

2. OVERVIEW OF ANALYTICAL METHODS FOR DRIED AND GROUND ASS SAMPLES

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To facilitate interpretation by regulatory authorities, the chemical methods detailed in these Guidelines have been adopted as the standards to be used for site assessments, Environmental Impact Assessments (EIA) or Environmental Management Plans (EM Plans).

The principal analytical methods for ASS and their standard symbols are listed in Tables F1.1–F1.7. The results of some methods can be used directly (eg. S_{CR}), while in other cases the calculated difference between a pair of determinations is used (eg. S_{POS} , calculated by $S_P - S_{KCl}$).

2.1 METHODOLOGY

ACIDITY METHODS

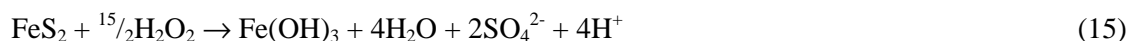
The ‘acid trail’ involves direct determination of acidity by titration, as opposed to the ‘sulfur trail’ which employs indirect means of predicting acidity using a combination of sulfur determinations and stoichiometric relationships.

(a) Potassium chloride pH (pH_{KCl}) and Titratable Actual Acidity (TAA)

Determination of actual acidity is necessary on soil with a laboratory pH_{KCl} of <5.5 ¹. The pH_{KCl} is measured in the laboratory after 4 h extraction with 1 M KCl (followed by overnight standing). Titratable Actual Acidity² is then determined by suspension titration to pH 6.5. For full description of the method, see Section B2.

(b) Peroxide oxidised pH (pH_{OX}) and Titratable Peroxide Acidity (TPA)

This method involves the use of 30% hydrogen peroxide to oxidise sulfides (usually pyrite) and produce sulfuric acid, as shown below.



Following oxidation pH_{OX} is measured. After peroxide decomposition and addition of KCl, Titratable Peroxide Acidity (TPA) is measured by suspension titration to pH 6.5.

Note: Where the pH after initial peroxide oxidation (pH_{OX}) is >6.5 , then a titration with HCl (to pH 4), followed by additional peroxide digestion must be performed. (This so-called ‘carbonate modification’ is particularly important when carbonate has been identified in the soil, for instance by testing for effervescence by adding 1 M HCl, sometimes referred to as the ‘fizz’ test, see Section H2). Where there is appreciable carbonate present in the soil, oxidation of pyrite by peroxide can be severely retarded, and unless the carbonate modification has been performed, complete oxidation of pyrite is not assured (with the risk that potential acidity is substantially underestimated). This applies equally to soils that have been limed. This procedure (of the HCl-titration and the additional peroxide digestion) enables the calculation

¹ Soils with a pH_{KCl} between 5.5 and 6.5 and no sulfides, are deemed to pose a lower risk and need not have TAA measured unless being analysed according to the SPOCAS suite. Soils with a pH_{KCl} in this range that do contain sulfides should have TAA measured.

² A method for measuring actual acidity involving the use of 0.5 M $BaCl_2$ as the extractant and suspension titration to pH 5.5 has been documented by Lin *et al.* (2000). They used a correction factor to convert ‘quick titration’ results to ‘long-term titration’ values, which they considered to be a complete measure of existing acidity in ASS. However work of McElnea *et al.* (2002b) indicated that these correction factors may be inappropriate for some soils, since long-term titration values can include a component of potential acidity. Therefore, the $BaCl_2$ method (Section G1, to be added) has not been included as a standard method. If the $BaCl_2$ extraction method is used, extractions should be restricted to 25 h and no correction factor applied. (A safety factor of at least 1.5 is still required for lime application). It is advisable to contact the relevant regulatory authority and provide justification before conducting substantial numbers of analyses.

of an 'excess acid neutralising capacity' (ANC_E) for materials/soil where ANC exceeds acidity generated by oxidation of sulfides (and which would otherwise only yield a TPA result of zero). For a full description of the method, see Section B3.

The TPA method is a measure of net acidity, since the acid produced by oxidation of sulfides has the opportunity to react with any acid buffering components in the sample (eg. carbonates). When the TPA is zero, it indicates that under laboratory conditions (using a finely-ground sample) the acid-neutralising components in the soil material exceed the acid-producing components. Often neutralising material (eg. coarse shell) present in the field may have low reactivity because of particle size and/or insoluble coatings. Thus, the TPA measured on finely ground samples in the laboratory could underestimate the net acid risk likely to be experienced in the field. To allow for the above, all measurements of the neutralising material (ANC) are divided by a fineness factor (FF) during acid base accounting (see Sections A2.2 and A3.3).

As mentioned in the previous section, for some ASS there is a scientific basis why acidity measured by titration methods may not correspond with acidity predicted from sulfur analyses. For example, using the earlier peroxide methods (POCAS, POCASm), Ward *et al.* (2002b) found that the low pH during the digestion with peroxide led to dissolution of clay minerals, and with titration of the filtered solution led to underestimation of acidity (eg. a lower TPA compared to that predicted using the S_{CR} method). However, modifications to the digestion and titration procedure employed in the new SPOCAS method has been shown by McElnea *et al.* (2002b) to have largely overcome such problems. This reinforces the instruction in these Guidelines that the **previous peroxide methods (eg. POSA, POCAS, POCASm) should not be used and should be replaced by SPOCAS when a peroxide based method is to be employed.**

The use of the TPA **alone** as a basis for the management of ASS materials (eg. to predict liming requirements) is not recommended. Acid base accounting (see Section A3) is the recommended approach for the assessment of ASS as a basis for their management, especially for the purpose of predicting lime requirements. The reasons for this are set out below. At least three situations may exist for a soil that has a TPA of zero: (i) the soil has no pyrite, (ii) the soil has a small amount of pyrite and a stoichiometric amount of carbonate, and (iii) the soil has a large amount of pyrite and carbonate. The TPA by itself cannot distinguish between these three possibilities. The third possibility is of most concern, as there could be considerable acid export in the field if the particle size of the carbonate source (eg. shell fragments) is large and the reactivity of the carbonate is low. A TPA of zero gives no indication of whether the appropriate excess of carbonate is present (eg. a minimum safety factor of 1.5). Hence the need for determining the excess acid neutralising capacity and some measure of pyrite content (eg. S_{CR} or S_{POS}).

Calculated acidity parameters

(c) Titratable Sulfidic Acidity (TSA)

Titratable Sulfidic Acidity is defined as the difference between TPA and TAA.

$$TSA = TPA - TAA$$

For unoxidised soil material in many situations (with negligible acid-buffering/acid-neutralising components) the TSA is comparable to the potential sulfidic acidity predicted from sulfur measurements (eg. S_{POS} , S_{CR}). In the absence of any appreciable ANC, where there is a difference between S_{POS} and TSA (when expressed in equivalent units), the general approach in acid base accounting (ABA) is to use sulfur measurements to estimate sulfidic acidity. However, should the TSA substantially exceed the sulfidic acidity predicted from the sulfur trail (eg. S_{POS} , S_{CR}) a cautionary approach is advisable. Such differences can indicate release of complexed iron and aluminium from organic sources and/or formation of simple organic acids during peroxide oxidation. While this acidity is commonly not rapidly released in the environment in the short term, it should not be

immediately dismissed as being of no consequence. The proponent should be aware that there may be some risk if soils are only managed according to the acidity from the sulfides. As a precaution in such circumstances, the proponent may want to increase the application rate of neutralising materials to nearer that indicated when TSA is substituted into the ABA equation.

SULFUR (AND ASSOCIATED CATION) METHODS

The ‘sulfur trail’ employs an indirect approach for predicting *potential acidity*, using a combination of sulfur determinations and stoichiometric relationships. This approach also needs to take into account the fact that some sulfur compounds are non-acid-producing (eg. gypsum), while other compounds can produce differing amounts of acid per mole of sulfur (eg. jarosite compared to pyrite). Unlike the acidity approach, sulfur methods alone cannot provide an estimate of net acid production. This is because no account is made of any inherent buffering/acid-neutralising components in the soil which may lessen or negate the acid risk. In soil material that is already strongly acidic (ie. a $\text{pH}_{\text{KCl}} < 5.5$) a measure of actual acidity (eg. using the TAA method) is also necessary.

(a) Total Sulfur (S_T)

Total sulfur (S_T) can be measured using a variety of chemical and instrumental techniques (see Section B5). The measurement of total sulfur provides a low-cost alternative for estimating the maximum potential environmental risk from acid produced by the oxidation of sulfides. It is widely used in the mining industry when estimating the maximum potential for acid drainage from sulfide sources, with predicted acid generation based on the stoichiometry of Eqn (9) (assuming all sulfur is present as sulfide).

When the content of sulfate salts (eg. gypsum) is appreciable, total sulfur may substantially overestimate the potential acid risk and can result in unnecessary or excessive application of lime to soil containing little or no sulfides. Additionally, no account is made of any acid-neutralising components in the soil. Furthermore, S_T measurements alone (like all sulfur-based methods) give no estimate of ‘actual acidity’ in soil that is already acidic due to previous oxidation of sulfides.

Instrumental total sulfur determination is a useful screening approach, but is generally not suitable for accurate determinations on soil with low sulfur contents (eg. sands) unless instruments have been specifically set up for low levels analysis. (Detection limits and reproducibilities can be very instrument-dependent). Moreover, total sulfur is not recommended for surface and/or highly organic soil, because S_T may exceed action limits (on non-sulfidic soil) purely due to sulfur in organic matter.

(b) Chromium Reducible Sulfur (S_{CR})

The Chromium Reducible Sulfur (S_{CR}) method (**Method Code 22B**) provides accurate, low-cost determinations of (non-sulfate) inorganic sulfur and is not subject to significant interferences from the sulfur, either in organic matter or sulfate minerals (eg. gypsum; Sullivan *et al.* 1999). The inorganic sulfur compounds measured by this method are: i) pyrite and other iron disulfides; ii) S_E , elemental sulfur; iii) thiosulfate, tetrathionate, polythionites; and iv) S_{AV} , acid volatile sulfides (eg. greigite, mackinawite, amorphous FeS), provided these have not been lost during sample transport and preparation. On wet samples, the chromium reduction method can be made specific to the iron disulfide fraction if pre-treatments are used to remove the acid volatile sulfide and elemental sulfur fractions. However, laboratories routinely oven-dry and grind samples, causing some or all of the acid volatile sulfides to oxidise (Bush and Sullivan 1997). Thus the S_{CR} results reported for oven-dry samples may only contain a small proportion of the acid volatile sulfur that was present in the original wet sample. With the exception of specific depositional environments (eg. drains and lake bottom sediments), this is not considered a significant issue as the sulfide content of most Australian ASS is generally dominated by pyrite.

The chromium reducible sulfur method is the preferred technique for estimating acid-producing inorganic sulfur in ASS, particularly near the action limits and on organic-rich samples.

If differences occur between results from various sulfur methods used to predict sulfidic acidity (eg. S_{CR} , S_{POS}) then the S_{CR} result should take precedence for use in the acid base account).

Note: If there is no obvious reason (eg. a highly organic/peaty sample) for a substantial difference (between S_{CR} and S_{POS}), then the first step is to conduct a repeat analysis to ensure the veracity of the analytical results.

(c) Peroxide Sulfur (S_P)

Peroxide sulfur is measured on a filtered solution, following soil digestion with peroxide and TPA titration. The S_P measurement by itself has limited application since it includes sulfate salts with no acid-generating potential (such as gypsum), sulfur from the oxidation of organic matter, as well as that derived from sulfides. The principal reason for measuring peroxide sulfur is to allow calculation of peroxide oxidisable sulfur (S_{POS}). In ASS without appreciable jarositic sulfur or other relatively insoluble acid-producing sulfates, the peroxide sulfur should approximately equal the total sulfur.

Note: In soil with $pH_{OX} > 6.5$ after initial peroxide digestion (but prior to TPA titration) particularly those containing carbonates, titration with HCl to pH 4 and further peroxide digestion must be performed to ensure complete oxidation of sulfides.

‘Peroxide’ calcium (Ca_P) and **‘peroxide’ magnesium (Mg_P)** can also be measured on the same filtered solution as S_P following the peroxide digestion and TPA titration.

(d) 1 M KCl extractable Sulfur (S_{KCl})

KCl-extractable sulfur is measured on a filtered solution following the TAA titration. This method provides a measure of adsorbed and soluble sulfate (including gypsum). It is used in combination with the S_P measurement to calculate peroxide oxidisable sulfur (S_{POS}). Additionally, it can be used in combination with HCl-extractable sulfur (S_{HCl}) to estimate net acid soluble sulfur (S_{NAS}).

KCl-extractable calcium (Ca_{KCl}) and **KCl-extractable magnesium (Mg_{KCl})** can also be measured on the filtered solution following the TAA titration. These determinations largely measure soluble (plus exchangeable) calcium and magnesium.

(e) 4 M HCl extractable Sulfur (S_{HCl})

HCl-extractable sulfur recovers soluble and adsorbed sulfate, sulfate from gypsum, as well as sulfur from relatively insoluble iron and aluminium hydroxy sulfate compounds (eg. jarosite, natrojarosite). It may include a contribution of sulfur from organic sources, particularly when sulfur is measured on an ICP-AES instrument (or another instrument that does not specifically measure sulfate). HCl-extractable sulfur (S_{HCl}) can be used in combination with KCl-extractable sulfur (S_{KCl}) to estimate retained acidity as net acid-soluble sulfur (S_{NAS}). Another common use of S_{KCl} is in the calculation of total oxidisable sulfur (S_{TOS}) when total sulfur (S_T) has also been determined.

HCl-extractable calcium (Ca_{HCl}) and **HCl-extractable magnesium (Mg_{HCl})** can be determined along with S_{HCl} . The 1:40 4 M HCl extraction employed should dissolve all calcium and magnesium carbonates, oxides and hydroxides in the soil, as well as extracting soluble and exchangeable calcium and magnesium.

(f) SPOCAS residual acid soluble sulfur (S_{RAS})

This 4 M HCl acid extraction procedure is performed on the soil residue remaining after the peroxide digestion in the SPOCAS method. As a result of the peroxide digestion procedure and subsequent washing of the soil residue, there should be no soluble, adsorbed or oxidisable sulfur remaining.

However, minerals such as jarosite and other ‘almost insoluble’ sulfate-containing compounds originally present in the soil material are largely unaffected by the peroxide digest. These compounds are soluble in HCl and are determined by this procedure. This sulfur measurement is used to estimate retained acidity, particularly from jarosite (see Eqn 11) and/or natrojarosite (Eqn 12).

Calculated sulfur (and cation) parameters

(g) Total Oxidisable Sulfur (S_{TOS})

Total oxidisable sulfur (S_{TOS}) is calculated from two sulfur measurements, total sulfur (S_T) and HCl-extractable sulfur (S_{HCl}), as shown below:

$$S_{TOS} = S_T - S_{HCl}$$

The limitations associated with this parameter generally include those associated with the determination of S_T and S_{HCl} . Typically, S_{TOS} is not suitable for accurate determinations on soil with low sulfur content (eg. sands). Moreover, it is not recommended for surface and/or highly organic soil, because S_{TOS} may exceed action limits (on non-sulfidic soil) due to sulfur in organic matter. Where the soil contains actual acidity, TAA needs to be measured. On soil material with jarositic salts present, or with pH <4.5 on a KCl extract, then measurement of S_{KCl} is also needed to estimate the contribution from such minerals. Despite these limitations, S_{TOS} provides a measure of oxidisable sulfur that is useful in screening soil for potential acidity.

(h) Peroxide Oxidisable Sulfur (S_{POS})

Peroxide oxidisable sulfur (S_{POS}) is calculated from peroxide sulfur (S_P) and KCl-extractable sulfur (S_{KCl}) measurements as shown below:

$$S_{POS} = S_P - S_{KCl}$$

As this method employs a strong chemical oxidant (30% w/w H_2O_2), it provides a measure of the maximum amount of potentially oxidisable sulfur in the soil sample and hence can be used to estimate the potential sulfidic acidity (Eqn 15). This method can overestimate the potential sulfidic acidity in soil where appreciable organic sulfur is present and is oxidised by the peroxide (eg. soil layers rich in organic matter). For soil with oxidisable sulfur results close to the action criteria, particularly sands (current action limit = 0.03 %S or 18 mol H^+ /t), the S_{CR} method generally gives a better estimate of the soil’s sulfide content. Whenever there is a discrepancy between the sulfur measurements used to calculate the potential sulfidic acidity, then those from the S_{CR} method will take precedence.

The S_{POS} can only estimate maximum sulfidic acidity as sulfur measurements give no indication of any acid-neutralising components in the soil. However, where calcium and magnesium have been determined on the same solutions used to measure S_P and S_{KCl} , an estimate of the acid neutralising ability of the soil can be made if ‘reacted’ calcium (Ca_A) and ‘reacted’ magnesium (Mg_A) are calculated.

$$Ca_A = Ca_P - Ca_{KCl}$$

$$Mg_A = Mg_P - Mg_{KCl}$$

Commonly, Ca_A and Mg_A reflect the amounts of ‘insoluble’ calcium and/or magnesium carbonates, oxides and hydroxides dissolved by the acid generated by the oxidation of sulfides in the peroxide digest. These values may include some calcium and magnesium from other soil minerals that may not have acid neutralising properties, and hence if used in acid base accounting the measurements may overestimate the effective ANC in soil with minimal carbonate. These measures of calcium and magnesium can be used in the ABA (see Tables A3.3 and 3.4), however their principal utility is as a confirmation of the presence of calcium and/or magnesium carbonates and hydroxides (and their

amounts) in the ABA when ANC has been calculated by other means. (See Section B15.1 for further details). Where Ca_A and Mg_A values do not exceed 0.1% they should be ignored in the ABA.

(i) Net acid-soluble Sulfur (S_{NAS})

Net acid-soluble sulfur (S_{NAS}) is calculated from HCl-extractable (S_{HCl}) and KCl-extractable (S_{KCl}) sulfur measurements as shown below:

$$S_{NAS} = S_{HCl} - S_{KCl}$$

This sulfur measurement is used to estimate retained acidity, particularly from jarosite (see Eqn 11) and/or natrojarosite (Eqn 12). In most soil materials S_{NAS} should approximately equal S_{RAS} , however usually only one of these determinations is performed on any sample.

Net acid-soluble calcium (Ca_{NAS}) and magnesium (Mg_{NAS}) can be calculated in a similar fashion.

$$Ca_{NAS} = Ca_{HCl} - Ca_{KCl}$$

$$Mg_{NAS} = Mg_{HCl} - Mg_{KCl}$$

Commonly, Ca_{NAS} and Mg_{NAS} reflect the **maximum** amounts of ‘insoluble’ calcium and/or magnesium carbonates, oxides and hydroxides dissolved by 4 M HCl. (These values may include some calcium and magnesium from other soil minerals that may not have acid neutralising properties, and hence if used in acid base accounting the measurements may overestimate the effective ANC). (See Section B15.2 for further details).

COMBINED (SPOCAS) METHOD

In the 1998 Laboratory Guidelines, the Peroxide Oxidation Combined Acidity & Sulfate (POCAS) method (Ahern *et al.* 1998) was included as the accepted peroxide-based laboratory procedures for determining the potential acidification of acid sulfate soils (ASS). It combined the principles of two commonly used peroxide oxidation methods: POSA (or peroxide oxidisable sulfuric acidity) (Lin and Melville 1993) which follows the ‘sulfur trail’ and the method of Dent and Bowman (1996) which follows the ‘acid trail’ (measuring TAA, TPA and by difference TSA). POCAS enabled the sulfur and acid trails of ASS to be directly compared using the one method. Where agreement between the acid and sulfur trails was poor, data provided by analysis of calcium and magnesium (indicating the presence of shell or naturally occurring carbonate) often accounted for the apparent discrepancy.

The **Suspension Peroxide Oxidation Combined Acidity & Sulfur (SPOCAS) method** (McElnea *et al.* 2002a; Latham *et al.* 2002) described in these Guidelines (Section B12) includes changes to the peroxide oxidation procedure that ensures quantitative recovery of pyritic sulfur and overcomes anomalies of sulfur loss and jarosite precipitation reported by Ward *et al.* (2002a, 2002b) using the earlier peroxide methods. Other changes include an increase in the titration pH end point (to 6.5) and the use of suspension titration. The complete SPOCAS method provides 12 individual analytes (plus 5 calculated parameters), enabling the quantification of some key fractions in the soil sample, leading to better prediction of its likely acid-generating potential (Table F1.2, Section F1). Put most simply, the SPOCAS method involves the measurement of pH, titratable acidity, sulfur and cations on two soil sub-samples. One soil sub-sample is oxidised with hydrogen peroxide and the other is not. The differences between the two values of the analytes from the two sub-samples are then calculated.

The Titratable Actual Acidity or **TAA** (the first component of the ‘**acidity trail**’) is a measure of the soluble and exchangeable acidity already present in the soil, often as a consequence of previous oxidation of sulfides. It is this acidity that will be mobilised and discharged following a rainfall event.

The Titratable Peroxide Acidity or **TPA** measurement (the second part of the acid trail) is the net result of the reactions between the acidifying and neutralising components in the soil (following peroxide digestion). A TPA of zero indicates that for a finely ground sample (under laboratory oxidation conditions), the soil's buffering/acid neutralising capacity exceeds (or equals) the potential acidity from oxidation of sulfides. A valuable feature of the TPA peroxide digestion component of the SPOCAS method is that for soil with $\text{pH}_{\text{OX}} > 6.5$, any excess acid neutralising capacity (ANC_{E}) can be quantified by means of an HCl titration. This feature is particularly useful when trying to confirm whether a soil has been treated with sufficient neutralising agent (including whether an appropriate liming safety factor has been applied, ie. verification testing). The TPA, being a measure of net acidity, includes a contribution from the material's ANC^3 .

The sulfidic acidity component is determined by the difference between TPA and TAA. This is termed Titratable Sulfidic Acidity (**TSA**).

The '**sulfur trail**' of SPOCAS (ie. S_{POS}) gives a measure of the **maximum** 'oxidisable' sulfur (usually predominantly sulfides) present in the soil sample. Since the chemical oxidising conditions employed in the laboratory are more rigorous than those experienced in the field, the S_{POS} result may, as a consequence, include some of the sulfur from the organic fraction in soil layers with appreciable organic matter. In such soil samples, S_{POS} is often slightly greater than S_{CR} (which specifically excludes organic forms of sulfur). Generally, S_{CR} and S_{POS} results are well correlated for reduced or PASS samples, but may differ on partially oxidised and surface samples. In some ASS, S_{CR} or S_{POS} may be below the action limit but the soil may still have an appreciable TPA. Sometimes this may reflect organic acidity, but it may also reflect acidity from oxidation and/or titration of iron- or manganese-containing compounds. This is particularly the case for peat soil and coffee rock. Various aluminium-containing compounds or complexes may also contribute to this acidity. This acidity may be present whether or not there is any appreciable potential sulfidic acidity (ie. any significant S_{CR} or S_{POS} result). While this acidity is commonly not rapidly released in the environment in the short term, it should not be immediately dismissed as being of no consequence. The proponent should be aware that there may be some risk if soils are only managed according to the acidity from the sulfides. As a precaution in such circumstances, the proponent may want to increase the application rate of neutralising materials to nearer that indicated when TSA is substituted into the ABA equation.

In the SPOCAS method, the S_{POS} (sulfur trail) result can be compared to the TSA (acid trail) result, provided the two quantities are expressed in equivalent units (eg. $\text{mol H}^+/\text{t}$). To do this, the stoichiometry of the pyrite oxidation reaction (Eqn 9) is assumed (ie. 2 moles of pyrite S produce 4 moles of H^+ acid). For example, the S_{POS} result (in units of %S) can be multiplied by 623.7 to convert it to 'equivalent' $\text{mol H}^+/\text{t}$. To signify that this result is in 'equivalent' **acidity** units, the S_{POS} symbol is prefixed by an '**a-**' (ie. $a\text{-}S_{\text{POS}}$). The TSA (in $\text{mol H}^+/\text{t}$) can similarly be converted to 'equivalent' sulfide **sulfur** units (in which case the result is prefixed by an '**s-**', ie. $s\text{-TSA}$).

Note: The convention of prefixing result symbols with an 'a-' or 's-' to signify that they have been converted to equivalent acidity and 'pyrite S' units has been adopted throughout these Guidelines. This is further described in Section F1.1.

In soil where the acid trail is lower than the sulfur trail (but the TPA is >0), calculation of the **reacted calcium** (Ca_{A}) and **magnesium** (Mg_{A}) can provide strong evidence for the presence of acid neutralising components in the soil. If it is assumed that this calcium and magnesium is derived from alkaline oxides, hydroxides or carbonates (and each mole of these elements provides 2 moles of acid neutralising), then these values can be converted to equivalent sulfur or acidity units and used in acid base accounting.

³ The usual limitations associated with sample preparation (eg. fine grinding of nominally 'unreactive' carbonates) apply (as discussed in sections A2.1b, B15.3 and elsewhere).

For example:

$$\text{Ca}_A (\% \text{Ca}) \times 0.8 = \text{s-Ca}_A (\text{equiv. \%S})$$

$$\text{Ca}_A (\% \text{Ca}) \times 499 = \text{a-Ca}_A (\text{equiv. mol H}^+/\text{t})$$

Similarly for Mg_A:

$$\text{Mg}_A (\% \text{Mg}) \times 1.319 \cong \text{s-Mg}_A (\text{equiv. \%S})$$

$$\text{Mg}_A (\% \text{Mg}) \times 822.9 = \text{a-Mg}_A (\text{equiv. mol H}^+/\text{t})$$

The sum of reacted calcium and magnesium (in equivalent acidity or sulfur units) can be compared to the difference between a-S_{POS} and TSA (or alternatively S_{POS} and s-TSA). It is common in soils with appreciable neutralising components for this sum to largely account for the difference between the acid and sulfur trails.

Reacted calcium and magnesium can be used in the ABA instead of the TSA, (particularly in soils with appreciable organic matter where the TSA may be elevated) yielding a lower net acidity and hence lower required liming rate.

Another useful parameter that can also be determined in the SPOCAS method (especially for soil with existing acidity and jarosite) is the **residual acid soluble sulfur (S_{RAS})**. This 4 M HCl acid extraction procedure is performed on the soil residue remaining after peroxide digestion and it measures sulfur from jarosite and other 'insoluble' sulfate-containing compounds originally present in the soil. (The acidity retained in these compounds is not recovered in the peroxide digest and subsequent titration). In some AASS (eg. particularly oxidised surface samples such as spoils), the acidity held in these compounds can be much greater than either the sulfidic or actual acidity. (See Section A3 for a discussion of sulfidic, actual and retained acidity).

In such soils, the retained acidity needs to be taken into account when calculating treatment or liming rates. The S_{RAS} value can be converted to an acid equivalent 'a-S_{RAS}' with a factor of 467.8 (see following conversion) in order to estimate 'retained' acidity, if it is assumed this sulfur has a similar 'per mole' acid-producing capacity as jarosite and/or natrojarosite sulfur (see Eqns 11 & 12). In such soil samples, TAA and a-S_{RAS} needs to be added to a-S_{POS} before calculating liming rates. (See Acid Base Accounting, Section A3 for details).

$$\text{S}_{\text{RAS}} (\%) \times 467.8 = \text{a-S}_{\text{RAS}} (\text{equiv. mol H}^+/\text{t})$$

Note: When using the SPOCAS method, S_{RAS} (or alternatively S_{NAS}) needs to be determined for all soil samples/horizons with pH_{KCl} ≤ 4.5. An exception to the need for S_{RAS} to be determined on all samples with pH_{KCl} ≤ 4.5 may be where a detailed soil profile description has been submitted by a 'skilled operator'⁴ verifying the absence of jarosite type minerals. In these instances, S_{NAS} must be determined on at least 20% of such samples (using those with the lowest pH_{KCl} values) to corroborate the conclusion that jarosite is absent. Organic samples are particularly difficult to interpret, though they present less of an interference to the S_{RAS} determination compared to S_{NAS}. Another exception may be where a sample from underneath the permanent (and undisturbed) watertable has a pH_{KCl} of ≤ 4.5.

⁴ An example of a skilled operator would be a qualified ASS consultant (such as a Certified Professional Soil Scientist, CPSS), experienced in ASS morphological descriptions.

Table A2.1. Acid yields for various iron and aluminium sulfates and hydroxy-sulfate minerals.

| Iron and aluminium sulfates and hydroxy-sulfates minerals | H⁺:Sulfur Ratio* |
|--|------------------------------------|
| $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3\downarrow + 2\text{SO}_4^{2-} + 3\text{H}^+ + \text{K}^+$ <p style="text-align: center;"><i>Jarosite: $pK_{SP} = 93$</i></p> | 1.5 |
| $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3\downarrow + 2\text{SO}_4^{2-} + 3\text{H}^+ + \text{Na}^+$ <p style="text-align: center;"><i>Natrojarosite</i></p> | 1.5 |
| $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{H}_2\text{O} \rightarrow 3\text{Al}(\text{OH})_3\downarrow + 2\text{SO}_4^{2-} + 3\text{H}^+ + \text{K}^+$ <p style="text-align: center;"><i>Alunite: $pK_{SP} = 85$</i></p> | 1.5 |
| $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}_2\text{O} + 2\text{SO}_4^{2-} + 3\text{H}^+ + \text{Na}^+$ <p style="text-align: center;"><i>Tamarugite</i></p> | 1.5 |
| $\text{Al}(\text{OH})\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{SO}_4^{2-} + 2\text{H}^+$ <p style="text-align: center;"><i>Jurbanite: $pK_{SP} = 17.8$</i></p> | 1.5 |
| $\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O} \rightarrow 4\text{Al}(\text{OH})_3 + 3\text{H}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+$ <p style="text-align: center;"><i>Basaluminite: $pK_{SP} = 117$</i></p> | 2.0 |
| $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 11\text{H}_2\text{O} + 3\text{SO}_4^{2-} + 6\text{H}^+$ <p style="text-align: center;"><i>Alunogen: $pK_{SP} = 7$</i></p> | 2.0 |

*Note: For comparison, the H⁺:Sulfur ratio for complete oxidation of pyrite is 2.0.

ACID NEUTRALISING CAPACITY (ANC), CARBON, CALCIUM AND MAGNESIUM METHODS

At this stage there is a clear need for further method development for the measurement of effective acid neutralising capacity (ANC) in ASS. The methods for estimating ANC that have been developed for acid rock drainage and/or limestone analysis are not necessarily directly transferable to acid sulfate soils. Typically, the ANC methods involve heating samples in an excess of a strong mineral acid, followed by a back-titration with alkali of the remaining 'unreacted' acid. When using such an approach on soils, some of the acid that is added is consumed through the breakdown of clay minerals and the release of aluminium, or other soil components by 'undesirable' reactions occurring at the very low pH of the acid digest. On some soils, an appreciable amount of the measured ANC may be due to these reactions that will only occur at low pH. It is desirable that the ANC measurements reflect the amount of the acid-neutralising material present in the soil that is capable of buffering (or maintaining) the soil at pH 6.5 or above. Finely-divided carbonate minerals are generally considered to be capable of providing this form of acid neutralising capacity.

The net acidity leached to the environment depends not only on the amount and rate of acid generation, but also on the amount and reactivity of the neutralising components in the soil. Coarse shell fragments in the soil may have little **effective** acid neutralising capacity due to their small surface area to volume ratio, and/or the presence of surface coatings. If coarse shell is not removed before soil grinding, the ANC measurement on the finely ground sample may poorly reflect the effective ANC in the field.

Note: A separate, large, unground sample is necessary for credible ANC analysis on soil where naturally occurring coarse shell or carbonates are present. To ensure representativeness of samples, 0.5 kg of sample will need to be picked clean of shell fragments.

Methods that add acid very slowly (eg. maintaining $\text{pH} \geq 4$), producing a titration curve, are more likely to correlate to field reactivity than those that add excess strong acid and back-titrate with base. As the ‘slow titration curve’ approach has rarely been conducted by commercial laboratories, the ANC data commonly supplied in the past was usually an overestimate of the soil’s effective ANC and may be of limited value.

Other chemical techniques detailed here (such as estimation of inorganic carbon, or reacted calcium and magnesium from SPOCAS) may more closely reflect the reactive calcium and/or magnesium carbonate content of soils and hence better reflect the effective acid neutralising capacity of the soil. However, again these measurements are made on finely ground soil samples and as such, these measurements may also poorly reflect the effective ANC in the field.

*Note: If the pH in KCl (pH_{KCl}) of the soil is less than or equal to 6.5, then this indicates that any acidity produced in the soil (eg. by sulfide oxidation) will not be able to be neutralised quickly enough in the soil to maintain a pH of 6.5 or above. Consequently, the ANC of samples in which pH_{KCl} is less than or equal to 6.5, **must be ignored** and considered to be zero. (There is no need to carry out any specific ANC analysis in this case where pH_{KCl} is < 6.5).*

In the acid rock drainage literature the acid neutralising capacity of the soil material has frequently been expressed in units of equivalent %CaCO₃. The ANC can also be expressed in ‘equivalent acid-neutralising units’ (mol H⁺/t) (see following conversion):

$$\text{ANC (\% CaCO}_3\text{)} \times 199.8 = \text{a-ANC (mol H}^+\text{/t)}$$

Similarly, to express ANC in ‘equivalent’ sulfur units for acid-base accounting purposes:

$$\text{ANC (\% CaCO}_3\text{)} / 3.121 = \text{s-ANC (equiv. \%S)}$$

Note: ANC is also expressed in kg CaCO₃/tonne soil (which can be converted to kg CaCO₃/m³ if the bulk density is known). (See Table F1.10 for conversions).

(a) ANC: Back-titration (ANC_{BT})

This approach involves the addition of a defined volume of standardised acid, followed by a hotplate digestion step. The excess acid remaining (ie. the added acid that has not been consumed by soil neutralising and buffering reactions—at very low pH) is ‘back-titrated’ to neutral pH using dilute NaOH solution. The 1 M HCl ‘rapid titration’ method (Method Code 19A1, Rayment and Higginson 1992, or Section B13.1) detailed in the 1998 *Laboratory Methods Guidelines* (Ahern *et al.* 1998) is not recommended for ASS for the reasons discussed earlier. Consequently, this method has been superseded and is replaced by another method (Method Code 19A2), which uses a more dilute (0.1 M) acid (see Section B13.2). Despite a lower concentration of acid being used, there are still reservations concerning the possibility that this method may still result in an overestimate of the effective ANC for ASS where the desired final pH of the soil material is ≥ 6.5 . With further research, this method may be modified in the future.

Note: If the pH_{KCl} is ≤ 6.5 , then ANC is treated as zero in the ABA equation, irrespective of the measured result.

(b) ANC: Excess—SPOCAS (ANC_E)

This measurement is carried out as part of the peroxide digestion component of the SPOCAS method. When the pH of the soil suspension is >6.5 after the initial peroxide oxidation stage, this may indicate the presence of carbonate or other alkaline minerals in the soil (eg. oxides/hydroxides of calcium and magnesium) in excess of that needed to neutralise the soil's sulfidic acidity. Soil suspensions should be titrated with HCl to pH 4, then digested again with peroxide. After this further peroxide digest, soil suspensions are titrated to pH 6.5 with NaOH (if pH <6.5). This NaOH titration result is subtracted from the HCl-titration result to give the **excess acid neutralising capacity** (ANC_E). As well as producing an estimate of excess ANC, this HCl-titration and re-digestion procedure is necessary to ensure complete peroxide oxidation of sulfides, which is slower and less efficient in the presence of excess carbonates.

Carbon methods for estimating carbonate content*(c) Carbon: Total (C_T)*

Total carbon (C_T) is determined by dry combustion in an oxygen charged furnace (eg. Leco™ furnace) or similar device. It is used in the calculation of total inorganic carbon (see Section B14).

(d) Carbon: Total Organic (C_{TO})

Total organic carbon is determined by a combustion furnace or similar device following acid pre-treatment to dissolve inorganic carbon (carbonate) and evolve CO₂ (see Section B14).

Calculated ANC parameters from carbon and alkali cation measurements*(e) Carbon: Inorganic (C_{IN})*

Total Inorganic carbon (C_{IN}) is calculated from total carbon (C_T) and total organic carbon (C_{TO}) measurements as shown below:

$$C_{IN} = C_T - C_{TO}$$

This carbon measurement is used to estimate carbonate content in the soil. Whilst calcium carbonates (or magnesium substituted CaCO₃, eg. dolomite) are likely to predominate in ASS, this approach is also likely to measure any iron or manganese carbonates in the soil⁵. Assuming the measured carbon is derived from calcium or magnesium carbonates then C_{IN} can be converted to its acid-neutralising equivalent 'a-C_{IN}' (see below):

$$C_{IN} (\%) \times 1665 = a-C_{IN} (\text{mol H}^+/\text{t})$$

(f) Reacted calcium (Ca_A) and magnesium (Mg_A)

Reacted calcium (Ca_A) is calculated from peroxide calcium (Ca_P) and KCl-extractable calcium (Ca_{KCl}) measurements as shown below:

$$Ca_A = Ca_P - Ca_{KCl}$$

Reacted magnesium (Mg_A) is calculated from peroxide magnesium (Mg_P) and KCl-extractable magnesium (Mg_{KCl}) measurements as shown below:

$$Mg_A = Mg_P - Mg_{KCl}$$

Commonly, Ca_A and Mg_A values reflect the amounts of 'insoluble' calcium and/or magnesium carbonates, oxides and hydroxides dissolved by the acid generated by the oxidation of sulfides in the

⁵ Iron-bearing carbonate minerals are also theoretically possible, but have not been identified in Qld ASS. Iron carbonate (siderite) is important in acid rock drainage. It is not an effective source of ANC since the ferrollysis reaction of the iron negates the acid neutralising reaction of the carbonate, and this can be a complication when measuring ANC by back-titration [Weber *et al.* (2004)]. When there is a substantial disagreement between the ANC calculated from ANC_{BT} and C_{IN}, this may be resolved by the measurement of Ca_{NAS} and Mg_{NAS}.

peroxide digest. In soil with excess carbonates, Ca_A and Mg_A will usually underestimate actual carbonate contents unless the HCl-titration procedure in SPOCAS has been performed. The reacted calcium and magnesium values can be converted to equivalent acid neutralising capacity (eg. a-Ca_A) assuming two moles of neutralising is provided per mole of calcium and magnesium:

$$\text{Ca}_A (\%) \times 499 = \text{a-Ca}_A (\text{mol H}^+/\text{t})$$

$$\text{Mg}_A (\%) \times 822.6 = \text{a-Mg}_A (\text{mol H}^+/\text{t})$$

Note: ANC values calculated from reacted calcium and magnesium may give higher results than ANC estimated from inorganic carbon (C_{IN}) measurements, since the latter is specific to carbonates and does not measure acid neutralising provided by CaO , Ca(OH)_2 , MgO , Mg(OH)_2 or similar alkaline compounds.

The recommended methods for ANC determination for the purpose of ABA are: ANC_{BT} (using 0.1 M HCl, Section B13.2), C_{IN} (Section B14), ($S_{POS} + s\text{-ANC}_E$), ($S_{POS} - s\text{-TSA}$) and reacted alkali cations (Ca_A and Mg_A) (from SPOCAS). The appropriateness of each of these values for use in determining ANC is given in Tables A3.1 to A3.4. The values derived from each of these methods need to be divided by the relevant fineness factor to yield an ANC value that can be used in an ABA. Whilst this does not preclude the use of other methods to estimate ANC, those other methods would need to be justified as appropriate to the relevant regulatory authorities.

Note: The use of C_{IN} without determining net acid soluble sulfur may be inappropriate for validation/verification testing where appreciable jarosite/retained acidity was present in the unameliorated soil. Jarosite is not recovered by the ANC_{BT} procedure.

SUMMARY OF MAIN METHODS

A number of decisions are necessary if submitting ASS (or suspected ASS) to laboratories for analysis. The first decision to make is whether samples should be submitted for conventional drying and grinding (and therefore 'Dry Analysis').

If samples are likely to contain significant monosulfides (eg. sludges or oozes from drains or lake bottoms), it is important that they are sampled (and stored) appropriately and analysed as wet samples. A flow diagram illustrating this fundamental decision-making process is shown in Figure A2.1.

Figure A2.1 shows that for dry samples it is easiest to select one of either the chromium or the SPOCAS suites of analysis, which will allow straight-forward calculation of net acidity using acid base accounting that should be readily acceptable to regulatory authorities. For those operators highly experienced in ASS, or for sites with previous analysis available, it is possible to select various combinations of methods in the Guidelines to conduct an acid base account. However, the onus will be on the consultant/proponent to clearly demonstrate the appropriateness of their selection/combination of methods for their particular site.

The advantage of the approach to use one of the main suites of analysis is that the laboratory follows a set of pre-determined rules to decide what analyses need to be conducted. The person submitting the samples need only decide between the two main options (eg. the Chromium or SPOCAS suites). Further explanation of the Chromium and SPOCAS suites is given in Section A2.2.

ASS ANALYSIS

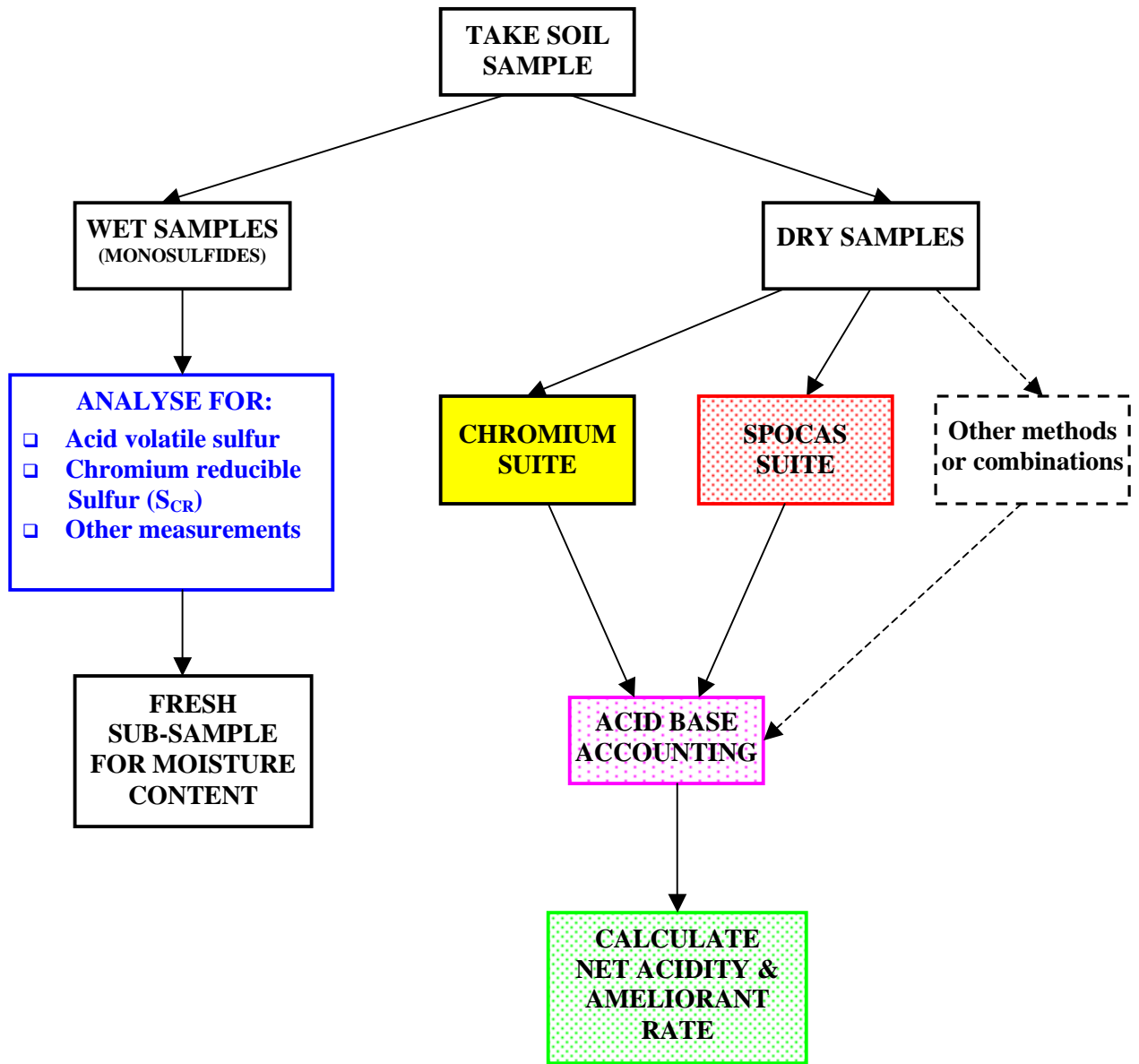


Figure A2.1. Flow diagram for analysis of ASS.

2.2 USING LABORATORY METHODS TO DETERMINE ACID RISK

Chemical analysis of ASS is undertaken to determine whether these soils are likely to generate any net acidity, and if so to quantify this acidity. From the analytical results, the amount of ameliorant needed to be added to these soils to prevent the possibility of net acid export is calculated. Fundamentally, what we are trying to measure is the net effect of acid generating processes in the soil balanced against any acid-neutralising (or basic) components that may be present. In other words, we are trying to construct an acid base account.

The acid base accounting (ABA) approach has long been used in the mining industry (both in Australia and overseas) in an effort to predict net acidity from oxidation of sulfidic material—with varying degrees of success. Whilst there are many similarities between the acid rock drainage and ASS situations, there are also fundamental differences. The principal difference is to do with the relative particle size of the sulfides in the two settings (ie. ores vs soils) (Caruccio 1975).

Generally, in ASS, sulfide crystals/particles are microscopic in size, typically with a diameter in the order of 0.5 µm for individual crystals (Bush and Sullivan 1999) or 20–50 µm for framboids (Hámor 1994) and are dispersed in a clay and silt particle size matrix with varying amounts of relatively inert sand present. This results in a substantially greater surface area and hence reactivity of sulfides in ASS compared to even finely ground rock in the acid rock drainage environment. Organic matter is usually present in ASS, ranging from minor amounts in some sands to extremely high levels in some peats. The presence of organic sulfur in many ASS represents a potential interference to some analytical methods that needs to be considered. Such components have a complicating effect both on analysis of ASS and on how they react in the environment. Organic sulfur compounds are generally not considered a significant environmental risk as they do not produce considerable net acidity on oxidation, in contrast to reduced inorganic sulfur compounds such as pyrite. Organic materials (particularly peats) however may contain significant organic acidity in the form of organic acids. Additionally, organic ligands can complex considerable quantities of iron and/or aluminium that may be released when the organic matter oxidises. These iron and aluminium ions may then produce acidity on hydrolysis. When attempting to raise the pH of an ASS by the addition of neutralising agents (such as agricultural lime), the effect of organic acidity needs to be factored in when formulating management plans, since this acidity needs to be neutralised along with acidity from pyrite oxidation when attempting to raise the pH of an acidic soil.

An ABA approach is widely used for predicting net acidity from sulfide oxidation of ASS. While several ABA models have been used for ASS, they all share a common underlying principle/approach, encapsulated in the following equation:

$$\text{Net Acidity} = \text{Potential Sulfidic acidity} + * \text{Existing Acidity} - \text{ANC}$$

For our purposes, existing acidity is defined as follows:

$$* \text{Existing Acidity} = \text{Actual Acidity} + \text{Retained Acidity}^6$$

and ANC as follows:

$$\text{ANC} = \text{measured ANC/fineness factor}$$

The components in the right hand side of the **Net Acidity** expression (or various combinations of these components) are determined using appropriate analytical methods. It is not usually necessary to determine every component in the expression. For example, the occurrence of existing acidity and acid neutralising capacity can be considered mutually exclusive for the purposes of ASS management to maintain the pH to >6.5 (ie. if a soil has existing acidity it has no effective acid neutralising capacity).

⁶* Refer to Acid Base Accounting (Section A3) for further explanation of terms.

In the mining industry, it has commonly been assumed that if the calculated *net acidity* is zero or negative (ie. there is supposedly '*net neutralising*'), then there is no risk. However, this assumption has proved invalid for many situations, and there have been cases where substantial environmental harm has occurred when this assumption has been made. Considerations such as the particle size or fineness of acid neutralising material and slowed reaction rates due to coating (or 'armouring') of particles with gypsum or iron precipitate, may prevent effective neutralisation and result in the net export of acid. The calculated net acidity in an ABA is critically dependent on which ANC method is used. As discussed earlier, ANC methods based on acid rock drainage procedures (in which excess acid is added and the soil digested at a very low pH, followed by back-titration with alkali) may overestimate the *effective* ANC in ASS⁷.

For all these reasons, the *measured* ANC in the previous equation is moderated by the use of a fineness factor (**FF**) when estimating the soil's ANC. The minimum fineness factor is 1.5 (in the case of fine agricultural lime), increasing to larger values (in the case of coarse shell or similar material).

There is no single 'right' way to determine each of the components of the ABA, and a number of alternatives are possible. However in this section, discussion will be limited to the two main approaches recommended for the calculation of net acidity.

USE OF LABORATORY METHODS TO DETERMINE AN ACID BASE ACCOUNT

It is strongly recommended that the ABA be conducted on dried samples. While the drying process may convert small amounts of sulfide to actual acidity, this acid is still accounted for in the ABA procedure. A dried sample has many advantages over wet samples. The drying and grinding process permits larger and more representative samples to be homogenised. Wet/moist and unground samples on the other hand are often heterogeneous. When making an ABA, it is important that the sub-samples taken to measure each of the components of the ABA expression are representative of the entire sample. This is difficult to achieve using a wet sample, and as a consequence each analysis must necessarily be replicated. Sub-sampling issues have not been adequately addressed for wet samples. It is strongly recommended that the ABA not be conducted on wet samples unless acid volatile sulfides (AVS) are suspected to be present.

Chromium suite

The Chromium suite is a set of independent analytical methods each of which determines a component of the acid base account. Only the required components of the acid base account are measured using this approach. To decide which components are needed, refer to the flow diagram (Figure A2.2). The initial step in the chromium suite is to measure the reduced inorganic sulfur content (by the chromium reducible sulfur method) to estimate the potential sulfidic acidity (the first component of the ABA equation), which must be determined in all cases.

Next, the pH_{KCl} of the soil must be assessed to determine whether it has existing acidity, or if it contains any ANC. The presence of **existing acidity** precludes the existence of any effective ANC and *vice versa*. If the pH_{KCl} is <5.5 , then **TAA** must be determined (ie. the **actual acidity** measured). If the pH_{KCl} is ≥ 5.5 and <6.5 , then TAA should also be determined if the S_{CR} result indicates the presence of sulfides (ie. the sulfidic acidity it is above the action limit for its texture). Where the pH_{KCl} is <4.5 (or when yellow mottles of jarosite/natrojarosite/schwertmannite etc. have been noted in the sample) an estimate of the **retained acidity** should be made, (from the measurement S_{KCl} , S_{HCl} and hence of **net acid soluble sulfur**, S_{NAS}).

⁷ For this reason, the use of 0.1 M HCl is recommended in ANC_{BT} methods (see Section B13.2).

If pH_{KCl} is >6.5 , the presence of carbonates⁸ (or other minerals/compounds capable of providing acid neutralising) is possible. The greater the pH is above 6.5, the more likely that the ANC will be effective ANC and therefore the more important it is to determine this. The measurement of ANC is desirable, since this will decrease the net acidity, and may even reveal that there is no net acidity present (ie. that there is net neutralising), meaning that the soil may not even require liming. An estimate of ANC can be made from: the **inorganic carbon** C_{IN} , (eg. by Leco™ furnace), the **net acid soluble calcium**, Ca_{NAS} (and Mg_{NAS} if dolomite/magnesite is present) if non-carbonate forms of neutralising are suspected, or from **acid neutralising capacity by back-titration** (ANC_{BT}). If the pH is between 5.5 and 6.5, no measure of ANC or existing acidity is necessary, as TAA is usually low. Obviously, if the S_{CR} result is below the action limits, then no measurement of ANC is necessary. The Chromium suite can also be used for verification testing to validate whether the required neutralising agent has been added to the ASS material (see Section A3.6).

⁸ An acid effervescence test (with 1 M HCl, see *Section H2*) indicates the presence of CaCO_3 , and making the determination of ANC worthwhile. However, this test should not be the only criterion, since non-carbonate forms of alkalinity (eg. calcium and magnesium oxides or hydroxides) do not give a positive result to the test, but are effective contributors to the ANC.

CHROMIUM SUITE

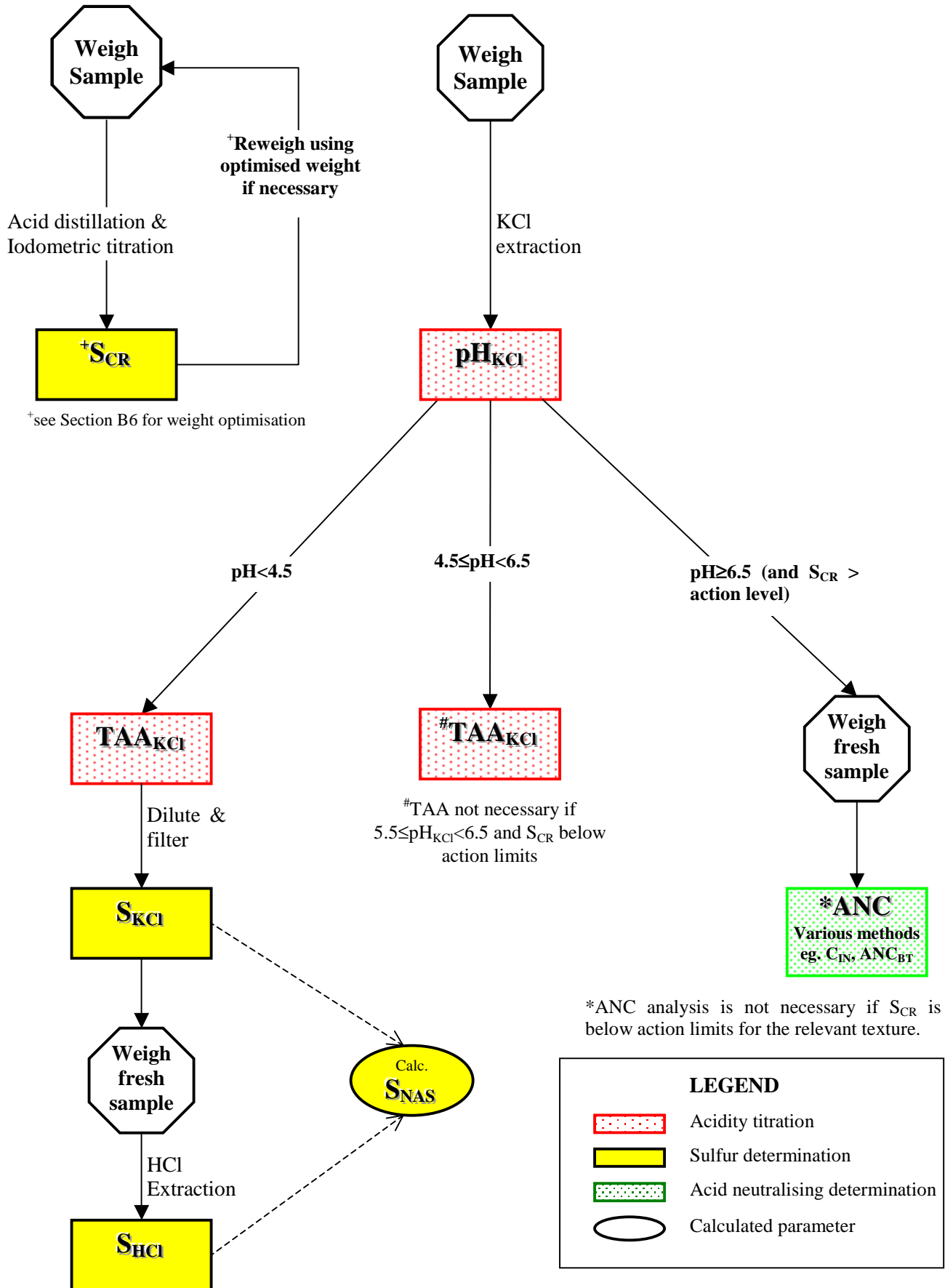


Figure A2.2. Flow diagram for Chromium suite.

SPOCAS Suite

A second approach is to perform the complete SPOCAS method (see Figure A2.3). The SPOCAS method is in essence a self-contained ABA. The TPA result of SPOCAS represents a measure of the net acidity, effectively equivalent to the sum of the soil's **potential sulfidic acidity** and **actual acidity**.

The initial step in the SPOCAS suite is to determine pH_{KCl} . If pH_{KCl} is ≥ 6.5 then the TAA is zero. Whether or not a TAA titration has been performed, KCl extractable sulfur (S_{KCl}), calcium (Ca_{KCl}) and magnesium (Mg_{KCl}) are then measured. Where the pH_{KCl} is < 4.5 (or when jarosite has been noted in the sample), then the **residual acid soluble sulfur (S_{RAS})**⁹ must be performed on the peroxide digested soil residue, since the TAA and TPA results do not measure the **retained acidity**.

The next stage in the SPOCAS suite is to perform the peroxide digestion procedure. After the addition of two aliquots of peroxide (and two hotplate heating steps) the pH_{OX} is measured. If pH_{OX} is ≤ 2 then the digest should be repeated using half the weight of soil. If the pH_{OX} is > 2 and ≤ 6.5 , then TPA is measured by titration with NaOH. If the pH_{OX} of the soil is > 6.5 (and the soil may be 'self-neutralising', ie. the TPA = 0), then the HCl-titration step in SPOCAS (ie. the carbonate modification) must be performed to ensure complete oxidation of sulfides. This allows calculation of the **excess acid neutralising capacity (ANC_{E})**, or in effect the **net alkalinity**.

Again, irrespective of which path has been followed (ie. determination of TPA or ANC_{E}) then the titrated suspension must be analysed for peroxide sulfur (S_{P}), calcium (Ca_{P}) and magnesium (Mg_{P}). In the final stage of the SPOCAS suite, for soil where pH_{KCl} is < 4.5 , then an extraction with 4 M HCl on the peroxide digested soil residue is performed to determine residual acid sulfur (S_{RAS}).

The SPOCAS suite can also be used for verification testing (see Section A3.6). The ANC_{E} (together with the S_{POS} and an appropriate fineness factor) is used in the ABA to determine whether or not additional treatment of the soil material is needed.

To perform the complete SPOCAS method, the S_{RAS} (or S_{NAS}) **must** be performed on soil with a pH_{KCl} of < 4.5 , and the HCl-titration **must** be performed where the pH_{OX} is > 6.5 . Anything less than this is unacceptable and does not constitute the complete SPOCAS method.

⁹ S_{NAS} can be used as an alternative measure of retained acidity.

SPOCAS: FLOW DIAGRAM

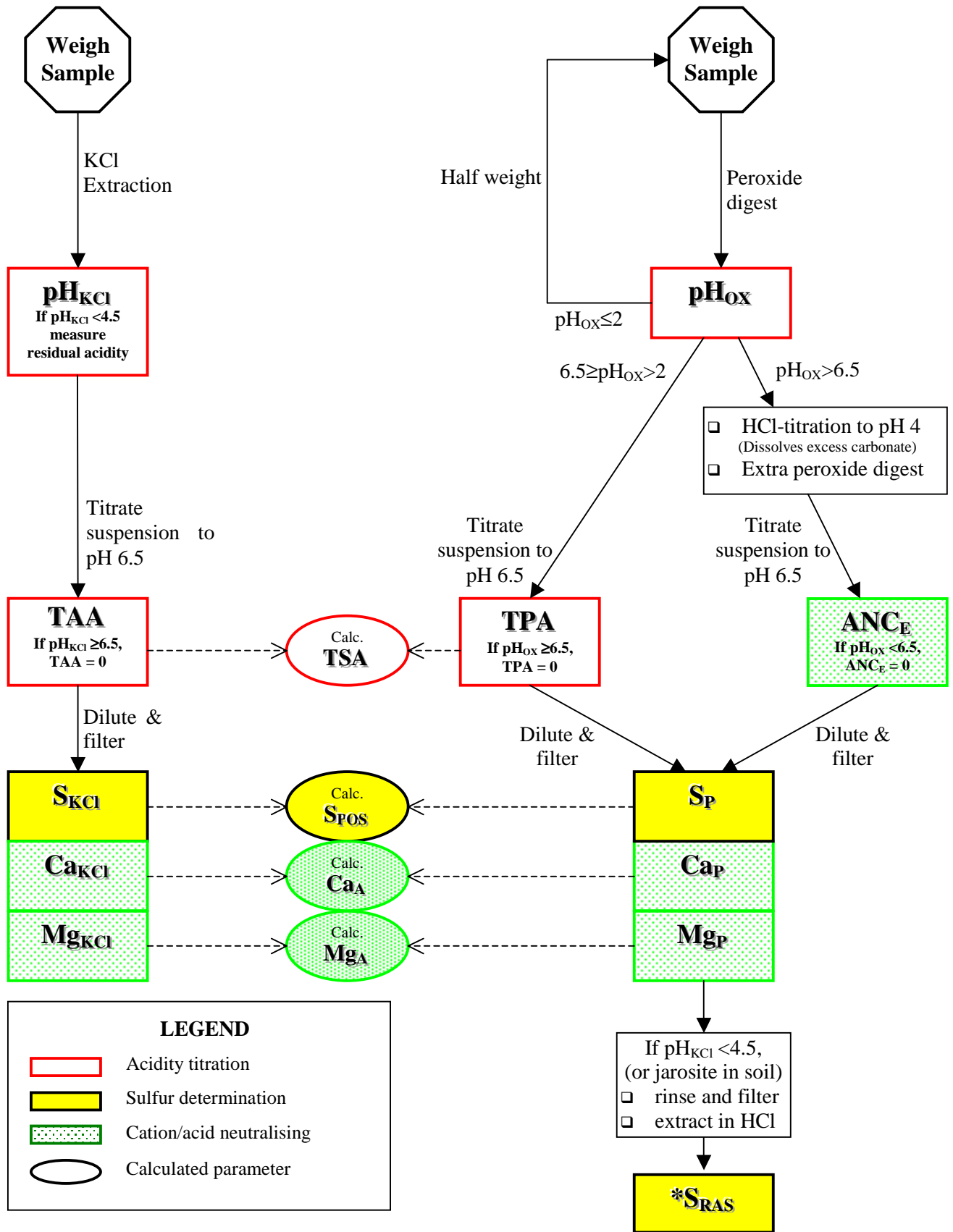


Figure A2.3. Flow diagram of SPOCAS suite.

* S_{NAS} may be substituted for S_{RAS}

2.3 CHOOSING A LABORATORY, SELECTING CONSULTANTS AND MEETING REGULATOR EXPECTATIONS

a) Choosing a laboratory

The selection of a laboratory to conduct ASS analysis is a commercial as well as a personal decision, commonly based on a combination of factors such as the laboratory's data quality and reliability, prices, location, sample turn-around time, equipment, and ability to interpret results.

It is expected that for any ASS analytical method used in the selected laboratory that there are strict quality assurance procedures in place. In most Australian states, NATA (National Association of Testing Authorities) accreditation of laboratories for each analytical method used is highly desirable. Where a laboratory is not NATA-accredited for a particular method then some further evidence of quality assurance will be necessary. Such evidence may take the form of a comparison between the selected laboratory and a NATA-accredited laboratory on a range of paired samples for that method. In the case of non-NATA-accredited methods, a request should also be made to the analysing laboratory to supply precision and validation data.

Further, it would be expected that laboratories conducting ASS analysis would take part in the Laboratory Sample Exchange Program for ASS, due to be conducted following final adoption of these Guidelines. (It would be reasonable to request information on the performance of the selected laboratory in the sample exchange program).

b) Selection of consultants

It is strongly recommended that consultants with qualifications in agricultural, environmental soil or geological science (specialising in soil chemistry, hydrology, pedology or geochemistry), experienced in acid sulfate soils management and accredited with a professional organisation (such as the Australian Society of Soil Science Inc.) be engaged to undertake soil investigations. Consultants familiar with the special sampling requirements for ASS are necessary.

c) Meeting regulator expectations

Approval authorities will principally be concerned with the selection of **appropriate methods** and on the **quality of the data**, since major developmental decisions are based on laboratory data. Generally, a regulator would expect a full Acid Base Account (ABA) to be conducted using the Chromium or SPOCAS suites on samples, in accordance with the latest sampling and assessment guidelines for the relevant state. Other combinations of methods from the Guidelines may be accepted on a case-by-case basis. After the data has been collated and assessed, further analysis may still be needed. (For instance, an S_{CR} determination may be added to the SPOCAS suite for samples where organic components may be contributing to an elevated S_{POS} result).

If other analytical methods (or variants of approved methods) are employed, a detailed justification will usually be required (eg. a regression analysis comparing the chosen method with an approved method). If variant or other methods are to be employed, their use should be negotiated with the approval authority prior to beginning analysis.

The *regulator or assessment manager* reviewing the final report/EIS/EM Plan will need to be convinced that the quantity and quality of sampling, analysis and relevant methods of analysis have been performed to adequately assess the site. Important information such as soil pH, actual acidity, potential acidity, jarosite or other acid producing compounds, and potential reactivity of inherent soil neutralising material will be needed (using appropriate laboratory analysis) to develop a cost-efficient, environmentally safe management plan. Field descriptions (eg. texture, inclusions and horizons) need to be integrated with the laboratory data to present an understanding of the layers/horizons likely to be encountered on disturbance. If any of these or other issues are deficient, then more drilling, sampling,

laboratory analysis or other types of analysis may be required to obtain development approval—often causing costly delays and frustration to all parties concerned.

In general, calculations from laboratory results of acid risk should take into account the need to neutralise **with a safety factor**, the sum of actual, retained and potential acidity from the eventual complete oxidation of all iron sulfides and complete hydrolysis of the oxidised products.

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