the quantity present. The differences between the results do not appear to be associated with the presence or absence of monosulfide, pyrite or organic sulfur. It seems likely that the differences are due to a lack of sensitivity where the amounts of sulfate are low. However, confidence in method 8 is provided by data in Table 4.3 that show good comparability between the analyses for standard mixtures prepared from analytical grade chemicals and the calculated values.

4.3.3 Total reduced sulfur (TRS)

Acidified chromium reduction, method 10, proved to be a straightforward and very successful method. Furthermore the procedure was precise and accurate. Reference to Table 4.2 demonstrates that this technique and ICP-AES were equally successful for determining the total reduced sulfur concentration. However these show great differences from those obtained by difference of total and acid-soluble sulfate as advocated in BS1377: 1990. Higher, lower and even negative values result from the lack of sensitivity of the total sulfur determination by method 15. 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 TR8, where monosulfide is also present. With methods 11 and 12, in which ICP-AES and AAS respectively were used for the copper determination, the trapping solutions required a dilution of between 8 to 10 times prior to analysis for copper, from which sulfur is then calculated. This gives the

Table 4.2 Sulfur speciation results for samples using standard (italics), proposed (bold) and other evaluated testing procedures

Determination	*Water-soluble sulfur (WSS) %S*		*Acid-soluble sulfur (ASS) %S*				
Method	1	***2***	3	*4*	***5***	*6*	*7*
Sample and sample description							
TR1- Carboniferous Mudstone	*0*	**0**	*0.01*	0.01	**0.01**	ND	ND
TR2- Permian Magnesian Limestone	*0*	**0**	*0.05*	0.21	**0.20**	0.20	0.19
TR3- Reworked Kimmeridge Clay	*0.01*	**0.01**	*0.16*	0.23	**0.21**	0.22	0.21
TR3B- Reworked Kimmeridge Clay	*0.12*	**0.19**	*0.83*	1.24	**1.08**	1.17	1.07
TR4- Mercia Mudstone	*0*	**0**	*0*	0.08	**0.06**	0.07	0.07
TR5- Glacial Till, with coal fragments	*0*	**0.01**	*0*	0.02	**0.02**	ND	ND
TR6- Lower Lias Clay	*0*	**0**	*0.04*	0.05	**0.04**	ND	ND
TR7- Slate	*0*	**0**	*0.02*	0	**0.01**	ND	ND
TR8- Pyritic Slate	*0.01*	**0.01**	*0.03*	0.01	**0.02**	ND	ND
TR9- Jurassic Oolitic Limestone	*0*	**0**	*0.03*	0.38	**0.37**	0.37	0.36
TR10- Slate	*0*	**0**	*0.06*	0.06	**0.07**	ND	ND
TR11D- Alluvial Sand with some gravel	*0.05*	**0.07**	*0.02*	0.07	**0.07**	ND	ND

Determination	*Monosulfide (MS) %S*		*Total reduced sulfur (TRS) %S*				*Total sulfur (TS) %S*						*Org. S % S*
Method	***8***	*9*	*Difference*	*10*	***11***	*12*	*13*	*14*	*15*	*16*	***17***	*18*	*Difference*
Sample			*15 - 3*										*17-5- (11+8)*
TR1	**0**	0	*-0.01*	0.10	**0.10**	0.10	0.04	0.03	*0*	0.05	**0.08**	0.09	0
TR2	**0**	0	*-0.01*	0	**0.05**	0.08	0.03	0.04	*0.04*	0.26	**0.25**	0.26	0
TR3	**0**	ND	*-0.11*	0.21	**0.21**	ND	0.06	0.05	*0.05*	0.30	**0.31**	0.31	0
TR3B	**0**	0	*0.55*	0.41	**0.41**	0.49	1.56	0.76	*1.38*	1.32	**1.39**	1.43	0
TR4	**0.13**	0.10	*0.06*	0.17	**0.17**	ND	0.04	0.03	*0.06*	0.10	**0.17**	0.17	0
TR5	**0**	ND	*0.32*	0	**0**	0	0.11	0.10	*0.32*	0.45	**0.11**	0.11	0.09
TR6	**0.18**	0	*0.68*	0.70	**0.70**	0.68	0.09	0.54	*0.72*	0.66	**0.73**	0.73	0
TR7	**0.15**	0.1	*0.05*	0.33	**0.33**	0.31	0.03	0.01	*0.07*	0.16	**0.31**	0.34	0
TR8	**0.32**	0	*2.47*	2.86	**2.86**	2.84	3.19	0.79	*2.50*	2.01	**2.97**	2.97	0.09
TR9	**0**	ND	*0.27*	0	**0**	0	0.06	0.04	*0.30*	0.43	**0.37**	0.37	0
TR10	**0.04**	0	*-0.06*	0.05	**0.05**	ND	0.10	0.04	*0*	0.09	**0.14**	0.14	0.02
TR11D	**0**	0	*0.24*	0.22	**0.22**	ND	ND	ND	*0.26*	0.31	**0.31**	0.31	0.02

ND = Not determined

Table 4.3 Results for the determination of standard mixtures to assess the accuracy and repeatability of the proposed test procedures

Method	*Form of sulfur*	*Actual S%*	*3 no analyses S%*	*Average S%*	*S (%)*	*sr (%)*
8	Acid-soluble (ASS)	4.287	4.173 / 4.162 / 4.195	4.177	0.017	0.40
		2.536	2.629 / 2.586 / 2.561	2.592	0.034	1.32
11	Total reduced (TRS)	2.39	2.33 / 2.34 / 2.35	2.34	0.010	0.43
		0.123	0.112 / 0.120 / 0.117	0.116	0.004	3.47
		5.48	5.39 / 5.43 / 5.40	5.41	0.021	0.39
		2.56	2.50 / 2.42 / 2.46	2.46	0.04	1.63
17	Total (TS)	3.73	3.56 / 3.61 / 3.67	3.61	0.055	1.52

s = *Standard deviation – The standard deviation of a population (data set) is the commonly used measure of dispersion of the results about a mean value. This is a measure of reproducibility of a procedure. The smaller the standard deviation the greater the precision.*

sr = *Coefficient of variation – This value is an estimate of the precision of measurement and is given by the standard deviation divided by the mean. The value is as a percentage.*

possibility of slight discrepancies, although according to the data none appear to be present here. Reference to Table 4.3, in which analyses for the standards are presented, indicates that a reasonable degree of accuracy was obtained with method 11 and it also demonstrates the reliability of methods 10 and 12. The results are presented as %S.

4.3.4 Total sulfur (TS)

In these tests, due to analytical errors, methods 15 and 16 were found to be insensitive to small quantities of sulfur and the technique was also time consuming. As is demonstrated in Table 4.2 some of the values are lower than for the other methods. Method 15, which is a lengthy procedure, was improved in method 16, by the use of ICP-AES for the direct determination of sulfur in the digestion extract. 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. These methods gave very similar results to each other. Table 4.3 indicates a good degree of comparability between method 17 and the calculated values for standards. Any errors introduced at the gravimetric determination stage of method 18 were eliminated by the use of ICP-AES.

These methods were not as straightforward as the LECO CS-244 analyser, method 13. It has been reported by Sparks (1996) that this older LECO type of analyser is not quite as accurate as wet chemical methods and this would appear to have been the case here. Subsequent models of the LECO automated analysers that use an infra red cell for the determination of total sulfur apparently show good agreement with wet geochemistry. Care needs to be taken with the choice of combustion equipment. In some models, the temperature attained and its duration during the combustion phase are insufficient to release all the sulfur present within a refractory matrix, such as occurs with mineral soils. Equipment also varied in terms of characterising the gas evolved and the manner of calibration (see Chapter 4.5).

Although XRF analysis, method 14, is a convenient and rapid method, comparisons of the values in Table 4.2 confirm that it may not be very accurate since the standards used for calibration tend to be lower in sulfur than the materials analysed here.

Determination directly by ICP-AES proved much more reliable than the gravimetric procedure. With improvements in ICP-AES UV filters, 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 utilised in the direct quantification of sulfate in water and acid extractions. The technique is especially suited where concentrations of extracted sulfur are low, since analyte dilutions may not be required for instrumental analysis. Where required, great care has to be exercised over the dilution procedure for higher sulfur concentrations.

The recommended more sensitive techniques for example ICP-AES, or iodometric titration should be used for the quantitative determination of sulfur. It should be noted that it is preferable to use ICP-AES as opposed to AAS since ICP-AES has a working range up to a magnitude greater than AAS, therefore less dilution is required. Older AAS equipment may be unable to analyse for sulfur directly, and AAS also proves to be less sensitive than ICP-AES for many other elements. Since ICP-AES is now one of the most widely used techniques for chemical analysis, its use is preferred and recommended.

4.4 Proposed analytical protocol

From the findings it appears that the analytical procedure presented in Figure 4.1 will allow the complete determination, for engineering applications, of the sulfur compounds common in geological materials to a high degree of accuracy and repeatability. Five tests are given, listed as Tests 1 to 5, which are shown on Figure 4.1 with the corresponding method number in brackets. The procedures are described in detail in Appendix C. As indicated in Figure 4.1, the procedure also includes the determination of sample pH, carbonate, organic carbon and chloride ions. Analyses for standards are presented in Table 4.3. The standards were prepared using analytical grade chemicals. The results provide confidence that the methods advocated provide accurate and repeatable results.

The five tests are described briefly below:

4.4.1 Test No.1: Water-soluble sulfur (WSS)

(Method 2)

BS1377: 1990 soluble sulfate extraction using a 2:1 water to soil extraction with the determination of soluble sulfate using ICP-AES.

4.4.2 Test No.2: Acid-soluble sulfur (ASS)

(Method 4)

Digestion in hydrochloric acid. Quantification of sulfates (gypsum) using ICP-AES.

4.4.3 Test No.3: Total reduced sulfur (TRS)

(Method 11)

Acidified chromium (II) reduction in a reducing atmosphere with trapping of evolved hydrogen sulfide gas. Quantification of disulfides using ICP-AES or iodometric titration. If desired, the pyrite concentration can be estimated by a correction for monosulfide using Test No.5 below.

4.4.4 Test No.4: Total sulfur (TS)

(Method 17)

Microwave digestion of the sample using aqua regia, with determination of the liberated sulfur in solution using ICP-AES. Alternatively, use of an appropriate Rapid High Temperature Combustion Analyser (Method 13) may be acceptable.

4.4.5 Test No.5: Monosulfide sulfur (MS)

(Method 8)

Digestion in hydrochloric acid with trapping of evolved hydrogen sulfide gas. Quantification of monosulfide species using ICP-AES. Method also yields acid-soluble sulfur by use of ICP-AES on the acid digest, as for Test No.2.

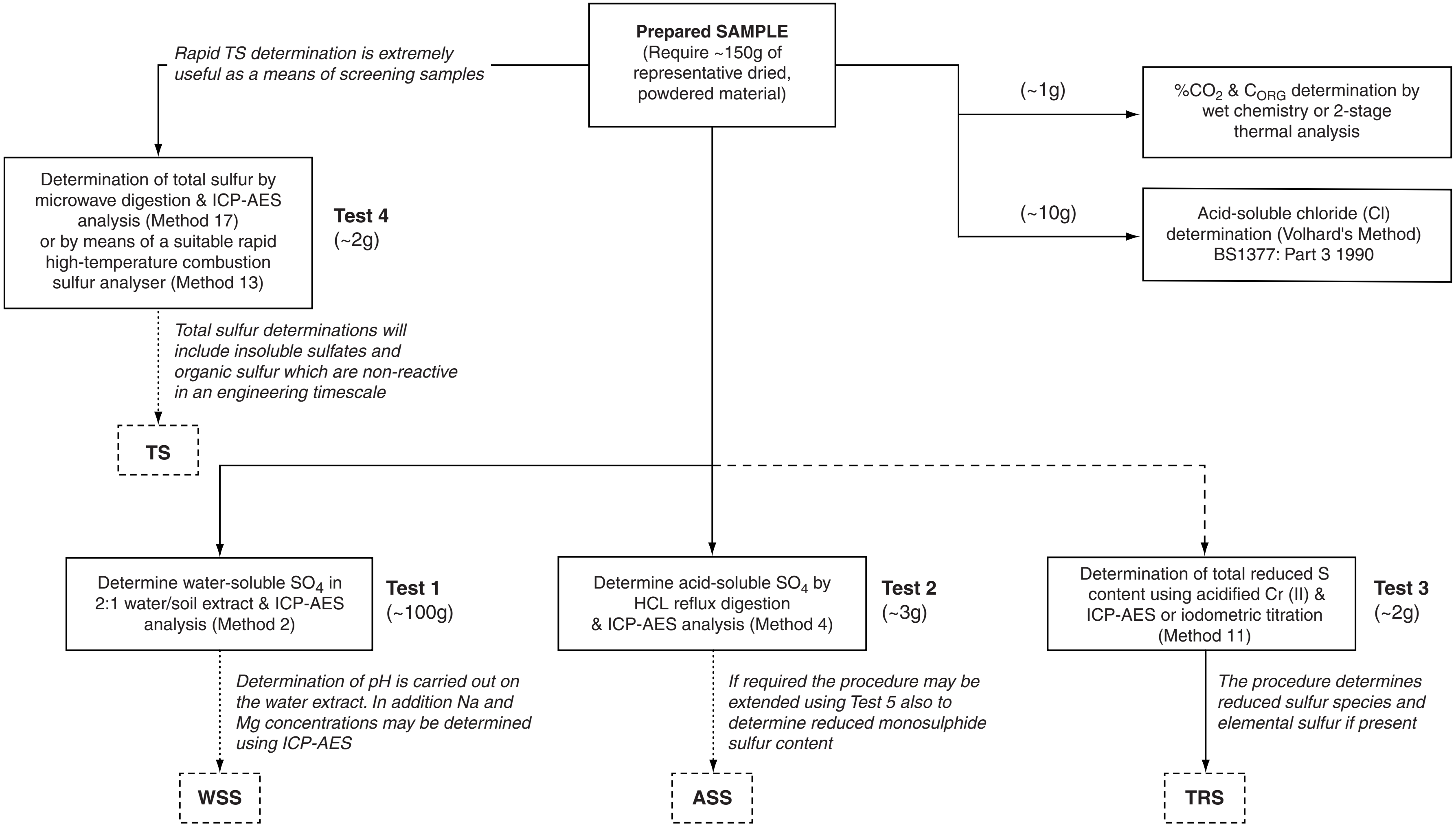


Figure 4.1 Analytical scheme for quantifying ground sulfur species (all results as %S)

Full details of the procedures for Tests No.1 to 5, and pro-formas for the test results, are given in Appendix C. Note that the new tests determine all sulfur compounds as %S. Where the sulfur is present as sulfate, the values have to be converted to SO_3 or SO_4 for comparison with limiting values. The conversion factors in Table 3.4 may be used.

4.5 Reproducibility trials

To evaluate the suitability of the proposed analytical protocol in commercial testing, a number of chemical testing houses were contacted during May 1999 and invited to take part in an assessment of the proposed test procedures (see Appendix A). A total of four testing houses initially agreed to take part in this programme but due to commercial constraints and work loads they were only able to oblige by analysing for water-soluble, acid-soluble and total sulfur species using in-house procedures. A further three agreed to comment on the proposed analytical protocol. Sets of six samples (see Table 4.4) with varying sulfur mineral contents were prepared at Sheffield University following the procedures outlined in Appendix C. The material was bagged as 150 to 200 gram quantities of unknown material and sent to the relevant testing houses for evaluation. The samples were also analysed at the University of Sheffield using the protocol described in Section 4.4. The results are presented in Table 4.5.

The participating laboratories were provided with the relevant parts of Appendix C for comment and the additional clarification shown in Appendix A was also provided in response to specific requests. A questionnaire designed to solicit comments on the performance of the tests and their suitability in an industrial context was also sent to the testing houses. The comments received from the testing houses were incorporated, where applicable, into the final test procedures presented in Appendix C.

LECO Instruments (UK) Limited kindly agreed to carry out total sulfur determinations on the samples using current state of the art rapid, high temperature combustion sulfur analysis instruments [HTC]. This was intended to check the comparability of results obtained using the proposed microwave digestion procedure and the HTC apparatus. The latter is preferred by some testing houses due to its ease of use and fast turn around time. In addition CERAM Research and GEOCHEM also determined total sulfur contents of the samples using HTC apparatus, the results of which are presented in Table 4.5.

The results for water and acid-soluble sulfur determinations (Table 4.5) show a moderate scatter in the results as can be seen from the high coefficient of variance values indicating a moderate to poor agreement between the results from different testing houses. Since testing houses used 'in-house' procedures rather than British Standard test methods, variations in results are to be expected.

Table 4.5 Sample sulfur analysis results *(All sulfur results are presented as %S unless otherwise stated)*

Testing house	*Sample ID*	*TR25*	*TR26*	*TR27*	*TR28*	*TR29*	*TR30*
Water-soluble sulfur determination [WSS]							
Geochem		0.107	0.078	0.102	0.001	0.002	0.016
Env. Analysis		0.154	0.016	0.116	0.001	0.002	0.021
Sheffield U.		0.181	0.178	0.122	0.001	0.005	0.034
	Mean	*0.147*	*0.091*	*0.113*	*0.001*	*0.003*	*0.024*
	S	*0.04*	*0.08*	*0.01*	*0.00*	*0.00*	*0.01*
	Sr	*25.42*	*90.15*	*9.06*	*0.00*	*57.74*	*39.26*
Acid-soluble sulfur determination [ASS]							
Geochem		0.15	0.25	0.28	0.39	0.13	0.07
Geochem (*)		0.25	0.16	3.31	0.14	0.00	0.06
Env. Analysis		0.28	0.22	8.84	0.14	0.01	0.04
Sheffield U.		0.19	0.21	7.42	0.53	0.00	0.05
	Mean	*0.218*	*0.210*	*4.963*	*0.300*	*0.035*	*0.055*
	S	*0.06*	*0.04*	*3.90*	*0.19*	*0.06*	*0.013*
	Sr	*26.91*	*17.82*	*78.68*	*64.46*	*181.4*	*23.47*
Total sulfur determination [TS]							
CERAM [Microwave digest]		0.91	1.68	8.04	9.00	1.07	2.30
CERAM [Leco CS-444]		0.98	1.59	10.62	9.57	1.03	2.52
Geochem [Leco CS-444]		0.83	1.57	6.85	6.69	1.03	2.32
LECO [Leco CS-444LS]		1.35	2.40	10.55	8.97	1.71	3.50
LECO [Leco SC-144DR]		0.90	1.47	7.13	3.29	0.95	2.35
Sheffield U. [Microwave digest]		0.93	1.68	8.27	8.98	1.09	2.35
	Mean	*0.98*	*1.73*	*8.58*	*7.75*	*1.15*	*2.56*
	S	*0.19*	*0.34*	*1.64*	*2.40*	*0.28*	*0.47*
	Sr	*18.92*	*19.44*	*19.18*	*31.02*	*24.43*	*18.33*

(*) The received sample was further ground prior to analysis.
s, sr as defined in Table 4.3.

The Geochem and Environmental Analysis results for water-soluble sulfur tend to be slightly lower than the Sheffield results. In the case of the acid-soluble sulfate-sulfur values, the Geochem results for 'as received' and 'further ground' material for sample TR27 differ greatly and are vastly different from the Environmental Analysis and Sheffield results. This is also seen in the results for the remaining samples. The Geochem 'in-house' procedure involved determination of acid-soluble sulfate by difference between total sulfur values on an acid pre-treated sample and untreated sample analysed using high temperature combustion (HTC) procedures. This procedure is totally different from the acid digestion approach in BS 1377: Part 3 (British Standards Institution, 1990), and produces different results.

Table 4.4 Sample details

Sample ID	*Material*	*Locality*	*Date collected*
TR25	Pyritic Alluvial Sand	Grange Farm, Hilton, Derbyshire [SK238318]	Collected June 1998
TR26	Lower Lias Clay	Blockley Brick pit, Gloucestershire [SP181371]	Collected November 1998.
TR27	Mercia Mudstone	British Gypsum Quarry, Cropwell Bishop, Notts [SK794430]	Collected April 1999
TR28	Mineraliferrous Sandstone	Silverband Mine, Barytes extraction works [NY717281]	Collected May 1999
TR29	Green Slate	Penhryn Quarry, Gwynned, N. Wales [SH620650]	Collected April 1999
TR30	Lias Alum Shale	Whitby, N. Yorks [SE184793]	Collected May 1999

Results for total sulfur determinations show generally good agreement, with a high degree of agreement for the microwave digestion procedure. Problems were apparent with use of the Leco Model SC-144DR HTC apparatus which employs a lower temperature resistance furnace (1500ºC) than the CS-444 model which achieves higher temperature (2000ºC) through the use of an induction furnace. Incomplete combustion of the samples has resulted using the SC-144 instrument. As analysis times are programmed into HTC instruments and range up to 90 seconds, highly refractory samples or temperature resistant minerals especially may undergo incomplete combustion. Such a problem is apparent with sample TR28 using the SC-144. In addition the reagents and glass wool used in the various traps in the HTC apparatus tend to absorb small amounts of sulfur so that until a few samples have been run, lower results are obtained. As this absorbed sulfur may be re-activated with instrument use, regular calibration of the equipment should be carried out as a check on the results. High sulfur standards are not available for HTC instrument calibration and therefore higher reported sulfur values tend to be extrapolated a long way from the calibration point, leading to inaccuracies.

With the intention of standardising sulfur species testing procedures, several chemical testing laboratories were contacted during late June 2000 and invited to take part in validation trials for the new testing procedures. Test 5 was not included in the trials, as it is only likely to be of interest for specialised investigations. Of the laboratories contacted only ECoS and TES Bretby were able to take part, although other laboratories contacted expressed an interest in the project, but they declined to take part due to busy summer workloads.

Suitable material was collected between the end of June and early July 2000 to provide a suite of materials containing levels of sulfur species frequently found in rocks and sediments encountered in construction projects within the UK (Table 4.6). A total of 5 samples were selected for testing, processed following the procedures set out in Appendix C and bagged as duplicates. Each testing house was supplied with 10 samples, which were numbered TRT01 to TRT10 inclusive. The fact that each sample was duplicated was unknown to the testing houses. This was done to evaluate the accuracy and the repeatability of the procedures.

A one-day workshop was held at Sheffield University on the 20th July 2000 for representatives from each testing house taking part in the trials to attend a demonstration of the procedure for total reduced sulfur (Test No. 3). In addition testing procedures were discussed for water and acid-soluble sulfur and total sulfur methods, and the equipment used at Sheffield University for the testing was viewed. On completion of the laboratory demonstration the representatives were each given the set of 10 prepared samples and a copy of the testing methods to be used.

The results are presented in Table 4.7. They show good agreement for the water-soluble sulfur and acid-soluble sulfur determinations as confirmed by low values of the standard deviation and coefficient of variance values presented.

Results for total sulfur using the microwave digestion procedure, which was carried out by Sheffield and ECoS, show generally good agreement between results with occasional differences as seen for example for sample TRT01. TES Bretby carried out total sulfur determinations using a HTC Leco CS-444 analyser, as a microwave digester was not available. The results are generally in good agreement with those of ECoS and Sheffield, as can be seen from the statistical analysis. This illustrates the importance of using an analyser with the capacity to digest pyrite, a point made in the consultations with laboratories earlier in 2000.

Results for total reduced sulfur are generally in very poor agreement as can be seen in Table 4.7. In general, the results from TES and ECoS are considerably higher than those from Sheffield. Total reduced sulfur values are higher than the total sulfur contents for samples TRT02/04, TRT03/07 and TRT08/09. TES Bretby undertook testing using 500mg and 250mg of material for each sample as hydrogen sulfide losses were suspected using 500mg of sample, which indicates that the gas flow rate used was too high. The reason for the differences between the laboratories is not clear. Determination of total reduced sulfur was by ICP-AES, in line with the procedure for the other test methods. An alternative determination is by iodometric end point determination. Iodometric titration is a commonly used and robust method which may offer greater accuracy and reproducibility as it alleviates the need for sample dilution and instrumental analysis which may introduce errors. Further study is required before the method can be recommended for routine use.

4.6 Recommended test methods

The reproducibility trials have confirmed that the proposed test methods for water-soluble sulfur (Test 1), acid-soluble sulfur (Test 2) and total sulfur (Test 4) are robust and repeatable in the environment of commercial laboratories. They are therefore recommended for routine

Table 4.6 Sample details

Sample ID	*Material*	*Locality*	*Date collected and contact*
TRT01 & TRT05	Pyritic Alluvial sand	Grange Farm, Hilton, Derbyshire [SK238318].	Trial Pit (1st June 1998) Kept refrigerated & dried.
TRT02 & TRT04	Weathered London clay	Colnbrook, Slough.	Material provided by M Reid from TRL compaction trial stockpile.
TRT03 & TRT07	Pink Shap granite	Shap Pink Quarry, Cumbria [NY556084].	
TRT06 & TRT10	Lower Lias clay	Morton Valence.	Donated by I. Longworth (BRE).
TRT08 & TRT09	Reading Bed clay	Knowl Hill Quarry [SU81657974].	Collected by M. Reid (19/06/2000).

Table 4.7 Validation trial sample sulfur analysis results ***(All sulfur results are presented as %S unless otherwise stated)***

Testing house	*Sample ID*	*TRT01/04*	*TRT02/04*	*TRT03/07*	*TRT08/09*	*TRT06/10*
Water-soluble sulfur determination [WSS]						
Sheffield U.		0.25 / 0.25	0.08 / 0.08	0.0 / 0.0	0.0 / 0.0	0.13 / 0.12
ECoS		0.27 / 0.27	0.08 / 0.08	0.0 / 0.0	0.0 / 0.0	0.12 / 0.12
TES Bretby		0.35 / 0.34	0.07 / 0.07	0.0 / 0.0	0.0 / 0.0	0.12 / 0.12
	Mean	*0.29*	*0.08*	*0.00*	*0.00*	*0.12*
	s	*0.04*	*0.01*	*0.00*	*0.00*	*0.00*
	sr	*15.57*	*6.74*	*0.00*	*0.00*	*3.36*
Acid-soluble sulfur determination [ASS]						
Sheffield U.		0.38 / 0.38	0.09 / 0.09	0.02 / 0.02	0.01 / 0.01	0.13 / 0.12
ECoS		0.39 / 0.35	0.08 / 0.08	0.04 / 0.03	0.01 / 0.01	0.14 / 0.13
TES Bretby		0.45 / 0.38	0.08 / 0.07	0.0 / 0.0	0.03 / 0.02	0.11 / 0.12
	Mean	*0.39*	*0.08*	*0.02*	*0.02*	*0.13*
	s	*0.03*	*0.01*	*0.02*	*0.01*	*0.01*
	sr	*8.53*	*9.22*	*87.39*	*55.78*	*8.39*
Total sulfur determination [TS]						
Sheffield U.		1.95 / 1.87	0.36 / 0.36	0.14 / 0.13	0.03 / 0.03	1.09 / 1.10
ECoS		2.52 / 2.48	0.45 / 0.43	0.14 / 0.14	0.01 / 0.0	1.36 / 1.28
TES Bretby		2.18 / 2.22	0.44 / 0.48	0.16 / 0.16	0.01 / 0.02	1.35 / 1.28
	Mean	*2.20*	*0.42*	*0.15*	*0.02*	*1.24*
	s	*0.34*	*0.05*	*0.01*	*0.02*	*0.13*
	sr	*15.55*	*11.17*	*3.45*	*90.00*	*10.78*
Total reduced sulfur determination [TRS]						
Sheffield U.		1.39 / 1.40	0.27 / 0.23	0.16 / 0.16	0.02 / 0.00	0.90 / 0.89
ECoS		1.26 / 1.81	0.72 / 1.11	0.64 / 0.75	0.42 / 0.40	0.69 / 0.55
TES Bretby		0.75 / 2.36	1.20 / 1.96	0.60 / 0.69	0.46 / 0.12	0.88 / 1.28
	Mean	*1.50*	*0.92*	*0.50*	*0.24*	*0.87*
	s	*0.54*	*0.65*	*0.27*	*0.21*	*0.25*
	sr	*36.36*	*71.41*	*53.62*	*89.98*	*28.51*
Sheffield U. known standard check		TS	TRS			
Standard [FeS_2] known content		4.25mg S	5.58mg S			
Standard [FeS_2] analysed content		4.19mg S	5.67mg S			

s, sr as defined in Table 4.3

use for determination of sulfur compounds in rocks, soils, fill materials and water samples. The survey also showed that the existing BS 1377: Part 3 and BS 1047 methods are effectively obsolete, in using the gravimetric determination of sulfate. A number of methods are being used at present by different laboratories, with no consistency in their application. There is a clear need for standard methods which can be used throughout industry, so that results from different laboratories may be compared. The proposed methods meet this need and should be adopted for all civil engineering applications.

The total reduced sulfur test (Test 3) shows considerable promise as a way of directly estimating the content of pyrite and other reduced sulfides. High accuracy and reproducibility were obtained by Sheffield University with this method (Table 4.3). However, in view of problems experienced by other laboratories, further work is required before this method can be recommended for routine use. It is likely that, following development, this method will become the standard method for the measurement of reduced sulfur compounds. However, at present it is recommended that this be estimated as the difference between the total sulfur and acid-soluble sulfur content. Using the new test methods, this quantity can be estimated much more accurately than using the old BS 1377: Part 3 and BS 1047 methods.

Test 5, monosulfide sulfur, is a specialised test that is only likely to be required where detailed investigations into the sulfur mineralogy of a particular material are required. It should therefore only be carried out by suitably equipped and qualified laboratories, and is not recommended as a test for routine use.

5 Site survey and joint testing exercises

5.1 Introduction

A site survey was carried out to obtain samples to evaluate the test methods described in Chapter 4. Sites were chosen because either the materials had been identified as being problematic or so that the sample set would include a suitable range of sulfur mineralogies. Full sample details are provided in Appendix B1. As noted in Appendix B1, previous testing had been performed on some of these materials, which provided the opportunity to compare earlier results with the present ones. The results of analyses on the site survey samples are presented in Appendix B2.

Tests were also carried out on further samples, listed in Appendix B1, that were donated by Halcrow Group Ltd from the thaumasite investigations on Lower Lias Clay from the M5 in Gloucestershire. These consisted of three groups of samples, some of which had been stored for some time prior to analysis. Samples TR14-1 to TR14-6 were from recently sampled cores that had been tested by TES Bretby and subsequently stored under refrigerated or non-refrigerated conditions by Halcrow. Samples TR14-7 to TR14-18 were newly sampled borehole cores, of which 7 samples were selected and split for parallel testing by TES Bretby using their British Standard based test procedures. Samples TR14-19 to TR14-25, which had been previously tested, were selected from the Halcrow core store to investigate the effects of storage conditions.

The test data from the 7 split samples jointly tested by TES Bretby and Sheffield University are directly comparable. Of the remaining samples tested, only samples TR14-19, TR14-20 and TR14-23 which had originally been tested by Halcrows, and subsequently stored in the core store provided test data, which are comparable with the present tests. The remaining samples were found to have either limited test data, or the samples had not been scheduled for testing by Halcrows. Therefore data were provided for adjacent samples, which had been tested. However, it became apparent that the material sampled was too variable for such a procedure to produce meaningful results.

Scott Wilson Kirkpatrick kindly provided test data for fill material from the A564 Foston-Hatton-Hilton bypass. Chemical test data were available for only 1 borrow pit sample that was tested by TES Bretby for water-soluble sulfate, acid-soluble sulfate and total sulfur using the existing British Standard based procedures. Sample description, grading and pH determinations were available for this and other samples. Trial pitting was undertaken as part of this project to obtain samples [TR11-D and TR11-D5] from undisturbed ground situated about 3 metres from the original borrow pit. The test data from these samples are considered to be comparable with the data for the single borrow pit sample mentioned above. Additionally 6 bagged sand and gravel samples that were collected from the borrow pit during the original construction period and then stored outside for 43 months in the site compound were tested to determine if any chemical changes had occurred as a result of this mode of storage.

The results of the comparative tests are presented in Appendix B3.

5.2 Results and interpretation

The results presented in Appendix B2 indicate the presence of reduced sulfide mineral species (pyrrhotite or pyrite) in many of the samples tested. Generally these mineral species are common in argillaceous materials such as mudrocks, slates and consolidated clays. However, it is seen from the results for samples TR10 and TR21 that not all argillaceous deposits contain these mineral species. If the procedures recommended in BS 1377: Part 3 had been followed, these minerals would not have been identified in granular, non-mudrock samples such as samples TR11-D, TR11-D5 and TR16-1 in which only sulfates would have been routinely determined. It was observed that the grey colour of these alluvial sand and gravel samples could be indicative of the presence of reduced sulfur species. Generally brown to yellow brown alluvial material was found to be associated with low sulfur contents. When summed up, the results of the sulfur species determinations were in good agreement with the total sulfur value, slight differences being due to the presence of organic sulfur. This is especially noticeable in sample TR23-3, where there was 5.09% excess in the total sulfur value present in what is interbedded clay and low grade coal.

The weathering state of samples was seen to affect the sulfate to reduced sulfides speciation. This can be seen in the results from samples TR14-1 to TR14-25. The material consisted of Lower Lias Clay ranging from unweathered in-situ material to both unweathered and weathered fill. Unweathered material such as samples TR14-1, TR14-3 and TR14-6 contained sulfur mainly in the reduced form (0.86 to 2.09 %S) with small quantities as sulfates (0.16 to 0.31%S). On the other hand, in samples TR14-2, TR14-20 and TR14-23, which were weathered material, the reduced sulfur contents were low (0.12 to 0.23%S) but the sulfate sulfur contents were relatively high (0.72 to 0.92 %S). Therefore it is important to evaluate the state of weathering of a sample when evaluating chemical data as this assists the evaluation of the material for changes induced by oxidation. Again, the high total reduced sulfur contents would not have been detected if only the existing BS 1377: Part 3 tests for sulfate had been carried out. The notes to the test procedure for sulfate in BS 1377: Part 3 state that, if pyrite is thought to be present, the total sulfur content should be determined by the BS 1047 method, and the difference between this value and the acid-soluble sulfate (total sulfate) should be attributed to pyrite. However, in practice this is rarely done.

The data in Appendix B3 show that there is good agreement between the results of the new test procedures and those of the British Standard test procedures. The water-soluble sulfate values are in overall agreement, but the new procedure has greater sensitivity. The differences between results range between 0.00 and 0.12 %S with the new method giving generally higher values.

The results for acid-soluble sulfate determinations are also in good agreement. The differences between methods range between 0.03 and 0.11 %S. There appear to be no particular factors influencing whether results are higher or lower than those obtained using the British Standard procedures. They are therefore probably due to the variable nature of the samples.

The results for the parallel chemical determinations on split samples and the single alluvial gravel sample (SWK – S934.1) for which comparable data are available are generally in good agreement for total sulfur determination. The differences between results usually ranges between 0.02 and 0.07%S, but for samples TR14-12 and TR14-17 the differences are respectively 0.18% and 0.49%. The average deviation of results about the mean is between 0.01 and 0.04% but at 0.09% and 0.25% respectively for samples TR14-12 and TR14-17 the deviation is higher in the latter cases. These differences are probably due to the presence of non-uniformly distributed sulfur compounds such as pyrite nodules or pockets of organic material containing sulfur, rather than the presence of sulfate crystals since the results for acid-soluble sulfate are in good agreement.

Direct comparisons are not possible for reduced sulfur species since only in the Sheffield tests was this determined directly and not by difference from the total sulfur and sulfate value. However, the values for total reduced sulfur in Appendix B3 are generally in reasonable agreement with the values obtained by the new procedures.

6 Sample storage

6.1 Storage tests

It is known that gypsum and pyrite may undergo degradation during short-term storage under atmospheric conditions. Many researchers have observed that oxidation of pyrite occurs when samples are maintained under standard sample storage conditions (Wilson, 1987; Hawkins and Pinches, 1987; Pye and Miller, 1990; Sandover and Norbury, 1993). Accordingly, to inform decisions concerning the suitability of storage conditions for samples intended for chemical testing, the effect of environmental conditions on sulfur compounds was investigated. The tests were conducted in two phases, in the first of which samples were specially pre-prepared for storage testing under different conditions while in the second, six Lower Lias Clay core samples (TR14-1 to TR14-6) were used as received. The results are given in Appendix B4.

Three samples (TR3B, TR6 and TR11-D) of varying sulfur mineralogy were selected for the phase one testing. These were oven dried at 60°C, until there was no further weight loss in successive weighings, and then the material was cooled, ground to a powder (except sample TR11D where grinding was not required) and homogenised. Fractions of each sample weighing about 60g were placed in glass test tubes, which were closed with a glass wool bung to prevent the entry of dust, and stored under the following conditions:

- Laboratory atmospheric conditions (see Table 6.1).
- Zero humidity, in a desiccator cabinet.
- Constant refrigerated conditions at ≤ 4°C.
- Constant 60°C in a fan assisted laboratory oven.
- Saturated controlled atmospheric conditions, at 90-95% relative humidity and laboratory temperatures (for temperature see Table 6.1).
- Incubated conditions at 34°C (for relative humidity see Table 6.1).

The samples were stored for a period of almost a year, and sub-sampled at intervals of 14, 44, 82, 112, 180, 241 and 346 days so that changes in sulfur speciation could be monitored.

Table 6.1 Laboratory conditions during the sample storage tests

Parameter	*Temperature °C*	*% Relative humidity*
Mean	20.4	54.2
Mode	21	65
Maximum	23	74
Minimum	17.5	30

The phase two samples were stored in the original core liner with an additional wrapping of polystyrene film, and replicate sub-sample fractions were stored in polythene sample bags. The aim was to replicate storage in sealed core liner and in containers allowing access to air. The samples were stored under the same laboratory conditions as the first phase samples (see Table 6.1) and sub-sampled at 79, 184 and 254 day intervals for acid-soluble sulfur and total reduced sulfur testing.

In addition to the above storage testing, sample TR6 was wrapped in a polythene bag and stored under laboratory conditions for a total of 475 days with sub-sampling and testing to monitor the sulfur phase changes at 278, 417 and 475 days. On completion of the storage tests the samples were also analysed for their carbonate content. The results are presented in Tables B4.1 to B4.5 of Appendix B4.

6.2 Results and interpretation

6.2.1 Phase One

It would be expected that as removal of reaction products during pyrite oxidation requires an aqueous phase, whatever the environmental conditions, chemical change would have been initially retarded as the samples were in a dry condition at the beginning of the test. However, the results from the first phase storage experiment showed quite evident loss of total reduced sulfur and gain in acid-soluble sulfur for the samples stored under humid and incubated conditions for all three samples tested. Sample TR8, which was an indurated slate with a high content of cubic pyrite crystals, showed the least amount of chemical change (Figures 6.1a and b). This would be because pyrite in this form is less reactive than finer grained and framboidal types present in other samples. Sample TR8 also showed a drop in the monosulfide sulfur content for all storage conditions, but no drastic change in the carbonate content over time.

Sample TR3B showed a clear decrease in total reduced sulfur for both the humid and incubated storage conditions over 3 months of storage. The sample stored under laboratory conditions also underwent a decrease in total reduced sulfur after 3 months of storage, and all three samples showed a general increase in acid-soluble sulfur content after 8 months of testing (Figures 6.2a and b). There was a small proportion of monosulfide sulfur detected in all the samples on completion of the storage experiment, which was not detected at the start of the experiment. This may be an intermediate product of pyrite oxidation although apparently aerobic conditions were maintained throughout the experiment. There was also a notable drop in carbonate content for the incubated, humid and to a lesser extent laboratory stored samples. This was probably due to reaction of calcite with pyrite reaction products to produce acid-soluble sulfur in the form of gypsum.

Sample TR11-D was recent alluvial sand containing framboidal pyrite. After 3 months of storage there was an evident decrease in total reduced sulfur for samples stored under humid, incubated and to a lesser extent laboratory conditions (Figures 6.3a and b). This was shadowed by an increase in the acid-soluble sulfur content after a period of 6 months of testing. Again, there was detectable

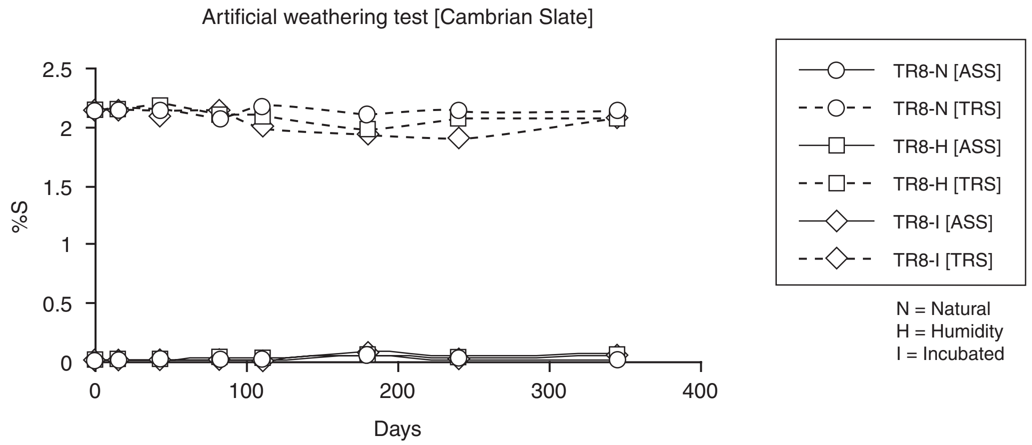


Figure 6.1a Sulfur specification changes due to storage method for TR8

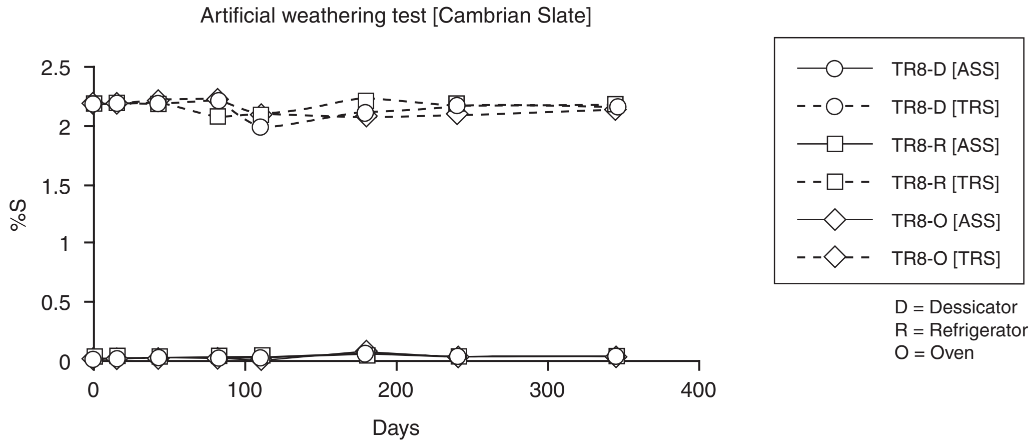


Figure 6.1b Sulfur specification changes due to storage method for TR8

monosulfide sulfur for all the samples tested after completion of the experiment. Total loss of carbonate occurred in the humid and incubated samples, and a decrease in the sample stored under laboratory conditions. This would probably have been consumed by pyrite reaction products to form acid-soluble sulfur. There was also an increase in water-soluble sulfur in incubated and humid samples, and an increase in the acidity of all the samples.

Small changes were recorded in the case of the oven-heated sample. This was probably due to moisture not being entirely eliminated by this treatment, as the samples were not sealed.

6.2.2 Phase Two

It should noted that although for phase one the samples were homogenised prior to the start of the experiment, in phase two, pieces of core were used as supplied. Because of this the sub-samples taken during the experiments may not have contained exactly the same initial mineralogy at the start of the test.

All but one sample in the phase two experiments showed a progressive loss in total reduced sulfur content, and a gain in the acid-soluble sulfur content (see Figures 6.4 to 6.10). As sample TR14-4 had a very low starting total reduced sulfur content, the changes here were slight. The results indicate a greater loss of total reduced sulfur in the bagged samples when compared with the core liner stored samples, with differences ranging from 20 to 71% greater loss of total reduced sulfur. There were evident carbonate content losses in only three of the six samples, with negligible changes in organic carbon content.

Sample TR6, which was stored in a sealed bulk bag, showed a marked loss in total reduced sulfur content within the first 8 months of storage, with a corresponding increase in acid-soluble sulfur content (Figure 6.4). There was also a clear decrease in the carbonate content but no detectable change in the amount of organic carbon.

The results from the storage experiment show clearly significant changes in sulfur and carbonate mineral species occur as a result of inappropriate storage conditions. Under laboratory, humid and incubated conditions, reduced sulfur minerals were degraded with the resulting loss of calcite and formation of gypsum. Therefore storage conditions are shown to have a drastic effect on the mineralogy of samples.

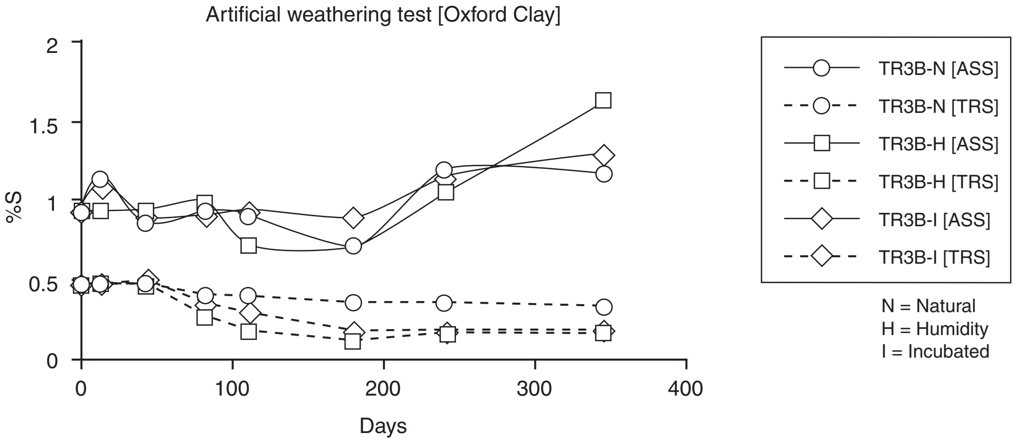


Figure 6.2a Sulfur specification changes due to storage method for TR3B

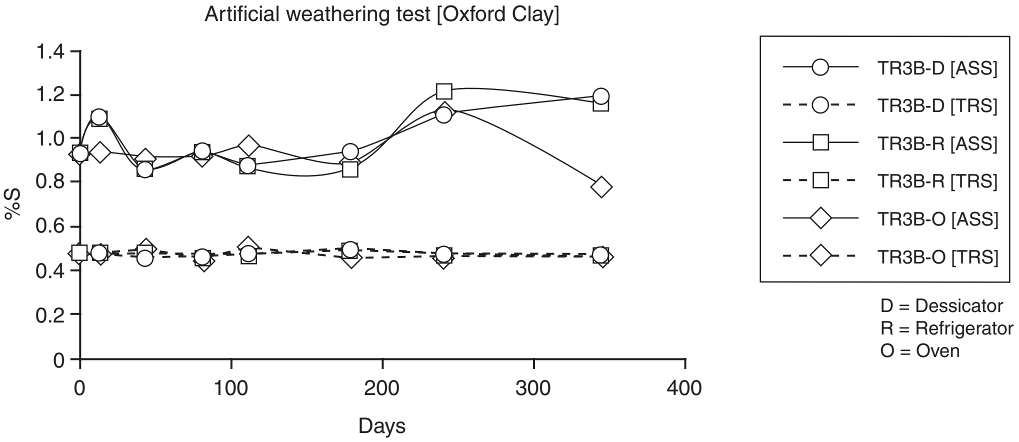


Figure 6.2b Sulfur specification change due to storage method for TR3B

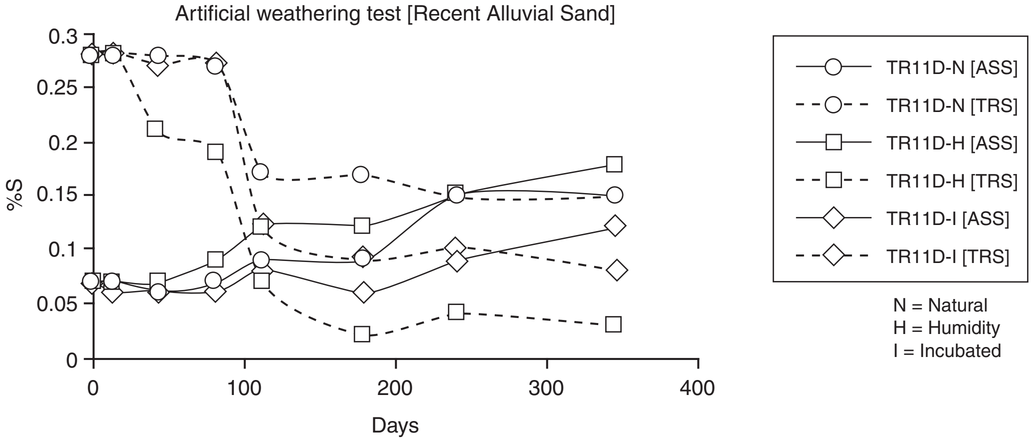


Figure 6.3a Sulfur specification changes due to storage method for TR11-D

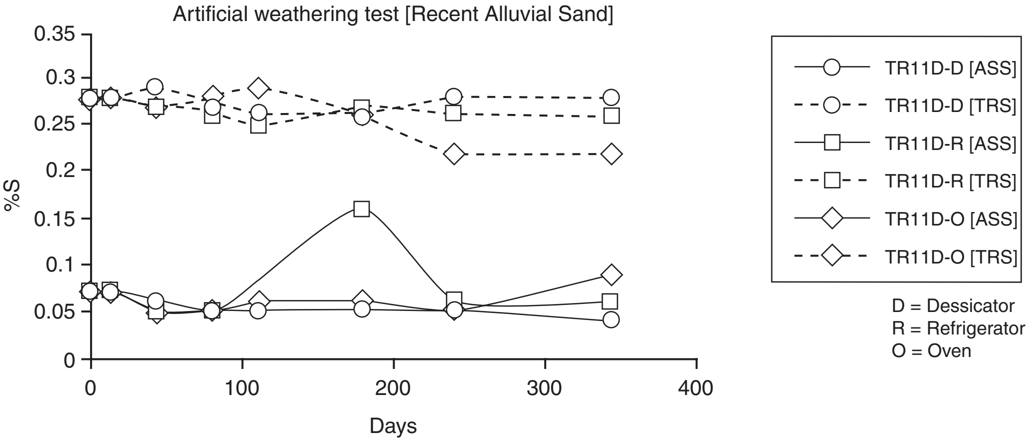


Figure 6.3b Sulfur specification changes due to storage method for TR11-D

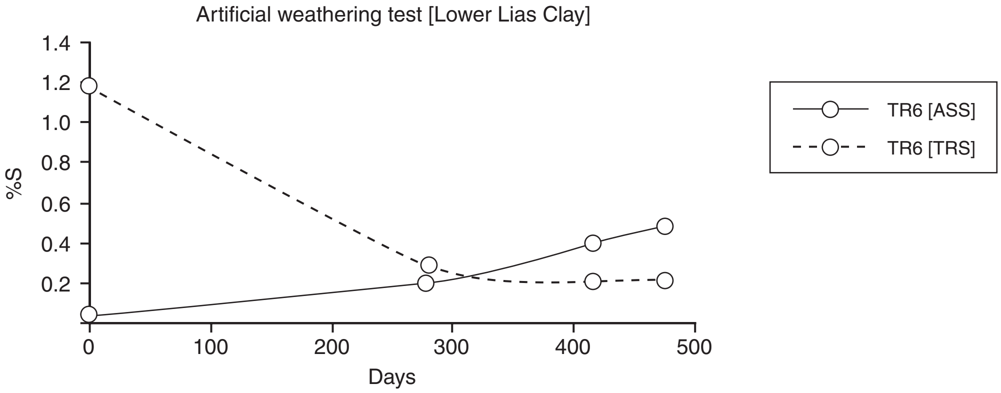


Figure 6.4 Sulfur specification change due to storage method for TR6 (Polythene wrapped block sample)

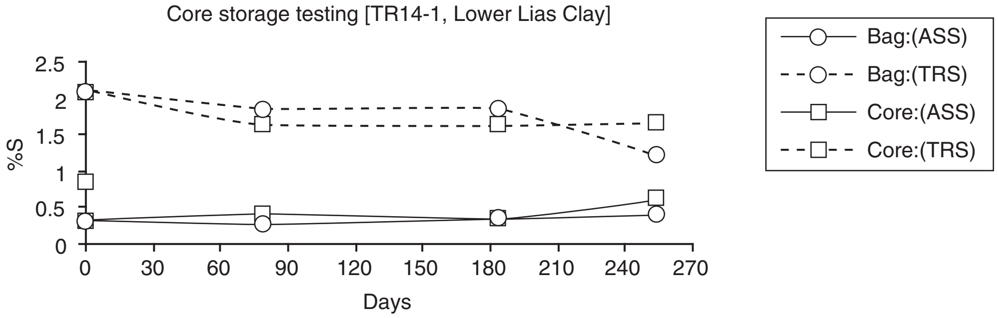


Figure 6.5 Sulfur specification changes due to storage method for TR14-1

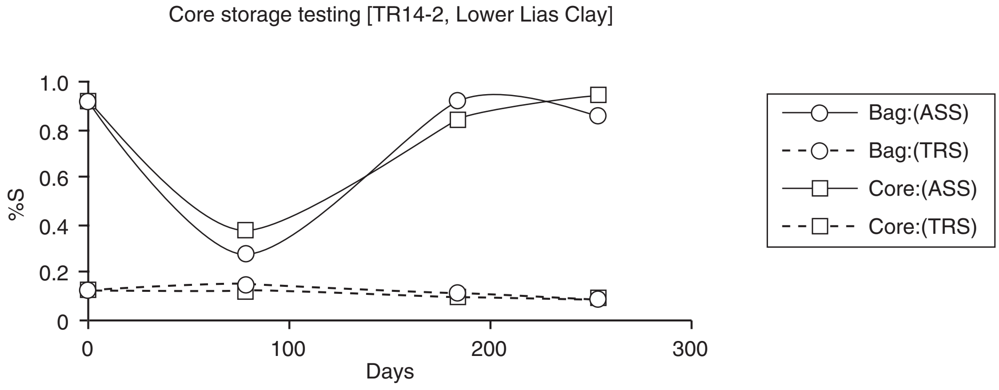


Figure 6.6 Sulfur specification changes due to storage method for TR14-2

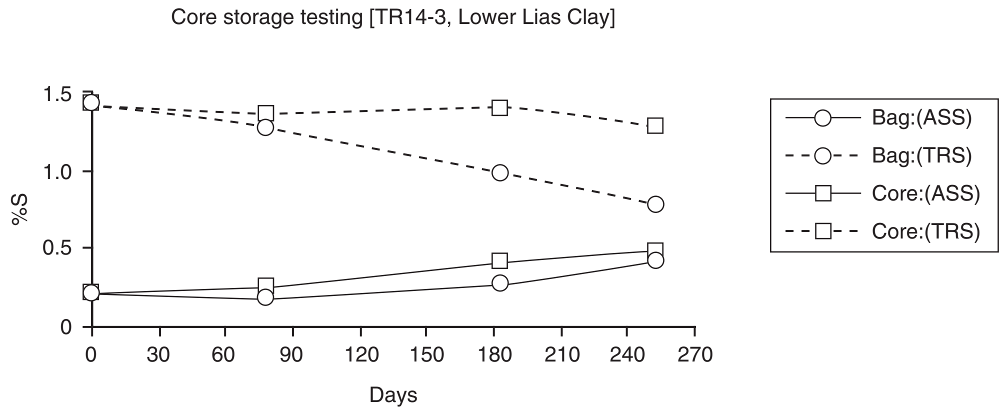


Figure 6.7 Sulfur specification changes due to storage method for TR14-3

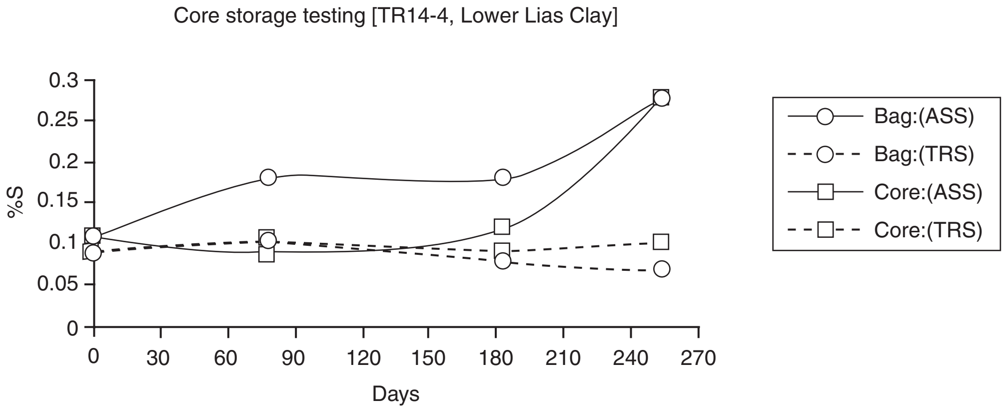


Figure 6.8 Sulfur specification changes due to storage method for TR14-4

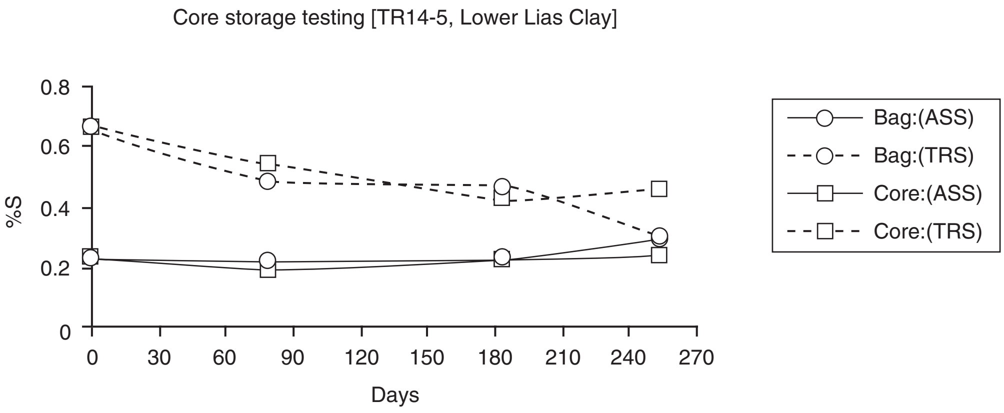


Figure 6.9 Sulfur specification changes due to storage methods for TR14-6

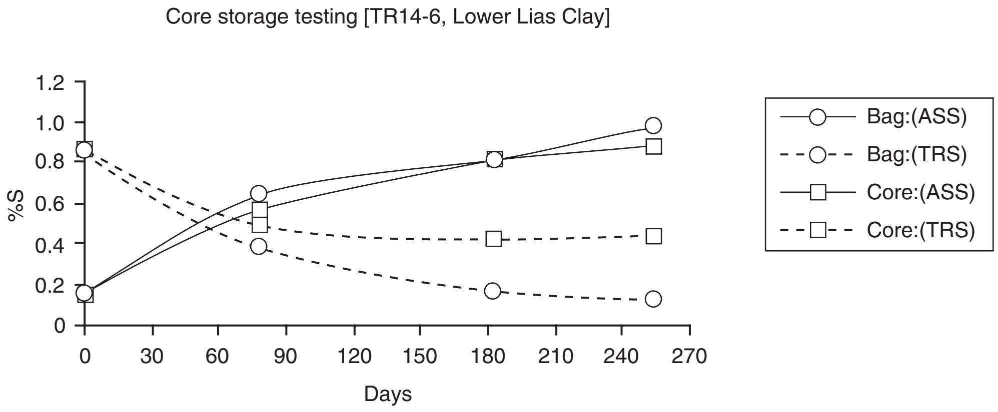


Figure 6.10 Sulfur specification changes due to storage method for TR14-5

The results presented in Table B4.4 (Appendix B4) give examples of the conversion of total reduced sulfur to acid-soluble sulfur under actual sample storage conditions. Three further samples, not listed in Table B4.4 (TR14-19, TR14-20 and TR14-23) had been kept in Halcrow's unheated core store for 8 months after being tested by TES Bretby at the time of sampling. The results show that there was a drastic decrease in total reduced sulfur content (0.14 to 0.08, 1.41 to 0.18 and 1.38 to 0.23 %S) and increase in acid-soluble sulfur (0.08 to 0.09, 0.08 to 0.72 and 0.15 to 0.90 %S). These reductions in total reduced sulfur show that core samples, even when stored in air-tight core liner, are liable to undergo chemical change. This is because pore water, interstitial water and oxygen are present within the sample.

The alluvial samples donated by SWK from the A564 by-pass work had been stored in sealed plastic bags for almost 4 years outdoors in a site compound. Test data for only one borrow pit sample were available from the original construction period and data for two additional samples taken in 1998 from near to this borrow pit were also obtained. The results show that the unweathered alluvium contains between 0.04 - 0.17 %S as acid-soluble sulfur and 0.22 - 0.58%S as total reduced sulfur. The six samples which had been stored for almost 4 years contained between 0.10 - 0.51 %S as acid-soluble sulfur and 0 - 0.02%S as total reduced sulfur. The results indicate that during storage the sulfides present in the samples had completely weathered to sulfate. Hence, to inhibit any chemical changes, samples need to be stored under dry or refrigerated conditions.

The results of the tests clearly demonstrate the importance of storing samples under conditions where changes in the sulfur mineralogy will not occur. It is recommended that samples be placed in airtight containers with a minimum amount of air. At least 1000g of sample is required for the sulfur compound tests. The sample containers should be stored on site at 0-4°C using a portable refrigerator or cool box. The samples should be transferred to the laboratory as soon as possible and stored in a refrigerator at 0-4°C. The dates of sampling, transference to the laboratory and all details of storage should be recorded. Samples should be analysed as soon as possible to minimise the opportunity for change in sulfur speciation and other chemical changes.

7 Case studies of pyrite oxidation

7.1 Roadford Dam

Roadford Dam is an embankment dam on the River Wolf in west Devon. The dam impounds a reservoir of some 37,000 ML, which is used primarily for water supply during the summer months. The embankment is 430 m in length with a maximum height of 41 m. It contains 970,000 m^3 of locally won low grade rockfill, 62,000 m^3 of drainage blanket material and has an upstream impermeable asphalt membrane. The dam was constructed between 1987 and 1989 and is owned and operated by South West Water.

The embankment material comprised fresh to moderately weathered mudstones, siltstones and sandstones of Carboniferous age. These materials combined to give a fairly homogeneous fill of free-draining, well-compacted granular material. Pyrite was present in the fresh mudstone, with an average content of 1.3% S, but was much less common in the other materials. The overall pyrite content of the embankment fill was estimated to be 0.6% S. The materials had negligible calcite content and were markedly acidic, with the pH ranging from 3.1 to 6.4.

There was concern that pyrite oxidation in the fill might lead to deterioration in the geotechnical properties of the fill and production of polluting drainage water from the embankment. Drainage from trial embankments constructed during the site investigation for the dam was found to be acidic with high concentrations of sulfate, iron and manganese. It was clear that oxidation would occur in the embankment, but the scale of the reactions was difficult to predict. An allowance was made in the design for some long term degradation in the shear strength of the fill, and the chemistry of the drainage waters was monitored during construction and operation to assess the rate of reaction within the embankment.

The composition of the drainage blanket material had a significant effect on the quality of the drainage water. The material was an altered dolerite which had a significant concentration of calcite, both as an alteration product to primary minerals and as a vein material. The average calcite content of the material was estimated to be 11.6%. Mass balances showed that if all the pyrite oxidised to sulfuric acid, it could in theory be neutralised by the calcite. Drainage from the embankment was found to have high sulfate concentrations and neutral pH from the start, indicating that pyrite oxidation and reaction between the sulfuric acid produced and the drainage blanket material was taking place. The sulfate concentration showed a seasonal pattern, with values much higher in winter than in summer. This is thought to reflect the greater flushing of weathering products out of the embankment in the winter months.

Estimates of the quantities involved in the reactions were based on the sulfate and calcium concentrations of the drainage waters. These can be related to the oxidation of pyrite and solution of calcite respectively. Quantities were calculated from the volume of the drainage water and the concentrations of sulfate and calcium, corrected for background levels in groundwater. Calculations showed that about 0.15% of the pyrite and 0.33% of the calcite had been consumed in chemical reactions over the period July 1990 to June 1991 (Table 7.1). These figures are indicative of the annual rate of pyrite oxidation and associated reactions in the early years of the life of the embankment.

Although the rate of reaction was very slow, it had a significant effect on the quality of the drainage water. This has required treatment to precipitate iron and manganese before discharge into the River Wolf downstream of the dam. The main potential impact of the oxidation reactions is thus environmental rather than geotechnical in this case.

7.2 Carsington Dam

Similar problems occurred during the reconstruction of Carsington Dam in Derbyshire. This 1200 m long embankment dam was initially constructed in the early 1980s, until a major slip occurred on the upstream face in 1984 when the embankment had nearly reached full height. A detailed investigation was carried out into the failure, following which the owners, Severn Trent Water, decided to rebuild the embankment on the same alignment but to a modified design. A further site investigation was carried out in 1987, and the dam was successfully reconstructed between 1989 and 1992. The dam retains a reservoir of 36,000 ML capacity, which is used to augment the flow of the River Derwent in summer. The history of the project is described by Banyard *et al.* (1992).

The dam is a zoned embankment with a clay core and shoulders of weathered mudstone. As at Roadford, the strata are of Carboniferous age, but here they are highly weathered to considerable depth and consist dominantly of marine mudstones with minor sandstones and carbonate bands. Because the materials are highly weathered, the fill has the consistency of clayey gravel and is not free draining. Drainage layers were thus incorporated in the original design to allow dissipation of porewater pressures. Local Carboniferous limestone was used for the drainage layers and the basal drainage blanket.

The fresh mudstone at depth has a pyrite content of about 3.5% S, a calcite content of about 7.5% $CaCO_3$ and near neutral pH. However, the deep weathering profile meant that most of the material used for embankment construction was weathered and had very high sulfate content and pH in the range 4 to 5, but low pyrite and calcite content. The pyrite had been oxidised and the resulting acid had dissolved the carbonate minerals. A summary of the properties of the materials used in embankment construction is given in Table 7.2.

The geochemical properties of the fill caused a number of problems. The acid waters from the mudstone fill reacted with the limestone in the drainage layers, clogging the drains with precipitates of gypsum and hydrous oxides of iron (ochre) (Plate 7.2) and generating carbon dioxide which travelled down the drains into the manhole system. This presented a major safety hazard. Corrosion of buried concrete was also noted when the dam was dismantled in 1989, particularly where drainage blankets were in contact with concrete (Plate 7.1). The movement of water and air through the drainage blanket allowed the reactions to proceed at a faster rate than where the concrete was in contact with the less permeable mudstone fill. There was concern that the chemical reactions might have contributed to a loss of strength in the fill material. Finally, the runoff from the dam was highly acidic with very high concentrations of iron and other metals. The runoff had to be collected and stored in large lagoons, where it was dosed

Table 7.1 Geochemical losses from Roadford and Carsington embankments

Parameter	*Roadford: July 1990 – June 1991*[1]	*Carsington: 1991*	*Carsington: 1992*	*Carsington: 1993*	*Carsington: 1994*	*Carsington: Average*
Weight FeS_2 lost (kg)	33,348	2,119	2,867	3,826	2,961	2,968
% Total FeS_2 lost by weight	0.15	0.0009	0.0012	0.0016	0.0013	0.00125
% Embankment fill lost by weight	0.0017	0.00004	0.00006	0.00008	0.00006	0.00006
Volume FeS_2 lost (m^3)	6.95	0.45	0.61	0.81	0.63	0.625
Weight $CaCO_3$ lost (kg)	49,222	5,755	5,089	5,901	4,822	5,392
% Total $CaCO_3$ lost by weight	0.33	0.0028	0.0025	0.0029	0.0023	0.0026
% Embankment fill lost by weight	0.0022	0.00012	0.00010	0.00012	0.00010	0.00011
Volume $CaCO_3$ lost (m^3)	18.2	2.12	1.88	2.18	1.78	1.99
Total weight lost (kg)	82,570	7,874	7,956	9,727	7,783	8,335
Total volume lost (m^3)	25.15	2.57	2.49	2.99	2.41	2.62
% Total fill lost by weight	0.0039	0.00016	0.00016	0.00020	0.00016	0.00017

[1] *Data from Davies and Reid (1997)*

Table 7.2 Geochemical data for embankment fill at Carsington Dam

	Type C (Core fill, head and residual mudstone)		*Type T (Transition fill, completely and highly weathered mudstone)*		*Type S (Shoulder fill, moderately and slightly weathered mudstone)*		*Total*
Parameter	*Average* **	*Range*	*Average* **	*Range*	*Average* **	*Range*	*Average* **
Volume (m^3)	2.12 x 10^5		1.31 x 10^6		1.14 x 10^6		2.66 x 10^6
Weight (kg)	3.12 x 10^8		2.31 x 10^9		2.27 x 10^9		4.89 x 10^9
Acid-soluble sulfate (%SO$_4$)	0.55	0.06 – 3.34	2.17	0.40 – 4.40	1.90	0.60 – 5.33	1.94
Pyrite (%S)	0.44	0.02 – 0.91	2.65	0.57 – 4.06	2.79	0.35 – 4.40	2.58
Total sulfur (%S)	0.62	0.20 – 1.14	3.37	0.74 – 4.53	3.42	0.59 – 4.91	3.23
CaCO$_3$ (%)	0.27	0.0 – 0.77	1.55	0.0 – 4.77	7.43	0.16 – 71.4	4.20
pH	4.3	3.1 – 5.4	4.7	2.9 – 7.1	5.9	2.8 – 7.5	–

* *Median values used for pH and CaCO$_3$*
** *Total values for volume and weight, average values for chemical species*

Plate 7.1 Concrete corrosion on spillway, Carsington Dam

with lime to precipitate the metals, before it could be discharged into the river downstream of the dam.

All the above aspects had to be addressed for the redesign of the embankment. The use of non-calcareous aggregates was specified for all drainage blankets and filters and the drainage system was designed to allow venting of gas to the atmosphere. Conditions for buried concrete with respect to sulfate attack were assessed as Class 5 according to BRE Digest 250 (1981), which was in force at the time. Leaching tests were carried out to assess the potential effect of weathering on the geotechnical properties of the fill (Anderson and Cripps, 1993) and an allowance for long-term degradation was made in the geotechnical design (Chalmers *et al.*, 1993). A layer of inert gravel was placed between the fill and topsoil on the downstream shoulder, to prevent vegetation being killed by acid from the fill. Two lagoons were constructed downstream of the dam to collect and treat all runoff and drainage to an acceptable standard.

The chemistry of the fill was monitored during reconstruction, and the results are summarised in Table 7.2. The chemistry of the drainage water was monitored during and after construction for pH, sulfate, alkalinity, iron, conductivity, turbidity and temperature, with occasional samples sent for more detailed analysis. A deposit of hydrous iron oxide (ochre) rapidly formed in the drainage outfall chamber and the channel leading from it to the lagoons, indicating that chemical reactions were still occurring within the embankment (Plate 7.3). The pH of the drainage was in the range 6.0 to 7.0, with the sulfate concentration fairly constant at about 90 mg/l, without the seasonal fluctuations observed at Roadford.

Plate 7.2 Chemical attack on limestone drainage blanket in acidic mudstone fill, Carsington Dam. Rupture surface to right of tape measure

Plate 7.3 Outfall showing precipitation of ochre in channel at Carsington Dam

The rate of pyrite oxidation was calculated by the same method as at Roadford, based on the rate of flow and concentrations of sulfate and calcium corrected for background levels in groundwater. Geochemical losses were calculated for the years 1991 to 1994. For pyrite, the annual losses ranged from 0.0009% to 0.0016% of the total pyrite, and for calcite from 0.0023% to 0.0029%. These values are much lower than those recorded at Roadford. This is ascribed to the more free draining nature of the fill at Roadford, which is more conducive to pyrite oxidation. A comparison of the total amounts lost from both embankments is given in Table 7.1.

As at Roadford, only a very small percentage of the pyrite was being oxidised each year. However, this was enough to have a major environmental impact and to require extensive precautions to avoid sulfate attack on buried concrete. As a result of these precautions, the condition causes no problem with the Dam and Reservoir or discharges.

7.3 A564: Hatton – Hilton – Foston Road improvement

Problems with corrosion of galvanised corrugated steel buried culverts occurred in this road improvement scheme in Derbyshire soon after construction. The steel was found to be severely corroded to the extent that holes were present in a number of culverts. The culverts had to be replaced before the road was opened to traffic, causing significant delays and additional expense to the contract. An example of the corrosion is shown in Plate 7.4.

The backfill to the structures was local alluvium, consisting of sand and gravel. Tests at the time of construction were for pH only. The results indicated that the material was acceptable but the rapid corrosion, which occurred following construction, indicated that another mechanism was at work. It is thought that rapid oxidation of pyrite in the fill took place when it was placed in the embankment, leading to the production of sulfuric acid which attacked the steel directly. Samples of material from adjacent to a borrow pit used for the structural backfill were obtained and tested in the course of this project (samples TR11-D and TR11-D5, Appendix B). The results show that the material contained 0.40 % S as total reduced sulfur (pyrite). A concentration of 0.40 % S would equate to a total potential sulfate (TPS)[†] concentration of 6.0 g/l SO_4. This is well above the limiting value of 0.3 g/l SO_4 for water-soluble sulfate for galvanised steel structures given in Chapter 8 of this report.

Sulfur species determination according to the British Standards procedure was carried out on one sample from the borrow pit during the construction period. The difference between total sulfur and acid-soluble sulfur gives a reduced sulfur content of 0.29% S, which equates to an oxidisable sulfides[††] concentration of 0.9 % SO_4. This is well above the limiting value given in Chapter 8 of this report. Had the testing regime proposed in Chapter 8 been carried out, the problem would have been identified and the material classed as unacceptable for structural backfill.

The alluvial material from the borrow pit was grey in colour. This indicates that reduced sulfur species may be present and could have been used as a pointer towards the need for detailed sample characterisation. The chemical test results in Table 5.2 show that the 6 original borrow pit samples which had been stored out of doors in sample bags for 4 years contained between 0.10 to 0.51% S as acid-soluble sulfur and 0 to 0.02 % S as total reduced sulfur.

Plate 7.4 Corrosion to corrugated steel buried culvert on A564

[†] *See Chapter 8 for explanation of TPS*

[††] *See Chapter 8 for explanation of oxidisable sulfides*

The fresh borrow pit material tested contained between 0.22 and 0.58 % S as reduced sulfur and only between 0.04 and 0.07 % S as acid-soluble sulfur. Therefore in an indeterminate period of up to 4 years the reduced sulfur in the form of pyrite had been completely converted to sulfate-sulfur.

The percentage of reduced sulfur is much lower in this material than in the Carboniferous mudstones in the embankment dam examples. River gravel is not normally considered a material likely to contain high amounts of pyrite, although similar cases have been reported (Sandover and Norbury, 1993). This case illustrates the importance of screening tests to identify materials having high total reduced sulfur content even in materials that do not have a history of corrosion problems.

7.4 M5 bridges on Lias Clay

In early 1998, the thaumasite form of sulfate attack was identified in a number of motorway bridge foundations on the M5 in Gloucestershire. All of the structures were founded on Lias Clay and the foundations had been backfilled with clay from the excavations for construction. The nature and form of the thaumasite attack are described by the Thaumasite Expert Group (1999). The limited test data at the time of construction, some 25 years before the problem was identified, indicate sulfate levels in Class 2. Tests on the backfill material during the investigation of the corrosion indicate that levels would now correspond with Class 4 and 5. The increase is thought to be due to oxidation of pyrite in the Lias Clay backfill. The oxidation is thought to have started when the clay was stockpiled beside the excavations during construction of the foundations.

Tentative calculations based on mineralogical and geochemical determinations on samples from excavations and boreholes in the fill and local undisturbed Lower Lias Clay have been used to indicate the apparent loss of pyrite from the fill since the construction. Taking data from a wide area indicated that the unweathered Lower Lias Clay contains about 1.05% total reduced sulfur (TRS), which compares with a total reduced sulfur content of about 0.53% in the weathered backfills at the site of the Tredington-Ashchurch Road Bridge. Data for other sites show similar trends. Only part of the sulfur released appears to have reacted with available calcite in the fill to produce gypsum (calcite decreases from 26% to 19% and gypsum increased to 0.7%), leaving about 0.48% sulfate available for thaumasite formation. Calculations of the amount of sulfur required for the thaumasite formed in the concrete from the volume of made ground associated with particular structures show that there is a large excess of sulfur available in the fill surrounding the affected structure. For instance, in the case of the central pier of the Tredington-Ashchurch Bridge there would be sufficient sulfur in only 46 m^3 of fill to account for the volume of thaumasite that was found in that structure. As the volume of fill associated with this pier is 325 m^3, only about 15% of the available sulfur is now present as thaumasite.

It is likely that the rate of acid and sulfate formation was most rapid during and shortly after excavation and backfilling during construction. At this time oxygen required for the oxidation of pyrite would be available but as this and the most accessible pyrite were consumed, the reaction rate would decrease. It would appear that at this particular site, further oxidation of the remaining pyrite could produce an amount of thaumasite similar to that already present. However, with the reduced rate of reaction and the longer flow paths for reactants now present, the amount is likely to be less than this.

8 Use of the new test methods

8.1 Terminology

Up to this point in the report, the test methods and results have been presented in terms of % S. This has advantages for analytical reasons and to enable comparison between the amount of sulfur present in different forms in a material. The determination of all sulfur species in terms of S has the advantage of allowing easy checks between the parameters for suspicious results. These are less obvious if some values are given as sulfate and some as sulfur. Some possible checks are given in the notes to Table 8.1. However, in order to interpret the results in terms of potential for attack on construction materials, it is necessary to transform the sulfur content into sulfate, either as mg/l SO_4 for water-soluble sulfate or % SO_4 for acid-soluble sulfate.

Table 8.1 Symbols for use with sulfur compounds

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	mg/l SO_4	–	15,000 x WSS	WS
Acid-soluble sulfate	% SO_4	–	3 x ASS	AS
Total potential sulfate	% SO_4	–	3 x TS	TPS
Oxidisable sulfides	% SO_4	–	TPS - AS	OS

Notes:

WS can also be expressed as % SO_4. The conversion factor is then WS (% SO_4) = 3 x WSS.

OS can also be determined from TRS. The conversion factor is OS = 3 x TRS.

Checks that can be employed on sulfur species include the following:
$TS \geq ASS + TRS$; $ASS \geq WSS$; $TRS \geq MS$; $TPS \geq AS$.

Example:
TR14-6, Lower Lias Clay (Appendix B2):
WSS = 0.16 % S; ASS = 0.16 % S; TRS = 0.99 % S; MS = 0.13 % S; TS = 1.17 % S.
WS = 2,400 mg/l SO_4 ; AS = 0.48 % SO_4 ; TPS = 3.51% SO_4; OS = 3.03 % SO_4.

In order to ensure clarity with respect to the form of sulfur, a set of symbols are proposed for use when dealing with sulfur compounds. The proposed symbols and their inter-relations are given in Table 8.1. Several of the symbols are already used by BRE in Special Digest 1 (Building Research Establishment, 2005). These have been maintained with their present meaning. The basic symbols WS, AS and TS refer to the forms of sulfur which are used in deciding the Design Sulfate (DS) Class. Thus they have different units: WS is as SO_4 in mg/l, AS as SO_4 in %, and TS as S in %. Using the old BS 1377: Part 3 gravimetric test (British Standards Institution, 1990), the results are obtained as sulfate (% SO_3), and can be converted to SO_4 by multiplying by 1.2.

With the introduction of ICP-AES, sulfur is determined as the element S, and has to be converted to SO_4 for use in classification systems. The new symbols are thus based on sulfur content rather than sulfate. New symbols WSS and ASS have been introduced for the determination of water-soluble and acid-soluble sulfur respectively using the new test methods. These figures can be converted to the equivalent WS and AS values using the conversion factors shown in Table 8.1. An example is given in the notes to Table 8.1.

The total potential sulfate (TPS) which could be generated by oxidation of reduced sulfur can be estimated conservatively from the total sulfur (TS) by assuming that all the sulfur in a sample will ultimately be converted to sulfate. TPS is expressed as % SO_4 and is calculated from 3 x TS, as shown in Table 8.1. Reduced sulfur may be estimated more accurately either by direct measurement of the total reduced sulfur (TRS), or by the difference between total sulfur (TS) and acid-soluble sulfur (ASS). As the total reduced sulfur test cannot be recommended for routine use at this stage, reduced sulfur may be estimated by TS - ASS. This is somewhat conservative, as unreactive species such as organic sulfur and barytes will be included, but the validation trial shows that both TS and ASS can be determined with a high degree of accuracy and repeatability using the new methods. The oxidisable sulfides (OS), which could be generated by oxidation of the reduced sulfur can then be calculated as shown in Table 8.1. OS is expressed as % SO_4, to enable the risk that the resulting sulfates pose to construction materials to be assessed.

8.2 Number of tests

The distribution of sulfur compounds in soils, rocks and fills can be extremely variable. It is therefore necessary to test sufficient samples to ensure that the true conditions are established. This aspect is addressed in Special Digest 1 (Building Research Establishment, 2005). This recommends that, if less than 5 samples are tested, the highest value should be taken as the characteristic value to determine the Design Sulfate (DS) Class for the site. If 5 to 9 results are available, the mean of the highest two results should be used as the characteristic value; and if 10 or more results are available, the mean of the highest 20% of the results should be taken as the characteristic value (Building Research Establishment, 2005). This method is also recommended for structural backfill materials. A minimum of 5 test results should be used when assessing the suitability of a material proposed for use as structural backfill. Samples should be taken, stored and analysed in accordance with the procedures described in Appendix C.

8.3 Factors affecting pyrite oxidation

The new test methods are designed to facilitate the reliable identification of structural backfill materials liable to cause corrosion of construction materials or other problems. The main agents of corrosion are acidity and sulfate ions. These can attack construction materials in a variety of ways: directly (e.g. acid attack on steel or concrete); by formation of secondary compounds which expand and cause disintegration of the construction material (e.g. sulfate attack on concrete by the formation of ettringite or thaumasite); or by creating a galvanic cell which enables electrochemical corrosion to take place (e.g. corrosion of corrugated steel buried structures or reinforcing elements in reinforced or anchored earth). In extremely reducing environments hydrogen sulfide formation can cause very rapid and severe corrosion of construction materials (Tiller, 1997). However, in most cases of structural backfill the environment will be oxidising and sulfate and acidity will be the main cause of corrosion.

The extent to which pyrite oxidation occurs depends on a number of factors. These include the grain size and crystal form of the sulfide compounds, the grading of the backfill, the access of air and water to the material, the temperature and microbiological activity. The most readily oxidised forms of sulfur are fine-grained clusters of pyrite known as framboids (see Plate 8.1). These may also occur as pockets or replacement features (see Plate 8.2). Monosulfides are also particularly susceptible to oxidation. These minerals are generally invisible to the naked eye and their presence can only be detected by electron microscopy or chemical methods. Coarser, crystalline varieties of pyrite are less readily oxidised as they are much denser than framboids (see Plate 8.3). The rate of reaction varies inversely with grain size, so large cubes of pyrite, visible to the naked eye, are very slow to oxidise.

Both air and water are required for oxidation, in the appropriate quantities (see Figure 2.1). Oxidation will usually be very slow below the water table. A flow of water assists the removal of reaction products, exposes fresh surfaces and allows the reaction to continue. Oxidation is most likely in freely draining granular backfills. Like most chemical reactions, oxidation proceeds much more rapidly in warm conditions. However, as it is an exothermic reaction, once initiated it will generate heat and enhance the rate of reaction. The rate of reaction is greatly increased if suitable species of bacteria are present.

The effect of pyrite oxidation on structural elements may also depend on the presence of any carbonate minerals in the backfill. The acid and sulfate released by the oxidation will react with carbonates to form gypsum and carbon dioxide (Figure 2.1), and more slowly with other minerals, including silicates. If sufficient carbonate is present, all the acidity and sulfate may be consumed in these reactions. However, this cannot be relied on, as the neutralising reactions also depend on factors such as grain size and crystallinity of the carbonates and their accessibility to the percolating acid and sulfate rich solutions. A straightforward acid/carbonate mass balance is unlikely to give an accurate prediction of the amount of sulfate available to attack construction materials.

Some case studies of pyrite oxidation in civil engineering situations are given in Chapter 7. The results are

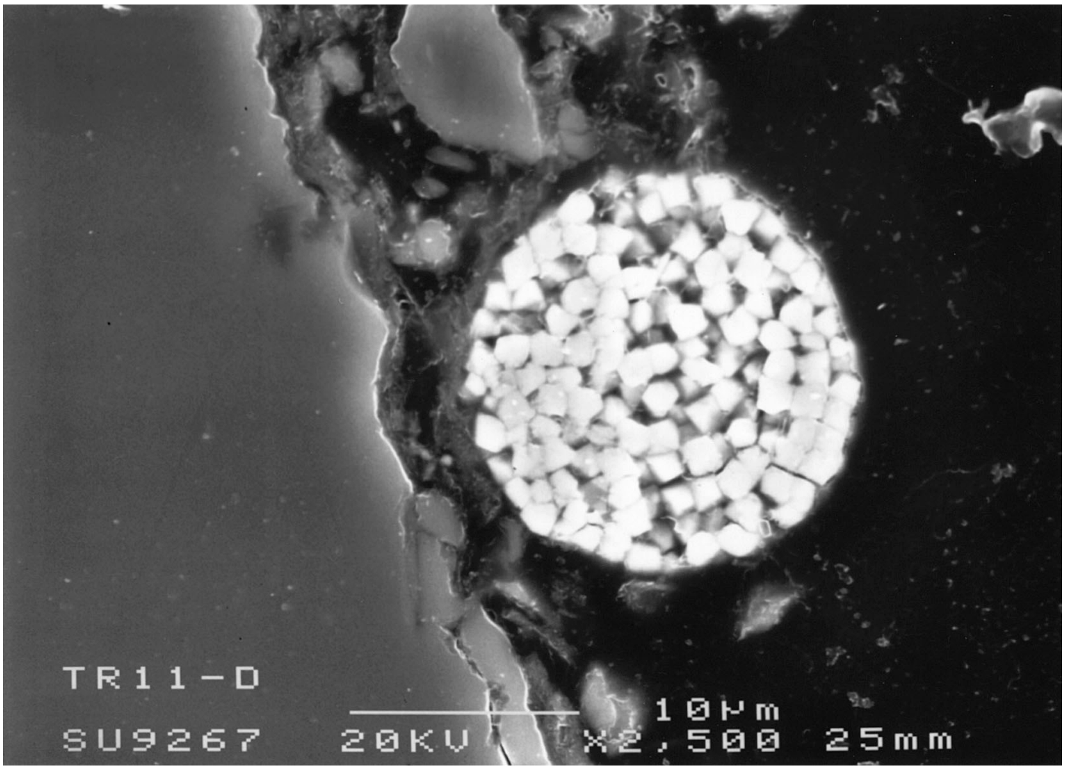


Plate 8.1 Framboidal pyrite from alluvial sand

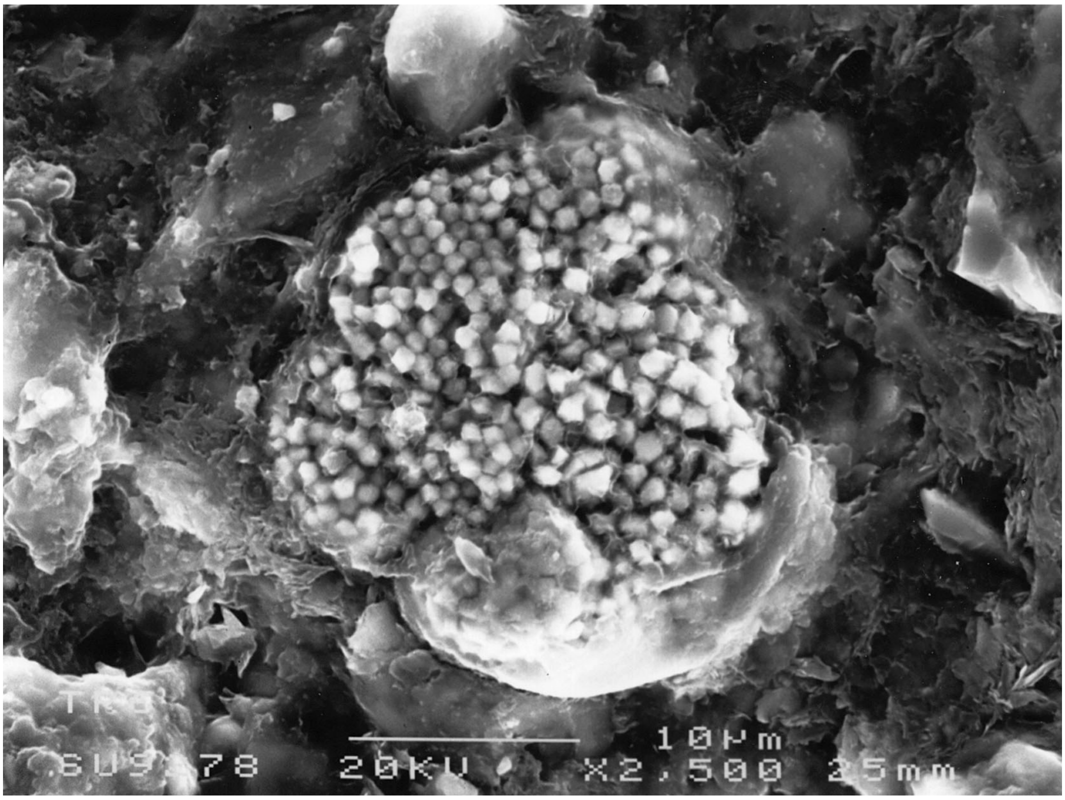


Plate 8.2 Framboidal pyrite replacing a calcite shell

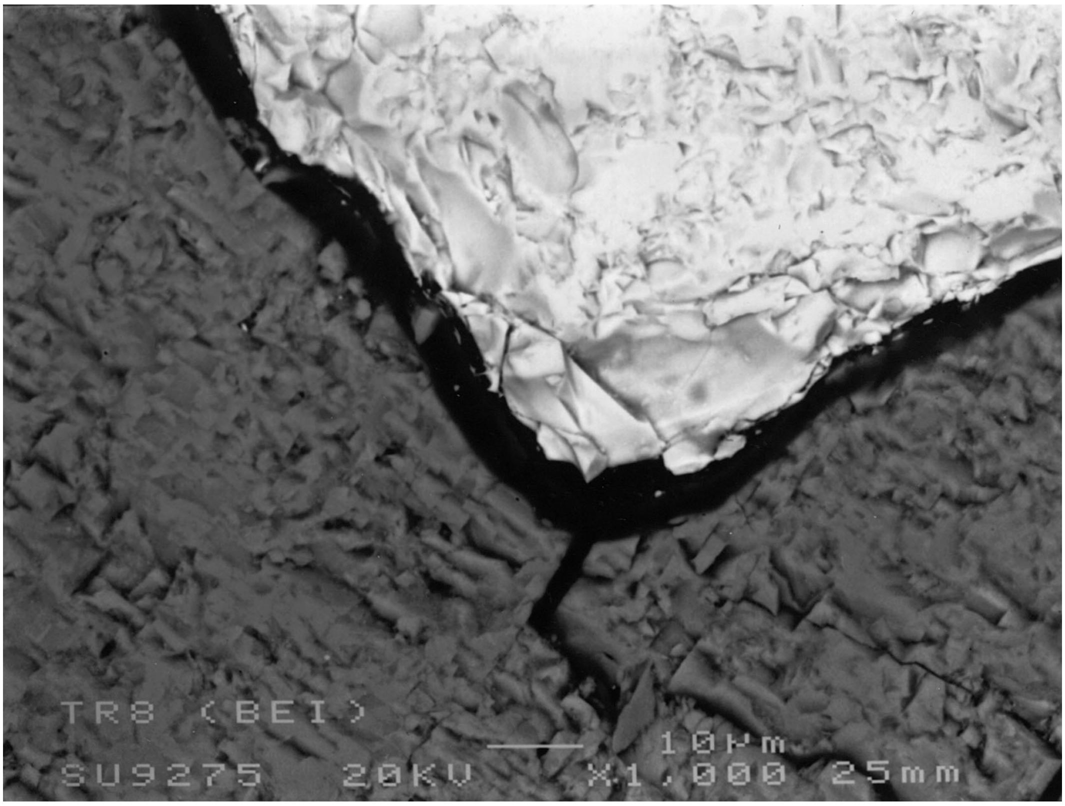


Plate 8.3 Pyrite cube in Cambrian Slate

summarised in Table 8.2. There are few recorded cases where it has been possible to estimate the proportion of pyrite that has been oxidised. From the data available, it appears that the oxidation of even small amounts of pyrite can have a dramatic impact on corrosion of construction materials. This has to be taken into account when setting limiting values for these species in structural backfills. If the amounts of fill are large there is also potential for pollution of surface waters or groundwater. These aspects also need consideration for structural backfills in highway works.

8.4 Assessment procedures

Existing limiting values for different categories of backfill material are set out in the MCHW and DMRB and are summarised in Tables 3.1 and 3.2 in this report. For attack on concrete, limiting values are given in Special Digest 1 (Building Research Establishment, 2005). The new test methods allow more accurate and reliable determination of the sulfur compounds and better estimation of the total potential sulfate (TPS) and oxidisable sulfides (OS) contents which could arise from oxidation of pyrite and other reduced sulfur compounds in the backfill materials.

Further research is needed on the rate of pyrite oxidation in backfill materials, a conclusion also reached by the Thaumasite Expert Group (1999). In the interim, it is proposed that it be assumed that all reduced sulfur present as monosulfides, disulfides or elemental sulfur will potentially oxidise to sulfate and be available to attack construction materials. The total potential sulfate (TPS) and oxidisable sulfides (OS) contents can then be

Table 8.2 Data from existing sites

Site	*Material*	*WS mg/l SO_4*	*OS % SO_4*	*TPS % SO_4*	*Rate of oxidation*	*Corrosion*
Roadford	Carboniferous mudstone	nd	nd	1.8	0.15% over 1 year	None
Carsington	Carboniferous mudstone	2,300	7.8	9.7	0.005% over 4 years	Attack on concrete in original dam. No attack on reconstructed dam.
A564 Hatton	Sand & Gravel (TR11D)	1,100	0.7	0.9	90% over 4 years	Severe attack on steel culvert.
M5 Bridges	Lias Clay (TR14-3)	1,600	4.3	4.8	15% - 50% over 25 years	Thaumasite attack on concrete.

nd: not determined

Notes

1 Significant environmental effects at Roadford and Carsington due to pollution of runoff and drainage.

2 Figures are representative values; considerable variation recorded at all sites.

3 pH of fill markedly acidic at Roadford, Carsington and A564, neutral at M5.

calculated as shown in Table 8.1. BRE Special Digest 1 (Building Research Establishment, 2005) includes limiting values for total potential sulfate (TPS) for materials in contact with buried concrete. The approach for structural backfill on highway schemes in contact with metallic elements, concrete or cement-bound material is described below.

For backfill to metallic elements such as corrugated steel buried structures, reinforced earth and anchored earth, the existing limiting values for WS have been retained, but translated from g/litre SO_3 to mg/litre SO_4. Limiting values have been set for OS, based on the limiting values for WS, translated into $\%SO_4$. Backfill must satisfy the requirements for both WS and OS. The limiting values for backfill to metals are much lower than those for backfill to concrete. No limiting values have been set for TPS, as it is felt this would have been excessively conservative given the limiting values for WS and OS.

The limiting values for material placed within 500mm of concrete, cement bound materials, other cementitious materials or stabilised capping are based on the boundaries between DS Class 2 and Class 3 in BRE Special Digest 1 (Building Research Establishment, 2005). The WS value has been translated from g/litre SO_3 to mg/litre SO_4. Limiting values for OS and TPS have been set. The value for OS has been derived by translating the value for WS into $\%SO_4$. The value for TPS is the upper boundary for DS Class 2 in BRE Special Digest 1 (Building Research Establishment, 2005). This is based on the old limiting values for AS from BRE Digest 250 (Building Research Establishment, 1981). Backfill must satisfy the requirements for WS, OS and TPS.

The limiting values are summarised in Table 8.3.

Table 8.3 Proposed limiting values

Parameter	*Units*	*Within 500mm of concrete or CBM (Clause 601.14)*[1]	*Within 500mm of metallic elements (Clause 601.15)*[2]	
			Galvanised	*Stainless steel*
WS	mg/l SO_4	1,500	300	600
OS	% SO_4	0.3	0.06	0.12
TPS	% SO_4	0.6	n/a	n/a

n/a: not applicable

Notes:

1 *Values equate to top of Class 2 (DS-2) conditions according to Table 2 of BRE Special Digest 1. WS and TPS values direct from Table 2, OS value by changing the WS value from mg/l to %.*

2 *Values for WS from existing Table 6/3 in SHW, transformed from SO_3 to SO_4. OS values equivalent to WS values but expressed as % instead of mg/l.*

WS = Water-soluble sulfate
OS = Oxidisable sulfides, derived from TPS - AS (or direct from TRS)
TPS = Total potential sulfate, derived from TS

At least five samples of each material should be tested. The mean of the highest two values should be used for comparison with the limiting values. This also applies if six to nine samples are tested. If ten or more samples are tested, the mean of the highest 20% of the results should be used for comparison with the limiting values.

The limiting values have been chosen to ensure that problems do not occur due to oxidation of reduced sulfur compounds such as pyrite. However, the limiting values only take account of the total amount of sulfur in each form, and do not allow consideration of factors such as grain size, mineralogy and access to air and water that affect the actual amount of oxidation that will take place in any given situation. As a result, the limiting values for OS and TPS are conservative, and may exclude materials that have been shown to perform satisfactorily as structural backfills. Examples of situations where materials may exceed the limiting values for structural backfills but still be acceptable include the following:

- Pyrite present as large cubic crystals visible to the naked eye. This will give high values of TPS and OS, but the rate of oxidation will be very slow because of the low specific surface area of the pyrite crystals (e.g. sample TR8, Plate 8.3).
- Unreactive sulfates such as barytes present as vein material or as a cement. This will give high values of TPS and OS, because the unreactive sulfate will not be detected by the AS test (e.g. sample TR28) However, it would give low values of TRS.

Where this occurs, enquiries should be made as to whether there is any history of corrosion problems with the material. A programme of detailed testing should be carried out on the material, using the new test methods, to establish its chemistry and mineralogy and ascertain more clearly its potential to cause corrosion. Mineralogical methods may include petrographic description using thin sections, X-ray diffraction or Scanning Electron Microscopy (SEM). If pyrite is present in framboidal form (Plates 8.1 and 8.2, sample TR11D), the material should be classified as unacceptable as structural backfill, because of the known tendency of this form of pyrite to oxidise rapidly in engineering situations.

The use of the material may be permitted as structural backfill if it can be established to the satisfaction of the Overseeing Organisation that:

1 the material has been used in the past as structural backfill without leading to problems with sulfur compounds; and

2 the reason why the material will not cause a problem is known, based on an understanding of its chemistry and mineralogy.

This approach has been used when preparing amendments to the MCHW and DMRB in Appendix D. Test methods 1, 2 and 4, listed in Section 4.4 and described in detail in Appendix C, should be used for all analyses. All references to sulfate as SO_3 have been replaced by the chemically correct form SO_4, to bring the MCHW and DMRB into line with the practice adopted by BRE Special Digest 1 and by the Thaumasite Expert Group Report.

An example of the use of this procedure for corrugated steel buried structures, galvanised reinforced earth elements and galvanised anchored earth elements is illustrated in Example 8.1 and shown on a flowchart in Figure 8.1.

A similar procedure is followed with regard to material placed within 500mm of concrete or cementitious material. The procedure is illustrated in Example 8.2 and in the flowchart in Figure 8.2.

The new test methods may also be applied to the case of buried concrete. The appropriate procedure and limiting values are those described in Special BRE Digest 1 (Building Research Establishment, 2005).

9 Recommendations

9.1 Sampling and storage protocols

- It is suggested that during drilling and sampling operations the use of water be avoided as much as possible, or kept to a minimum when obtaining samples for chemical testing.
- Samples selected for chemical testing should be placed in airtight containers as soon as possible with a minimum amount of air, thus minimising oxidation of sulfides. This may be achieved by filling a suitable container with as much sample as possible thus displacing air or using sealable polythene bags from which the excess air has been expelled. Detailed sample records should be kept for samples as oxidation of pyrite may still proceed due to availability of air and water within the sample.
- The samples should be stored on site at temperatures of between 0 - 4°C and delivered to the laboratory or store house as soon as is practicably possible where they should be stored under refrigerated conditions (0 - 4°C).
- Samples should preferably be sub-sampled for chemical testing, and dried in an oven at 60°C and tested within a few days of delivery. Samples or sub-samples which are required to be stored should be dried at 60°C, placed in air-tight containers and kept under refrigerated conditions.
- As core store conditions do not prevent breakdown of sulfide mineral species, diary records should be kept for all dates of sampling, transportation, processing, testing and storage conditions. These records should be easily accessible so that they can be taken into account when the results of chemical tests are being interpreted.
- Full details of sampling and sample preparation procedures are given in Appendix C.

9.2 Screening tests and determination of sulfur speciation

- Representative samples should be subjected to screening tests for pH and total sulfur.
- Determination of sulfur compounds should be carried out by the new methods. Test No. 1 (water-soluble sulfur, WSS), Test No. 2 (acid-soluble sulfur, ASS) and Test No. 4 (total sulfur, TS) are recommended for routine use in commercial laboratories. Test No. 3 (total reduced sulfur, TRS) requires further work but is potentially suitable for routine use. Test No. 5 (monosulfide sulfur, MS) is appropriate for materials such as industrial fills, mineral processing wastes and recent anaerobic organic rich sediments.
- At least 5 tests should be carried out for each material proposed for use as structural backfill. The mean of the highest two value should be used for comparison with the limiting values. If between 6 and 9 tests are carried out, the average of the 2 highest values should be used for comparison with the limiting values. If 10 or more tests are carried out, the mean of the highest 20% of the results should be taken for comparison with the limiting values.

9.3 Limiting values for acceptability of structural backfills

- Carry out water-soluble sulfur test (WSS) using Test No. 1 and convert to WS (mg/l SO_4); if greater than limiting values in Table 8.3, material is unacceptable.
- Carry out total sulfur test (TS) using Test No. 4 and acid-soluble sulfur test (ASS) using Test No. 2. Calculate oxidisable sulfides (OS) as % SO_4; if OS is greater than limiting values in Table 8.3, material is unacceptable.
- For backfill to concrete, calculate total potential sulfate (TPS) from TS; if TPS is greater than the limiting value in Table 8.3, material is unacceptable.
- If the material is classified as unacceptable because of OS or TPS values but has been used satisfactorily as structural backfill in the past, seek expert advice, consider history of material and carry out detailed testing using Test Nos.1 to 5 as appropriate.
- The above method applies for backfill to metallic reinforcing elements, culverts, pavement concrete, cementitious materials and structural concrete. The procedures are illustrated in Figures 8.1 and 8.2 and Examples 8.1 and 8.2 for metallic elements and fill to concrete respectively.
- For concrete placed in the ground, the procedures in BRE Special Digest 1 (2005) should be followed, using the new test methods.

9.4 User guide

Overseeing organisation

- Incorporate new test methods and assessment procedures into standard procedures by means of amendments to MCHW and DMRB.
- Ensure all designers and contractors are aware of the methods and use them.
- Monitor effectiveness of new procedures in avoiding use of potentially corrosive material as structural backfill.

Designer

- Specify new test methods for site investigations and main civil engineering contracts.
- Ensure samples are taken and stored in accordance with the new methods.

- Ensure sample preparation and testing are carried out in accordance with the new methods.
- Ensure at least five tests are carried out to give a representative picture of each material.
- Monitor test results and check against limiting values
- Order additional testing and consult an expert geochemist if material has been used satisfactorily in the past but OS and/or TPS exceed limiting values.

Site investigation contractor

- Ensure samples are taken on site and stored in accordance with the new test methods.
- Carry out tests in accordance with the new test methods; if these are done by a specialised testing laboratory, ensure the laboratory adheres to the new procedures.
- Keep detailed sample QA records including sampling details, storage, sub-sampling and testing conditions.
- Report the results in accordance with the new procedures.

Main civil engineering contractor

- Ensure at least five tests are carried out on any material proposed for use as structural backfill
- Investigate history of material and carry out additional testing if material has been used satisfactorily in the past but OS and/or TPS exceed limiting values.

10 Further work

The results of the storage experiments showed that the exclusion of air, drying, and refrigeration would retard pyrite oxidation in samples. Further work is required to investigate the exact limits on the conditions, temperatures and the times over which storage would be acceptable.

Collection of case histories concerning use of pyrite bearing fills and the performance of structures would be valuable, especially where chemical data are available. This would enable a better estimate to be made of the proportion of reduced sulfur, which is likely to oxidise when placed as backfill. This has implications for the use of materials as bulk fill as well as structural backfill.

The total reduced sulfur (TRS) test (Test No. 3) has the potential to allow direct estimation of the oxidisable sulfides (OS). This would be more accurate than the present method, which determines OS from the difference between the total sulfur (TS) and acid-soluble sulfate (AS) content. Further work is required to enable this test to be used on a routine basis by commercial laboratories.

11 Conclusions

The existing specification and design notes are inadequate in respect of testing for sulfur compounds in structural backfills, in that they only consider water-soluble sulfate and do not allow for oxidation of reduced sulfur compounds such as pyrite. Recent examples have shown how oxidation of pyrite can lead to corrosion of corrugated steel buried culverts and the thaumasite form of sulfate attack on buried concrete.

Existing test methods for sulfate and total sulfur suffer from a number of limitations, and there is no adequate existing standard for reduced sulfur species such as pyrite. New test methods have been developed building on the existing methods and using advances in analytical techniques, to allow better characterisation of sulfur compounds in rocks, soils and fill materials. Full details of the test methods are given in Appendix C. Five tests are proposed, comprising:

Test No.1: Water-soluble sulfur (WSS)
Test No.2: Acid-soluble sulfur (ASS)
Test No.3: Total reduced sulfur (TRS)
Test No.4: Total sulfur (TS)
Test No.5: Monosulfide sulfur (MS)

Tests No. 1, 2 and 4 are recommended for routine use by commercial laboratories for the determination of sulfur compounds and assessment of the risk to construction materials. Test No. 3 requires further work before it can be recommended for routine use. Test No. 5 is appropriate in certain specialised situations. The test methods proposed above are in addition to the existing test methods for other species that can cause corrosion, such as pH, chloride and organic content. These should be determined and included in a corrosion assessment in the usual way.

The sulfur content of samples can change considerably during storage if conditions are not correct, due to oxidation of reduced sulfur species. Experiments with storage of samples under different conditions indicates that samples should be retained in airtight containers, stored in a refrigerator at 0 - 4°C and tested within a few days. Where storage of longer than one week is necessary, samples should be dried at 60°C, placed in air-tight containers and stored at 0 - 4°C.

At least five samples of each material should be tested. The mean of the highest two values should be used for comparison with the limiting values. This also applies if six to nine samples are tested. If ten or more samples are tested, the mean of the highest 20% of the results should be used for comparison with the limiting values.

For assessment of the acceptability of materials for structural backfills, the new test methods for water-soluble sulfur (Test No. 1), acid-soluble sulfur (Test No. 2) and total sulfur (Test No. 4) should be used. Limiting values for water-soluble sulfate (WS) in Table 8.3 should be used. The oxidisable sulfides (OS), which could develop from oxidation of reduced sulfur, should be calculated from total sulfur (TS) minus acid-soluble sulfate (AS). If this is greater than the limiting values in Table 8.3, the material should not be used for structural backfill. For backfill to concrete, the total potential sulfate (TPS), calculated from the total sulfur (TS) also needs to be considered. A limiting value is given in Table 8.3.

If a material is unacceptable because of the OS or TPS values, but has been used satisfactorily in the past, expert

Example 8.1 Fill to CSBS, RE and AE structures

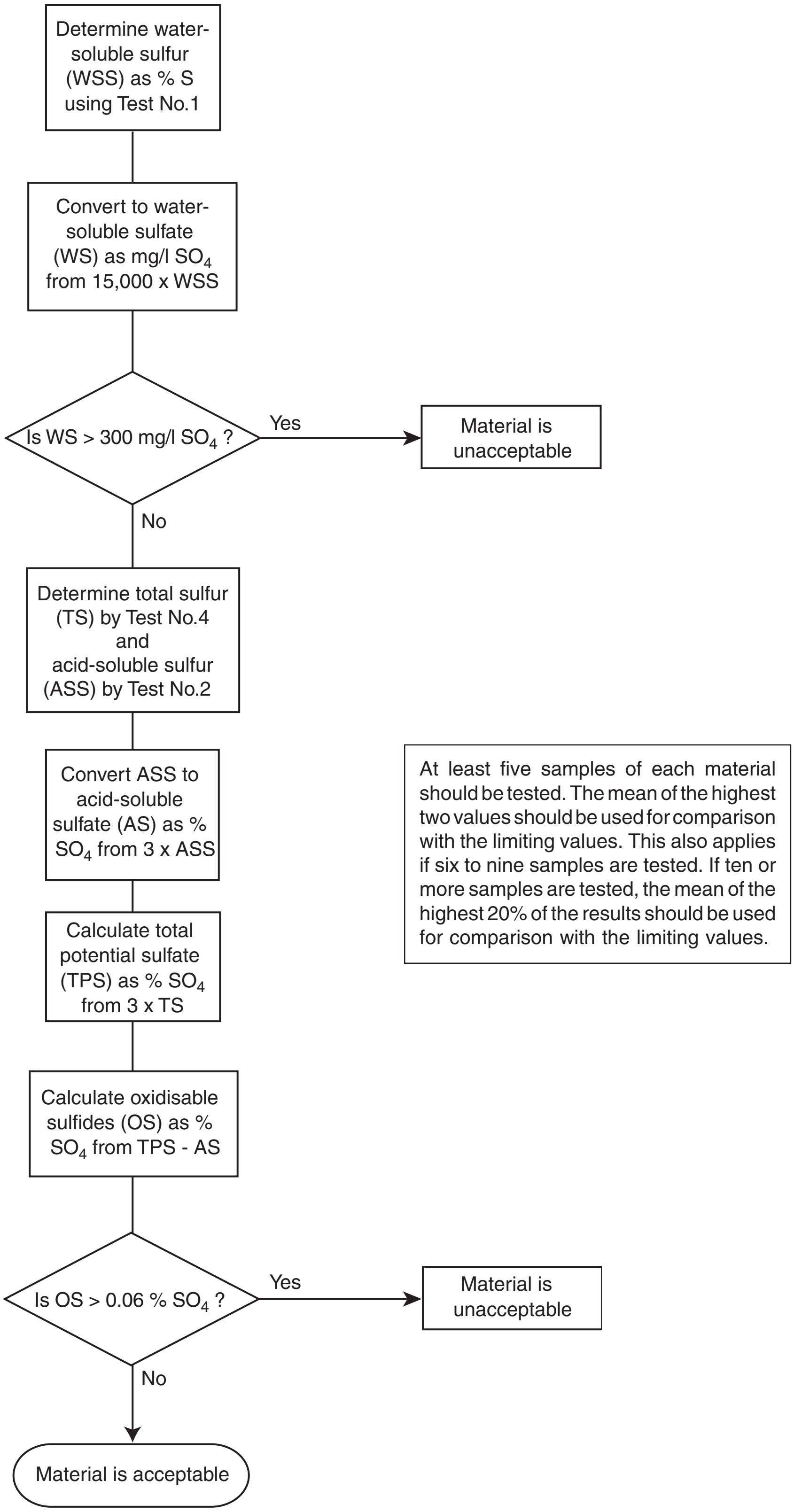
Present procedure:

1. Determine water-soluble sulfate (as SO_3) by BS 1377: Part 3.
2. If greater than 0.25 g/l (galvanised) or 0.50 g/l (stainless steel), material is unacceptable.

Proposed procedure:

1. Determine water-soluble sulfur (WSS) as % S by Test No.1 and convert to water-soluble sulfate (WS) as mg/l SO_4 from 15,000 x WSS (%S).
2. If greater than 300 mg/l SO_4 (galvanised) or 600 mg/l SO_4 (stainless steel), material is unacceptable.
3. Determine total sulfur (TS) as % S by Test No. 4 and acid-soluble sulfur (ASS) as % S by Test No. 2.
4. Convert TS to TPS (as $\%SO_4$) from 3 x TS and ASS to AS (as $\%SO_4$) from 3 x ASS.
5. Calculate oxidisable sulfides (OS) as % SO_4 from TPS - AS.
6. If OS greater than 0.06 % SO_4 (galvanised) or 0.12 % SO_4 (stainless steel), material is unacceptable.
7. If WS and OS are less than or equal to the limiting values, the material is acceptable.
8. If OS is greater than the limiting values but the material has been used successfully in the past, seek expert advice, consider history of material and carry out detailed mineralogical and chemical testing using new test methods.

   At least five samples of each material should be tested. The mean of the highest two values should be used for comparison with the limiting values. This also applies if six to nine samples are tested. If ten or more samples are tested, the mean of the highest 20% of the results should be used for comparison with the limiting values.



At least five samples of each material should be tested. The mean of the highest two values should be used for comparison with the limiting values. This also applies if six to nine samples are tested. If ten or more samples are tested, the mean of the highest 20% of the results should be used for comparison with the limiting values.

Figure 8.1 Flow chart assessment of structural backfill to galvanised steel elements

Example 8.2: Fill to concrete structures

Present procedure:

1 Determine water-soluble sulfate (as SO_3) according to BS 1377: Part 3.

2 If greater than 1.9 g/l (as SO_3), material is unacceptable.

Proposed procedure:

1 Determine water-soluble sulfur (WSS) as % S by Test No.1 and convert to water-soluble sulfate (WS) as mg/l SO_4 from 15,000 x WSS (%S).

2 If greater than 1,500 mg/l SO_4, material is unacceptable.

3 Determine TS (% S) by Test No. 4 and ASS (% S) by Test No. 2.

4 Convert TS to TPS (as %SO_4) from 3 x TS and ASS to AS (as %SO_4) from 3 x ASS.

5 Calculate oxidisable sulfides (OS) as % SO_4 from TPS - AS.

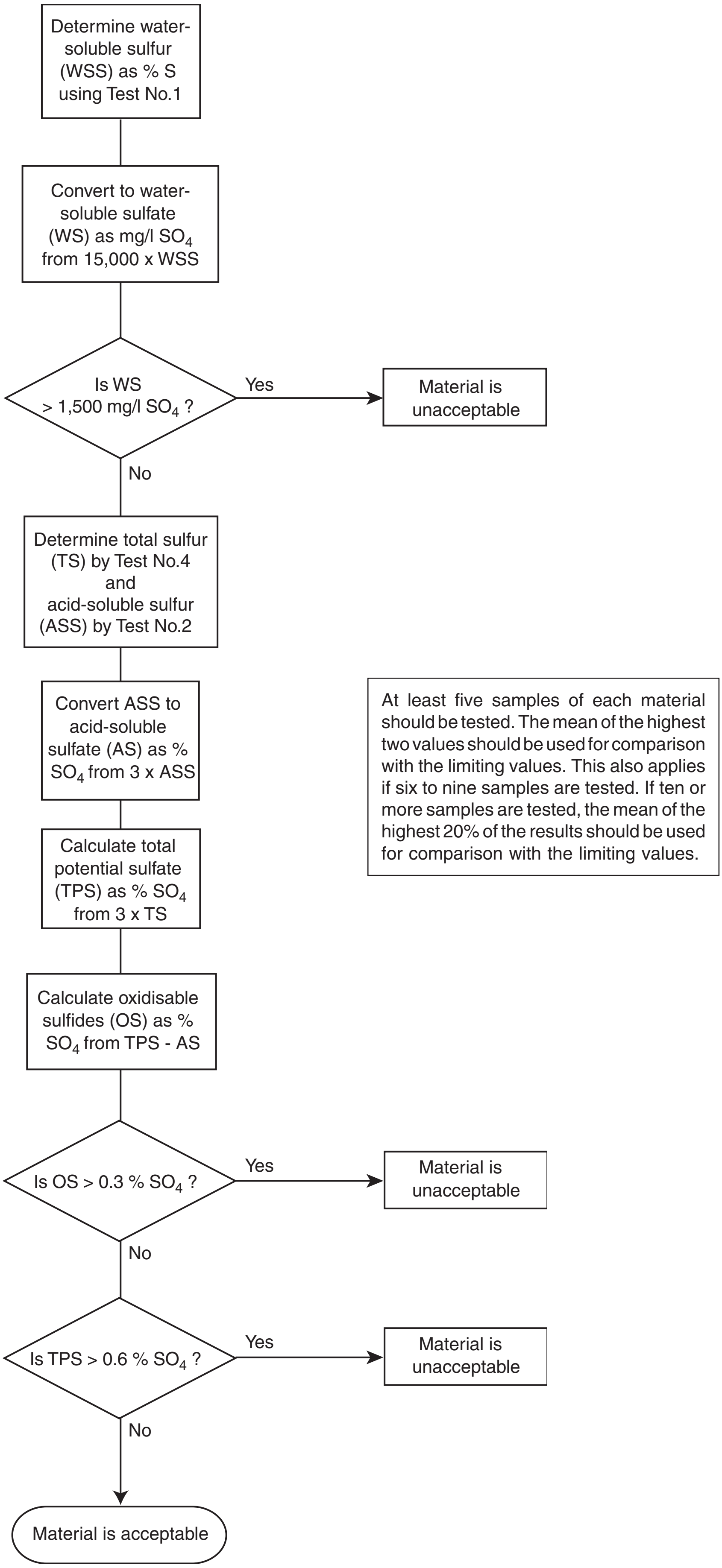
6 If OS greater than 0.3 % SO_4, material is unacceptable.

7 If TPS greater than 0.6 % SO_4, material is unacceptable.

8 If WS, OS and TPS less than or equal to the limiting values, material is acceptable.

9. If TPS and /or OS are greater than the limiting values but the material has been used successfully in the past, seek expert advice, consider history of material and carry out detailed mineralogical an chemical testing using new test methods.

At least five samples of each material should be tested. The mean of the highest two values should be used for comparison with the limiting values. This also applies if six to nine samples are tested. If ten or more samples are tested, the mean of the highest 20% of the results should be used for comparison with the limiting values.



At least five samples of each material should be tested. The mean of the highest two values should be used for comparison with the limiting values. This also applies if six to nine samples are tested. If ten or more samples are tested, the mean of the highest 20% of the results should be used for comparison with the limiting values.

Figure 8.2 Flow chart assessment of fill placed within 500mm of concrete or cement bound materials advice should be taken. The history of the material should be established and detailed testing to establish its mineralogy and chemistry using the full suite of new test methods should be carried out. The use of the material may be permitted as structural backfill if it can be established to the satisfaction of the Overseeing Organisation that:

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

The proposed changes were implemented by making a number of amendments to the Manual of Contract Documents for Highway Works in November 2003. Further amendments will be made in November 2005 as a result of changes to BRE Special Digest 1 in June 2005. For classifying ground conditions for sulfate level in respect of design of buried concrete, the recommendations of Special BRE Digest 1 should be followed.

Experience from embankment dam and highway construction projects, where materials containing pyrite have been used as fill, show that oxidation of the pyrite can lead to the production of acidic drainage water with high concentrations of iron, manganese, aluminium and sulfate. This drainage can cause pollution of surface waters, such that the drainage may have to be collected and treated before it can be discharged to watercourses. The case studies revealed that the oxidation of only a small proportion of the pyrite could cause major problems with both quality of drainage water and attack on construction materials. The environmental aspects should be given equal consideration with the potential for attack on construction materials when assessing potential materials for structural work. This applies to bulk fill as well as structural backfill.

12 Acknowledgements

The authors are grateful to the following for their assistance with sampling, the provision of test samples, testing or advice: Mr M Floyd (Halcrow Group Ltd), Mr I Longworth (Building Research Establishment), Mr N Loudon, Dr D Bush and Mr C G Duffell (Highways Agency), Scott Wilson Kirkpatrick & Co Ltd, Mr B Archer (Grange Farm, Hilton), Mr D O'Farrell (Cumbria C.C), Ms Jean Straher (Mott MacDonald), Mr J Dixon and Mr R Wheeler, Dr T Mannerings and Mr P Ryan (LECO Instruments UK), and TES Bretby and ECoS Environmental for taking part in the validation trial. Plate 7.4 is reproduced courtesy of Scott Wilson Kirkpatrick & Co. Ltd.

The permission of South West Water and Severn Trent Water Ltd. to publish the case studies on Roadford and Carsington Dams respectively is gratefully acknowledged.

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Appendix A: Consultations

A1 Consultees

Building Research Establishment	Mr Ian Longworth
Halcrow Group	Mr Mike Floyd Mr Dom Wimpenny Ms Imelda Cuffe Mrs Barbera Pieda
Scottish Executive Development Department	Mr Forbes MacGregor
Highland Council	Mr Bill Robins
R J McLeod	Mr Hector MacDonald
South Ayrshire Council	Mr Douglas Hemmings
Welsh Office	Mr John Collins
Highways and Engineering Department, Gwynedd	Mr Dennish Patel
Technical Services Department, Neath & Port Talbot	Mr Martin Jarvis
Independent Consultant	Mr Brian Hunnibell
Sir Owen Williams & Partners	Mr Ian Blackstock Mr John Dickson
Cheshire County Council	Mr Phil Watkins
Mott MacDonald	Dr John Perry Mr Hugh Kent Miss Jean Straher
Scott Wilson Kirkpatrick	Mr Guy Thomas Mr Keith Alford Mr John Goodacre
Cumbria County Council	Mr Dave O' Farrell
TRL Limited	Dr Ken Brady Mr Doug Boden Mr Donald MacNeil Dr John Temporal
Highways Agency	Mr David Patterson Mr Alex Kidd Mr Chris Duffell Mr Neil Loudon Dr David Bush
L G Mouchel and Partners	Mr John Watson
LECO Instruments UK Ltd., Stockport	Dr Tony Mannerings Mr Peter Ryan

A2 Laboratories participating in the reproducability trial

Testing and commenting:

- Geochem Group, Chester.
- CERAM, Stoke-on-Trent.
- Environmental Analysis, Hastings.
- LECO Instruments Ltd.

Comment only:

- TES Bretby, Burton-on-Trent.
- Eclipse Scientific, Kent.
- Hyder Laboratories, Birmingham.
- ECoS Environmental, Bradford.

A3 Laboratories participating in the validation trial

- TES Bretby, Burton-on-Trent.
- ECoS Environmental, Bradford.

Appendix B: Test results

B1: List of test samples

Sample	*Suppliers Ref.*	*Locality*	*Description*
TR1		M1/M62, S.Yorks. [SE325267]	Carboniferous Coal Measures Mudrock.
TR2		Roman Road, S. Yorks. [SK515113]	Permian Magnesian limestone.
TR3		Princes Risborough.[SP745074]	Kimmeridge Clay.
TR3-B		Princes Risborough.[SP745074]	Kimmeridge Clay.
TR4		Arnold, Nottingham. [SK596473]	Mercia mudstone.
TR5		M8, East Glasgow. [NS449695]	Glacial till.
TR6		Blockley Qy, Glouc. [SP181371]	Lower Lias Clay.
TR7		Penhryn Qy, N. Wales. [SH620650]	Cambrian purple slate.
TR8		Penhryn Qy, N. Wales. [SH620650]	Cambrian green slate.
TR9		Fishhill Quarry, A44, [SP129359]	Jurassic oolitic limestone.
TR10		Dolebole Qy, Cornwall. [SX043820]	Devonian slate.
TR11-D		Hilton, Derbyshire. [SK238318]	Alluvial sand and gravel.
TR11-D5		Hilton, Derbyshire. [SK238318]	Alluvial sand and gravel.
TR11-1	81131/3/NE/1	Hilton bypass, B/P sample.[SK236320]	Bagged alluvial sand and gravel.
TR11-2	81131/4/SW/2	Hilton bypass, B/P sample.[SK236320]	Bagged alluvial sand and gravel.
TR11-3	81131/2/NW/2	Hilton bypass, B/P sample.[SK236320]	Bagged alluvial sand and gravel.
TR11-4	81131/2/CE/2	Hilton bypass, B/P sample.[SK236320]	Bagged alluvial sand and gravel.
TR11-5	81131/GF/CW/1	Hilton bypass, B/P sample.[SK236320]	Bagged alluvial sand and gravel.
TR11-6	81131/3/CE/1	Hilton bypass, B/P sample.[SK236320]	Bagged alluvial sand and gravel.
TR12-1	TP1: 1.10-1.20m	M1/A50, Jn.24, Derbyshire.[SK471290]	Alluvial sand with some gravel.
TR12-2	TP2: 3.00-3.40m	M1/A50, Jn.24, Derbyshire.[SK471290]	Alluvial sand with some gravel.
TR12-3	TP3: 1.10-1.30m	M1/A50, Jn.24, Derbyshire.[SK471290]	Alluvial sand with some gravel.
TR12-4	TP8: 3.00-3.20m	M1/A50, Jn.24, Derbyshire.[SK469287]	Alluvial sand with some gravel.
TR13		Achnasheen, Scotland.[NH162585]	Micaceous schist and soil backfill.
TR14-1	98S0034/298	M5, Gloucestershire.	Unweathered Lower Lias Clay.
TR14-2	98S0034/299	M5, Gloucestershire.	Weathered Lower Lias Clay.
TR14-3	98S0034/300	M5, Gloucestershire.	Unweathered Lower Lias Clay.
TR14-4	98S0034/301	M5, Gloucestershire.	Weathered Lower Lias Clay.
TR14-5	98S0038/140	M5, Gloucestershire.	Unweathered Lower Lias Clay.
TR14-6	98S0038/138	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-7	98S0044/116	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-8	98S0044/117	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-9	98S0044/119	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-10	98S0044/121	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-11	98S0044/123	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-12	98S0044/125	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-13	98S0044/149	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-14	98S0044/138	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-15	98S0044/140	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-16	98S0044/142	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-17	98S0044/144	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-18	98S0044/156	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-19	98S0044/35	M5, Gloucestershire.	Sample store, Lower Lias Clay core.
TR14-20	98S0046/10	M5, Gloucestershire.	Sample store, Lower Lias Clay core.
TR14-21	98S0073/143a	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-22	98S0073/143b	M5, Gloucestershire.	Lower Lias Clay fill.
TR14-23	98S0046/6	M5, Gloucestershire.	Sample store, Lower Lias Clay core.
TR14-24	98S0029/455	M5, Gloucestershire.	Sample store, Lower Lias Clay core.
TR14-25	98S0029/444	M5, Gloucestershire.	Sample store, Lower Lias Clay core.
TR15		M3, Shepperton Qy.[TQ056673]	Alluvial sand and gravel.
TR16-1		M56, Preston Brook.[SJ568807]	Alluvial sand.
TR16-2		M56, Preston Brook.[SJ568807]	Silty clay backfill.
TR16-3		M56, Preston Brook.[SJ568807]	Silty clay, Glacial Till.
TR17-1		Workington, Cumbria.[NY986285]	Crushed ironmaking slag.
TR17-2		Workington, Cumbria.[NY986285]	Uncrushed ironmaking slag.
TR17-3		Workington, Cumbria.[NY986285]	Uncrushed metalliferous slag.
TR18-1		A4212, Bala, Wales. [SH816392]	Rock and soil fill.
TR18-2		A4212, Bala, Wales. [SH777382]	Rock and soil fill.
TR19		Baglan, S. Wales. [SS748924]	Coal Measures rock and soil fill.
TR20-1	S1	A16T, Lincolnshire. [TF244196]	Clay, silt, sand, chalk fill.
TR20-2	WN1	A16T, Lincolnshire. [TF260259]	Clay, silt, sand, chalk fill.
TR20-3	WN6	A16T, Lincolnshire. [TF267291]	Clay, silt, sand, chalk fill.
TR21		M60, Boothroyd Bridge.[SD182816]	Carboniferous (Namurian) mudrock fill material.
TR22		A2, Gaylors Hill [TQ674697]	Sand & gravel, Harwich Formation.

Continued ....

B1 (Continued): List of test samples

Sample	*Suppliers Ref.*	*Locality*	*Description*
TR23-1		A2, Gaylors Hill [TQ674697]	Sand & clay Woolwich and Reading Beds.
TR23-2		A2, Gaylors Hill [TQ674697]	Shelly clay. Woolwich and Reading Beds.
TR23-3		A2, Gaylors Hill [TQ674697]	Lignitic clay Woolwich and Reading Beds
TR24		Purton Clay Pit, Swindon, Wiltshire	Lower Oxford Clay.
TR25		Hilton, Derbyshire [SK238318]	Alluvial sand and gravel
TR26		Blockley Quarry, Gloucs. [SP181371]	Lower Lias Clay
TR27		B.G. Cropwell Bishop [SK794430]	Mercia Mudstone
TR28		Silverband Mine [NY717281]	Carb. Lst. Unit - Sandstone
TR29		Penhryn Quarry [SH620650]	Cambrian green slate
TR30		Whitby, Teeside [SE184793]	Lias Alum Shale
TRT01/05		Hilton, Derbyshire [SK184793]	Alluvial sand and gravel
TRT02/04	TRL Stockpile	Colnbrook, Slough	Weathered London Clay
TRT03/07		Shap Pink Granite Qy [NY556084]	Pyritic Granite
TRT06/10	BRE Core	Morton Valence, Gloucs.	Lower Lias Clay
TRT08/09		Knowl Hill Quarry [SU81657974]	Reading Beds Clay

B2: Site survey chemical test results

Sulfur speciation, pH, carbon speciation and chloride test results for the samples *(All results as % S unless stated otherwise).*

Sample	*WSS*	*ASS*	*MS*	*TRS*	*TS*	*%CO_2*	*%C_{ORG}*	*%Cl*	*pH*	*<2mm*	*Material*
TR1	0	0.01	0	0.10	0.09	0.37	1.23	<0.01	7.55	100%	ARG
TR2	0	0.02	0	0.05	0.26	46.86	0	0.04	8.70	100%	LST
TR3	0.01	0.21	0	0.21	0.31	22.49	1.06	<0.01	8.08	100%	ARG
TR3-B	0.19	1.08	0	0.41	1.43	10.46	2.11	<0.01	7.60	100%	ARG
TR4	0	0.06	0.13	0.17	0.17	6.70	0.68	<0.01	8.19	100%	ARG
TR5	0	0.02	0	0	0.11	0	0.86	<0.01	8.07	100%	TILL
TR6	0	0.04	0.18	0.70	0.73	4.80	1.53	<0.01	7.91	100%	ARG
TR7	0	0.01	0.15	0.33	0.34	0	0.10	<0.01	9.09	100%	ARG
TR8	0.10	0.02	0.32	2.86	2.97	0.20	0.12	<0.01	8.64	100%	ARG
TR9	0	0.37	0	0	0.37	41.18	0	<0.01	8.24	100%	LST
TR10	0	0.07	0.04	0.05	0.14	0.97	0.28	<0.01	8.76	100%	ARG
TR11-D	0.07	0.07	0	0.22	0.31	0.12	1.06	<0.01	3.64	48.3%	AL-Grey
TR11-D5	0.05	0.04	0	0.58	0.60	0.10	0.96	<0.01	3.66	37.8%	AL-Grey
TR11-1	0.07	0.10	0	0	0.09	0.23	0	<0.01	4.04	37.2%	AL-Brown
TR11-2	0.27	0.44	0	0.01	0.45	0.26	0	<0.01	5.53	40.8%	AL-Brown
TR11-3	0.16	0.18	0	0	0.19	0	0	<0.01	4.35	40.3%	AL-Brown
TR11-4	0.18	0.23	0	0.02	0.25	0	0	<0.01	3.82	35.3%	AL-Brown
TR11-5	0.38	0.42	0	0	0.42	0.09	0	<0.01	3.85	33.9%	AL-Brown
TR11-6	0.45	0.51	0	0.02	0.52	0.07	0	<0.01	2.74	58.1%	AL-Brown
TR12-1	0	0.05	0	0	0.05	0.22	0	<0.01	7.24	32.6%	AL-Yellow
TR12-2	0	0.01	0	0	0	0.07	0	<0.01	7.39	52.4%	AL-Yellow
TR12-3	0	0.01	0	0	0.01	0.24	0	<0.01	7.25	95.0%	AL-Yellow
TR12-4	0	0.01	0	0	0.02	0	0	<0.01	7.39	71.7%	AL-Yellow
TR13	0	0.11	0	0	0.10	0	0	0.08	7.55	100%	MET.Fill
TR14-1	0.15	0.31	0.13	2.22	2.30	15.12	1.02	<0.01	6.84	100%	ARG
TR14-2	0.18	0.92	0.01	0.13	1.03	7.51	0.54	0.03	7.24	100%	ARG
TR14-3	0.11	0.22	0	1.42	1.59	7.89	1.17	0.02	6.56	100%	ARG
TR14-4	0.08	0.11	0	0.09	0.20	8.57	0.50	0.03	7.13	100%	ARG
TR14-5	0.07	0.23	0	0.66	0.86	10.07	0.96	0.02	7.70	100%	ARG
TR14-6	0.16	0.16	0.13	0.99	1.17	3.56	1.05	<0.01	7.22	100%	ARG
TR14-7	0.09	0.09	0.02	0.17	0.25	1.19	0.78	<0.01	7.31	100%	ARG
TR14-8	0.02	0.02	0.01	0.20	0.20	1.18	0.78	<0.01	7.16	100%	ARG
TR14-9	0.14	0.14	0.03	0.21	0.29	1.32	0.79	<0.01	7.38	100%	ARG
TR14-10	0.17	0.19	0	0.19	0.35	1.00	0.89	<0.01	7.38	100%	ARG
TR14-11	0.16	0.18	0	0.21	0.37	1.28	0.82	<0.01	7.42	100%	ARG
TR14-12	0.17	0.31	0	0.45	0.70	3.31	0.91	<0.01	7.25	100%	ARG
TR14-13	0.16	0.33	0	0.04	0.37	1.45	0.88	0.02	7.26	100%	ARG
TR14-14	0.03	0.03	0.05	0.21	0.26	1.19	0.84	<0.01	7.58	100%	ARG
TR14-15	0.05	0.06	0.01	0.12	0.17	1.22	0.76	<0.01	7.62	100%	ARG
TR14-16	0.05	0.05	0.04	0.10	0.16	0.91	0.83	<0.01	7.46	100%	ARG
TR14-17	0.18	0.37	0	0.06	0.42	1.75	0.79	<0.01	7.38	100%	ARG
TR14-18	0.08	0.10	0	0.15	0.27	1.06	0.88	<0.01	7.54	100%	ARG
TR14-19	0.09	0.09	0.02	0.10	0.18	0.87	1.02	<0.01	7.41	100%	ARG
TR14-20	0.15	0.72	0.09	0.27	1.35	21.6	1.94	<0.01	7.44	100%	ARG
TR14-21	0.01	0.14	0.01	0.25	0.36	18.76	1.04	<0.01	7.90	100%	ARG
TR14-22	0.13	0.63	0.13	0.38	1.05	18.64	1.07	<0.01	7.50	100%	ARG
TR14-23	0.16	0.90	0.12	0.35	1.50	19.62	5.44	<0.01	7.55	100%	ARG
TR14-24	0.02	0.23	0.01	0.07	0.27	20.28	0.63	<0.01	7.99	100%	ARG
TR14-25	0.09	0.16	0.01	0.02	0.18	8.91	1.12	<0.01	7.72	100%	ARG
TR15	0.01	0.09	0	0	0.08	0	0	<0.01	8.91	31.1%	AL-Yellow
TR16-1	0.02	0.12	0	0.10	0.19	0.84	0.86	<0.01	7.40	100%	AL-Grey
TR16-2	0.01	0.05	0	0	0.04	0.54	5.59	0.03	7.88	100%	ARG
TR16-3	0.01	0.04	0	0.17	0.22	5.87	0	<0.01	8.75	100%	ARG
TR17-1	0.21	0.69	0.29	1.77	2.31	1.15	0	0.02	12.01	100%	Slag
TR17-2	0.10	0.53	0.31	0.41	0.95	2.35	0	0.02	9.72	100%	Slag
TR17-3	0.34	0.84	0.15	2.1	2.96	0	0	0.03	11.75	100%	Slag
TR18-1	0	0.02	0.01	0.12	0.12	0.15	3.42	<0.01	6.28	100%	IG.Fill IG.Fill
TR18-2	0.01	0.02	0.02	0.02	0.04	0.17	0.50	<0.01	5.94	100%	IG.Fill IG.Fill
TR19	0.02	0.08	0.03	0.20	0.29	0.43	3.15	<0.01	8.08	100%	ARG
TR20-1	0.01	0.03	0	0	0.04	3.79	0.14	<0.01	7.78	100%	CH.Fill CH.Fill
TR20-2	0.01	0.05	0	0	0.07	6.51	0.19	<0.01	8.36	100%	CH.Fill
TR20-3	0	0.12	0	0.01	0.18	11.43	2.96	<0.01	8.01	100%	CH.Fill
TR21	0	0.08	0.01	0.03	0.09	0.08	0.69	<0.01	7.70	100%	ARG
TR22	0	0.02	0	0	0.02	0.06	0	<0.01	6.00	42.9%	AL-Yellow

Continued ....

B2 (Continued): Site survey chemical test results

Sulfur speciation, pH, carbon speciation and chloride test results for the samples *(All results as % S unless stated otherwise)*.

Sample	*WSS*	*ASS*	*MS*	*TRS*	*TS*	*%CO_2*	*%C_{ORG}*	*%Cl*	*pH*	*<2mm*	*Material*
TR23-1	0.08	0.14	0	1.09	1.29	0	1.38	<0.01	7.21	100%	ARG
TR23-2	0.18	0.38	0	6.92	7.50	6.13	6.89	<0.01	7.03	100%	ARG
TR23-3	0.15	0.69	0	10.28	16.06	1.35	27.34	<0.01	4.97	100%	ARG
TR24	0.14	0.27	0.11	1.14	1.37	3.95	1.90	<0.01	7.76	100%	AL-Grey
TR25	0.18	0.19	0.12	0.80	0.93	N/D	N/D	N/D	3.16	100%	AL-Grey
TR26	0.18	0.21	0.26	1.29	1.68	N/D	N/D	N/D	7.29	100%	ARG
TR27	0.12	7.42	0.00	0.42	8.27	N/D	N/D	N/D	7.74	100%	ARG
TR28	0.00	0.53	0.00	0.13	8.98	N/D	N/D	N/D	6.84	100%	M-SST
TR29	<0.01	0.00	0.00	1.12	1.09	N/D	N/D	N/D	8.47	100%	ARG
TR30	0.03	0.05	0.17	2.26	2.35	N/D	N/D	N/D	7.85	100%	ARG
TRT01	0.25	0.38	N/D	1.39	1.91	N/D	N/D	N/D	2.90	100%	AL-Grey
TRT02	0.08	0.09	N/D	0.25	0.36	N/D	N/D	N/D	7.15	100%	ARG
TRT03	0.00	0.02	N/D	0.16	0.14	N/D	N/D	N/D	8.90	100%	Granite
TRT06	0.13	0.13	N/D	0.90	1.10	N/D	N/D	N/D	7.82	100%	ARG
TRT08	0.00	0.01	N/D	0.01	0.03	N/D	N/D	N/D	7.88	100%	ARG

WSS = Water-soluble sulfur; ASS = Acid-soluble sulfur; MS = Monosulfide sulfur;
TRS = Total reduced sulfur (includes monosulfide sulfur); TS = Total sulfur; N/D = Not determined.
ARG = Argillaceous material including mudrocks, slate and consolidated clays
LST = Limestone
TILL = Glacial sand and clay deposits
AL = River alluvium consisting of sand and gravel, including colour of the material
Slag = Metalliferous ironmaking slag
MET.Fill = Fill made up of metamorphic rock including schist
IG.Fill = Fill made up of igneous material including basalt
CH.Fill = Fill made up of chalk and clay
M-SST = Mineraliferous sandstone

Table B3.1 Results for the sulfur speciation testing carried out by Sheffield & TES Bretby on Lower Lias Clay from the M5

Sample	*Equivalent Sample Ref.*	*Water-soluble Sulfur %S*		*Acid-soluble Sulfur %S*		*Monosulfide %S*		*Total Sulfur %S*		*TRS %S*	
[Sheffield]	*[TES Bretby]*	*[Sheffield]*	*[TES Bretby]*	*[Sheffield]*	*[TES Bretby]*	*[Sheffield]*	*[TES Bretby]*	*[Sheffield] [ ]= ASS+MS+TRS*	*[TES Bretby]*	*[Sheffield]*	*[TES Bretby] [Total S-ASS]*
TR14-7	44/116a	0.09	0.10	0.09	0.16	0.02	<0.0001	0.25 [0.26]	0.23	0.17	0.07
TR14-8	44/117a	0.02	0.05	0.02	0.10	0.01	<0.0001	0.20 [0.22]	0.18	0.20	0.08
TR14-10	44/121a	0.17	0.06	0.19	0.13	<0.01	<0.0001	0.37 [0.38]	0.42	0.19	0.29
TR14-12	44/125a	0.17	0.05	0.31	0.20	<0.01	<0.0001	0.70 [0.76]	0.88	0.45	0.68
TR14-14	44/138a	0.03	0.04	0.03	0.07	0.05	<0.0001	0.26 [0.24]	0.19	0.21	0.12
TR14-16	44/142a	0.05	0.05	0.05	0.08	0.04	<0.0001	0.16 [0.15]	0.19	0.10	0.11
TR14-17	44/144a	0.18	0.11	0.37	0.31	<0.01	<0.0001	0.42 [0.43]	0.91	0.06	0.60
TR14-19	44/32	0.09	0.08	0.09	0.08	0.02	0.0002	0.18 [0.19]	0.22	0.10	0.14
TR14-20	46/17b	0.15	0.03	0.72	0.08	0.09	<0.0001	1.35 [0.99]	1.49	0.18	1.41
TR14-23	46/14	0.16	0.13	0.90	0.15	0.12	<0.0001	1.50 [1.25]	1.53	0.23	1.38

ASS = Acid-soluble Sulfur: MS = Monosulfide: TRS = Total Reduced Sulfur

Table B3.2 Comparative test results for the A564 Foston-Hatton-Hilton by-pass

Sample and date received [Sheffield]	*Equivalent Sample ref. and date sampled [TES Bretby]*	pH		<2mm Sieve %		WSS %S		ASS %S		TS %S		TRS %S	TRS %S [TS – ASS]
		[Sheff]	*[TES]*	*[Sheff]*	*[TES]*	*[Sheff]*	*[TES]*	*[Sheff]*	*[TES]*	*[Sheff]*	*[TES]*	*[Sheffield]*	*[TES Bretby]*
TR11-D (1.6.98)	S934.1 (21.10.94)	3.64	4.30	34	38	0.07	0.05	0.07	0.17	0.31	0.46	0.22	0.29
TR11-D5 (1.6.98)	S934.1 (21.10.94)	3.66	4.30	48	38	0.05	0.05	0.04	0.17	0.60	0.46	0.58	0.29
[Mean]		[3.65]	[4.30]	[41]	[38]	[0.06]	[0.05]	[0.06]	[0.17]	[0.45]	[0.46]	[0.40]	[0.29]
TR11-1 (1.6.98)	3/NE/1 (17-27.1.95)	4.04	3.8	37	32	0.07	n/d	0.10	n/d	0.09	n/d	0	n/d
TR11-2 (1.6.98)	4/SW/2 (17-24.1.95)	5.53	4.9	41	32	0.27	n/d	0.44	n/d	0.45	n/d	0.01	n/d
TR11-3 (1.6.98)	2/NW/2 (1-14.2.95)	4.35	6.6	40	34	0.16	n/d	0.18	n/d	0.19	n/d	0	n/d
TR11-4 (1.6.98)	2/CE/2 (1-14.2.95)	3.82	5.8	35	42	0.17	n/d	0.23	n/d	0.25	n/d	0.02	n/d
TR11-5 (1.6.98)	GF/CW/1 (3-27.2.95)	3.85	5.4	34	29	0.38	n/d	0.42	n/d	0.42	n/d	0	n/d
TR11-6 (1.6.98)	3/CE/1 (17-27.1.95)	2.74	2.9	58	63	0.45	n/d	0.51	n/d	0.52	n/d	0.02	n/d

n/d = Not determined. WSS = Water-soluble Sulfur: ASS = Acid-soluble Sulfur: TS = Total Sulfur: TRS = Total Reduced Sulfur

Table B4.1 Storage experiment: acid-soluble sulfur (ASS) and total reduced sulfur (TRS) test results (all results as % S)

Date	*03/06/98*		*17/06/98*		*24/07/98*		*31/08/98*		*30/09/98*		*07/12/98*		*06/02/99*		*21/05/99*	
Sample	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*
TR8(N)	0.02	2.15	0.01	N/D	0.01	2.16	0.02	2.08	0.02	2.19	0.05	2.11	0.01	2.15	0.01	2.15
TR8(D)	0.02	2.15	0.03	N/D	0.01	2.14	0.02	2.18	0.01	1.96	0.01	2.09	0.01	2.15	0.02	2.13
TR8(H)	0.02	2.15	0.02	N/D	0.02	2.16	0.03	2.10	0.04	2.09	0.05	1.97	0.04	2.08	0.06	2.08
TR8(R)	0.02	2.15	0.02	N/D	0.01	2.15	0.02	2.05	0.02	2.07	0.02	2.19	0.01	2.15	0.01	2.15
TR8(O)	0.02	2.15	0.02	N/D	0.01	2.18	0.01	2.20	0.02	2.08	0.05	2.05	0.02	2.07	0.02	2.11
TR8(I)	0.02	2.15	0.02	N/D	0.02	2.10	0.02	2.14	0.02	2.00	0.09	1.94	0.05	1.90	0.08	2.08
TR3B(N)	0.93	0.47	1.13	N/D	0.85	0.47	0.92	0.39	0.89	0.39	0.70	0.34	1.18	0.35	1.17	0.32
TR3B(D)	0.93	0.47	1.10	N/D	0.86	0.45	0.94	0.46	0.88	0.47	0.94	0.49	1.11	0.47	1.19	0.47
TR3B(H)	0.93	0.47	0.92	N/D	0.92	0.45	0.97	0.25	0.72	0.17	0.70	0.11	1.04	0.15	1.63	0.15
TR3B(R)	0.93	0.47	1.09	N/D	0.86	0.47	0.93	0.45	0.87	0.46	0.86	0.48	1.21	0.46	1.16	0.46
TR3B(O)	0.93	0.47	0.94	N/D	0.91	0.49	0.92	0.45	0.96	0.50	0.89	0.45	1.13	0.46	0.78	0.46
TR3B(I)	0.93	0.47	1.09	N/D	0.89	0.49	0.90	0.35	0.92	0.29	0.88	0.17	1.14	0.17	1.28	0.17
TR11D(N)	0.07	0.28	0.07	N/D	0.06	0.28	0.07	0.27	0.09	0.17	0.09	0.17	0.15	0.25	0.15	0.15
TR11D(D)	0.07	0.28	0.07	N/D	0.06	0.29	0.05	0.27	0.05	0.26	0.05	0.26	0.05	0.28	0.04	0.28
TR11D(H)	0.07	0.28	0.07	N/D	0.07	0.21	0.09	0.19	0.12	0.07	0.12	0.02	0.15	0.04	0.18	0.07
TR11D(R)	0.07	0.28	0.07	N/D	0.05	0.27	0.05	0.26	0.08	0.25	0.16	0.27	0.06	0.26	0.06	0.26
TR11D(O)	0.07	0.28	0.07	N/D	0.05	0.27	0.05	0.28	0.06	0.29	0.06	0.26	0.05	0.22	0.09	0.22
TR11D(I)	0.07	0.28	0.06	N/D	0.06	0.27	0.06	0.27	0.08	0.12	0.06	0.09	0.09	0.12	0.12	0.13

N= Stored under natural laboratory conditions: D= Stored in a desiccator: H= Stored under 95% Relative Humidity conditions: R= Refrigerated storage at 4°C: O= Oven storage at 60°C: I= Storage under incubated conditions, at 35°C.

Table B4.2 Storage experiment: acid-soluble sulfur (ASS), total reduced sulfur (TRS), carbonate and organic carbon test data for a Lower Lias clay polythene wrapped block sample stored under non controlled laboratory conditions

Date	*12/04/98*				*15/01/99*		*02/06/99*		*30/07/99*			
Sample	*ASS*	*TRS*	*% CO_2*	*$\%C_{ORG}$*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*% CO_2*	*$\%C_{ORG}$*
TR6	0.04	1.18	4.80	1.53	0.20	0.29	0.40	0.21	0.48	0.21	3.75	1.56

Table B4.3 Storage experiment: monosulfide (MS), water-soluble sulfur (WSS), pH and carbonate test results

Date	*03/06/98*				*21/05/99*			
Sample	*MS*	*WSS*	*pH*	*%CO$_2$*	*MS*	*WSS*	*pH*	*%CO$_2$*
TR8(N)	0.32	N/A	N/A	0.2	0.17	N/D	N/D	0.21
TR8(D)	0.32	N/A	N/A	0.2	0.10	N/D	N/D	0.23
TR8(H)	0.32	N/A	N/A	0.2	0.15	N/D	N/D	0.18
TR8(R)	0.32	N/A	N/A	0.2	0.10	N/D	N/D	0.19
TR8(O)	0.32	N/A	N/A	0.2	0.18	N/D	N/D	0.20
TR8(I)	0.32	N/A	N/A	0.2	0.15	N/D	N/D	0.25
TR3B(N)	0	N/A	N/A	10.46	0.09	N/D	N/D	9.54
TR3B(D)	0	N/A	N/A	10.46	0.09	N/D	N/D	10.21
TR3B(H)	0	N/A	N/A	10.46	0.07	N/D	N/D	7.88
TR3B(R)	0	N/A	N/A	10.46	0.09	N/D	N/D	10.36
TR3B(O)	0	N/A	N/A	10.46	0.06	N/D	N/D	9.79
TR3B(I)	0	N/A	N/A	10.46	0.11	N/D	N/D	7.93
TR11D(N)	0	0.07	3.64	0.12	0.17	0.07	3.45	0.03
TR11D(D)	0	0.07	3.64	0.12	0.03	0.06	3.57	0.07
TR11D(H)	0	0.07	3.64	0.12	0.03	0.13	3.05	0
TR11D(R)	0	0.07	3.64	0.12	0.11	0.06	3.55	0.08
TR11D(O)	0	0.07	3.64	0.12	0.13	0.07	3.45	0.08
TR11D(I)	0	0.07	3.64	0.12	0.09	0.09	3.30	0

Table B4.4 Core sample storage experiment: acid-soluble sulfur (ASS) and total reduced sulfur (TRS) test results

Date	*19/11/98*		*06/02/99*		*21/05/99*		*30/07/99*	
Sample	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*	*ASS*	*TRS*
TR14-1 (B)	0.31	2.09	0.26	1.85	0.35	1.85	0.39	1.19
TR14-1 (C)	0.31	2.09	0.40	1.63	0.32	1.63	0.62	1.67
TR14-2 (B)	0.92	0.12	0.28	0.14	0.91	0.11	0.85	0.08
TR14-2 (C)	0.92	0.12	0.37	0.12	0.84	0.15	0.94	0.10
TR14-3 (B)	0.22	1.42	0.18	1.27	0.28	0.98	0.41	0.77
TR14-3 (C)	0.22	1.42	0.25	1.35	0.42	1.39	0.48	1.28
TR14-4 (B)	0.11	0.09	0.18	0.10	0.18	0.08	0.28	0.07
TR14-4 (C)	0.11	0.09	0.09	0.10	0.12	0.09	0.28	0.10
TR14-5 (B)	0.23	0.66	0.22	0.48	0.23	0.46	0.30	0.29
TR14-5 (C)	0.23	0.66	0.19	0.54	0.22	0.42	0.24	0.45
TR14-6 (B)	0.16	0.86	0.64	0.38	0.81	0.17	0.98	0.13
TR14-6 (C)	0.16	0.86	0.57	0.50	0.81	0.43	0.88	0.45

Table B4.5 Core sample storage experiment: carbonate and organic carbon test results

Date	*19/11/98*		*30/07/99*	
Sample	*% CO$_2$*	*%C$_{ORG}$*	*% CO$_2$*	*%C$_{ORG}$*
TR14-1 (B)	15.12	1.02	15.12	1.10
TR14-1 (C)	15.12	1.02	15.41	1.16
TR14-2 (B)	7.51	0.54	7.83	0.64
TR14-2 (C)	7.51	0.54	7.25	0.45
TR14-3 (B)	7.89	1.17	7.94	1.32
TR14-3 (C)	7.89	1.17	7.37	1.00
TR14-4 (B)	8.57	0.50	8.26	0.73
TR14-4 (C)	8.57	0.50	8.06	0.53
TR14-5 (B)	10.07	0.96	9.73	1.01
TR14-5 (C)	10.07	0.96	9.87	0.82
TR14-6 (B)	3.56	1.05	3.00	1.06
TR14-6 (C)	3.56	1.05	3.02	0.70

(B) = Bag sample; (C) = Core sample

Appendix C: Test procedures for the determination of sulfur species

C.1 Sample preparation

Samples should be taken and stored in accordance with the recommendations given in Section 6.2. Samples should be prepared in accordance with the general procedures and recommendations described in BS1377 (British Standards Institution, 1990) and Head (1992) with modifications that are designed to preserve the original chemistry of the materials. The systematic procedure is as follows:

1 Drying of samples

Soils and sediments shall be dried at a temperature of between 60 and 75 °C using a fan-assisted or conventional oven until any difference in successive weighings, carried out at intervals of 4 hours, does not exceed 0.1% of the original mass of the samples (BS1377). (This will generally take between 48 and 72 hours). The samples shall then be allowed to cool to room temperature in a desiccator.

Rock samples shall be oven dried at a temperature of between 100 and 105 °C, using a fan-assisted or conventional oven until any difference in successive weighings, carried out at intervals of 4 hours, does not exceed 0.1% of the original mass of the samples (BS1377). (This will generally take about 48 hours). The samples shall then be allowed to cool to room temperature in a desiccator.

2 Mechanical processing

Previously dried coarse grained (non-cohesive) material shall be dry sieved using 5mm and 2mm sieves. Material retained on the sieves shall be examined using a binocular microscope of magnification x 35 or similar. If the retained fraction consists of inert material such as quartz etc, then the material shall be brushed clean of any adhering particles which should be added to the <2mm fraction and the inert fragments retained for weighing. If the material consists of weakly cemented grains, they shall be broken down by means of gentle pounding action using an agate or ceramic pestle and mortar and re-sieved. If the retained material consists of cemented clay, mudstone or any material considered to be a potential host for sulfur minerals it shall be added to the fraction passing the 2mm sieve which is retained for testing. The <2mm fraction and the inert fraction (>2mm) shall be weighed and their respective percentages of the total content recorded.

Previously dried fine grained (cohesive) material shall be broken down using a ceramic mortar and rubber-coated glass rod. Any gravel size (>2mm) material shall be removed for examination under a binocular microscope. Any fragments of inert material shall be brushed clean of any adhering particles, which shall be added to the disaggregated material and retained for weighing. If the retained material consists of cemented clay, mudstone or any material considered to be a potential host for sulfur minerals it shall be added to the disaggregated fraction which is retained for testing. The disaggregated fraction and inert fraction shall be weighed and their respective percentages of the total content recorded.

After being dried, rock samples shall be brushed clean of any loose debris, and then broken down into sub-centimetric sized fragments using an industrial fly press; alternatively a hammer and steel plate or a steel pestle and mortar may be used. The material is retained for testing. (Care must be taken when using mechanical crushing devices to ensure that samples do not become heated beyond 105°C).

3 Subdividing

The material retained for testing shall be mixed thoroughly and subdivided by cone and quartering or riffling until a representative sub-sample of between 200 and 300 g is obtained.

4 Particle size reduction

The representative sub-samples shall be subjected to particle size reduction producing a powdered sample of <212µm grain size. The particle size reduction shall be accomplished using a tungsten carbide disc shatter mill, or an equivalent type of mill. The samples shall be subjected to between 10 and 15 seconds of milling. Longer periods may cause oxidation of sulfur minerals. The powdered sample shall be passed through a 212µm sieve, with any material retained on the 212µm sieve being re-ground.

5 Storage

Where storage before testing is required the powdered samples shall be oven dried for a further 24 hours at a temperature of between 60 and 75°C. The samples shall then be allowed to cool to room temperature in a desiccator, placed in air tight containers and stored at a temperature of 0 - 4°C to await testing.

C.2 Chemical testing

The description of each of the tests comprises a step-by-step procedure starting with dry powdered material. The relevant forms for recording the test results and examples of the calculations are also given.

Careful assessment should be made of the level of skills required to carry out the determinations, as personnel may need training to carry them out competently and safely. This is particularly the case with Test Nos. 3, 4 and 5.

The end-point determinations for several of the tests is by the use of inductively coupled plasma - atomic emission spectroscopy (ICP-AES) equipment. It is anticipated that extractions that have been prepared in accordance with the procedures described here will be submitted to an analyst who operates the equipment. If dilution of the sample is necessary for analysis it shall be undertaken by the analyst and the total concentration value corrected appropriately. The result should be presented in milligrams per litre (mg/l) and, where dilution was required, this fact should be reported. The sulfur content of blank solutions should be determined as a procedure check and, if this reveals any contamination, the tests should be repeated.

Care must be taken with the ICP-AES analysis as the equipment must be carefully calibrated against an appropriate standard and checks run to make sure there are no instrument fluctuations which may result in errors. Extreme care must be taken with the dilution for ICP analysis, as slight operational errors may result in large errors in the sulfur determination. Good practice in chemical testing requires that duplicate specimens should be tested. If more than one specimen has been tested and the individual results differ by no more than 0.1% S (0.3% S for total reduced sulfur (TRS) determinations), the mean result should be calculated. If they differ by more than 0.1% S (0.3% S for total reduced sulfur (TRS) determinations) the test should be repeated with two new portions of the prepared sample until this level of precision is achieved.

Test No. 1 - Determination of water-soluble sulfur (WSS)

This procedure will determine total water soluble sulfur species including highly soluble sulfates such as epsomite and partly soluble sulfates such as gypsum, ionic sulfides and sulfites if present. All these sulfur species can have a detrimental effect on concrete and steel and therefore an accurate assessment of the immediate risk to construction materials may be made using this procedure.

The extraction procedure is the same as that specified in BS1377 (British Standards Institution, 1990), but the determination of sulfur in solution is by ICP-AES rather than gravimetric means. The result is expressed in terms of water-soluble sulfur (WSS) in percent and water-soluble sulfate (WS) in mg/l. All data shall be recorded on Data Sheet No.1.

The test may also be used for samples of groundwater by omitting the extraction procedure and going directly to the determination of sulfur in solution by ICP-AES.

Apparatus and chemicals

A 250ml capacity clean and dry, leakproof screw cap, rigid plastic or HDPE container (Glass containers are susceptible to damage from the soil particles during the extraction stage);
A rotary tumbler or mechanical shaker;
30-50ml capacity sterile polystyrene or polypropylene leakproof screw cap sample bottles;
Vacuum filter funnel, flask and Whatman No. 542 (or equivalent) filter paper;
0.45µm membrane syringe filter;
Calibrated electronic pH meter;
Laboratory glassware;
De-ionised water;
Analytical grade concentrated nitric acid, 1.42 g/ml (solution = 70%) (if samples need to be stored).

Procedure

1. Weigh out a 30 to 50 g (m_1) representative portion of the oven-dried sample into the 250ml capacity container. Record the weight to an accuracy of 0.001g. Add between 60 ml and 100 ml of de-ionised water, recording the exact amount (V_1), to the sample to make a 2:1 water to soil mixture and stopper the extraction bottle tightly. Retain a blank of around 10 ml of the de-ionised water used for each batch of extractions for ICP-AES analysis.
2. Place the extraction vessel in a mechanical shaker or mechanical rotator and agitate for 16 hours (overnight).
3. Filter the soil suspension under vacuum through the filter funnel into the filter flask, using the filter paper. If the filtrate is still cloudy further filtration using a 0.45 µm membrane syringe filter will be necessary. Do not add any more water. Retain an aliquot of around 20 ml of the sample for sulfur determination and measure the pH of the remaining solution using a calibrated electronic pH meter.
4. If the sample is to be stored prior to analysis acidify to 1-2% by volume with concentrated nitric acid (or whatever concentration is necessary to produce the same matrix as for the calibration standard).
5. Analyse the sulfur concentration using ICP-AES ($\mathbf{r}_1$). If dilution of the sample is necessary for analysis it shall be reported. Also determine the sulfur content of the blank solution.
6. Calculate the water soluble sulfur content of the sample. Present the value as % **WSS** (**WSS** = water-soluble sulfur).
7. Calculate the water-soluble sulfate **(WS)** of the sample. Present the value as **mg/l** $\mathbf{SO_4}$.
8. **WS = 15,000 x WSS**.

Calculation - see Data Sheet No. 1

m_1 = 35500 mg of sample

V_1 = 71 ml of de-ionised water

r_1 = 792.0 mg/l of sulfur in the solution

NB: 0.001 mg/g = 1 mg/l

Calculate the mass of sulfur in solution (**m_2**). Adjust the measured concentration for the volume of water used in the extraction and convert to mg of sulfur in the extract.

$(r_1 \times V_1)$ $\div$ 1000 = **m_2** $\therefore$ $(792.0 \times 71) \div 1000 = 56.232$ mg S in the solution.

Convert to percent (water-soluble sulfate) sulfur in the sample:

(**m_2** $\times$ 100) $\div$ **m_1** = % **WSS**. $\therefore$ $(56.232 \times 100) \div 35500$ = **<u>0.158 % WSS</u>**

Equivalent water-soluble sulfate **(g/l WS) : g/l WS = 15 × % WSS**

$\therefore$ 0.158 % WSS × 15,000 = 2,376 mg/l SO_4 WS

Express to nearest 100 mg/l = **<u>2,400 mg/l SO_4 WS</u>**

Test No. 2 - Determination of acid-soluble sulfur (ASS)

This test is used to determine the quantities of acid-soluble sulfates in samples. These include gypsum, and highly soluble sulfates such as epsomite. The extraction described will not dissolve mineral sulfates such as barytes or take sulfur in organic matter into solution. Organic sulfur and mineral sulfates do not usually lead to attack on engineering materials.

The test requires the preparation of de-aired dilute hydrochloric acid. During the extraction, which should be carried out in a fume cupboard, acid-soluble sulfur compounds are taken into solution, which is then analysed for sulfur. The data are recorded on Data Sheet No.1. The results are expressed as acid-soluble sulfur (ASS) in percent and acid-soluble sulfate (AS) in percent.

Apparatus and chemicals

250 ml capacity quickfit, round bottom flask;
Analytical grade concentrated hydrochloric acid (HCl), 1.18 g/ml (solution = 35% HCl);
Water cooled condenser;
Long delivery stem quickfit dropping funnel or a jumbo syringe with a long delivery stem;
Electric heating mantle (or alternative heat source);
Vacuum filter funnel, flask and Whatman No. 542 (or equivalent) filter paper;
0.45µm membrane syringe filter;
30-50 ml capacity sterile polystyrene or polypropylene leakproof screw cap sample bottles;
Laboratory glassware;
De-ionised water;
Oxygen-free nitrogen or argon;
Lead acetate paper.

Reagents

Prepare a 25% hydrochloric acid solution by volume using analytical reagent grade acid and de-ionised water. De-air the hydrochloric acid solution by passing oxygen-free nitrogen (or argon) through it for 10 minutes prior to use. Alternatively prepare beforehand. Heat the hydrochloric acid solution to boiling, maintain the solution at boiling point for 10 minutes and then immediately transfer it to an appropriate sealed vessel, cool and store until required.

Procedure

1. Weigh out a 0.80 - 1.0 g (m_1) representative portion of the oven-dried sample to an accuracy of 0.001g and place the sample in the round bottom reaction flask.
2. Connect the condenser to the flask and establish the condenser water flow.
3. Add exactly 100 ml of 25% de-aired hydrochloric acid (V_1) using the dropping funnel or jumbo syringe through the condenser. Retain a 10 ml quantity of each batch of de-aired hydrochloric acid prepared for blank analysis.
4. Lower the reaction vessel into the heating mantle and bring the contents rapidly to the boil. Maintain the reaction at boiling point under reflux for 15 minutes [*1].
5. Allow the contents of the reaction flask to cool to room temperature with the condenser attached.
6. Filter the residual solution in the reaction flask under vacuum into a dry filter flask. If the filtrate is still cloudy further filtration using a 0.45 µm membrane syringe filter will be necessary. Do not add any more water. Retain an aliquot of around 20 ml of the sample for sulfur determination.
7. Analyse the sulfur concentration using ICP-AES (r_1). If dilution of the sample is necessary it shall be reported. Also determine the sulfur content of the blank solution.
8. Calculate the acid soluble sulfur content of the sample. Present the value as % **ASS** (**ASS**= acid-soluble sulfur).
9. Calculate the acid-soluble sulfate (AS) content of the sample. Present the value as **% SO_4 AS. AS = 3 x ASS**.

Calculation – see data sheet No. 1

m_1 = 1000 mg of sample

V_1 = 100 ml (hydrochloric acid solution for dissolution)

r_1 = 21.98 mg/l of sulfur in the diluted digestion solution

NB: 0.001 mg/g =1mg/l

Calculate the mass of sulfur present in solution ($\mathbf{m_2}$). Adjust the measured concentration for the volume of hydrochloric acid used in the extraction and convert to mg of sulfur in the extract.

$(\mathbf{r_1} \times \mathbf{V_1}) \div 1000 = \mathbf{m_2} \therefore (21.98 \times 100) \div 1000 = 2.198$ mg S

Convert to percent acid-soluble sulfur (ASS) in the sample.

$(\mathbf{m_2} \times 100) \div m_1 = \%$ ASS $\therefore (2.198 \times 100) \div 1000 =$ **<u>0.220 % ASS</u>**

Equivalent acid-soluble sulfate **(% AS) : % AS = 3 × % ASS**

$\therefore$ 0.220 % ASS × 3 = **<u>0.660 % SO_4 AS</u>**

Express to 2 decimal places = **<u>0.66 % SO_4 AS</u>**

Notes

*1 The exhaust gas should be tested for the presence of hydrogen sulfide using lead acetate paper. If this darkens to black, monosulfide minerals are present and the fact should be reported in ‘remarks’. Such minerals may be quantified using Test No. 5.

Test No. 3 - Determination of total reduced sulfur (TRS)

This test is used to determine the quantity of sulfur present either as elemental or reduced sulfide forms. Thus it is appropriate for the determination of pyrite, although if elemental sulfur or monosulfide is present they will be included in the test result. Other forms of sulfur, such as organics, water-soluble and acid-soluble are not included. The test includes all reduced sulfur species which could oxidise to produce sulfate. The TRS value is used to calculate the oxidisable sulfides (OS) content.

Reduced sulfur compounds are a significant cause of problems in engineering situations as they may oxidise producing acidic and sulfate rich conditions. This leads to attack on construction materials. Under some circumstances the oxidation process may occur long after construction is completed.

The apparatus required for the test is shown in Figure C1. The preparation of various reagents is required, the apparatus for which is shown in Figure C2. The extraction leads to the evolution of sulfur as hydrogen sulfide gas, which is trapped in an acidified copper nitrate solution leading to the precipitation of copper sulfide. The extraction should be carried out in a fume cupboard. The amount of sulfur evolved by the reaction is quantified by determining the loss of copper from the trapping solution. This may be carried out using Procedure A: ICP-AES method, or using procedure B: iodometric titration. The results are recorded on Data Sheet No.2. The results are expressed as percent total reduced sulfur and may be converted to oxidisable sulfides (OS) in percent sulfate.

Apparatus and chemicals

250 ml capacity 2 neck quickfit reaction flask;

75 ml quickfit reagent reservoir with air tight tap or jumbo syringe attachment;

Oxygen-free nitrogen or argon gas;

Tapered quickfit air inlet tube;

Condenser;

Sulfur resistant tubing[*1;]

2 No 75 ml Trapping vessels: Dreschel type sintered bottle head with a sintered disc of porosity grade P40, (see BS1752), in a quickfit test tube assembly;

300ml conical glass flask;

Heating mantle or other suitable heat source;

Type 2c chromatography column (for the Jones reductor);

Filter funnel, 500ml capacity flask and Whatmans No.540 (or equivalent) filter paper;

Laboratory glassware;

20-30 mesh pure zinc (Zn);

Hydrochloric acid (HCl);

De-ionised water;

Absolute ethanol (C_2H_5OH);

Mercuric nitrate (mercury (II) nitrate 2-hydrate: $Hg_2(NO_3)_2.2H_2O$) or mercuric chloride (mercury (II) chloride: $HgCl_2$);

Analytical grade chromic chloride (Chromium (III) chloride 6-hydrate: $CrCl_3.6H_2O$);

Analytical grade concentrated hydrochloric acid, 1.18 g/ml (solution = 35% HCl);

Analytical grade copper nitrate (Copper (II) nitrate 3-hydrate: $Cu(NO_3)_2.3H_2O$);

Analytical grade concentrated nitric acid, 1.42 g/ml (solution = 70% HNO_3);

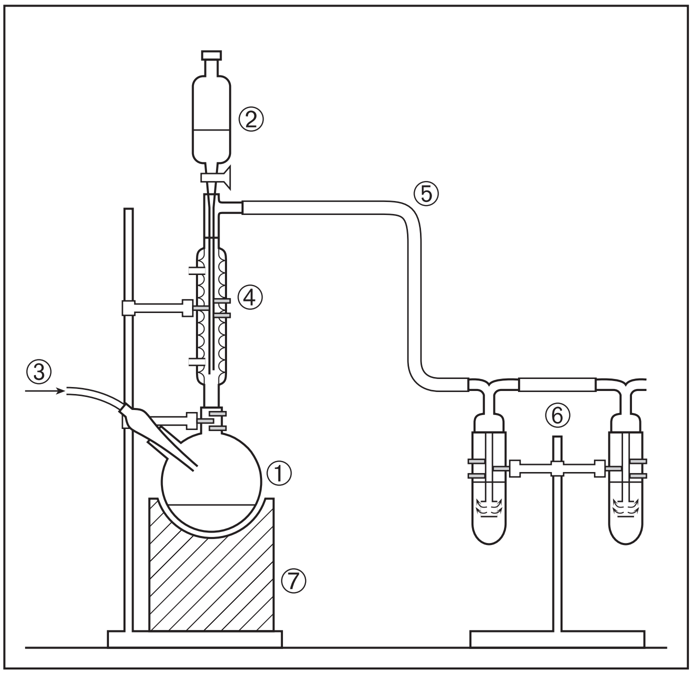
Lead acetate paper.

Preparations

A. Jones reductor (see Figure C2).
This should be carried out in a fume cupboard (Ref.1).

1 Place ~200 g of 20-30 mesh pure zinc in a beaker, wash and decant twice with 5% by volume hydrochloric acid, then cover with 200 ml of 5% by volume hydrochloric acid.

2 Add the required quantity of mercuric nitrate or mercuric chloride to make a 2% solution (2 g in 200 ml). Stir for 3-5 minutes, decant the solution, wash and decant a further 3 times using tap water. The zinc amalgam should have a shiny appearance.



1 = 250 ml 2 neck quickfit reaction flask;
2 = 75 ml quickfit reagent reservoir with air tight tap or jumbo syringe attachment;
3 = Nitrogen/argon gas introduced via quickfit side arm spout;
4 = Condenser;
5 = Sulfur resistant tubing;
6 = 2 No 75 ml Dreschel head gas bubbler type trapping vessels;
7 = Heating mantle.

Figure C1 Schematic diagram of the apparatus for total reduced sulfur (TRS) determination

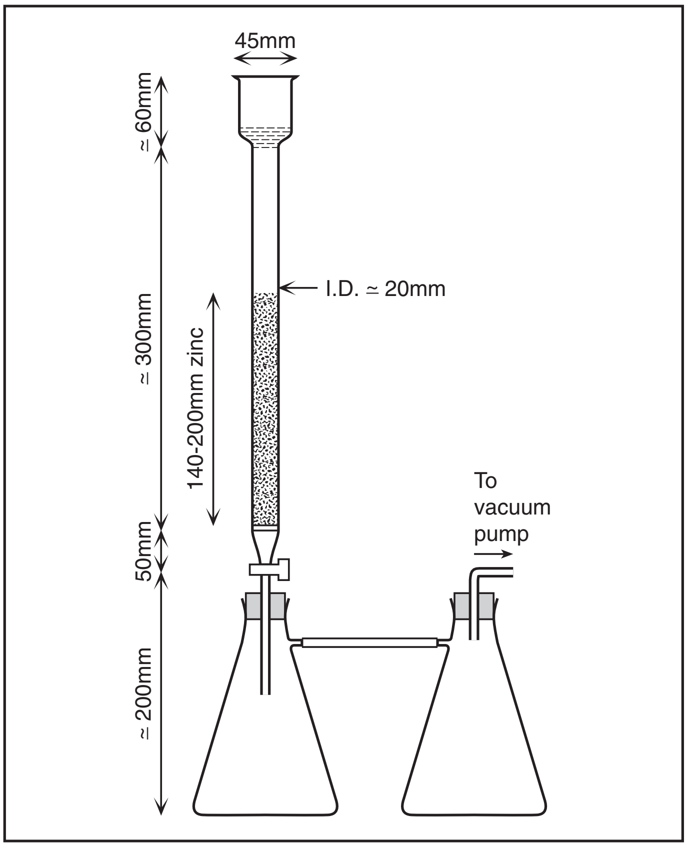


Figure C2 Jones reductor assembly

3 Prepare the Jones reductor by packing the amalgamated zinc into the glass column and store under de-ionised water containing 1-2 drops of concentrated hydrochloric acid.

4 Activate the Jones reductor immediately prior to use. To do this slowly pass through it 100 ml of 5% by volume hydrochloric acid.

B. Reagents

1 Chromium (III) solution [266 g/l chromic chloride solution acidified to 4.5% by volume with concentrated hydrochloric acid].

> *Dissolve 266 ± 0.5 g of chromic chloride in 200 ml of de-ionised water, add 45 ml of analytical grade concentrated hydrochloric acid and make up to 1000 ml in a volumetric flask.*

2 Chromium (II) solution

Pass the 266 g/l chromic (III) chloride solution (which has been acidified to 4.5% by volume with analytical grade concentrated hydrochloric acid) through the activated Jones reductor. On reduction, the chromic (III) solution changes valence state to chromic (II), which is observed as the colour changes from green to blue down the column. Due to atmospheric oxidation this solution is unstable and should be prepared every two to three days. Store the prepared solution in a stoppered glass vessel out of direct light.

3 Copper nitrate solution ~200 mg/l acidified to 3.15% by volume with concentrated nitric acid.

> *Dissolve exactly 0.76 g of copper nitrate in 200 ml of de-ionised water, transfer to a volumetric flask, add 31.5 ml of analytical grade concentrated nitric acid and make up to 1000 ml with de-ionised water.*

Procedure A: copper determination by ICP-AES

1 Weigh out a 0.5 g (**m_1**).representative portion of the oven-dried sample to an accuracy of 0.0001 g. Also run a blank with no sample.

2 Place the sample in a 250 ml quickfit, side arm round bottom reaction flask and add 10 ml of absolute ethanol.

3 Connect the condenser (see Fig. C1), and establish the condenser water flow.

4 Using air-tight sulfur resistant tubing [*1] connect the two in-line gas washing tube trapping vessels. Each trapping vessel shall contain exactly 50 ml of 200 mg/l acidified copper nitrate solution (combined total of 100 ml = (**V_2**)). Retain exactly 100 ml of the copper nitrate solution for a blank determination (**V_1**).

5 To the side arm attach a gas inlet tube connected to the oxygen-free nitrogen (or argon) gas supply, and establish a slow steady flow of gas [*2]. Flush the reaction flask for 5 minutes to displace the air.

6 Stop the gas flow and add 50 ml of the chromium (II) solution and 20 ml of analytical grade concentrated hydrochloric acid, using the a long stem dropping funnel or jumbo syringe fitted to the condenser and restart the gas flow [*3].

7 Allow the reaction to proceed in the cold for 15 minutes and then apply heat (~150°C) bringing the solution to a gentle boil and leave the mixture gently boiling under reflux for 1½ hours [*4].

8 When the digestion has been completed, if ICP-AES analysis is to be used, filter the contents of each of the trapping vessels into the 500ml volumetric flask. Also carefully wash out the bottle head and quick fit test tube with de-ionised water into the filter paper. Wash the residue in the filter paper with de-ionised water. Discard the black solid CuS precipitate on the filter paper. Make the blank and absorbent solutions up to 500 ml with de-ionised water [i.e. ×5 dilution (blank, **d_1**; absorbent, **d_2**)] in the volumetric flasks for the determination of copper using ICP-AES.

9 If iodometric titration is to be used, filter the contents of each of the trapping vessels into the same 300ml conical flask. Also carefully wash out the head and quickfit test tubes with a minimum of de-ionised water into the filter paper. Wash the residue in the filter paper with a minimum of de-ionised water. Discard the black solid CuS precipitate on the filter paper.

10 Analyse the copper concentration using ICP-AES [blank (**r_1**) and test (**r_2**) solutions] **OR** alternatively determine the copper concentration of the test and blank solutions using iodometric titration as presented in Test No.3 procedure B. If dilution of the sample is necessary for ICP-AES analysis it shall be reported, and the total concentration value corrected appropriately.

11 Calculate the total reduced sulfur content of the sample. Present the value as % **TRS** (TRS = Total reduced sulfur).

12 Calculate the equivalent oxidisable sulfides **(OS)** content of the sample. Present the value as % SO_4 **OS.**
(% OS = 3 x% TRS)

Calculation using ICP-AES - See data sheet No. 2

Determine the amount of sulfur equivalent to the loss of copper from the solution by considering the reaction and the atomic weights of copper and sulfur

$FeS_2 + 2H_2 = 2H_2S + 2Cu(NO_3)_2 = 2CuS \downarrow + 2HNO_3 + H_2$

So for every g of Cu, 0.504 g of S have been precipitated.

$\boldsymbol{V_1}$ = 100 ml blank absorption solution

$\boldsymbol{V_2}$ = 100 ml test absorption solution

$\boldsymbol{m_1}$ = 500 mg of sample

$\boldsymbol{r_1}$ = 40.50 mg/l of copper in the diluted blank solution

$\boldsymbol{r_2}$ = 22.28 mg/l of copper in the diluted test solution

$\boldsymbol{d_1}$ = ×5 (dilution of blank solution)

$\boldsymbol{d_2}$ = ×5 (dilution of test solution)

NB: 0.001 mg/g = 1mg/l

Concentration of copper in blank solution: $\boldsymbol{r_1 \times d_1 = \mathrm{Tr}_1} \therefore 40.50 \times 5 = 202.5$ mg/l

Concentration of copper in test solution: $\boldsymbol{r_2 \times d_2 = \mathrm{Tr}_2} \therefore 22.28 \times 5 = 111.4$ mg/l

Convert concentrations of the solutions used into amount of copper in test quantity.

In the blank solution the concentration of copper is 202.5 mg/l.

$\therefore$ In 100 ml of blank $(\mathbf{Tr_1} \times \boldsymbol{V_1}) \div 1000 = \mathbf{p_1} \therefore \mathbf{p_1} = (202.5 \times 100) \div 1000 = 20.25$ mg Cu.

In the test solution the concentration of copper is 111.4 mg/l.

$\therefore$ in 100 ml of test solution $(\mathbf{Tr_2} \times \mathbf{V_2}) \div 1000 = p_2 \therefore p_2 = (111.4 \times 100) \div 1000 = 11.14$ mg Cu.

As 1 atom of sulfur combines with 1 atom of copper, knowing the quantity of copper used, the amount of sulfur liberated in the reaction may be determined i.e. 1.0 g of copper = 0.504 g of sulfur.

$(\mathbf{p_1} - \mathbf{p_2}) \times 0.504 = \mathbf{m_2} \therefore (20.25 - 11.14) \times 0.504 = 4.59$ mg S

In 500 mg of test sample there is 4.59 mg ($\mathbf{m_2}$) of sulfide-sulfur

$(\mathbf{m_2} \times 100) \div \boldsymbol{m_1}$ = % **TRS** : $(4.59 \times 100) \div 500$ = **<u>0.918 % TRS</u>**

Express to 2 decimal places = **<u>0.92 % TRS</u>**

Equivalent oxidisable sulfides **(OS)** as % SO_4: % **OS = 3 x % TRS** $\therefore$ **0.92 (% S) TRS = <u>2.76 (% SO_4) OS</u>**

Notes

*1 Use only H_2S- resistant line (for example Bev-A-Line®, Tygon® etc, consult manufacturer about suitability) for connection from condenser to the absorption cell as other rubber lines may react giving off sulfur-bearing gas. The gas line should be suitably attached to all connections producing an air tight joint.

*2 A carrier gas flow rate should be established which creates a steady flow of gas bubbles from the sinter head and does not create frothing at the surface of the absorbent solutions contained in the gas traps. This will vary with use of the sintered heads and generally a supply pressure of between 3-5 psi (20 – 35 kPa) has been found suitable.

*3 If the quickfit dropping funnel tap or jumbo syringe connection does not create an air tight seal when the gas flow is resumed then the dropping funnel should be removed and the inlet port blocked using a quickfit stopper. It is suggested that an air-tight seal is confirmed prior to testing by setting up the equipment and placing a small quantity of liquid in the dropping funnel and switching on the gas supply.

*4 The exhaust gas should be tested with lead acetate paper for the presence of hydrogen sulfide, which will cause it to darken to black. If this occurs the flow rate should be reduced and the fact reported. If darkening of the lead acetate persists the test should be repeated with a smaller sample (see below).

- The volumes of copper nitrate solution used must be accurately measured out using a calibrated pipette.
- The reaction digestion vessel should be washed out as soon as it is cool enough to be handled as the contents may solidify.
- 200 mg/l copper nitrate absorbant solution is suitable for samples with up to 1.7% TRS for 500 mg sample tested (3.18% equivalent FeS_2 for pyrite). If high quantities of TRS (>1.7%) are expected or detected the determination should be repeated using smaller quantities of sample i.e. 300 mg or using copper nitrate solutions of 500 mg/l or 1000 mg/l strengths. Extracts from such samples will need appropriate dilution for ICP-AES analysis.

Reference

1. Bassett J, Denney R C, Jeffery G H and Mendham J (1978). *Vogel's textbook of inorganic analysis*. 4th edition, Longman Group limited.

Procedure B: copper determination by iodometric titration

The sulfur extraction is carried out in exactly the same way as for procedure A; steps 1 to 9. To carry out the titration a calibration curve must be determined using a commercially available or made-up standard copper solution. This forms steps 4 to 7 of this procedure, which then continues with the titration to determine the amount of copper present in the blank and test solutions.

Apparatus and chemicals

Electric heating mantle or other suitable heat source;
250 ml capacity conical flasks;
Laboratory glassware;
Soluble starch;
De-ionised water;
De-aired deionised water;
Potassium iodide (KI);
Potassium thiocyanate (KSCN);
Sodium thiosulfate ($Na_2S_2O_3.5H_2O$);
Sodium carbonate (Na_2CO_3);
Copper standard.

1 Prepare a starch solution by combining 1 g of soluble starch with enough de-ionised water to make a thick paste. Pour this into 100 ml of boiling de-ionised water and stir for a few seconds. Remove the flask from heat and add 2-3 g of potassium iodide. Allow the mixture to cool and store in a stoppered bottle out of direct sunlight. Make fresh starch solution every 2-3 days.

2 Prepare potassium iodide solution by dissolving 10 g of potassium iodide in 100 ml of de-ionised water and store this in a stoppered bottle.

3 Prepare potassium thiocyanate solution by dissolving 10 g of potassium thiocyanate in 100 ml of de-ionised water and store this in a stoppered bottle.

4 Prepare sodium thiosulfate solution (24.8 g/l) by dissolving exactly 24.82 g of sodium thiosulfate and 0.1 g of sodium carbonate in de-aired, de-ionised water and make up to 1000 ml and store in a stoppered bottle. Make a fresh stock each week.

5 Standardise the sodium thiosulfate solution using a prepared (~1000 mg/l) or commercially available copper standard by pipetting 5 ml, 10 ml, 20 ml and 50 ml of the copper standard into separate 250 ml conical flasks, and making the solutions up to 50 ml with de-ionised water.

6 Titrate each copper solution with the sodium thiosulfate solution by adding 10 ml of potassium iodide solution to the copper solution. Then add the potassium thiosulfate from a micro-burette whilst swirling the contents of the flask until the colour of the titration solution changes from a pale brown to a pale yellow. Add 2 ml of the starch indicator solution. Continue the titration slowly until the colour shows signs of changing from black to purple. Add 10 ml of potassium thiocyanate solution and continue to titrate adding the sodium thiosulfate solution dropwise whilst continually swirling the mixture. The end-point is detected by a sudden colour change from purple to white. This end-point is drop sensitive therefore care should be taken when adding the sodium thiosulfate solution. Record the amount of sodium thiosulfate used in the titration. Perform the titration on the remaining copper standard solutions.

7 Once the titrations have been completed, construct a graph of copper concentration against quantity of thiosulfate used and calculate the calibration of the thiosulfate solution.

8 For the iodometric titration procedure transfer exactly 100 ml of the diluted copper blank solution (V_1) prepared for analysis at step 4 in procedure A into a 250 ml conical flask.

9 Add exactly 10 ml of the potassium iodide solution and titrate with the standardised sodium thiosulfate solution from a micro-burette until pale yellow.

10 Add 2 ml of the starch solution and slowly titrate until the colour changes from black to purple.

11 Add 10 ml of the potassium thiocyanate solution and immediately complete the titration, the end point is detected by a sudden colour change from purple to white.

12 Record the volume of titrant used (**Vt_1**) for the blank solution.

13 Repeat the titration procedure with the diluted test solution (**V_2**) prepared for analysis at step 9 in procedure A and record the relevant volume of titrant (**Vt_2**) used.

14 Correct the results for volumetric dilution and calculate the sulfur content by the difference in copper content of the stock absorbent and the absorbent solution. Present the result as percent total reduced sulfur **(TRS)**.

15 Present the equivalent oxidisable sulfides (OS) content of the sample, as % SO_4 **OS**.

16 % **OS = 3 x % TRS**

Calculation using iodometric titration

V_1 = 100 ml blank absorption solution

V_2 = Solution containing 100 ml of test absorption solution combined with de-ionised wash water

m_1 = 500 mg of sample

St = Standardisation of thiosulfate solution (i.e. from calibration curve, 1 ml thiosulfate = 6.30 mg copper)

Vt_1 = 3.215 ml thiosulfate solution used in the blank solution titration

Vt_2 = 1.770 ml thiosulfate solution used in the test solution titration

NB: 0.001 mg/g = 1 mg/l

Calculate the amount of copper present in the blank solution.

$\mathbf{Vt_1 \times St = p_1} \therefore \mathbf{p_1} = (3.215 \times 6.30) = 20.254$ mg Cu

Calculate the amount of copper present in the test solution.

$\mathbf{Vt_2 \times St = p_2} \therefore \mathbf{p_2} = (1.770 \times 6.30) = 11.151$ mg Cu

As 1 atom of sulfur combines with 1 atom of copper, knowing the quantity of copper used, the amount of sulfur liberated in the reaction may be determined i.e. For CuS, S = 0.504 × Cu

Calculate the amount of sulfur present in the solution.

$(\mathbf{p_1 - p_2}) \times 0.504 = \mathbf{m_2} \therefore \mathbf{m_2} = (20.254 - 11.151) \times 0.504 = 4.59$ mg S

Calculate the concentration of total reduced sulfur.

In 500 mg of test sample there is 4.59 mg (m_2) of sulfide-sulfur.

$(m_2 \times 100) \div m_1 = \%$ **TRS** $\therefore (4.59 \times 100) \div 500 =$ **<u>0.918 % TRS</u>**

Express to 2 decimal places = **<u>0.92 % TRS</u>**

Equivalent oxidisable sulfides **(% OS) : % OS = 3 x% TRS**

∴ 0.92 (% S) TRS = <u>2.76 (% SO_4) OS</u>

Notes

A procedure for iodometric titration of similar accuracy using zinc acetate is presented in Sulfides in Waters and Effluents 1983, Tentative Methods for the Examination of Waters and Associate Materials, HMSO, London.

Test No. 4 - Determination of total sulfur (TS)

Two procedures are presented for the determination of total sulfur in samples. The microwave digestion method is preferred as this is less liable to be affected by differences in the operation of the equipment.

Procedure A: Microwave digestion

The procedure in this test releases all sulfur present in a sample into solution. The sulfur is then determined by ICP-AES analysis. The microwave digestion should be performed according to the manufacturer's instructions supplied with the specific instrument used. The results are recorded on Data Sheet No. 3. The results are expressed as percent total sulfur (TS). From TS and the acid-soluble sulfur (AS), the oxidisable sulfides (OS) may be calculated.

Apparatus

Reverse aqua-regia solution (3 parts analytical grade concentrated HNO_3: 1 part analytical grade concentrated HCl by volume);

De-ionised water;

Microwave digestion apparatus with PTFE pressure reaction vessel;

Centrifuge;

Laboratory glassware.

Procedure

1 Weigh out accurately about 300 mg (m_1) of powdered, oven dried sample to 0.0001 g, and place in a clean PTFE reaction vessel.

2 In a fume cupboard carefully add 20 ml of prepared reverse aqua-regia solution into the PTFE reaction vessel.

3 For each batch of samples analysed run 1 blank analysis using reverse aqua-regia only.

4 Seal the reaction vessels, place them in the microwave digester carousel and pressurise each vessel. Select the required programme for shale/coal dissolution from the manual that accompanies the brand of digester being used. This should digest the sample for a minimum of 60 minutes at increments between 100-170°C under incremental pressures ranging from 415 to 1100 kPa (60 psi to 160 psi).

5 Once the digestion is completed and the system has cooled to room temperature as indicated by the apparatus, carefully remove the reaction vessel, and dismantle it in a fume cupboard. Carefully transfer all the reaction solution into a 50 ml centrifuge tube by washing with de-ionised water. Centrifuge for 15 minutes at 4500 rpm.

6 Transfer the supernatant liquid into a 200 ml volumetric flask. Then wash and centrifuge the residue twice using between 30 and 50 ml of de-ionised water, transferring the supernatant liquid into the volumetric flask each time.

7 Make up the supernatant and wash solutions to 200 ml in the volumetric flask using de-ionised water (d_1).

8 Analyse the sulfur concentration using ICP-AES (r_1). If dilution of the sample is necessary for ICP-AES analysis it shall be reported, and the total concentration value corrected appropriately. Also determine the sulfur content of the blank solution as a procedure check.

9 Calculate the total sulfur content of the sample. Present the value as %**TS** (TS = total sulfur).

10 Calculate equivalent oxidisable sulfides **(OS)** content of the sample. Present the value as % **OS**.

11 **% OS = (3 x% TS) – %AS** (AS = acid-soluble sulfate, Test No. 2).

12 Calculate equivalent total potential sulfate (PS) content of the sample. Present the value as % **SO_4 TPS**.

13 % **TPS = 3 × % TS.**

Calculation -see Data Sheet No. 3

m_1 = 300 mg of sample

d_1 = 200 ml volume of test sample with de-ionised wash and dilution water

r_1 = 29.99 mg/l

NB: 0.001 mg/g = 1mg/l sulfur in the test solution

Calculate the amount of sulfur in the extract. Adjust the measured concentration for the volume of extract and convert to mg of sulfur in the extract.

$(\mathbf{r}_1 \times d_1) \div 1000 = \mathbf{m}_2 \therefore (29.99 \times 200) \div 1000 = 5.998$ mg S in the solution.

Convert to percent total sulfur in the sample: $(\mathbf{m}_2 \times 100) \div m_1 = \%$ **TS** $\therefore (5.998 \times 100) \div 300 =$ **2.00 TS as % S**

Equivalent oxidisable sulfides **(% OS) : % OS = (3 x% TS) – % AS**

$\therefore$(3 x 2.00) % TS – 0.66 % AS = 5.34 OS as % SO_4

Equivalent total potential sulfate **(% TPS) $\therefore$ % SO_4 (TPS) = 3 × % TS**

$\therefore$2.00 % OS × 3 = 6.0 TPS as % SO_4

Procedure B: Rapid High Temperature Combustion (HTC) analysis

Total sulfur contents of samples may be determined using suitable HTC apparatus such as the Leco CS-444 carbon-sulfur analyser. Care should be exercised when using HTC procedures in selecting an analyser which is capable of reaching the required combustion temperature within the analysis period (i.e. the instrument reaches temperatures in excess of 2000°C rapidly within a 40 second analysis period). Generally such instruments utilise induction furnaces.

When using HTC procedures, blanks should be run with samples as a quality check on the performance of the instrument.

Suitable standards should be used to calibrate HTC analysers. Sulfur rich samples may yield results that are beyond the calibrated range of the instrument. Such results may be prone to error and should be treated with caution.

The results should be presented as % TS. The equivalent oxidisable sulfides (OS) and total potential sulfate (TPS) may be calculated from the TS and acid-soluble sulfate (AS) values.

Test No. 5 - Determination of monosulfide sulfur (MS)

This test is used where it is suspected that monosulfide minerals such as mackinawite, greigite and pyrrhotite are present in samples. Such minerals are very reactive in engineering situations and, if present must be taken in to account in the assessment of the material. Any monosulfide (MS) present will be included in the total reduced sulfur (TRS) and total sulfur (TS) determined respectively in test Nos. 3 and 4. Monosulfide (MS) is not determined in the acid-soluble sulfur (ASS) or sulfate (AS) determinations, as it is evolved as hydrogen sulfide gas during the acid extraction process. In this test the hydrogen sulfide gas produced by the dissolution of monosufide minerals is trapped in copper nitrate solution by the precipitation of copper sulfide. The sulfur is then quantified by measuring the loss of copper from the trapping solution. This may be done using either ICP-AES analysis or by iodometric titration of the test and a blank solution, as in Test No. 3 for total reduced sulfur (TRS). The test for monosufide (MS) can be combined with the acid-soluble sulfur (ASS) determination described in Test No. 2, by attaching the trapping vessel to the condenser outlet, where the contents of the reaction vessel containing acid-soluble sulfur compounds are analysed for sulfur using ICP-AES analysis. The results are recorded on Data Sheet No. 2. The results are expressed as percent monosulfide (MS).

Apparatus and chemicals

250 ml capacity 2 neck quickfit reaction flask;

75 ml quickfit reagent reservoir with air tight tap or jumbo syringe attachment;

Oxygen-free nitrogen or argon gas;

Tapered quickfit air inlet tube;

Condenser;

Sulfur resistant tubing*[1];

1 No 75 ml Trapping vessels: Dreschel type sintered bottle head with a sintered disc of porosity grade P40, (see BS1752), in a quickfit test tube assembly;

Electric heating mantle or other suitable heat source;

Vacuum filter funnel and Whatmans No. 540 (or equivalent) filter paper;

0.45μm membrane syringe filter;

Laboratory glassware;

Lead acetate paper;

Copper nitrate (Copper (II) nitrate 3-hydrate: $Cu(NO_3)_2.3H_2O$);

Analytical grade concentrated nitric acid, 1.42 g/ml (solution = 70% HNO_3);

Analytical grade concentrated hydrochloric acid, 1.18 g/ml (solution = 35% HCl);

Tin (II) chloride (Tin (II) chloride 2-hydrate: $SnCl_2.H_2O$);

De-ionised water.

Reagents

Prepare ~200 mg/l copper nitrate solution acidified to 3.15% by volume with analytical grade concentrated nitric acid by dissolving about 0.76 g of copper nitrate in 200 ml of de-ionised water. Transfer this to a volumetric flask, add 31.5 ml of analytical grade concentrated nitric acid and make up to 1000 ml with de-ionised water.

Prepare a 25% by volume hydrochloric acid solution using analytical grade concentrated hydrochloric acid and de-ionised water. De-air the hydrochloric acid solution by passing oxygen-free nitrogen (or argon) through it prior to use. Alternatively prepare beforehand by heating the hydrochloric acid solution to boiling. Maintain the solution at boiling point for 10 minutes and then transfer it to an appropriate sealed vessel, cool and store until required.

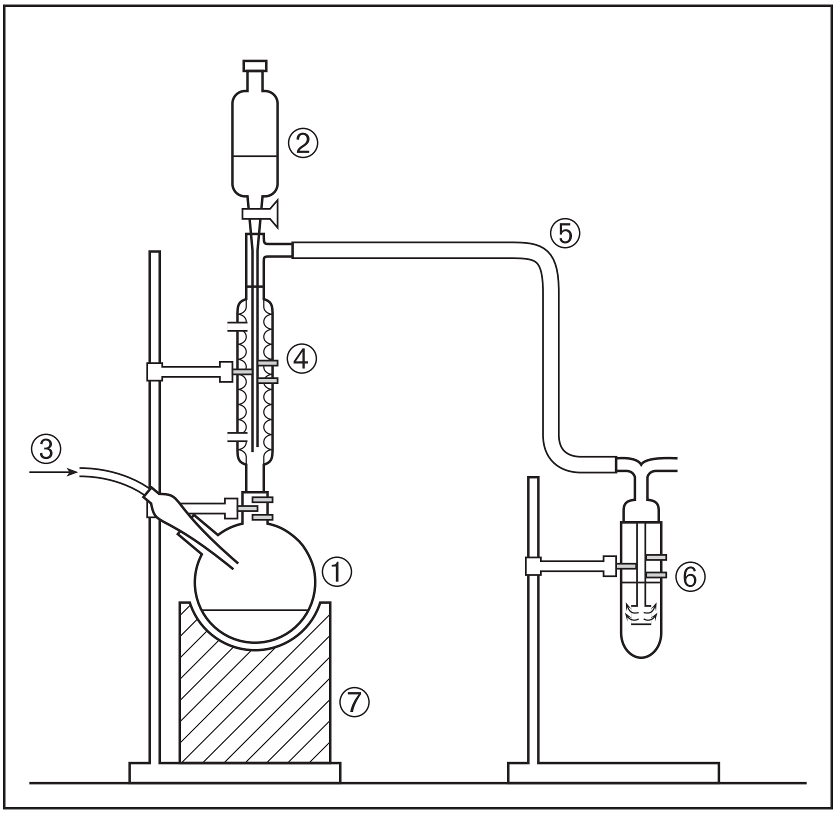
Procedure

1 Accurately weigh out between 0.80 and 1.0 g of powdered, oven dried sample to 0.0001g (m_1). Also run a blank with no sample.

2 Place the sample in the reaction flask and add approximately 1.6-2 g of tin (II) chloride.

3 Connect the condenser (see Fig. C3), and establish the condenser water flow.

4 Using air-tight sulfur resistant tubing *[1] connect the condenser to an in-line gas washing tube trapping vessel containing exactly 50 ml of the 200 mg/l acidified copper nitrate solution (V_2). Retain exactly 50 ml of the copper nitrate solution for a blank determination (V_1) by ICP-AES, or (IV_1) by iodometric titration.



1 = 250 ml 2 neck quickfit reaction flask
2 = 75 ml quickfit reagent reservoir with air tight tap or jumbo syringe attachment
3 = Nigtrogen/argon gas introduced via quickfit side arm spout
4 = Condenser
5 = Sulfur resistant tubing
6 = 75 ml Dreschel head gas bubbler type trapping vessel
7 = Heating mantle

Figure C3 Schematic diagram of the apparatus used for monosulfide (MS) determination

5 To the side arm attach a gas inlet tube to an oxygen-free nitrogen (or argon) gas supply, and establish a slow steady flow of gas[*2]. Flush the reaction flask for 5 minutes to displace the air.

6 Stop the gas flow and add exactly 100 ml of 25% de-aired hydrochloric acid **(dV_1)** using the dropping funnel or jumbo syringe through the condenser and restart the gas flow[*3]. Retain a 10 ml quantity of each batch of de-aired hydrochloric acid prepared for blank analysis.

7 Lower the reaction vessel into the heating mantle and bring the contents rapidly to the boil. Maintain the reaction at boiling point under reflux for 30 minutes [*4].

8 Allow the contents of the reaction flask to cool to room temperature with the condenser attached.

9 Meanwhile filter the copper nitrate absorption trap solution and wash the residue in the filter paper with de-ionised water. Dilute the blank and absorbent solutions for copper determination by ICP-AES. The blank and absorbent solutions should be diluted by placing 50 ml quantities of the stock and test solutions in 250 ml volumetric flasks and making these up to 250 ml with de-ionised water i.e. ×5 dilution (blank, d_1; absorbent, d_2). Determine the copper concentration using ICP-AES blank (r_1) and test (r_2) solutions.

10 If iodometric titration is to be used, filter the contents of the trapping vessel into a 250 ml conical flask **(IV_2)**. Also carefully wash out the head and quickfit test tube with a minimum of de-ionised water into the filter paper. Wash the residue in the filter paper with a minimum of de-ionised water. Discard the black solid copper sulfide (CuS) precipitate on the filter paper. Determine the copper content of the blank solution and test solution using iodometric titration as detailed in Test No. 3 procedure B.

11 Calculate the monosulfide sulfur content and present as % **MS** (MS = monosulfide sulfur).

12 Where acid-soluble sulfur **(ASS)** and sulfate **(AS)** analyses are also required filter the residual solution in the reaction flask under vacuum into a dry filter flask. If the filtrate is still cloudy further filtration using a 0.45 µm membrane syringe filter will be necessary. Do not add any more water. Retain an aliquot of around 20 ml of the sample for sulfur determination.

13 Analyse the sulfur concentration using ICP-AES (sr_1). If dilution of the sample is necessary for analysis it shall be reported, and the total concentration value corrected appropriately. Also determine the sulfur content of the blank solution as a procedure check.

14 Calculate the acid-soluble sulfate content of the sample. Present the value as **%SO_4 AS** (AS = acid-soluble sulfate). **AS = 3 x ASS**.

Calculation using ICP-AES determination – see Data Sheet No. 2

The procedure includes the calculation of the amount of acid-soluble sulfur (ASS) and sulfate (AS) present.

V_1 = 50 ml blank absorption solution
V_2 = 50 ml test absorption solution
m_1 = 1000 mg of sample
r_1 = 48.20 mg/l of copper in the blank solution
r_2 = 41.30 mg/l of copper in the test solution
d_1 = × 5 dilution of blank solution (for ICP-AES procedure only)
d_2 = × 5 dilution of test solution (for ICP-AES procedure only)
sr_1 = 21.98 mg/l of sulfur in the diluted digestion solution
dV_1 = 100 ml of hydrochloric acid solution
NB: 0.001 mg/g =1mg/l

Concentration of copper in the blank solution: $r_1 \times d_1 = \mathrm{Tr}_1 \therefore 48.20 \times 5 = 241.00$ mg/l

Concentration of copper in the test solution: $r_2 \times d_2 = \mathrm{Tr}_2 \therefore 41.30 \times 5 = 206.50$ mg/l

Convert concentrations of the solutions used into concentration of copper in test quantity.

In the blank solution the concentration of copper is 241.00 mg/l.

∴ in 50 ml of blank $(\mathrm{Tr}_1 \times V_1) \div 1000 = \mathrm{p}_1 \therefore \mathrm{p}_1 = (241.00 \times 50) \div 1000 = 12.05$ mg Cu.

In the test solution the quantity of copper is 206.50 mg/l.

∴ in 50 ml of test solution. $(\mathrm{Tr}_2 \times \mathrm{V}_2) \div 1000 = \mathrm{p}_2 \therefore \mathrm{p}_2 = (206.5 \times 50) \div 1000 = 10.325$ mg Cu.

As 1 atom of sulfur combines with 1 atom of copper, knowing the quantity of copper used the amount of sulfur liberated in the reaction may be determined i.e. For CuS,

S = 0.504 × Cu

$(\mathrm{p}_1 - \mathrm{p}_2) \times 0.504 = \mathrm{m}_2 \therefore \mathrm{m}_2 = (12.05 - 10.325) \times 0.504 = 0.869$ mg S

In 1000 mg of test sample there is 0.869 mg **(m_2)** of sulfide-sulfur.

$(\mathrm{m}_2 \times 100) \div m_1 = \%$ **MS**: $(0.869 \times 100) \div 1000 =$ **0.0869 % MS**

Express to 2 decimal places = **0.09 % MS**

Calculate the amounts of acid-soluble sulfur (ASS) and sulfate (AS) present.

Calculate the mass of sulfur present in solution **(m_2)**. Adjust the measured concentration for the volume of hydrochloric acid used in the extraction and convert to mg of sulfur in the extract.

$(\mathrm{sr}_1 \times \mathrm{d}V_1) \div 1000 = \mathrm{m}_2 \therefore (21.98 \times 100) \div 1000 = 2.198$ mg S

Convert to percent acid-soluble sulfur (ASS) in the sample.

$(\mathrm{m}_2 \times 100) \div m_1 = \%$ ASS $\therefore (2.198 \times 100) \div 1000 =$ **0.220 % ASS**

Express to 2 decimal places = **0.22 % ASS**

Equivalent acid-soluble sulfate **(% AS) : % AS = 3 × % ASS**

∴ 0.22 % ASS × 3 = 0.66 % SO_4 AS

Calculation using iodometric titration

IV_1 = 50 ml blank absorption solution

IV_2 = solution containing 50 ml of test absorption solution combined with de-ionised wash water

m_1 = 1000 mg of sample

St = Standardisation of thiosulfate solution = (i.e. from calibration curve 1 ml thiosulfate = 6.30 mg copper)

$\mathbf{Vt_1}$ = 1.610 ml thiosulfate solution used in the blank solution titration

$\mathbf{Vt_2}$ = 1.336 ml thiosulfate solution used in the test solution titration

NB: 0.001 mg/g = 1 mg/l

Calculate the amount of copper present the blank solution

$\mathbf{Vt_1 \times St = p_1 \therefore p_1} = (1.610 \times 6.30) = 10.143$ mg Cu

Calculate the amount of copper present in the test solution

$\mathbf{Vt_2 \times St = p_2 \therefore p_2} = (1.336 \times 6.30) = 8.419$ mg Cu

As 1 atom of sulfur combines with 1 atom of copper, knowing the quantity of copper used the amount of sulfur liberated in the reaction may be determined i.e. For CuS,

S = 0.504 × Cu

Calculate the amount of sulfur trapped in the solution

$\mathbf{(p_1 - p_2)} \times 0.504 = \mathbf{m_2 \therefore m_2} = (10.143 - 8.419) \times 0.504 = 0.869$ mg S

In 1000 mg of test sample there is 0.869 mg ($\mathbf{m_2}$) of sulfide-sulfur. Calculate the concentration of monosulfide sulfur.

$(\mathbf{m_2} \times 100) \div m_1 = \%$ **MS** : $(0.869 \times 100) \div 1000 =$ **0.0869 % MS**

Express to 2 decimal places = **0.09 % MS**

Notes

*1 Only use H_2S- resistant line (for example Bev-A-Line®, Tygon® etc, consult manufacturer for information about suitability) for connection from condenser to the absorption cell as other rubber lines may react giving off sulfur-bearing gas. The gas line should be suitably attached to all connections producing an air tight joint.

*2 A carrier gas flow rate should be established which creates a steady flow of gas bubbles from the sinter head and does not create frothing at the surface of the absorbent solutions contained in the gas traps. This will vary with use of the sintered heads and generally a supply pressure of between 20 – 35 kPa (3-5 psi) has been found suitable.

*3 If the quickfit dropping funnel tap or jumbo syringe connection does not create an air tight seal when the gas flow is resumed then the dropping funnel should be removed and the inlet port blocked using a quickfit stopper. It is suggested that an air-tight seal is confirmed prior to testing by setting up the equipment and placing a small quantity of liquid in the dropping funnel and switching on the gas supply.

*4 Test the exhaust gas with lead acetate paper for hydrogen sulfide gas, which if present will cause the paper to darken to black. If this occurs reduce the gas flow rate and report the incident in ‘remarks’. If after reducing the gas flow rate hydrogen sulfide continues to be present repeat the test using a smaller amount of sample.

- The volumes of copper nitrate solution used must be accurately measured out using a calibrated pipette.

Data Sheet No. 1 Water-soluble sulfur (WSS) or acid-soluble sulfur (ASS)

Samples of sediment/ rock/ other*

Sample no:	Date received:
Sample description:	Sample processing details:
Sample storage details:	Comments:
Test method*	Water-soluble sulfur / Acid-soluble sulfur

Sample reference					
Mass of original sample w_1 **g**					
Mass of sample passing 2mm test sieve w_2 **g**					
Percent finer than 2mm in original sample $(w_2 \div w_1) \times 100$ **%**					
Mass of test sample used m_1 **mg**					
Extraction vessel number					
Volume of deionised water V_1 or acid used V_1* **ml**					
Total sulfur concentration by ICP-AES r_1 **mg/l**					
Percent of ***water-soluble sulfur*** in sample material finer than 2mm $(V_1 \mathbf{r}_1) \div 1000 = \mathbf{m}_2$ $(\mathbf{m}_2 \times 100) \div m_1 =$ **% WSS**					
Percent of ***acid-soluble sulfur*** in sample material finer than 2mm $(\mathbf{r}_1 \times V_1) \div 1000 = \mathbf{m}_2$ $(\mathbf{m}_2 \times 100) \div m_1 =$ **% ASS**					
pH					
Equivalent ***water-soluble sulfate*** (mg/l SO_4 **WS**) 15,000 × % **WSS = WS** (mg/l SO_4)					
Equivalent **acid-soluble sulfate** (% SO_4 **AS**) 3 × % **ASS = AS** (% SO_4)					

Remarks:	Operator:	Checked:	Approved:

* Delete as appropriate

Data Sheet No. 2 Total reduced sulfur (TRS) or monosulfide (MS)

Samples of sediment/ rock/ other*

Sample no:	Date received:
Sample description:	Sample processing details:
Sample storage details:	Comments:
Test method*	Total reduced sulfur / Monosulfide by Chromium reduction

Sample reference						
Mass of original sample w_1	**g**					
Mass of sample passing 2mm test sieve w_2	**g**					
Percent finer than 2mm in original sample $(w_2 \div w_1) \times 100$	**%**					
Mass of test sample used m_1	**mg**					
Volume of Cu blank solution retained V_1	**ml**					
Volume of Cu absorbent solution used V_2	**ml**					
Volumetric dilution of Cu blank solution d_1	**(ie. ×5)**					
Volumetric dilution of Cu absorbent solution d_2	**(ie.×5)**					
Copper conc. of blank by ICP-AES r_1	**mg/l**					
Copper conc. of absorbent by ICP-AES r_2	**mg/l**					
Percent of ***[total reduced sulfur / monosulfide]**** in sample material finer than 2mm Blank $r_1 \times d_1 = \mathbf{Tr_1}$ Absorbent $r_2 \times d_2 = \mathbf{Tr_2}$ Blank $(\mathbf{Tr_1} \times V_1) \div 1000 = \mathbf{p_1}$ Absorbent $(\mathbf{Tr_2} \times V_2) \div 1000 = \mathbf{p_2}$ $(\mathbf{p_1} - \mathbf{p_2}) \times 0.504 = \mathbf{m_2}$ (mg S) $(\mathbf{m_2} \times 100) \div m_1 =$ **% TRS / % MS***						
Equivalent oxidisable sulfides (% SO_4 **OS**) **OS** (% SO_4) = 3 x% **TRS**						

Remarks:	Operator:	Checked:	Approved:

* Delete as appropriate

Data Sheet No. 3 Total sulfur (TS) by microwave digestion

Samples of sediment/ rock/ other*

Sample no:	Date received:
Sample description:	Sample processing details:
Sample storage details:	Comments:
Equipment used	

Sample reference						
Mass of original sample w_1	**g**					
Mass of sample passing 2mm test sieve w_2	**g**					
Percent finer than 2mm in original sample $(w_2 \div w_1) \times 100$	**%**					
Mass of test sample used m_1	**mg**					
Reaction vessel number						
Diluted final volume of extract d_1	**(ie. 200 ml)**					
Sulfur concentration by ICP-AES r_1	**mg/l**					
Percent of **total sulfur** in sample material finer than 2mm $(r_1 \times d_1) \div 1000 = m_2$ $(m_2 \times 100) \div m_1 =$	**% TS**					
Equivalent oxidisable sulfides (**OS**) as % SO_4 (3 × % **TS**) - **% AS = % OS**						
Equivalent total potential sulfate (%SO_4 **TPS**) 3 × **% TS = TPS** (% SO_4)						

Remarks:	Operator:	Checked:	Approved:

* Delete as appropriate

Abstract

Problems have been experienced on recent highway schemes with corrosion of galvanised steel buried structures (CSBS) due to chemical reaction from structural backfill. The corrosion has been attributed to the presence of sulfates and sulfides in the structural backfill. A review by TRL (Reid and Perry, 1996) indicated that improvements could be made in the identification and assessment of sulfur compounds in the current Specification for Highway Works (MCHW1) and related documents. The present project was undertaken to develop appropriate test methods for sulfur compounds in structural backfills, to determine appropriate limiting values for the various sulfur compounds and to prepare modifications to MCHW1 and related documents. This report includes a review of existing specifications and test methods for sulfur compounds in soils and rocks and describes the development of new test methods which allow a fuller characterisation of sulfur species. The concept of oxidisable sulfides content is introduced, as the amount of sulfate which would be produced by complete oxidation of the reduced sulfur in a material. Limiting values are given for oxidisable sulfides and total potential sulfate. Detailed protocols for the new test methods and suggested amendments to the MCHW and DMRB are given. The updated 2005 edition contains revised limiting values for backfill to concrete.

Related publications

TRL505	*Swell test requirements for lime stabilised materials* by D J MacNeil and D P Steele. 2001 (price £40, code H)
TRL447	*Sulfate specification for structural backfills* by J M Reid, M A Czerewko and J C Cripps. 2001 (price £60, code N)
PR1	*Durability of corrugated steel buried structures* by KC Brady and W McMahon. 1993 (price £40, code J)
RR97	*An evaluation of unburnt colliery shale as fill for reinforced earth structures* by G West and M P O'Reilly.1987 (price £25, code B)

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