

### 3. PROCEDURE FOR PREDICTING ACID RISK VIA THE ACID BASE ACCOUNT (ABA)

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#### 3.1 BACKGROUND TO ACID BASE ACCOUNTING

As stated in Section A2.2, the ABA approach is not new; it has had a long history in one form or another in acid rock drainage, where the oxidation of various sulfide or disulfide minerals is problematic. Miller (1986) defined the term **Net Acid Generating Potential (NAGP)** for use in the mining industry as:

$$\text{NAGP} = 3.13 \times \text{S} (\%) - \text{ANC} \quad (\% \text{CaCO}_3)$$

This is the essentially the same form as the ABA equation given in Section A2.2—except that it does not contain a term for the existing acidity which is common in acid sulfate soils. The sulfur result substituted into the NAGP expression was commonly total sulfur ( $S_T$ ).

Mulvey (1993) adapted the NAGP concept to ASS, using more precise measures of pyritic sulfur.

*Note: The similarities and differences between the acid rock drainage and ASS situations are discussed in Section A2.2.*

Mulvey and Willett (1996) defined NAGP in terms of kg  $\text{H}_2\text{SO}_4/\text{t}$ :

$$\text{NAGP} = 30.6 \times \text{S} (\% \text{ sulfide S}) - \text{ANC} \quad (\text{kg H}_2\text{SO}_4/\text{t})$$

Equally, this equation/relation can be expressed in units of %S:

$$\text{NAGP} = \text{S} (\% \text{S}) - \text{ANC} (\% \text{CaCO}_3) / 3.125 \quad (\% \text{S})$$

**Obviously, these expressions are only applicable to PASS. Written more generally:**

$$\text{Net Acidity} = \text{Potential Sulfidic Acidity} - \text{Acid Neutralising Capacity}^*$$

A refinement of the above ABA concepts to allow for the use of these methods for AASS as well as PASS, was made by Sullivan *et al.* (2001) who defined Net Acidity as below:

$$\text{Net Acidity} = \text{Potential Sulfidic Acidity} + \text{Actual Acidity} - \text{Acid Neutralising Capacity}$$

**This ABA** has been used widely in NSW for prediction of Net Acidity in ASS materials.

As has been discussed previously, there are various ways by which each of the components of the ABA expression can be measured. However, the net result can depend critically on which results are substituted into the ABA expression, and more particularly the methods used to determine them. We shall discuss each of the ABA expression's components in turn.

### 3.2 MEASUREMENT OF POTENTIAL SULFIDIC ACIDITY

The first component of the ABA is the **potential sulfidic acidity** (which must be measured in all cases of acid base accounting for ASS, irrespective of soil pH). Potential sulfidic acidity can be measured with varying degrees of sophistication. The simplest approach is to measure **total sulfur** and take this as the sulfide content. This is a cheap, easy approach analytically and has often been used in the mining industry (eg. NAGP; Miller 1986), however it is likely to be an overestimate of the potential sulfidic acidity/sulfide content in ASS, leading to excessive (sometimes even unnecessary) liming, (particularly when appreciable sulfur is present as soluble sulfate salts or organic sulfur in surface soil where sulfide content may be negligible). Substituting  $S_{TOS}$  into the equation provides a better estimate of potential sulfidic acidity, with sulfur species soluble in 4 M HCl salts removed from the total sulfur result. Whether the  $S_T$  or the  $S_{TOS}$  approach is used, it is vital that the  $S_T$  value be accurate—especially where  $S_T$  is low, or where  $S_{TOS}$  is low.

A preferable approach is to use  $S_{CR}$ , or the  $S_{POS}$  result from the SPOCAS method as estimates of potential sulfidic acidity. The most accurate approach and the preferred one for organic samples and those with low levels of sulfide (close to the action limit) is the use of the  $S_{CR}$  result. The methods for estimating potential sulfidic acidity have become more sophisticated and accurate in recent times. This has culminated in the two main approaches of  $S_{CR}$  and  $S_{POS}$  for acid base accounting purposes.

Having determined or estimated the potential sulfidic acidity it is necessary to measure either the **existing acidity**, or the **acid neutralising capacity**. To establish which one of these two quantities has to be measured it is necessary to measure the  $pH_{KCl}$  of the soil. If the  $pH_{KCl}$  is  $<5.5$ , then the existing acidity must be determined. If the pH is  $\geq 6.5$  then the ANC should be determined, unless the sulfur result ( $S_{CR}$  or  $S_{POS}$ ) is less than the action limit for the relevant texture class.

### 3.3 MEASUREMENT OF ACID NEUTRALISING CAPACITY

While techniques for measuring acid neutralising capacity are relatively easy to perform in the laboratory, the results obtained do not necessarily reflect the material's effective acid neutralising capacity in the environment. There has been relatively little research conducted on the measurement of acid neutralising capacity in ASS. With refinement in estimates of potential sulfidic acidity, the focus is now shifting to improving the accuracy of the measurement of ANC. Some of the methods used for ASS, which have been derived from the acid rock drainage or lime analysis disciplines are unsuitable, as they can be an overestimate of the soil's effective ANC. When  $S_T$  was the index used for sulfidic acidity, accuracy of the ANC measurement was less critical, but with the use of  $S_{CR}$  or  $S_{POS}$ , then if the ANC result used is an overestimate, there is the risk of net acidity production in the environment, despite calculations indicating there should be **no net acidity**. Kinetic factors, such as the rate of acid production compared to the rates at which the neutralising materials dissolve becomes more important. Coatings on the neutralising materials (eg. iron oxides, gypsum) may further decrease their effectiveness.

While relatively small amounts of ANC can be provided by cation exchange or from organic matter, this acid buffering is often inconsequential in comparison to that required to neutralise the acidity produced by the oxidation of sulfides. It is desirable that any acid neutralising components in the soil maintain pH at or above 5.5 (and preferably at or above 6.5). Such ANC is commonly provided by calcium and magnesium carbonates<sup>1</sup>. Some of the methods available for estimating ANC (especially those that involve acid digestion and back-titration of unreacted acid) have the potential to include buffering as a result of the breakdown of clay minerals at the low pH of the acid digest solution. Clearly this is undesirable. The current ANC back-titration method ( $ANC_{BT}$ ) is incapable of distinguishing between the contributions of exchangeable bases and organic matter from the buffering

<sup>1</sup> In treated materials, oxides and hydroxides of calcium and magnesium may be present, depending on the ameliorant used.

provided by the breakdown of clay minerals. It has the potential to overestimate the soil's effective ANC (particularly if titration of suspension is not performed).

*Note: Any ASS material with a  $pH_{KCl}$  of  $<6.5$  must be assumed to have an effective ANC of zero (even if shell is present in the sample). Clearly, if the pH has dropped below 6.5 then acid neutralising components in the soil are not reactive/available enough to keep pace with acid generation from sulfide oxidation and to maintain pH of the material above 6.5 (the desired level). Measurement of ANC on soil with  $pH_{KCl} < 6.5$  (especially using the acid digest/back-titration approaches) can sometimes give a substantial result, but this ANC is not effective in maintaining the ASS material at or above pH 6.5.*

To minimise the chance that ANC is overestimated, it is desirable to use methods that are more specific to the measurement of the soil's calcium and magnesium carbonate.

An approach that is less likely to overestimate effective ANC is to use the reacted calcium ( $Ca_A$ ) and magnesium ( $Mg_A$ ) results from the SPOCAS method. The technique that is least likely to overestimate the soil's effective ANC is the measurement of inorganic carbon ( $C_{IN}$ , eg. by combustion furnace), which is specific to carbonates. However, this technique does not quantify neutralising from oxide and hydroxide minerals, so has the potential to underestimate ANC in some cases. Where the neutralising agent used is 'red mud' or similar 'non-carbonate' or 'non-oxide' material, measurements of carbonate or alkali cation content (eg.  $C_{IN}$ ,  $Ca_A$  and  $Mg_A$ ) are clearly inappropriate. The use of the  $ANC_{BT}$  method or  $ANC_E$  from SPOCAS would appear the best alternatives in such cases, but the research has yet to be conducted.

Analytical precision of the ANC measurements is not the only consideration. An important issue is the effectiveness of the acid neutralising materials. The presence of almost unaltered coarse shell material (except for surface iron staining) commonly observed in very acidic oxidised ASS is testament to the lack of neutralising effectiveness of such coarse shell material. The effectiveness of carbonates (and other neutralising components in the soil) is dependent on their form (eg. finely divided vs coarse). The typical laboratory sample preparation (which includes fine grinding) may greatly alter the size (and hence reactivity) of  $CaCO_3$  in shell fragments and may artificially increase the reactivity of the neutralising components. In the field, even when  $CaCO_3$  is added as finely divided, high quality agricultural lime, problems such as coating, slow reaction kinetics or poor mixing through the soil decreases its effectiveness. These considerations are part of the rationale of the 1.5 safety factor required when neutralising the soil. Despite the presence of coarse shell material (or other neutralising soil constituents), if they are unreactive to such an extent that the acid produced by sulfide oxidation cannot be neutralised effectively enough to maintain  $pH_{KCl} \geq 6.5$ , then the ANC must be considered to be **zero**. There is clearly a need to account for particle size and reactivity of neutralising materials and this is done by the application of a fineness factor.

#### ***a) Application of a fineness factor (FF) to the ANC measured in ASS***

These Guidelines deal with the limitations of methods for determining ANC on ASS materials by dividing the **measured ANC** by a **fineness factor** (FF). When ameliorating PASS by mixing it well with finely-divided, pure agricultural lime, a safety factor of 1.5 must be applied. Equally, this reasoning (of a minimum 1.5 safety factor) should be applied to any naturally occurring ANC that is present in the soil. The minimum fineness factor that should be applied to any ANC is 1.5, however larger factors (eg. 2, 2.5 or 3) may be applicable for shell or other forms of neutralising inclusions in the soil. For application of fineness factors in the ABA, see Tables A3.1–A3.4.

### 3.4 MEASUREMENT OF EXISTING ACIDITY

If soils are already acidic (eg.  $\text{pH}_{\text{KCl}} < 6.5$ ), the ABA equation needs to include the **existing acidity** component (unless  $\text{pH}_{\text{KCl}}$  is  $> 5.5$ , and the  $S_{\text{CR}}$  or  $S_{\text{POS}}$  is below action limits for that soil's texture).

**Existing acidity is comprised of both actual acidity and retained acidity, ie.**

$$\text{Existing Acidity} = \text{Actual Acidity} + \text{Retained Acidity}$$

*Note: Existing acidity may be determined where the  $\text{pH}_{\text{KCl}}$  is between 5.5 and 6.5, but it is not mandatory (many coastal non-ASS can fall in this pH range) unless the SPOCAS method is being performed.*

Whilst the research into the measurement of existing acidity in ASS has been neglected in the past (in favour of the measurement of sulfidic acidity), this is changing. Methods for measuring actual acidity are becoming more refined, though a considerable research effort needs to be expended into the measurement of retained acidity.

To measure actual acidity (ie. the soluble and exchangeable acidity) it is necessary to measure the titratable actual acidity (TAA, Section B2). The retained acidity is usually only appreciable when the pH is  $< 4.5$  (and particularly when  $\text{pH}_{\text{KCl}}$  is  $< 4$ ), where jarosite and other hydroxy sulfate minerals are stable and sometimes present in substantial amounts. Knowledge of the form and abundance of the various iron and aluminium hydroxy sulfate minerals in ASS is relatively poor, as is the understanding of the rate of release of acidity from the hydrolysis/decomposition of these compounds.

#### a) Retained acidity via the Chromium suite

If the **Chromium suite** (Section A2) has been followed, an estimate of retained acidity can be obtained by the difference between sulfur determined on the titrated TAA suspension (ie.  $S_{\text{KCl}}$ ), and the sulfur extracted by 4 M HCl on a separate soil sub-sample ( $S_{\text{HCl}}$ ). This will yield the **net acid soluble sulfur** result ( $S_{\text{NAS}} = S_{\text{HCl}} - S_{\text{KCl}}$ ), from which retained acidity can be calculated (see theoretical conversion below), if it is assumed that this sulfur will produce 1.5 moles of acidity per mole of sulfur, as is the case for jarosite and natrojarosite (see Eqns 11 and 12, Section A1.2c).

$$\mathbf{a-S_{NAS}} \text{ (mol H}^+\text{/t)} = S_{\text{NAS}} \text{ (\%)} \times \mathbf{0.75} \times \mathbf{623.7}$$

#### b) Retained acidity using the SPOCAS suite

If the **SPOCAS suite** (Section A2) has been used, then the measurement of **residual acid soluble sulfur** ( $S_{\text{RAS}}$ ) can be used to calculate retained acidity:

$$\mathbf{a-S_{RAS}} \text{ (mol H}^+\text{/t)} = S_{\text{RAS}} \text{ (\%)} \times \mathbf{0.75} \times \mathbf{623.7}$$

Alternatively, if a 4 M HCl extraction on another sub-sample has been conducted,  $S_{\text{NAS}}$  can be calculated from  $S_{\text{HCl}} - S_{\text{KCl}}$  (as described above *via* the Chromium suite) rather than measuring residual acid soluble sulfur ( $S_{\text{RAS}}$ ).

The amount of acidity released per mole of sulfur is variable [eg. basaluminite and  $\text{AlOHSO}_4$  produces 2 moles of acidity per mole sulfur, while jarosite produces 1.5 moles (Table A2.1)]. Further research is needed into the release of acidity from the various hydroxy sulfate minerals.

The **SPOCAS method** represents an all-in-one acid base account. The TPA result of SPOCAS represents a measure of the net acidity, effectively equivalent to the sum of potential sulfidic acidity and actual acidity. Where the  $\text{pH}_{\text{KCl}}$  is  $< 4.5$ , then the  $S_{\text{RAS}}$  component of SPOCAS should be performed, since the TPA result does not measure the retained acidity.

In soil horizons, jarosite is frequently concentrated along root channels, soil cracks and on ped faces, while the remainder of the soil can remain largely unoxidised and at near neutral pH. Therefore a dried and ground soil sample may have a pH higher than 4.5, but still contain appreciable jarosite. This is one of the reasons why a pH higher than the pH of <3.7 needed for jarosite formation, (ie. a pH of 4.5), has been chosen as the cut-off point for measurement of retained acidity. It is important if jarosite has been noted that retained acidity be analysed for, irrespective of soil pH.

### 3.5 *GENERAL ABA EQUATION*

In summary, the general form of the ABA applicable to ASS is shown below:

$$\text{Net Acidity} = \text{Potential Sulfidic Acidity} + \text{Existing Acidity} - \text{measured ANC/FF}$$

This further expands to:

$$\text{Net Acidity} = \text{Potential Sulfidic Acidity} + \text{Actual Acidity} + \text{Retained Acidity} - \text{measured ANC/FF}$$

The following tables illustrate which results are needed to complete the ABA equation for various  $\text{pH}_{\text{KCl}}$  ranges using the Chromium suite and SPOCAS suite approaches. (Tables are given both in acidity units and sulfur units, see Tables A3.1–A3.4). Once the **Net Acidity** has been calculated from these tables, it is a simple matter of looking up the conversion table (**Table F1.10**) and applying the appropriate safety factor to calculate the required liming rate (taking into account the neutralising value of the ameliorant being applied).

**Table A3.1. Chromium suite acid base accounting—sulfur units. Analyses required.**

<b>Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF</b>
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Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
<b>pH<sub>KCl</sub> ≥ 6.5</b> if S <sub>CR</sub> < action limit, do not need ANC	S <sub>CR</sub>			– [s-C <sub>IN</sub> /FF]*
	S <sub>CR</sub>			– [s-ANC <sub>BT</sub> /FF]*
<b>5.5 ≤ pH<sub>KCl</sub> &lt; 6.5</b>	S <sub>CR</sub>	+ Optional**		
<b>4.5 ≤ pH<sub>KCl</sub> &lt; 5.5</b>	S <sub>CR</sub>	+ s-TAA		
<b>pH<sub>KCl</sub> &lt; 4.5</b>	S <sub>CR</sub>	+ s-TAA	+ s-S <sub>NAS</sub>	

An empty field indicates that the determination of that property is not required

\*FF = Fineness factor (at least 1.5)

\*\*s-TAA not required if S<sub>CR</sub> is below action limits for relevant soil texture

**Table A3.2. Chromium suite acid base accounting—acidity units. Analyses required.**

Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
<b>pH<sub>KCl</sub> ≥ 6.5</b> if S <sub>CR</sub> < action limit, do not need ANC	a-S <sub>CR</sub>			– [a-C <sub>IN</sub> /FF]*
	a-S <sub>CR</sub>			– [a-ANC <sub>BT</sub> /FF]*
<b>5.5 ≤ pH<sub>KCl</sub> &lt; 6.5</b>	a-S <sub>CR</sub>	+ Optional**		
<b>4.5 ≤ pH<sub>KCl</sub> &lt; 5.5</b>	a-S <sub>CR</sub>	+ TAA		
<b>pH<sub>KCl</sub> &lt; 4.5</b>	a-S <sub>CR</sub>	+ TAA	+ a-S <sub>NAS</sub>	

An empty field indicates that the determination of that property is not required

\*FF = Fineness factor (at least 1.5)

\*\*TAA not required if S<sub>CR</sub> is below action limits for relevant soil texture

**Table A3.3. SPOCAS suite acid base accounting—sulfur units. Analyses required.**

<b>Net Acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity – measured ANC/FF</b>
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Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
TPA = 0 pH <sub>KCl</sub> ≥ 6.5	S <sub>POS</sub>			– [(S <sub>POS</sub> +s-ANC <sub>E</sub> )/FF]* or – [(s-Ca <sub>A</sub> +s-Mg <sub>A</sub> )/FF]*
TPA >0 pH <sub>KCl</sub> ≥ 6.5	S <sub>POS</sub>			– [(S <sub>POS</sub> – s-TSA)/FF]* or – [(s-Ca <sub>A</sub> +s-Mg <sub>A</sub> )/FF]*
TPA >0 4.5 ≤ pH <sub>KCl</sub> < 6.5	S <sub>POS</sub>	+ s-TAA		
TPA >0 pH <sub>KCl</sub> < 4.5	S <sub>POS</sub>	+ s-TAA	+ **s-S <sub>RAS</sub>	

An empty field indicates that the determination of that property is not required

\*FF = Fineness factor (at least 1.5)

\*\*S<sub>RAS</sub> may alternatively be substituted by S<sub>NAS</sub> if available.

**Table A3.4. SPOCAS suite acid base accounting—acidity units. Analyses required.**

Preliminary Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
TPA = 0 pH <sub>KCl</sub> ≥ 6.5	a-S <sub>POS</sub>			– [(a-S <sub>POS</sub> +a-ANC <sub>E</sub> )/FF]* or – [(a-Ca <sub>A</sub> +a-Mg <sub>A</sub> )/FF]*
TPA >0 pH <sub>KCl</sub> ≥ 6.5	a-S <sub>POS</sub>			– [(a-S <sub>POS</sub> – TSA)/FF]* or – [(a-Ca <sub>A</sub> +a-Mg <sub>A</sub> )/FF]*
TPA >0 4.5 ≤ pH <sub>KCl</sub> < 6.5	a-S <sub>POS</sub>	+ TAA		
TPA >0 pH <sub>KCl</sub> < 4.5	a-S <sub>POS</sub>	+ TAA	+ **a-S <sub>RAS</sub>	

An empty field indicates that the determination of that property is not required

\*FF = Fineness factor (at least 1.5)

\*\*S<sub>RAS</sub> may alternatively be substituted by S<sub>NAS</sub> if available.

### 3.6 VERIFICATION TESTING

The objective when ameliorating ASS with alkaline material is to ensure that there will be no chance that net acidity will be generated from the complete oxidation of any sulfides in these soils. Verification testing is a tool that is used to confirm whether sufficient ameliorant (neutralising agent) has been incorporated into the ASS to prevent any future acidification. During the verification phase of the sampling, soil that has been treated with a neutralising agent such as agricultural lime is analysed. If the results of the verification testing indicate a failure (to comply with the performance criteria for the site), then the soil should be re-treated. The acid base account (and specifically the ABA equation) is used in verification testing to assess whether ASS have the potential to produce net acidity. In the ABA equation, any measured ANC is moderated by the use of a fineness factor (using a minimum of 1.5) to take into account the fineness of the acid neutralising material, reactivity, incomplete mixing, coatings etc.

Verification testing helps ensure that appropriate treatment of ASS has occurred, and provides some security against later accusations of insufficient treatment of these soils/litigation. The more comprehensive the initial soil sampling and site characterisation, and the better the mixing of the neutralising agent, the more likely soils are to pass verification.

When submitting ameliorated samples for analysis it should be made clear to the laboratory that the soil requires verification testing and also whether the soil contained jarosite prior to being ameliorated. The neutralising agent used in amelioration (especially if it is not  $\text{CaCO}_3$ /agricultural lime) is also valuable information to provide to the laboratory and regulatory authorities. The methods in these Guidelines have not been tested for uncommon neutralising agents.

Previously, the TPA result from the POCAS or POCASm methods has been used to assess whether sufficient ameliorant has been added (in the absence at the time of specific methodology for the purpose). A TPA value of zero was typically the benchmark used for verification testing. There are a number of reasons why a TPA result by itself is no longer acceptable. The first reason relates to the need to ameliorate the soil with at least 1.5 times the acid neutralising material theoretically required to neutralise the potential acidity. The TPA by itself cannot assess whether there is sufficient excess acid neutralising present to meet the minimum 1.5 'safety' factor. To do this, a measure of oxidisable sulfur must also be made. Moreover, recent work has shown that TPA in isolation is inadequate because the peroxide digest of POCAS and POCASm does not ensure complete oxidation of sulfides in the presence of large amounts of carbonates. (Hydrogen peroxide oxidation of pyrite is less efficient at alkaline pH in the presence of carbonates) (See Section A2.1b).

#### *a) Using the SPOCAS suite*

The use of the SPOCAS suite and the associated ABA is one option for verification testing. The SPOCAS method overcomes problems with the peroxide digest procedures of POCAS and POCASm by use of a titration with HCl that ensures that complete oxidation of sulfides occurs, as well as quantifying the soil's excess acid neutralising capacity ( $\text{ANC}_E$ ). The  $S_{\text{POS}}$  result can be compared to the  $\text{ANC}_E$  result to determine whether the appropriate safety factor has been achieved.

Obviously, in a properly ameliorated soil, the  $\text{pH}_{\text{KCl}}$  should be  $\geq 6.5$  and TAA equal to zero. Similarly, the  $\text{pH}_{\text{OX}}$  should be  $> 6.5$  and the TPA equal to zero. Additionally, the **net acidity** result from the ABA should be zero or negative (having applied the appropriate fineness factor to the ANC). To see what conditions should be met and what data should be substituted into the ABA, refer to Tables A3.5–A3.6. See Section F1.10 for an example of calculating net acidity from verification testing results using the SPOCAS suite.

**Table A3.5. SPOCAS suite acid base accounting—acidity and sulfur units. Verification.**

UNITS	Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
SULFUR	TPA = 0	S <sub>POS</sub>		–	[(S <sub>POS</sub> +s-ANC <sub>E</sub> )/FF]*
	pH <sub>KCl</sub> ≥ 6.5^^	S <sub>POS</sub>		–	[(s-Ca <sub>A</sub> +s-Mg <sub>A</sub> )/FF]*
ACIDITY	TPA = 0	a-S <sub>POS</sub>		–	[(S <sub>POS</sub> +a-ANC <sub>E</sub> )/FF]*
	pH <sub>KCl</sub> ≥ 6.5^^	a-S <sub>POS</sub>		–	[(a-Ca <sub>A</sub> +a-Mg <sub>A</sub> )/FF]*

An empty field indicates that the determination of that property is not required.

\*FF = Fineness factor (at least 1.5).

^^If an ameliorated soil fails the pH<sub>KCl</sub> criterion (ie. pH<sub>KCl</sub> is <6.5), then the decision tree/flow diagram (Fig. A2.3) should be followed and the net acidity calculated using the relevant equations in Tables A3.3 and A3.4.

### b) Using the Chromium suite

Another approach for verification is to use the Chromium suite of analyses. Again, in a properly ameliorated soil, pH<sub>KCl</sub> should be ≥6.5 and TAA should be zero. The S<sub>CR</sub> result is compared to a measure of soil ANC (either the back-titration approach, ANC<sub>BT</sub>, or measurement of inorganic carbon, eg. C<sub>IN</sub> by induction furnace) and it then can be assessed whether the appropriate safety factor has been met. In any case, if the **net acidity** from the ABA equation is zero or negative (with the appropriate fineness factor applied to the ANC) then the soil has passed verification. There is however an exception to this for soil that contained retained acidity (eg. jarosite) prior to amelioration (see Section A3.5c below). See Section F1.10 for an example of calculating net acidity from verification testing results using the Chromium suite.

**Table A3.6. Chromium suite acid base accounting—acidity and sulfur units. Verification.**

UNITS	Analysis Results	Potential Acidity	Actual Acidity	Retained Acidity	ANC
SULFUR	pH <sub>KCl</sub> ≥ 6.5^^	S <sub>CR</sub>		–	[s-C <sub>IN</sub> /FF]*#
	retained acidity NOT present	S <sub>CR</sub>		–	[s-ANC <sub>BT</sub> /FF]*
	pH <sub>KCl</sub> ≥ 6.5^^	S <sub>CR</sub>		+	s-S <sub>NAS</sub>
	retained acidity present before liming	S <sub>CR</sub>		+	s-S <sub>NAS</sub>
ACIDITY	pH <sub>KCl</sub> ≥ 6.5^^	a-S <sub>CR</sub>		–	[a-C <sub>IN</sub> /FF]*#
	retained acidity NOT present	a-S <sub>CR</sub>		–	[a-ANC <sub>BT</sub> /FF]*
	pH <sub>KCl</sub> ≥ 6.5^^	a-S <sub>CR</sub>		+	a-S <sub>NAS</sub>
	retained acidity present before liming	a-S <sub>CR</sub>		+	a-S <sub>NAS</sub>

An empty field indicates that the determination of that property is not required.

\*FF = Fineness factor (at least 1.5).

#The use of C<sub>IN</sub> is not appropriate where a non-carbonate or oxide neutralising agent has been used (see Section 3.3).

^^If an ameliorated soil fails the pH<sub>KCl</sub> criterion (ie. pH<sub>KCl</sub> is <6.5), then the decision tree/flow diagram (Fig. A2.2) should be followed and the net acidity calculated using the relevant equations in Tables A3.1 and A3.2. If pH<sub>KCl</sub> is <4.5, retained acidity obviously also needs to be measured.

*Note: This approach can be slightly modified, for example by the substitution of another estimate of sulfide content in place of the S<sub>CR</sub> value (eg. S<sub>TOS</sub>).*

*c) Jarosite complications*

A complication arises when soil material that contains jarosite (and similar minerals) is treated with low solubility alkaline products such as agricultural lime ( $\text{CaCO}_3$ ). Jarosite and  $\text{CaCO}_3$  should not naturally co-exist in a soil at equilibrium. In a lime-treated soil material that contained jarosite, there may have been insufficient time and/or moisture for all the jarosite to hydrolyse/decompose and reach equilibrium. Hence, in a lime-treated soil, field and lab pH are likely to be poor indicators of the presence or absence of jarosite. This means that even if the  $\text{pH}_{\text{KCl}}$  is  $\geq 6.5$  in the TAA analysis (because of the presence of carbonate), one cannot be sure that the long-term equilibrium pH will not be strongly acidic. Kinetic factors mean that jarosite may not have had sufficient time to react.

In the peroxide digest of the SPOCAS suite, most or all of the jarosite dissolves/reacts in the presence of excess  $\text{CaCO}_3$ . Under these conditions the retained acidity is neutralised by the ameliorant present. Thus an  $\text{ANC}_E$  result will have accounted for retained acidity (unlike other measures of ANC, eg.  $\text{ANC}_{\text{BT}}$  and  $\text{C}_{\text{IN}}$ ).

If using the chromium suite on treated soil that contained jarosite, the situation is slightly different. It is necessary to measure  $\text{pH}_{\text{KCl}}$  (and TAA if the  $\text{pH}_{\text{KCl}}$  is  $< 6.5$ ), as well as  $S_{\text{KCl}}$  and  $S_{\text{HCl}}$  (in order to calculate  $S_{\text{NAS}}$ ). The measurement of  $S_{\text{NAS}}$  is necessary as the estimation of ANC by either the inorganic carbon method ( $\text{C}_{\text{IN}}$ ) or the back-titration method ( $\text{ANC}_{\text{BT}}$ ) are essentially unaffected by the presence or absence of jarosite. Therefore retained acidity also needs to be measured by  $S_{\text{NAS}}$  in this situation.

In summary, if the SPOCAS suite is used for verification of treated soil material, it is not necessary to know whether jarosite is present as the results will account for the presence of jarosite. In contrast, if the chromium suite is used it is essential that the laboratory be notified that jarosite may be present and that  $S_{\text{KCl}}$  and  $S_{\text{HCl}}$  are measured. Failure to take  $S_{\text{NAS}}$  into account could result in an erroneous acid base account. If you are unsure of the jarosite status of the soil either use the SPOCAS suite for verification, or alternatively include measurement of  $S_{\text{NAS}}$  if using the chromium suite.

**3.7 PRESENTATION OF RESULTS**

With the multitude of results generated by ASS methods and the need to perform various calculations and conversions so that results are in the appropriate units to allow the construction of an acid base account, the way in which these results are presented is an important consideration. A standard format (or standard formats) for the presentation of laboratory data, or at least a consistent order in which analytes are listed in spreadsheets has advantages for laboratories, their clients, consultants and regulators. Suggested formats for SPOCAS and chromium suites and combined data (as well as field data) are provided in the Appendix (Section I, Tables I1.1–I1.3). Excel template files for calculation of an acid base account will be available by contacting Kristie Watling (e-mail [Kristie.Watling@nrm.qld.gov.au](mailto:Kristie.Watling@nrm.qld.gov.au)) or Angus McElnea (e-mail [Angus.McElnea@nrm.qld.gov.au](mailto:Angus.McElnea@nrm.qld.gov.au)), QASSIT Qld Department of Natural Resources and Mines, Gate 2, Block C, 80 Meiers Road, Indooroopilly Qld 4068.

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