

SECTION A: OVERVIEW

1. BACKGROUND TO ACID SULFATE SOIL ANALYSIS

CR Ahern, AE McElnea and LA Sullivan

1.1 THE PURPOSE OF THE GUIDELINES

The *Acid Sulfate Soils Laboratory Methods Guidelines* set out the standard methods for routine laboratory analysis of existing acidity (ie. actual and retained acidity) and of the potential acid production from oxidation of iron sulfides in estuarine and coastal sediments that should be used to provide information for the assessment and management of acid sulfate soil (ASS). The Guidelines also recommend best practice methods in the sampling, handling and transport of soil samples.

These guideline methods are not the only tools available for assessing ASS. It is acknowledged that there are many more variations of these methods, plus more complex or costlier ‘research methods’ available for analysing ASS. Some of these other methods may be equally suitable or more appropriate in some circumstances. However, in order to develop assessment standards and formulate regulations, some standardisation of methodology is necessary. Therefore, unless otherwise negotiated initially with the approving authorities, the laboratory analysis results submitted as part of any site assessment or investigation should use at least one, and in many cases a combination, of the standard methods listed in these Guidelines.

Other methods may supplement the standard ones, but fuller explanations of any ‘non-standard method’, together with their interpretation and correlations with standard approaches will normally be necessary. Provided the submissions made are logical and based on rational soil science, sedimentological and geomorphological principles, assessors/regulators should be prepared to judge each submission on its merit.

a) Significant changes and developments since *Laboratory Methods Guidelines, 1998 ASS Manual*

These Guidelines have been expanded (in size) from the Chapter in the 1998 ASS Manual (Stone *et al.* 1998). To facilitate easier use, the Guidelines have been divided into a number of sections (detailed below):

- ❑ Section A: Overview
- ❑ Section B: Dried Samples
- ❑ Section C: Wet Samples
- ❑ Section D: Soil Physical Methods
- ❑ Section E: ASS Water Methods
- ❑ Section F: Codes
- ❑ Section G: Miscellaneous Research Methods
- ❑ Section H: Field Methods
- ❑ Section I: Appendix

As ASS research continues, there will be further revisions and/or additions to the methods described in these Guidelines. (Note: See also previous section on ‘Reviewing and Updating the Guidelines’). A

greater emphasis is now placed on measuring existing acidity (including forms of iron and aluminium that contribute to acidity), particularly that derived from prior oxidation of reduced inorganic sulfur, since it is this acidity that may be exported in the next rainfall event. In contrast, reduced inorganic sulfur compounds such as pyrite represent a threat only if they are allowed to oxidise. (This statement is not intended to downplay the risk posed by oxidation of sulfides, which can be rapid when ASS are exposed).

Revised procedure/s are included for measuring actual acidity. Additionally, a method for estimating retained acidity (the ‘less available’ existing acidity) that may be released by hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, and other iron and aluminium hydroxy sulfates) is included. Such compounds do not necessarily require oxygen to hydrolyse and produce acidity, however for jarosite and natrojarosite, the rate at which acid is released is likely to be limited by their extremely low solubility.

The digestion procedure for peroxide-based methods has also been improved as a result of recent research (McElnea *et al.* 2002a, 2002b). This has improved recoveries, lessened the potential for jarosite formation and overcome potential sulfur and acid loss problems identified by Ward *et al.* (2002a, 2002b). **The improved *Suspension POCAS method (SPOCAS)* must now be used in place of the outdated POCAS and POCASm versions** (see Section B12). New result and method codes (eg. Method Code 23, see Section F, Table F1.2) have been added to distinguish SPOCAS results in databases from those results obtained using the previous POCAS or POCASm methods (Method Code 21).

In the 1998 Methods Guidelines, the chromium reducible sulfur (S_{CR}) method was a late addition as a ‘Miscellaneous Research Method’. Due to considerable research (Sullivan *et al.* 1998, 1999, 2000) and experience with the method in a number of Australian laboratories, it is now firmly established as a relatively straight-forward routine method, albeit a method that does involve the use and production of very toxic chemicals. At present, it provides the most reliable and direct measure of reduced inorganic sulfur over the wide range of values encountered in ASS (provided that the optimum sample weight is used, McElnea *et al.* 2002a). The S_{CR} method is particularly recommended for measuring sulfide contents close to the action limits, and on soil with appreciable organic sulfur (see Section B6).

Some methods have been added for measuring carbonate content (Section B14) and acid neutralising capacity (Section B13), while less appropriate ones have been removed. A *fineness factor* (FF) has been introduced to account for variation in reactivity associated with the particle size of shell and other acid neutralising material. Miscellaneous ‘Research methods’ and soil physical methods (eg. soil moisture, bulk density) are detailed in separate sections to be included in a later version. A method for the quantification of ‘total acidity’ in acid sulfate waters (Section E1) will also be added in a later version.

With the development of new and/or improved methods, the Total Sulfur (S_T) and Total Oxidisable Sulfur (S_{TOS}) approaches have become less relevant and are appropriate only as screening methods. However they may still be used where laboratories can demonstrate that their equipment can provide sufficient accuracy both at low sulfur values (eg. below the action criteria¹) and throughout the entire (large) range of sulfur values encountered in ASS analysis. (Note: Detection limits and reproducibilities for these techniques can be very instrument-dependent).

Standard analysis suites

To simplify assessment, particularly for development proposals, a number of general rules have been applied to selecting soil analyses to allow routine laboratories to provide a more effective service and to give regulators sufficient information to properly assess the proposed management plan based on complete laboratory data. These general rules have been translated into two standard analytical suites

¹ See the *Soil Management Guidelines* (Dear *et al.* 2002) for information about the acid sulfate soil texture-based action criteria.

for ASS. **At least one of two main suites of analyses will normally be required** for most acid sulfate soil situations:

- ❑ the *chromium suite* (Figure A2.2), or
- ❑ the *SPOCAS suite* (Figure A2.3).

—these are discussed in later sections.

Acid Base Accounting

A new section (Section A3) on acid base accounting for calculating **net acidity** has been included. It requires input of results from the Chromium suite or the SPOCAS suite. Other methods listed in these Guidelines (but which are not part of the Chromium or SPOCAS suites) may be used, but it will usually be necessary to justify departures from the main approaches (with additional explanations and interpretation of data provided, eg. to regulatory bodies). With the adoption of these Guidelines, **calculations for quantity of neutralising materials will need to be based on the net acidity from acid base accounting** (section A3).

Wet sample techniques

A separate section for the analysis of **wet samples** (Section C) will be included in a later version. Recent research (Sullivan and Bush 2000; Bush *et al.* 2002) has shown that substantial quantities of ‘monosulfides’ or acid volatile sulfides (AVS) can accumulate in drains, which if disturbed (eg. in drain maintenance, or in storm/flood events) can produce acidity and deoxygenate water, with disastrous environmental consequences. Proper sampling and storage of monosulfide-containing samples prior to their analysis is critical and they must be analysed wet. Methods for measuring AVS and elemental sulfur in wet sediments are therefore contained in a discrete section (Section C) of these Guidelines.

b) Summary

Identification, and assessment of the distribution and severity of acid sulfate soils is the first step in land use assessment. Because acid sulfate soils are highly variable and have extremely dynamic characteristics, identification in the field and quantification of potential hazards can be extremely difficult. Therefore, the identification and assessment of acid sulfate soils is highly dependent on appropriate appraisal of these soils by field survey, field and laboratory analysis, and sound interpretation of the results.

The number of laboratory analyses undertaken for any proposal will depend on the level of risk that it represents, which will be a function of the size and type of the proposed disturbance, the presence of any existing and/or potential acidity, as well as other soil characteristics. The sampling and analysis program should provide sufficient information to ensure the proposal can be managed in an ecologically sustainable manner. Other guidelines exist detailing the amount of sampling required for ASS disturbances, eg. *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998* (Ahern *et al.* 1998).

1.2 CHEMICAL PROPERTIES OF ACID SULFATE SOIL

To interpret the results from analysis of ASS, it is necessary to have at least a rudimentary knowledge of the chemical processes involved. Some fundamental processes and properties of acid sulfate soil, particularly with regard to iron sulfides and pyrite (FeS₂) oxidation are summarised below.

a) Oxidation of pyrite

Potential acid sulfate soils (PASS) are typically waterlogged soils, rich in pyrite, which have not been oxidised. Any disturbance which exposes PASS to the air (oxygen) can lead to the development of

extremely acidic soil layers or horizons with field pH values of ≤ 4 . These highly acidic soil horizons (with $\text{pH} \leq 4$) are termed actual acid sulfate soils (AASS). Actual and potential acid sulfate soils can occur together in the same profile, with actual ASS typically overlying potential ASS. Commonly, in the zone of oxidation, AASS (ie. soil with $\text{pH} \leq 4$) may still have reserves of unoxidised sulfides (ie. potential sulfidic acidity).

The mechanism by which the oxidation of pyrite is initiated is not comprehensively understood. One mechanism suggests that the initial step in pyrite oxidation is the production of elemental sulfur and ferrous ion, 'Fe²⁺' (White and Melville 1993):



The elemental sulfur is then oxidised to sulfate and acid (ie. sulfuric acid):



Other mechanisms for the oxidation of pyrite exist (eg. McKay and Halpern 1958, Singer and Stumm 1970, Moses *et al.* 1987, Luther III 1987) and are reviewed in Evangelou (1995) and Evangelou and Zhang (1995).

The conversion of pyrite to ferrous ion and sulfate can be written as:



The soluble ferrous ion may then be oxidised to ferric ion, Fe³⁺:



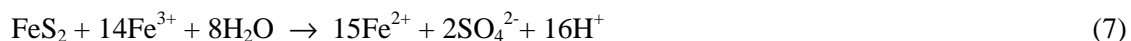
If the pH is greater than 4, then various pH-dependent precipitation reactions may occur, one of which is the precipitation of ferric hydroxide and the liberation of more acid in a reaction termed hydrolysis:



If equations 4 and 5 are added together, the net result of the oxidation of ferrous iron is the production of 2 moles of acidity per mole of ferrous iron.



If the pH is less than 4, Fe³⁺ can remain in solution. The dissolved Fe³⁺ greatly accelerates the oxidation process of pyrite (by a rapid electron-transfer mechanism) and does not require oxygen to oxidise pyrite:



The reaction can result in considerable acid production when existing ASS containing Fe³⁺ are re-flooded or buried under water without neutralising the existing acidity. This is because oxidation reactions (such as the oxidation of pyrite by ferric ion, see Eqn 7) do not necessarily need oxygen to occur. The notion that oxygen must be present for pyrite to oxidise is a popular misconception. Some initial oxidation is required to produce ferric ion, but once it is present, exclusion of oxygen alone may not prevent further acid generation until all ferric ion is consumed.

However, if the buried material is completely denied oxygen, the oxidation process eventually ceases when all Fe³⁺ is consumed. Generally, oxygen is required to produce more Fe³⁺ by Eqn 4. So,

although some further oxidation can occur on burial (and produce additional acid), this management approach is still a better option than leaving material untreated and exposed to oxygen, where ultimately all acid potential may be realised.

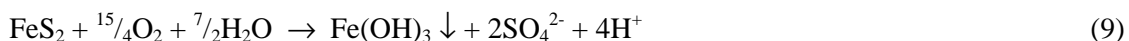
Note: Another possible source of acidity in ASS that have been buried can be from hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, schwertmannite and other iron and aluminium hydroxy sulfates).

The soluble ferrous ion, Fe^{2+} (produced in Eqns 1, 3 or 7) can easily be transported downstream where the following reaction (Eqn 8) removes dissolved oxygen from the water during the oxidation process to produce more acid:



(Various forms of iron oxy-hydroxides can precipitate, depending on pH).

The overall equation for the complete oxidation of pyrite can be written as:



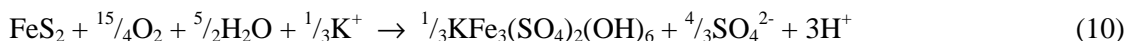
The prediction of the maximum theoretical acid production from reduced inorganic sulfur, peroxide oxidisable sulfur, or total oxidisable sulfur analysis is based on the stoichiometry of Eqn (9) (ie. one mole of pyrite ultimately produces 4 moles of H^+ acidity). However, there are many pathways for acid production and removal of products where the ultimate result is not that of Eqn (9).

b) Iron oxidation products

There are characteristic iron oxidation reactions that are frequently associated with the development of actual acid sulfate soils and the transport of acidic leachate (White and Melville 1993). In streams for example, the secondary oxidation of Fe^{2+} can produce characteristic iron oxy-hydroxides flocs, usually reddish or yellowish brown in colour (eg. goethite, FeO.OH) (Eqn 8). The oxidation of Fe^{2+} and hydrolysis of Fe^{3+} can liberate large amounts of acid, often a significant distance away from the oxidation of pyrite in the acid sulfate soil (Eqns 4 and 5). Many other products of iron sulfide oxidation are also observed in the soil, such as the characteristic yellow mottles of jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, or natrojarosite $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, minerals that typically form at or below pH 3.7 under strongly oxidising conditions (White and Melville 1993). Another iron hydroxy sulfate mineral that is increasingly being found in ASS areas is schwertmannite [$\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$]. Such minerals can act as a store of acidity which can be slowly released on hydrolysis, without the need for oxygen.

c) Jarosite, and iron and aluminium hydroxy sulfate compounds

Jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, is an acidic by-product of ASS oxidation commonly found in disturbed or drained ASS. Its formation (Eqn 10) represents incomplete hydrolysis of Fe^{3+} during the oxidation of pyrite (Dent 1986):



Jarosite is relatively insoluble and most stable at a pH between 3 and 4, though it can persist at higher pH under dry conditions. In moist environments, jarosite slowly decomposes (usually by hydrolysis) releasing iron and acid into waterways, and is often a major source of acidity in waterways draining areas of ASS have been disturbed sometime in the past. One mole of jarosite releases 3 moles of acidity (as per Eqn 11):

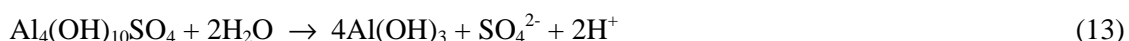


Natrojarosite, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, an insoluble hydroxy sulfate mineral similar to jarosite (but with Na^+ replacing K^+ in the mineral structure), also provides 3 moles of acidity on hydrolysis:



Many sparingly soluble sulfate salts of iron and aluminium which can release acid on hydrolysis may be present in AASS.

By way of example, basaluminite, $\text{Al}_4(\text{OH})_{10}\text{SO}_4$, is an aluminium hydroxy sulfate mineral that can release acidity by hydrolysis as pH rises (as shown by Eqn 13):



The S_{POS} and S_{CR} methods do not measure acidity retained in these iron or aluminium hydroxy-sulfate compounds. However, the SPOCAS method can provide an estimate of these sulfates if the digested soil residue is extracted with 4 M HCl to calculate S_{RAS} (or residual acid soluble sulfur) (**Method Code 23R**). Alternatively, the difference between 4 M HCl extractable sulfur (S_{HCl}) and 1 M KCl extractable sulfur (S_{KCl}) (ie. the net acid soluble sulfur or S_{NAS} , **Method Code 20J**) can also be used to estimate the amount of iron or aluminium hydroxy-sulfate compounds present.

Note: Titratable Actual Acidity (TAA) and Titratable Peroxide Acidity (TPA) methods do not quantitatively recover retained acidity from jarosite (McElnea et al. 2002b), despite a widely held view to the contrary.

d) Existing acidity

Existing acidity in ASS includes ‘**actual**’ acidity and ‘**retained**’ acidity. Actual acidity is largely readily soluble and exchangeable acidity measured in the laboratory by titration of a 1 M KCl suspension and is termed Titratable Actual Acidity (TAA) (**Method Code 23F**). Retained acidity is the acidity stored in largely insoluble compounds such as jarosite and other iron and aluminium sulfate minerals, which tends not to be measured by the TAA titration. These ‘insoluble’ sulfur compounds can be extracted by 4 M HCl and then the sulfur determined. The difference between the sulfur in the HCl extraction (S_{HCl}) and sulfur in the KCl extraction (S_{KCl}) is attributed to these acid-producing sulfur compounds and is referred to as retained or ‘net acid soluble’ sulfur (S_{NAS}) in these Guidelines. The retained or net acid-soluble sulfur **acidity** ($a\text{-}S_{\text{NAS}}$) can be estimated from S_{NAS} by assuming 1 mole of net acid-soluble sulfur produces 3 moles of acidity (as is the case for jarosite or natrojarosite) (See Sections A3.4 and F1–6 for explanation and calculation). Alternatively, a 4 M HCl extraction performed on the washed soil residue after peroxide digestion gives the residual acid soluble sulfur (S_{RAS}) which can also be used to estimate retained acidity. These retained forms of existing acidity are held transiently in the soil and may be subject to slow re-mobilisation by wetting and drying, or if geochemical conditions change (eg. as a consequence of liming, or re-flooding with brackish water, etc.).

While on a ‘per weight’ basis, jarosite is not as acid-producing a mineral as pyrite (eg. in PASS, or AASS with reserves of pyrite), in disturbed sites substantial crusts of jarosite and similar minerals may form on soil surfaces, making acidity from jarosite an important issue in such cases.

e) Monosulfides

Modern sediments may contain reactive reduced sulfur phases (such as iron ‘monosulfides’) that oxidise readily on contact with air. Iron monosulfides (\approx ‘FeS’) are often associated with organic-rich

new sediments, drains and lake bottoms, and oxidise rapidly when exposed to oxygen. These monosulfides include ‘amorphous FeS’, mackinawite ($\cong \text{FeS}$) and greigite ($\cong \text{Fe}_3\text{S}_4$) (Bush and Sullivan 1997). These compounds are often referred to as acid volatile sulfides (or AVS). Due to their high reaction rates in air, if their contents in sediments are to be accurately measured then these samples require specialised sampling and treatment², and should not be dried prior to analysis. The Acid Volatile Sulfur (S_{AV}) method (**Method Code 22A**) should be used to analyse for these compounds and sequentially chromium reducible sulfur to measure the remaining reduced inorganic sulfur compounds. As acid volatile sulfur measurements are made on wet samples, a moisture determination on another sub-sample is necessary to convert the result to a dry weight basis. Normally analyses performed using small weights of wet sample need to be conducted at least in duplicate.

Note: Most of the routine laboratory methods in these Guidelines are designed primarily to determine pyrite sulfur. Most calculations are based on the assumption that ‘non-sulfate’ sulfur is present as iron disulfide (FeS_2). The presence of monosulfides with variable iron to sulfur ratios complicates predictions using the common stoichiometric calculations. However, monosulfides are usually present in only minor amounts in most acid sulfate soils (Bush and Sullivan 1998). Nevertheless, amounts can be appreciable in bottom sediments of rivers, lakes and drains (Sullivan and Bush 2000).

f) Acid neutralising capacity of soil material

The acid neutralising capacity (or ANC) is a measure of a soil’s inherent ability to buffer acidity and resist the lowering of the soil pH. A variety of definitions for ANC and methods for its determination exist in the literature. Acid buffering in the soil may be provided by dissolution of calcium and/or magnesium carbonates (eg. shell), cation exchange reactions, and by reaction with the organic and clay fractions. Additionally, other soil minerals can provide some neutralisation of acid, the amount dependent on particle size and degree of weathering. The effectiveness of these buffering components in maintaining soil pH at acceptable levels (eg. pH 6.5–9.0) will depend on the types and quantities of clay minerals in the soil, and on the type, amount and particle size of the carbonates or other minerals present.

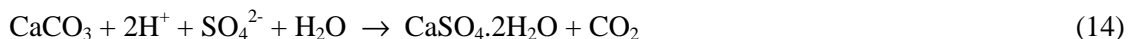
Note: Exo-skeletons of fossilised marine micro fauna (eg. foraminifera) can also be a source of carbonate or neutralising compounds in certain soils, which may not be visible to the naked eye.

The presence of carbonates, in excess of the potential acidity held by sulfides, does not necessarily prevent soil acidification if the carbonates’ acid buffering is not readily or rapidly available (eg. if it is locked up in shells, or as unreactive coarse fragments). Formation of insoluble or sparingly soluble surface coatings (eg. of iron oxides, gypsum, etc.) can also limit the neutralising ability and reactivity of calcium carbonate. It is extremely important to know the *in situ* form and distribution of the carbonates in the sediment to enable a correct interpretation of analytical results and the choice of appropriate management techniques. It should be noted that normal laboratory soil preparation (especially the grinding process) affects the fineness and reactivity of shell, yielding an analytical acid neutralising capacity in excess of that which would normally be available from the soil *in situ*.

Finely divided CaCO_3 (eg. agricultural lime) is commonly used as a source of neutralising capacity. The reaction of calcium carbonate with the acid produced from pyrite oxidation can result in precipitation of calcium sulfate (usually gypsum) and the generation of carbon dioxide, though the

² If specialised sampling and treatment is not used then it is highly likely that partial or complete oxidation of monosulfides has taken place, producing some acidity and elemental sulfur. Therefore in addition to S_{AV} and S_{CR} , a measure of pH (pH_{KCl}) and, if necessary, of actual acidity (TAA) is needed on AVS-containing sediments that have not been treated appropriately.

neutralisation product (gypsum) is sparingly soluble in water (ie. 2.6 g/L). The complete reaction is as follows:



1 mole CaCO_3 will theoretically neutralise 2 moles H^+ (1 mole $\text{CaCO}_3 = 100.0873$ g)

1 mole H_2SO_4 contains 2 moles H^+ (1 mole $\text{H}_2\text{SO}_4 = 98.0795$ g)

Thus, on a weight basis, 1 g H_2SO_4 requires (100.0873/98.0795) or 1.0205 g of pure CaCO_3 to totally neutralise it.

Note: An excess of calcium carbonate is always required, as this reaction does not go to completion at near-neutral or alkaline pH values (eg. pH >6.5) (Rose and Daub 1994; Nicholson et al. 1988) due to the equilibrium with bicarbonate ions (HCO_3^-). Ultimately, this bicarbonate provides buffering against formation of very low pH (<4), but in order to keep pH values around neutral, excess calcium carbonate is required. Ward et al. (2002c) documented that for certain acid sulfate soils, oxidation of pyrite may be quicker in soil limed at less than the calculated stoichiometric rate compared to unlimed ASS. This reinforces the need for safety factors of at least 1.5 to 2. Coarse-textured neutralising material may require much larger safety factors.

In many of the acid sulfate soils in Australia the amounts of shell deposits, carbonates or natural clay buffering capacity are **insufficient** to neutralise the acid produced by pyrite oxidation (White and Melville 1993). However, ‘self-neutralising’ ASS are not uncommon in northern and central coastal Queensland (eg. East Trinity Cairns; Latham *et al.* 2002) particularly where fine shell and coral associated with the Great Barrier Reef detritus/debris can occur. Recent studies in southern Australia (eg. Merry *et al.* 2003) have found areas of ASS associated with deposits of powdered shell or carbonate, particularly in areas influenced by erosion of naturally occurring limestone (eg. the erosion of limestone cliffs common on coastlines adjacent to the Southern Ocean).

g) Soil texture

Soil texture is an important factor that influences the acid buffering capacity of the soil. For example, in pyritic sandy deposits, in the absence of significant quantities of shell material there is little acid-buffering capacity due to a lack of cation exchange sites on the soil minerals (which are typically highly weathered). Conversely, clay size minerals commonly have a greater acid buffering capacity than sands. ‘Action criteria’ which trigger the need for management of acid sulfate soils are linked to three broad texture groups, as acid-buffering capacity generally increases, from little or none in sands to higher levels in heavy clays. Recent data from Southern Cross University suggests that the action criteria for peat ASS materials should be the same as those for sandy textured materials (Sullivan *pers. comm.*).

Note: Soils in the same broad texture categories can have substantially different acid-buffering capacities, depending on the mineralogy of the soil. A proponent may be able to provide the necessary evidence to show that their particular soil(s) has a greater buffering or neutralising ability than acid producing potential.

1.3 COMPLEXITY OF ASS AND ASSOCIATED ANALYSES

The main aim of ‘static’ laboratory tests is to provide realistic, cost-effective estimates of *existing acidity* and predict future acid generation from oxidation of sulfides (ie. *potential sulfidic acidity*). Affordability is a key consideration, given the variable nature of acid sulfate soils, both spatially and

with time. Thus a balance needs to be struck between conducting highly detailed and exact analyses on a limited number of samples and the need for the analysis of a sufficient number of samples to adequately characterise a site.

Laboratory testing also aims to predict the amount of neutralising agent required (including safety factors) to prevent any future soil acidification under any conceivable conditions and hence avoid the export of acid, iron, aluminium and heavy metals into the receiving environment.

‘Static’ laboratory tests cannot be expected to *accurately* predict how soils will perform in any particular environment or climate, but do provide an indication of their probable behaviour. The use of more time-consuming ‘kinetic’ or ‘temporal’ testing (eg. over a period of a few months to several years, using incubation or leaching column approaches) is likely to give a better estimate of the ultimate behaviour of ASS over time. However, such tests are extremely costly and not likely to be used extensively, other than for large-scale projects or research (eg. McElnea and Ahern 2000a). Ultimately, it is difficult to predict how a large volume of ASS will behave over time in a particular environment. Temperature, rainfall, porosity, oxygen supply, wetting and drying regimes, pH, hydraulic conductivity, soil texture, sulfide content, sulfide crystal size, bacteria, coatings, soil minerals, neutralising material, shell size and other factors combine to control the ultimate rate of oxidation of sulfides, the by-products formed and the extent of acidification (if any) in the soil. The static tests are designed to ensure that under any feasible management regime soils will not produce net acidity if they have been ameliorated at dosing rates calculated from these tests and using appropriate safety or fineness factors.

The range of oxidation states of sulfur (–2 to +6) in sulfur minerals and the variety of oxidation products present makes the analysis of sulfur components in ASS complicated. Superimposed on the complex sulfur chemistry of ASS is the chemistry of acid generation and the by-products generated by this acid (eg. iron, manganese and aluminium species). In addition, these species’ subsequent interaction with and neutralisation within the soil matrix further increases the complexity of ASS analysis (McElnea and Ahern 2000b). Hydrolysis of iron and aluminium species can be a major source of acidity (eg. Eqns 5, 11, 12 and 13). Only some of the reactions of acid sulfate soils are summarised in Section A1.2; there are many more reactions and compounds that occur in ASS.

It is clear that sulfur in soil can exist in many forms:

- ❑ organic compounds
- ❑ readily soluble sulfates (eg. of sodium, potassium and magnesium)
- ❑ sparingly soluble sulfates (eg. gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
- ❑ ‘almost insoluble’ sulfate minerals (eg. jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$; and natrojarosite $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ and other iron or aluminium sulfates)
- ❑ disulfide minerals (eg. pyrite or marcasite, FeS_2)
- ❑ monosulfide minerals (eg. greigite, Fe_3S_4 ; mackinawite, $\cong \text{FeS}$; and various other iron monosulfides)
- ❑ elemental sulfur

Not all these forms of sulfur produce acid (eg. gypsum does not produce acid) and those that do produce acid can produce differing amounts per mole of sulfur present (eg. pyrite compared with jarosite). Hence, some fractionation of the various sulfur compounds is necessary in order to use stoichiometric relationships to more accurately predict future acid generation. Even when the various sulfur components are accurately quantified, the use of sulfur analysis to predict acid generation is still an indirect approach based on various theoretical assumptions and may not reflect the situation that occurs in the natural environment.

Note: Sulfur analysis alone provides no measure of actual acidity in ASS. Neither does it take into account the effect of any acid neutralising reactions in the soil (that may decrease or negate the potential acidity).

A direct approach for measuring acidity is to titrate it (to a defined pH end point) using a base (such as NaOH). In order to measure potential sulfidic acidity it is necessary first to chemically oxidise any sulfides present (eg. using 30% hydrogen peroxide) and then titrate the acidity generated. Some of the issues associated with the titration approach are:

- ❑ the pH end point
- ❑ the use of suspensions or filtered extracts
- ❑ the chemical oxidation conditions used
- ❑ organic matter and organic acidity effects
- ❑ recovery of acidity from insoluble compounds (eg. jarosite)
- ❑ that titrations usually reflects the net acidity (as some acid may be neutralised by various soil components, eg. carbonates)

Note: Further discussion of these and other issues associated with the measurement of acidity in ASS can be found in McElnea et al. (2002a, 2002b).

Hence, for some ASS, there are fundamental reasons why acidity measured by titration methods does not correspond with acidity predicted from sulfur analyses.

Given the complexity associated with ASS analysis, it is unrealistic to expect that there will be a universal, low cost, single analytical procedure that provides all the required information to effectively manage ASS. These Guidelines detail a variety of methods that can be used to predict net acid production in ASS to provide a basis for the sound management of ASS materials.

References

- Bush RT, Sullivan LA (1997) Morphology and behaviour of greigite from a Holocene sediment in Eastern Australia. *Australian Journal of Soil Research* **35**, 853–861.
- Bush RT, Sullivan LA (1998) Acid volatile sulfur distribution in acid sulfate soil and some implications for management. In 'Proceedings of the National Soils Conference'. pp. 1–6. (Australian Society of Soil Science Inc.: Brisbane, Australia)
- Bush RT, Sullivan LA, Fyfe DM (2002) Distribution and occurrence of monosulfidic black ooze (MBO) in coastal acid sulfate soil landscapes. In 'Fifth International Acid Sulfate Soil Conference'. 25–30 August 2002 (Eds LA Sullivan, BCT Macdonald, A Keene) p. 13, (Tweed Shire Council: Murwillumbah, NSW)
- Dent D (1986) 'Acid sulphate soils: a baseline for research and development.' (International Institute for Land Reclamation and Improvement: Wageningen, The Netherlands).
- Evangelou VP (1995) 'Pyrite oxidation and its control: solution chemistry, surface chemistry, acid mine drainage (AMD), molecular oxidation mechanisms, microbial role, kinetics, control, ameliorates and limitations, microencapsulation.' (CRC Press, Inc.: Boca Raton)
- Evangelou VP, Zhang YL (1995) A review: pyrite oxidation mechanisms and acid mine drainage prevention. *Critical Reviews in Environmental Science and Technology* **25**, 141–199.
- Latham NP, Grant IJC, Lyons D, McElnea AE, Ahern CR (2002) Peroxide oxidation of self-neutralising soils. In 'Fifth International Acid Sulfate Soil Conference'. 25–30 August 2002 (Eds LA Sullivan, BCT Macdonald, A Keene) Addendum pp. 20–21, (Tweed Shire Council: Murwillumbah, NSW)
- Luther III GW (1987) Pyrite oxidation and reduction: Molecular orbital theory considerations. *Geochimica et Cosmochimica Acta* **51**, 3193–3199.
- McElnea AE, Ahern CR (2000a) Effectiveness of Lime and Cement Kiln Dust as Acid Sulfate Soil Ameliorants – Leaching Column Experiments. In 'Acid Sulfate Soils: Environmental Issues,

- Assessment and Management, Technical Papers'. (Eds CR Ahern, KM Hey, KM Watling, VJ Eldershaw) pp. 30/1–30/12 (Queensland Department of Natural Resources: Brisbane)
- McElnea AE, Ahern CR (2000b) Issues associated with laboratory methods for assessing acid sulfate soil risk—particularly hydrogen peroxide-based methods. In 'Proceedings of Workshop on Remediation and Assessment of Broadacre Acid Sulfate Soils'. (Ed. P Slavich) pp. 1–15. (ASSMAC: Australia)
- McElnea AE, Ahern CR, Menzies NW (2002a) Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soil. *Australian Journal of Soil Research* **40**, 1115–1132.
- McElnea AE, Ahern CR, Menzies NW (2002b) The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* **40**, 1133–1157.
- McKay DR, Halpern J (1958) A kinetic study of the oxidation of pyrite in aqueous suspension. *Transactions of the Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers* **212**, 301–309.
- Merry RH, Fitzpatrick RW, Barnett EJ, Davies PJ, Fotheringham DG, Thomas BP, Hick WS (2003) South Australian Inventory of Acid Sulfate Soil Risk (Atlas). Final project report to Coastal Acid Sulfate Soils Program (CASSP) pp. 38 (CSIRO: Australia).
- Moses CO, Nordstrom DK, Herman JS, Mills AL (1987) Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochimica et Cosmochimica Acta* **51**, 1561–1571.
- Nicholson RV, Gillham RW, Reardon EJ (1988). Pyrite oxidation in carbonate-buffered solution: 1. Experimental kinetics. *Geochimica et Cosmochimica Acta* **52**, 1077–1085.
- Rose AW, Daub GA (1994) Simulated weathering of pyritic shale with limestone and lime. In 'Proceedings of the International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage'. Vol. 2, pp. 334–340. (US Department of the Interior, Bureau of Mines Special Publication SP 06B-94: Pittsburg, PA)
- Singer PC, Stumm W (1970) Acidic mine drainage: The rate-determining step. *Science* **167**, 1121–1123.
- Stone Y, Ahern CR, Blunden B (1998). 'Acid Sulfate Soils Manual 1998' (Acid Sulfate Soils Management Advisory Committee: Wollongbar, NSW).
- Sullivan LA, Bush RT, McConchie D, Lancaster G, Clark M, Norris N, Southon R, Saenger P (1998). Chromium Reducible Sulfur (S_{CR}) – Method 22B In 'Acid Sulfate Soils Laboratory Methods Guidelines.' (Eds CR Ahern, B Blunden, Y Stone). (Acid Sulfate Soils Management Advisory Committee: Wollongbar, NSW).
- Sullivan LA, Bush RT (2000). The behaviour of drain sludge in acid sulfate soil areas: Some implications for acidification and waterways management. In 'Proceedings of Workshop on Remediation and Assessment of Broadacre Acid Sulfate Soils'. (Ed. P Slavich) pp. 43–48. (ASSMAC: Australia)
- Sullivan LA, Bush RT, McConchie D, Lancaster G, Haskins PG, Clark MW (1999) Comparison of peroxide oxidisable sulfur and chromium reducible sulfur methods for determination of reduced inorganic sulfur in soil. *Australian Journal of Soil Research* **37**, 255–65.
- Sullivan LA, Bush RT, McConchie D (2000) A modified chromium-reducible sulfur method for reduced inorganic sulfur: optimum reaction time for acid sulfate soil. *Australian Journal of Soil Research* **38**, 729–734.
- Ward NJ, Sullivan LA, Bush RT (2002c) Sulfide oxidation and acidification of acid sulfate soil materials treated with $CaCO_3$ and seawater-neutralised bauxite refinery residue. *Australian Journal of Soil Research* **40**, 1057–1067.
- Ward NJ, Sullivan LA, Bush RT, Lin C (2002a) Assessment of peroxide oxidation for acid sulfate soil analysis. 1. Reduced inorganic sulfur. *Australian Journal of Soil Research* **40**, 433–442.
- Ward NJ, Sullivan LA, Bush RT, Lin C (2002b). Assessment of peroxide oxidation for acid sulfate soil analysis. 2. Acidity determination. *Australian Journal of Soil Research* **40**, 443–454.
- White I, Melville MD (1993). 'Treatment and containment of potential acid sulphate soils'. CSIRO Centre for Environmental Mechanics, Technical Report No. 53.