

**DRAFT IDENTIFICATION  
AND INVESTIGATION OF  
ACID SULFATE SOILS**

**Acid Sulfate Soils Guideline  
Series**

Prepared by  
Land & Water Quality Branch

DEPARTMENT OF ENVIRONMENT

DRAFT FOR COMMENT

May 2006

# Notice

This guideline may be applicable to decision-making authorities, proponents, consultants and other interested parties involved in the planning, development and land use of areas potentially containing acid sulfate soils. The DoE should be consulted where guidance on policy issues is not covered in this guideline or where further clarification and explanation is required.

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# Acknowledgments

The Department of Environment would like to acknowledge the guidelines and manuals produced by the following committees and organisations that were used in the development of this guideline:

- Queensland Acid Sulfate Soils Investigation Team;
- Queensland Acid Sulfate Soil Management Advisory Committee;
- NSW Acid Sulfate Soils Management Advisory Committee;
- National Committee for Acid Sulfate Soils; and
- Southern Cross University.

## Preface

This guideline forms part of a comprehensive statutory and policy framework for the identification, assessment and management of acid sulfate soils in Western Australia.

The Acid Sulfate Soils Guideline Series contains the following guidelines:

- Preparation of Acid Sulfate Soil Management Plan (April 2003)
- Guidance for groundwater management in urban areas on acid sulfate soils (October 2004)
- Treatment and management of disturbed acid sulfate soils (October 2004)

Other guidelines include:

- General guidance on managing Acid Sulfate Soils (August 2001)
- Is my house built on Acid Sulfate Soils? (Draft) (June 2004)
- Proposed Framework for Managing Acid Sulfate Soils (June 2004)

Copies of these guidelines are available from the DoE's website at [www.environment.wa.gov.au](http://www.environment.wa.gov.au).

### **We welcome your feedback**

A publication feedback form can be found at the back of this publication.

**If you wish to make comment on this document please forward written comments by 1 September 2006 to:**

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The recommended reference for this publication is: Identification and Investigation of Acid Sulfate Soils, Department of Environment, Government of Western Australia, Acid Sulfate Soils Guideline Series, May 2006.

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# 1 Introduction

Acid Sulfate Soils (ASS) are naturally occurring soils, sediments or organic substrates (e.g. peat) formed under waterlogged conditions that contain iron sulfide minerals (predominantly as the mineral pyrite) or their oxidation products. When exposed to air due to the lowering of the watertable (e.g. dewatering, groundwater abstraction or drainage), or by excavation, the sulfides in these soils readily oxidise, releasing sulfuric acid and iron into the soil and groundwater, often in harmful quantities. This acid can, in turn, release aluminium, nutrients and heavy metals (particularly arsenic) held within the soil matrix.

Once mobilised in this way, the acid, metals and nutrients can seep into waterways, killing fish, other aquatic organisms and vegetation, and can degrade concrete and steel pipes and structures to the point of failure.

It is estimated that there are more than 90,000 square kilometres of naturally occurring acid sulfate soils throughout Australia of which about 77,500 km<sup>2</sup> of land has a high probability of containing ASS (NatCASS, 2006). More than 30% of Australia's acid sulfate soils are located in coastal Western Australia.

The disturbance of ASS can cause environmental harm. Causing serious or material environmental harm is an offence under the *Environmental Protection Act 1986*.

## 2 Purpose of this Guideline

The purpose of this guideline is to provide practical guidance in relation to the minimum level of investigation required to:

- identify the presence or the absence of ASS in areas to be potentially disturbed by a proposed development or other project; and if present
- define the nature and extent of ASS and the likely amount of existing and potential acidity in order to determine appropriate management measures.

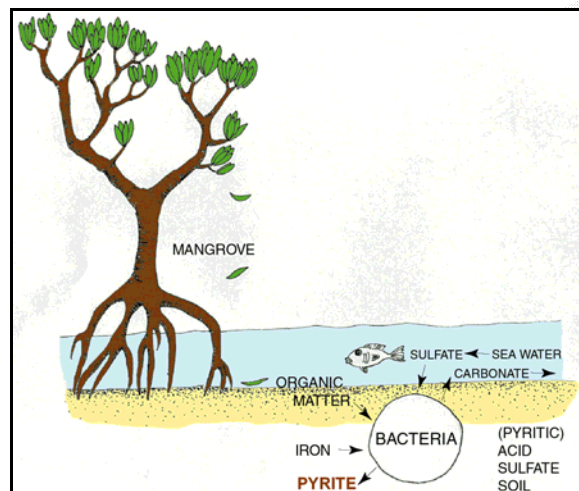
This document provides information on the identification and investigation of ASS. Guidance on management measures for acid sulfate soils can be obtained from the document entitled *Treatment and management of acid sulfate soil disturbance*. **(Insert reference when new management guideline is finalised)**

This guideline should be used in conjunction with any other relevant guidelines (including the DoE's *Contaminated Sites Management Series*), standards and information sources as well as professional experience and judgement to develop the most appropriate investigation program for a site.

## 3 Background Information

### 3.1 Acid Sulfate Soils Formation

In Australia, the soils/sediments which are of most concern are those which formed within the last 10,000 years, after the last major sea level rise. When the sea level rose and inundated the land, sulfate in the seawater mixed with land sediments containing iron oxides and organic matter (Figure 1). The resulting chemical reaction produced large quantities of iron sulfides in waterlogged environments.



**Figure 1: Iron sulfides such as pyrite are formed in sediments of coastal lowlands where there is sufficient sulfur present. The sulfides are stable until exposed to air at which point they produce sulfuric acid.**

For the purposes of this guidance, the term 'Acid Sulfate Soils' (ASS) includes both Potential Acid Sulfate Soils (PASS) and Actual Acid Sulfate Soils (AASS).

- Potential acid sulfate soils (PASS) are soils or sediments which contain iron sulfides and/or other sulfidic minerals that have not been oxidised by exposure to air. The field pH of these soils in their undisturbed state is more than pH 4 and is commonly neutral to alkaline (pH 7 to pH 9). These soils or sediments are invariably saturated with water in their natural state. The waterlogged layer may be peat, clay, loam, silt, or sand and is usually dark grey and soft but may also be dark brown, or medium to pale grey to white.
- Actual acid sulfate soils (AASS) are soils or sediments which contain iron sulfides and/or other sulfidic minerals that have previously undergone some oxidation to produce sulfuric acid. This results in existing acidity (pH <4) and often a yellow and/or red mottling (jarosite/iron oxide) in the soil profile. AASS commonly also contain residual un-oxidised iron sulfides or potential acidity as well as existing acidity.

### 3.2 Distribution of Acid Sulfate Soils in Western Australia

Acid Sulfate Soils are widespread around coastal regions of the State, and are also locally associated with freshwater wetlands and saline sulfate rich groundwater in some agricultural areas.

In Western Australia, shallow ASS are known to be present in the following general locations:

- riverine, estuarine and coastal lowland areas such as mangroves, brackish lakes, tidal flats, salt marshes, salt pans, swamps and seasonally inundated plains;
- wetland areas;
- saline inland areas;
- between the Moore River and Dunsborough on the Swan Coastal Plain, over 10% (or 88,000 Ha) is considered to have a risk of shallow ASS formations, while about 60% (around 430,000 Ha) have ASS at depth of more than 3 metres below surface; and
- on the Scott Coastal Plain, extensive areas of shallow ASS up to 40 metres above sea level have been identified.

Particular areas of concern in Western Australia include:

- Peaty wetlands in the Perth Metro such as Stirling, Gwelup, Bayswater and Ashfield;
- Estuarine, floodplain, damp land and seasonal wetland areas between Perth and Dunsborough, such as the Peel-Harvey estuarine system, Leschenault and the Vasse-Wonnerup estuarine system;
- Tidal, intertidal and supratidal flats along the northern coastline, including the Pilbara and Kimberley coasts;
- The Scott Coastal Plain; and
- Parts of the Wheatbelt where secondary land salinisation has occurred.

The Department of Environment (DoE) has produced ASS Risk Maps for the Swan Coastal Plain and for the Albany-Torbay region. For more information see section 4.1.

In general, ASS can be found in the following areas:

- a) Areas depicted on geology and/or geomorphological maps as geologically recent such as:
  - i) shallow tidal flats or tidal lakes
  - ii) shallow estuarine, shallow marine deposits
  - iii) stranded beach ridges and adjacent swales
  - iv) interdune swales or coastal sand dunes
  - v) coastal alluvial valleys
  - vi) wetlands
  - vii) floodplain
  - viii) waterlogged areas
  - ix) scalded areas
  - x) sump land
  - xi) marshes
  - xii) swamps
- b) Areas depicted in vegetation mapping as:
  - i) mangroves
  - ii) wetland dependent vegetation such as reeds and paperbarks (*Melaleuca spp.*)
  - iii) areas where the dominant vegetation is tolerant of salt, acid and/or waterlogging conditions e.g. mangroves, saltcouch, swamp-tolerant reeds, rushes, paperbarks and swamp oak (*Casuarina spp.*)
- c) Areas identified in geological descriptions or in maps as:
  - i) bearing acid sulfide minerals
  - ii) former marine or estuarine shales and sediments

- iii) coal deposits
- iv) mineral sand deposits
- d) Areas known to contain peat or a build up of organic material.
- e) Areas where the highest known watertable level is within three (3) metres of the surface.
- f) Land with elevation less than 5 metres above Australian Height Datum (AHD).
- g) Any areas in Western Australia (including inland areas) where a combination of all the following pre-disposing factors exist:
  - i) organic matter
  - ii) iron minerals
  - iii) waterlogged conditions or a high watertable
  - iv) sulfidic minerals
  - v) deep estuarine sediments below ground surface.

The extent of inland ASS is largely unknown and research into their behaviour is limited.

### 3.3 Other Potentially Problematic Acid-generating Substrates

Some types of soils or subsurface substrates, whilst perhaps not fitting the traditional description of ASS, nonetheless have some acid generating potential and can release a significant amount of acidity and/or iron when disturbed. These soils, which are outlined below, have many of the same properties as ASS and subsequently should be investigated and managed as would be ASS.

#### 3.3.1 Recent Sand Units - Pale Grey Sands and Iron Cemented Organic Rich Sands (Coffee Rock)

Recent experience has indicated that dewatering or other disturbance of some sand units (including Bassendean Sands and Spearwood Sands) often results in acidification of the shallow groundwater aquifer and the mobilisation of iron, aluminium and other metals into the groundwater system and/or the surrounding environment.

Of particular concern are variably cemented iron and/or organic rich sands (commonly referred to as "coffee rock"). These sands may be shallow ('B' horizon<sup>1</sup>), but may also form deeper within profiles (particularly in areas mapped as medium ASS risk). Coffee rock forms by the precipitation of humates and iron from groundwater mainly in the zone of watertable fluctuation units and may vary between bright orange, orange-brown and dark brown to black.

Laboratory analyses indicate that coffee rock horizons contain stored potential acidity in a number of forms. They may contain inorganic sulfides, including di-sulfides (pyrites) and iron mono-sulfides; as well as potential acidity stored in poorly crystalline and easily hydrolysable iron and manganese oxides. Oxygen transported into such layers, by either convective transport or direct exposure to air by lowering of ground-water levels, can result in the oxidation of such minerals and the generation of acidity.

To date, investigations have identified sulfur concentrations of up to 0.72 % w/w (weight for weight) in coffee rock horizons. As with all potentially acidic soil materials when waterlogged, the coffee rock unit itself may be acidic to slightly alkaline (Field pH 4.1 to 9.0/ p<sub>H</sub><sub>KCl</sub> 3.2 to 8.3) (Degens and Wallace-Bell, *in press*).

<sup>1</sup> **B HORIZON:** Subsoil horizons consisting of one or more mineral layers differing to the A Horizon by: clay, iron, aluminium or organic matter concentrations; structure and/or consistence; and colour.

The 'A' horizon<sup>2</sup> of these coffee rock soil profiles is typically pale grey to white quartz sands, with a heavily leached appearance and little silt or clay. The 'A' horizon is often moderately acidic but may be alkaline (pH 4-10) and may also contain small amounts of sulfides, mobilised from the 'B' horizon. Sulfur concentrations of up to 0.87 % w/w in Bassendean Sand 'A' horizons have been reported to DoE.

The shallow groundwater aquifers associated with coffee rock soil profiles typically also contain dissolved hydrogen sulfide and organic carbon.

Due to the geochemical complexity of acid storage and release in coffee rock soil profiles, current investigation techniques may be underestimating the amount of acid generating potential within these profiles which typically possess nil to negligible buffering capacity. For example iron in both jarosite and schwertmannite can undergo hydrolysis and result in the release of acidity into the receiving environment. It is recommended that the acid released through transformation of meta-stable schwertmannite and jarosite to goethite should be incorporated into acid base accounting models (Sullivan & Bush, 2004).

### 3.3.2 Dredge spoil

Many estuaries in the urban areas including canal developments are dredged periodically to maintain the required water depths. Where sediments contain high concentrations of pyrite, or contain highly reactive iron monosulfides, they require innovative disposal techniques that minimise sulfide oxidation. Inappropriate disposal of estuarine sediments including dredge spoils can also provide ideal conditions for secondary pyrite formation. As the sediments age, there will be an increase in pyrite content due to sulfate reduction while the carbonate buffering capacity is depleted over time. Older dredge spoils have little or no buffering capacity and if these sediments are disturbed and exposed on a large scale, sulfide oxidation will quickly deplete the limited bicarbonate buffering capacity and cause offsite impact with large amounts of acidic and potentially metal-rich waters.

## 3.4 ASS Disturbance Processes

Acid sulfate soils are benign when in a waterlogged environment. However, when these soils are drained or excavated, oxygen from the atmosphere reacts with the iron sulfides in the soil. This results in the production of sulfuric acid. The acid can cause a breakdown of the soil structure releasing aluminium and other metals, precipitates and nutrients, which remain in the soil until rainfall or groundwater flow is sufficient to leach them out. The acid and metals may then be mobilised into groundwater aquifers, and into nearby water bodies, often with deleterious environmental and economic impacts.

Projects and developments in ASS risk areas which involve excavation, lowering of the watertable (temporarily or permanently), compaction of saturated soils or sediments and/or lateral displacement of previously saturated sediments may adversely disturb ASS.

The types of development which may cause acid sulfate soil problems include, but are not restricted to:

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<sup>2</sup> **A HORIZONS:** The surface mineral horizons where some have organic matter accumulation. They are usually darker in colour than the lower horizons. If they are lighter in colour, then the horizons have lower silicate clay content .

- urban developments such as residential estates, canal estates, tourist developments, marinas and golf courses;
- dewatering operations;
- drainage works;
- groundwater abstraction;
- ditching for mosquito control;
- artificially deepening lakes, waterways and wetlands;
- de-sludging or other cleaning of open drains;
- removal or mining of sulfidic peat;
- infrastructure projects such as canals, bridges, roads, port facilities, flood gates, dams, rail tunnels and detention basins;
- mining and quarrying operations;
- dredging operations;
- developments involving disturbance to wetlands, mangrove swamps, salt marshes, lakes and waterways;
- rural drainage which lowers the watertable;
- flood mitigation works including construction of levees;
- compacting saturated soils or sediments, ie through pre-loading;
- laterally displacing previously saturated sediments, resulting in groundwater extrusion and aeration of ASS; and
- aquaculture developments, such as prawn farms in mangrove communities.

### 3.5 Potential Impacts of the Disturbance of ASS

The disturbance of ASS has the capacity to directly impact upon the basic natural assets of soil, water, and biota, and thus may affect agriculture, fishing, aquaculture, recreation, tourism, as well as human health and visual amenity. The environmental, social and economic consequences that may result include:

- soil acidification;
- adverse changes to the quality of soil and water (groundwater, surface water, wetlands, watercourses and estuaries);
- degradation of wetlands, water-dependant ecosystems and ecosystem services;
- loss of habitat and biodiversity;
- invasion and dominance of wetlands and waterways by acid-tolerant water plants and plankton species;
- reduction of soil stability and fertility;
- loss of/deterioration in quality of water sources for stock, irrigation and human use by increasing acidity and heavy metal concentrations;
- creation of acid surface scalds in discharge areas;
- loss of visual amenity by rust coloured stains, scums and slimes from iron precipitates;
- risk of long-term infrastructure damage through acidic water corroding metallic and concrete structures (concrete cancer) such as roads, bridges, pumps, sub-surface pipes, retaining walls, brick course work and foundations;
- blockage of reticulation systems and other small pipe systems by iron precipitates;
- acidification of surface water bodies increasing mosquito breeding, which may increase the prevalence of mosquito-borne diseases such as Ross River virus; and
- increased financial burden of treating and rehabilitating affected areas, and maintenance of infrastructure.

The impacts of ASS leachate may persist over a long time, or peak seasonally (after dry periods with the first drought-breaking rains). In some areas of Australia, ASS drained 100 years ago is still releasing acid (Sammut, 2000).

Any works in areas containing ASS should be governed by the guiding principle that the disturbance of acid sulfate soils should be avoided wherever possible.

The accurate identification of ASS and their associated risk is the first step to ensure that disturbance of land containing ASS is planned and managed to avoid potential adverse effects on the natural and built environment.

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## 4 When Do Sites Need to be Investigated for Acid Sulfate Soils?

Investigations to determine the presence and distribution of ASS should ideally be undertaken in the early stages of land-use planning processes (e.g. Structural Planning). Identification of ASS at this stage will allow the design of development works to be modified so as to avoid or minimise the disturbance of ASS.

Proponents proposing to carry out developments which involve ground disturbance or a change of groundwater levels in areas susceptible to ASS, as listed in Section 3.2, need to conduct investigations to determine whether or not ASS are present and, if so, to fully characterise their nature and extent (WAPC, 2003). ASS investigations should be undertaken prior to the disturbance of any soil, surface water or groundwater.

Sites should be investigated for acid sulfate soils if **any** of the following works are proposed:

- soil or sediment disturbance greater than 100m<sup>3</sup> in the ASS high risk areas (e.g. construction of roads, foundations, drainage works, land forming works, dams and aquaculture ponds or sand or gravel extraction);

or

- lowering of the watertable, whether temporary or permanent (e.g. for groundwater abstraction, dewatering, installation of new drainage, modification to existing drainage) in areas depicted in the ASS risk map as “high risk of AASS or PASS occurrence” or dewatering operations in areas depicted in the ASS risk map as “moderate to low risk of AASS or PASS occurrence” within 500m from the high risk areas;

or

- Where there is evidence of a significant risk of disturbing acid sulfate soils in the Moderate to Low Risk areas exceeding 3.0m below natural surface

or

- any dredging operations;
- extractive industry works (e.g. mineral sand mining); or
- flood mitigation works including construction of levees and flood gates;

or

- in **any** of the areas listed in Section 3.2.

### 4.1 Risk Maps

The DoE has compiled ASS risk maps for several regions of Western Australia which provide a broad-scale indication of the areas where ASS are most likely to exist. The majority of these ASS risk maps are based on review of existing geomorphological, geological and hydrological information. In coastal fringes of the lower Swan Coastal Plain, on-ground landscape investigations have been carried out to improve mapping of the high risk areas. At the time of publication, risk maps have been produced for the Swan Coastal Plain and the Albany/Torbay

area. Mapping projects are continuing in other key areas of WA including the lower south-west, the Scott Coastal Plain, and the Albany–Denmark Coastal region and limited north-west coastal areas. For further information contact the Land and Water Quality Branch of the DoE.

It needs to be emphasised that the risk maps are designed to be used for broad-scale planning purposes and are not appropriate for use at an individual property level. The maps should be read at the scale of their intended use, 1:50,000.

The ASS risk maps are not intended to provide site specific ASS information. The information derived from the maps cannot be used in the assessment of the potential to effectively manage ASS in a particular development.

When using ASS risk maps, the following must always be kept in mind:

- Extreme variations in the nature and distribution of ASS can be expected; and
- Depth to the ASS layer can be highly variable. The depths indicated should be used as a guide only and not used for specific assessment of development potential.

Digital versions of the ASS risk maps, compatible with standard GIS systems, are available for purchase from the DoE (contact Information Services Branch). Hard copies of the ASS Risk Map for the Swan Coastal Plain are included within the Western Australian Planning Commission's (WAPC) publication "WAPC Planning Bulletin 64" available directly from the WAPC.

Use of the ASS risk map will not replace the need to undertake a detailed desktop assessment and site inspection.

## 4.2 Investigation Process

A two- to three-step investigation process will usually be required:

- Step 1: Desktop Assessment and Site Inspection
- Step 2: Soil Sampling
- Step 3: Laboratory Analysis
- Step 4: Reporting Results

Proponents should allow sufficient project timing to ensure that ASS investigations are finalised well before earth works commence.

The ASS Investigation Process is illustrated in Figure 2.

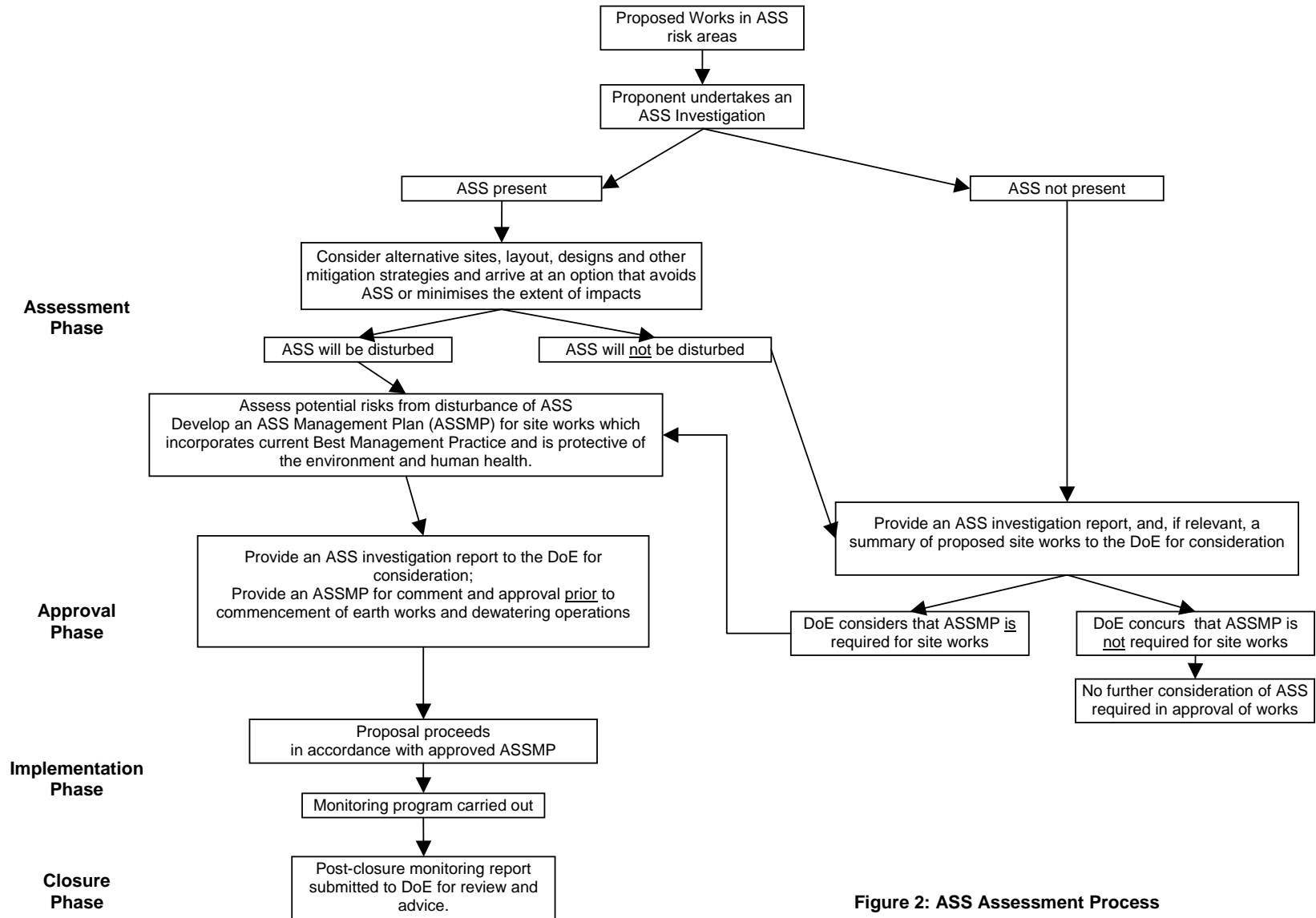


Figure 2: ASS Assessment Process

# 5 Step 1: Desktop Assessment and Site Inspection

Step 1 involves a desktop assessment and a site visit to identify indicators of ASS. A minimum of 3 to 4 weeks should be allowed for completion of this stage of the investigation.

## 5.1 Desktop assessment

The desktop assessment is a preliminary appraisal of ASS risk within the project area. This involves gathering information from ASS risk maps, generic soil maps, environmental geological maps, topographic maps, aerial photographs and other local investigations or environmental impact reports to assess the likelihood of ASS occurrence.

## 5.2 Site inspection

In all cases, a site inspection should be undertaken to support the findings of the desktop assessment. The site inspection should include, as a minimum:

- Visual assessment of topography and geomorphology;
- Visual assessment of surface water and hydrology;
- Visual assessment of prevalent plant communities; and
- Examination of surface soils and the soil profile (hand auger may be sufficient at this stage).

When reporting on a site assessment, it is important to describe the area of the total site, with emphasis on the area of any proposed disturbance. As ASS do not recognise property boundaries, it is important to also inspect the surrounding area.

When inspecting a site, consideration should be given to the identification of both potential acid sulfate soils (PASS) and actual acid sulfate soils (AASS). Also note that it is common to have an AASS that also contains some un-oxidised iron sulfides, or potential acidity.

Table 1 provides a list of soil, water and vegetation indicators that are suggestive of the presence of ASS. Some of the indicators will only be visible when boreholes are drilled/dug/augered.

Table 1: Indicators of ASS

<b>Soil Type</b>	<b>Indicators</b>
<b>Potential Acid Sulfate Soil (PASS)</b>	<p><b>Soil characteristics</b></p> <ul style="list-style-type: none"> <li>• waterlogged soils – unripe muds (soft, sticky and can be squeezed between fingers, blue grey or dark greenish grey mud with a high water content), silty sands or sands (mid to dark grey) or bottom sediments (dark grey to black e.g. iron monosulfides “black oozes”) possibly exposed at sides and bottom of drains or cuttings, or in boreholes;</li> <li>• peat or peaty soils;</li> <li>• coffee rock horizons; or</li> <li>• a sulfurous smell e.g. hydrogen sulfide or ‘rotten egg’ gas.</li> </ul>

	<p><b>Water characteristics</b></p> <ul style="list-style-type: none"> <li>• waterlogged soils;</li> <li>• water pH usually neutral but may be acidic; or</li> <li>• oily looking iron bacterial surface scum (the similar appearances of iron bacterial scum and a hydrocarbon slick can be differentiated by disturbing the surface with a stick: bacterial scum will separate if agitated whereas a hydrocarbon slick will adhere to the stick upon removal).</li> </ul> <p><i>NB: Caution should be taken when inspecting highly altered landscapes in the field (e.g. where inert fill has been placed over ASS material, dredge spoil, etc). Soil, water and landscape indicators may be masked by past landscape and drainage modifications and this should be taken into consideration when determining borehole locations.</i></p> <p><b>Vegetation characteristics</b></p> <ul style="list-style-type: none"> <li>• Dominant vegetation is tolerant of salt, acid and/or waterlogging conditions e.g. mangroves, saltcouch, <i>Phragmites</i> (a tall acid tolerant grass species), swamp-tolerant reeds, rushes, paperbarks (<i>Melaleuca spp.</i>) and swamp oak (<i>Casuarina spp.</i>).</li> </ul>
<p><b>Actual Acid Sulfate Soil (AASS)</b></p>	<p><b>Soil characteristics</b></p> <ul style="list-style-type: none"> <li>• presence of corroded shell;</li> <li>• sulfurous smell e.g. hydrogen sulfide or 'rotten egg' gas; and</li> <li>• any jarositic horizons or substantial iron oxide mottling in surface encrustations or in any material dredged or excavated and left exposed.</li> </ul> <p><b>Water characteristics</b></p> <ul style="list-style-type: none"> <li>• water of pH &lt;5.5 (and particularly below 4.5) in surface water bodies, drains or groundwater (this is not a definitive indicator as organic acids may contribute to low pH in some environments such as <i>Melaleuca</i> swamps);</li> <li>• unusually clear or milky blue-green water flowing from or within the area (aluminium released by ASS acts as a flocculating agent);</li> <li>• extensive iron stains on any drain or pond surfaces, or iron-stained water and ochre deposits; and</li> <li>• oily looking bacterial surface scum (differentiated from a hydrocarbon slick of similar appearance as described for PASS).</li> </ul> <p><b>Vegetation characteristics</b></p> <ul style="list-style-type: none"> <li>• dead, dying, stunted vegetation*;</li> <li>• scalded or bare low-lying areas*;</li> <li>• poor vegetation regrowth in previously disturbed areas.</li> </ul> <p><b>Infrastructure</b></p> <ul style="list-style-type: none"> <li>• corrosion of concrete and/or steel structures* (including foundations, fences, masonry/brick walls, pipes).</li> </ul> <p><i>* May also be due to excessive salinity or to salinity in combination with AASS.</i></p>

Often AASS will directly overlay PASS, with the fluctuating watertable level marking the boundary between the two units.

If the results of the desktop assessment and site inspection suggest that ASS may be present, or the results are inconclusive, an intrusive investigation involving soil sampling and analysis should be undertaken.

The only instances in which soil sampling and laboratory analysis would not be required are:

- a) where soils and groundwater at a site will not be disturbed; and/or
- b) where the findings of the desktop assessment and site inspection show no indications of ASS.

An example of the latter would be: no geomorphological, hydrological or vegetation indicators were identified and inspection of the soil profile found it comprised of clean yellow quartz sand overlying Tamala Limestone to at least one metre beyond the maximum expected depth of disturbance; or no geomorphological, hydrological or vegetation indicators were identified and inspection of the soil profile found it comprised white sand to at least one metre beyond the maximum expected depth of disturbance.

In these instances the proponent may submit this evidence (i.e. desk top assessment report, photographs and detailed soil description) to support non-completion of soil sampling and laboratory analysis.

## 6 Step 2: Soil Sampling

The Soil Sampling and Laboratory Analysis (Step 2) stage of an ASS assessment comprises the collection and analysis of soil samples from the site and interpretation of these results.

An estimated minimum of 1 to 3 months should be allowed for completion of this stage of the investigation.

The aim of Step 2 is to:

- 1) conclusively determine whether or not ASS are present; and if present,
- 2) to delineate the lateral and vertical extent of ASS horizons;
- 3) quantify the maximum amount of existing and potential soil acidity that will require treatment and management if ASS is disturbed; and
- 4) gather data upon which to base the development of effective management strategies for any ASS disturbance.

### 6.1 Occupational health and safety considerations

It is important to note that there are occupational health and safety issues related to intrusive investigations for ASS, particularly in regard to digging soil inspection pits, working around drill rigs, use and handling of hydrogen peroxide and dangers associated with hydrogen sulfide gas poisoning.

The *Occupational Safety and Health Act 1984* places a clear obligation on a person to ensure the safety and health of anyone they engage to do work (such as drillers, earthmoving contractors and consultants). It is therefore recommended that Health, Safety and Environment Plans (HSEPs) be produced and the contents adequately communicated to all site personnel prior to the commencement of site works.

Any risks to the public, such as adjacent landowners/occupants, should also be identified and measures implemented to minimise them.

Guidance on the contents of HSEPs can be obtained from the Department of Consumer and Employment Protection website ([www.safetyline.wa.gov.au](http://www.safetyline.wa.gov.au)).

### 6.2 Minimum number of sampling locations required

The minimum number of sampling locations required is dependant on the area (hectares) of the site to be disturbed, or for linear disturbances, the length.

Table 2 summarises the minimum number of sample locations required for non-linear and linear disturbances.

Table 2: Minimum number of sample locations required

Type of disturbance	Extent of site project	Number of sampling locations
Non-linear	Project Area	
	< 1 ha	4
	1 – 2 ha	6
	2 – 3 ha	8
	3 – 4 ha	10
	> 4 ha	2 per hectare
Linear	Minor <sup>3</sup> width and volume and low S (%)	@ 100 m intervals
	Major <sup>4</sup> width and volume and/or high S (%)	@ 50 m intervals

The sampling location density outlined in Table 2 relates to the pre-design phase, as opposed to sampling requirements after the project design has been established and a management plan needs to be developed (See Section 8 for guidance on requirements for further investigations to support management plans).

For projects disturbing small volumes (<1,000m<sup>3</sup>) or existing stockpiles of ASS, see Section 6.8.

*For large projects (>50 ha) the DoE may accept reduced sampling densities, providing the investigation program is designed to satisfactorily characterise the various geological/geomorphological units at a site.*

### 6.3 Location of sampling points

The findings of the Desktop Assessment and Site Inspection should be used in conjunction with an understanding of the nature of the development disturbance to judge the best locations for investigative boreholes. Undertaking a mapping exercise, which seeks to delineate the lateral and vertical extent of ASS horizons, is usually more useful than a grided sampling pattern, particularly for large project areas.

Factors to consider when deciding upon sample locations include:

- nature of the disturbance (e.g. excavation, dewatering, drainage, surcharging);
- specific location or locations of disturbance (including any underground service pipes such as sewerage or drains);
- total area of the site to be disturbed;
- volume of material to be disturbed;
- maximum depth of disturbance;
- topography/geomorphology;

<sup>3</sup> Minor Linear Disturbance – e.g. underground infrastructure, pipe lines, narrow shallow drains (<1 metre below ground level; mBGL)

<sup>4</sup> Major Linear Disturbance – e.g. roads, railways, canals, deep sewer, wide or deep drains, dredging projects

- sensitivity of the surrounding environment;
- location of sensitive environmental receptors; and
- estimated extent of cone of depression during dewatering.

Soil sampling locations should be representative of the site, and particularly of the area of disturbance. Care should be taken to ensure representative samples are collected especially on sites with more than one type of geological/geomorphological unit, or clearly different land surface elevations, so that sampling is representative of the entire area.

## 6.4 Depth of sampling points

Soil sampling locations need to extend to at least 1 metre below the maximum depth of disturbance.

Where alteration of groundwater levels by drainage, pumping, etc. is envisaged, then sampling to at least 1m below the depth of the lowest estimated groundwater level should be completed.

## 6.5 Sampling equipment

Choice of equipment for sample collection depends on the sensitivity of the site, soil texture, soil moisture, sampling depth required, and accessibility.

A range of manual and mechanical equipment is available for soil sampling including a variety of drilling rigs (usually tracked) which are able to drill on soft ground. In some instances, where soils are very soft, hand augering may be most appropriate.

## 6.6 Soil sampling procedure

The following information should be recorded as part of the soil sampling procedure:

- the full grid reference of each sampling location using Australian Metric Grid and its current surface height (AHD);
- the exact location of each sampling location shown on an appropriately scaled map;
- an exact description of the vertical dimensions of the borehole or test pit relative to existing surface height and AHD, so that accurate cross-sections can be produced;
- a brief description of the equipment and methods used to retrieve the samples;
- a field description for each soil profile including:
  - soil texture, grain size, roundness, sorting and sphericity using the Australian Soil and Land Survey Field Handbook (McDonald *et al.*, 1990) as a guide;
  - colour using a Munsell colour chart; and
  - mottling, organic matter, moisture content, watertable level and other diagnostic features (e.g. jarosite, shell);
- photographs of the soil profile clearly identifying each strata in the soil profile.

An example of a field log is presented as Table 8. Once boreholes have been drilled and/or test pits dug, and the profiles described and photographed, soil samples should be collected from each profile. Starting from the present ground surface, soil samples should be collected at intervals not exceeding 0.25 m intervals down the profile. Where individual soil units or soil horizons are encountered with a thickness of less than 0.25 m, sampling frequency should be increased to ensure that at least one sample is collected from each unit or horizon. Figure 3 shows correct sample collection from a hypothetical soil profile.

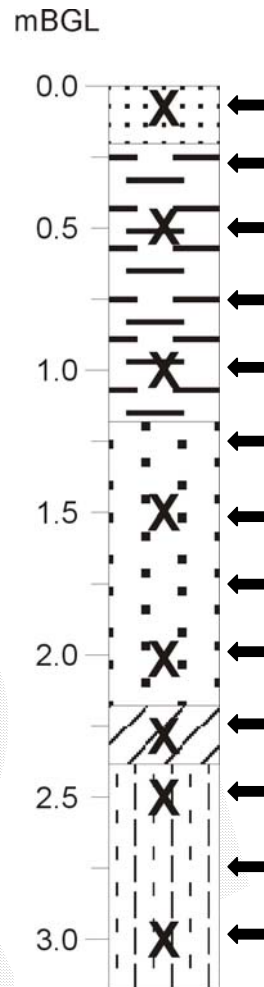


Figure 3: Correct sample collection (←) and laboratory analysis (X) from a hypothetical soil profile.

The field operator should identify any significant changes with depth down the profile in field description properties (such as colour, texture, moisture content, field  $pH_F$  and  $pH_{FOX}$  test results etc.). Soils with clearly different physical, visual or chemical properties should not be 'bulked' together, as this will affect how the laboratory results can be interpreted. Again, field personnel should keep in mind that investigations should aim to fully characterise each soil unit at the site.

Ideally, each soil sample should constitute 200-500 grams to allow sufficient sample mass for physical and chemical analysis. It is important to note that compositing over too large a vertical interval to achieve this sample weight will tend to skew results. The absolute mass required will be dependent upon the specific gravity of the sample medium (i.e. will require a greater volume of peat than would be required for clay). Check with the chosen National Association of Testing Authorities, Australia (NATA) accredited analytical laboratory for the required soil sample quantity.

Any visible shell or carbonate nodules should be removed from the soil sample in the field. Laboratories routinely sieve samples (<2 mm) submitted for ASS testing, after drying, and prior to grinding and analysis. However, this sieving is often difficult, particularly on clayey samples as these often set hard on drying, making removal of shell or carbonate nodules without breakage/shattering extremely difficult. Shells or carbonates disturbed in this manner have an increased reactive surface area which can lead to an overestimation of the true neutralising

capacity of a soil. Most drilling techniques also shatter some shell and carbonate materials and this should be considered when selecting appropriate sampling methods for a site.

The presence of shell, its location within the profile, size and abundance must be recorded on field logging sheets for later interpretation with laboratory data.

When collecting samples in the field it is important to prevent oxidation of the soil as much as possible. This can be achieved by immediately placing the sample in plastic snap-lock bags or other suitable containers, excluding air, then placing in a field freezer or with sufficient ice in an esky. Samples should also be kept out of direct sunlight. The samples should be carefully marked (using a waterproof pen) for easy identification, and be frozen or specially dried (as per *Acid Sulfate Soils Laboratory Methods Guidelines, Ahern et al., 2004*) within 24 hours of collection.

All samples should be retained in storage (frozen or specially dried) until the field investigation report and any related ASS management strategy has been assessed for the purposes of the development, pending approval. Until this time, further laboratory analysis may be required to clarify results, or provide a more accurate understanding of the soil for management purposes.

Further information on how to undertake ASS sampling can be found in the *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland (Ahern et al., 1998)* available at <http://acidsulfatesoils.environment.wa.gov.au>.

## 6.7 Sediment sample collection

For sampling purposes, dredging/de-sludging of coastal rivers, lakes, dams, drains, canals and wetlands should be treated as a major linear disturbance. Sampling of the material to be dredged should be undertaken at 50m intervals. Where possible, samples should be collected from the sediment profile as per Section 6.6 to at least 1 metre below the maximum depth of expected material extraction, ensuring that samples from all sedimentary layers are collected.

Care must be taken when sampling bottom sediments in drains or sediments likely to contain iron monosulfides, commonly known as monosulfide black oozes (MBOs). These will require special sampling, storage, and treatment. Iron monosulfides readily oxidise within hours (and even within minutes) at room temperature and are therefore required to be frozen immediately after sample collection. Guidelines for handling such samples are currently being developed by Queensland Acid Sulfate Soils Investigation Team (QASSIT). Sediments containing monosulfides will require analysis by the acid volatile sulfur method of Bush and Sullivan (1998).

Careful attention must be paid in collecting underwater sediment samples to ensure that all sediment particle sizes are collected. The fine silt and clay fraction (typically less than 65µm) of the dredged material may contain high concentrations of sulfide, but this material can easily drain/disperse from the sample during collection. In some wet dredging operations, fine grained, sulfide rich sediment (fine silt and clay fractions) can separate from the coarse grained, sulfide poor, carbonate rich sediments (sands and carbonates) during stockpiling. Assessment of such dredged material may require that the constituent fractions of the resource be separated and tested accordingly. Interpretation of soil analysis on the dredge material may be complicated due to the neutralising influences of fine shell material or trapped pore water within the sample.

Laboratory methods suitable for analysis of sediments are fully described in the *Acid Sulfate Soils Laboratory Methods Guidelines* produced by the Queensland Department of Natural Resources, Mines and Water, Queensland (Ahern et al., 2004). These guidelines are available at <http://acidsulfatesoils.environment.wa.gov.au>.

## 6.8 Stockpile sample collection

Some sites may contain existing stockpiles of suspected or known ASS materials (e.g. dredge spoil stockpiles, excavated peat or sand stockpiles). These are most likely to be found in areas where there has been historic development prior to the widespread adoption of ASS management procedures within the State.

When encountered, such stockpiles should be assessed for their acid generating potential. The minimum number of samples which should be collected from such stockpiles is dependent upon the volume of the stockpile, as outlined in Table 3.

Table 3: Minimum number of samples to be collected from stockpiles, based on volume in cubic metres.

Volume (m <sup>3</sup> )	Number of Samples
< 250	2
251 - 500	3
501 to 1000	4
> 1,000	1 per 500m <sup>3</sup>

Samples should be collected in such a way as to be properly representative of the material contained within the stockpile i.e. samples should be collected from various depths and locations within the stockpile. It is not sufficient to collect only surface or near surface samples.

Any material taken to landfill should be sampled according to the DoE guideline *Landfill Waste Classification and Waste Definitions (As amended)* (2005).

## 6.9 Field Tests

Soil field pH (pH<sub>F</sub>) and field pH peroxide tests (pH<sub>FOX</sub>) may be helpful in identifying ASS and/or may help with soil sample selection for laboratory analysis. The pH<sub>F</sub> test measures the existing acidity of a soil:water paste, and is therefore used to help identify actual acid sulfate soils (AASS). The pH<sub>FOX</sub> test may be used to give an indication of the presence of stored (potential) acidity. APPENDIX 1 provides information on how to perform and interpret the results of soil field pH<sub>F</sub> and pH<sub>FOX</sub> tests.

It is important to note that whilst a useful exploratory tool, soil field pH<sub>F</sub> and pH<sub>FOX</sub> tests are indicative only and cannot be used as a substitute for laboratory analysis to determine the presence or absence of ASS. Recent review of field pH<sub>F</sub> and pH<sub>FOX</sub> tests in Western Australian soils indicates that these tests provide an accurate identification of ASS in only 60% to 80% of cases and are capable of providing both false positives and false negatives (i.e. may underestimate or overestimate acid-generating potential). Underestimation of acid-generating potential appears to be most common in clays and may be due to poor mixing during the field test.

Other semi-qualitative tests such as examination under a microscope for pyrite and its reaction with peroxide on the slide may be useful tools to identify pyrite presence, but they require experience and training.

## 7 Step 3: Laboratory Analysis

### 7.1 Submission of Soil Samples for Quantitative Laboratory Analysis

The number of samples that should be submitted to a laboratory for analysis is dependant on the size and type of disturbance as outlined below.

#### 7.1.1 Linear disturbances, any disturbance $>1000\text{m}^3$ and/or for any groundwater disturbance

Starting from the present ground surface, soil samples should be submitted for quantitative laboratory tests at intervals not exceeding 0.5 m down the profile from each sampling location. Where individual soil strata units or soil horizons are encountered with a thickness of less than 0.5 m, the frequency of laboratory analysis will need to be increased to ensure that at least one sample is analysed from each unit or horizon. Figure 3 shows the correct sample selection for laboratory analysis from a hypothetical soil profile, and Table 2 indicates the number of sampling locations required.

Laboratory analysis confirming the absence of sulfides is just as important as determining the actual sulfide content on a positive sample.

#### 7.1.2 Small-scale non-linear disturbance ( $<1000\text{m}^3$ ) with no groundwater disturbance

For small scale non-linear disturbances (i.e.  $< 1000\text{m}^3$  and not drains or trenches) where no dewatering or groundwater pumping is to be conducted, a reduced number of laboratory analyses may be performed (refer to Table 4), provided sufficient information is collected upon which to base sound management practices.

Samples should be collected as per the standard protocol for disturbances  $>1000\text{m}^3$  (see Section 6.1 through to Section 6.6), including the appropriate number of sample locations, detailed soil profile descriptions and sample collection at minimum intervals of 0.25 m etc.

The sampling protocol outlined below can be used as a guide to selecting samples for laboratory analysis:

- Using the field observations and the soil profile descriptions as a guide, select the sample location(s) most likely to contain ASS;
- From these selected location(s), select the one sample that is most likely to contain ASS from each metre interval;
- Additionally, select a minimum of one sample most likely to contain ASS from each of the other sampling locations; then
- Submit the selected samples for laboratory analysis, and store the remaining samples frozen or specially dried for possible future use.

All soil samples should be retained until the application has been assessed by the DoE. The DoE will compare the laboratory results with the field logs and if dissatisfied with the sample selection, may request that additional samples be analysed.

Table 4 shows the minimum number of samples to be submitted for laboratory analysis under this protocol.

Table 4 Minimum number of soil samples to be submitted for laboratory analysis for small-scale non-linear disturbances (<1000m<sup>3</sup>) with no dewatering or groundwater pumping.

	Maximum disturbance depth			
	<1 m	1 – 2 m	2 – 3 m	3 – 4 m
	Borehole depth 2 m	Borehole depth 3 m	Borehole depth 4 m	Borehole depth 5 m
Volume of disturbed soils ≤ 250 m <sup>3</sup>	3	4	5	6
Volume of disturbed soils 251 - 1000m <sup>3</sup>	4	5	6	7

*Note: Number of samples to be analysed per total volume of soil to be disturbed, not per borehole. Depth of disturbance to be measured from ground surface. Borehole depth must be 1m below maximum proposed depth of disturbance.*

### 7.1.3 Stockpiles

Quantitative laboratory tests need to be conducted on all samples collected as per the procedures outlined in section 6.8.

## 7.2 Quantitative laboratory analysis

### 7.2.1 Acid-base accounting

Chemical analysis is undertaken as part of an ASS investigation to determine whether these soils are likely to generate any net acidity and, if so, to quantify this acidity. The analytical results can be further used to calculate the amount of neutralising materials required to be added to these soils to counteract any potential and existing acidity.

Quantitative laboratory analyses for ASS have been developed to measure the net effect of acid generating processes in the soil, balanced against acid-neutralising (or basic) components that may be present i.e. an Acid-Base Account (ABA).

The underlying principle of Acid-Base Accounting is outlined in the following equation:

$$\text{Net Acidity} = \text{Potential Acidity} + \text{Existing Acidity} - \text{Acid Neutralising Capacity (ANC)}$$

Existing acidity is defined as follows:

$$\text{Existing Acidity} = \text{Actual Acidity} + \text{Retained Acidity}^5$$

<sup>5</sup> Refer to *Acid Sulfate Soils Laboratory Methods Guidelines* produced by the Queensland Department of Natural Resources, Mines and Water, Queensland (Ahern et al. 2004) for further explanation of terms. These guidelines are available at <http://acidsulfatesoils.environment.wa.gov.au>.

ANC is defined as follows:

$$\text{ANC}^6 = \text{measured ANC} / \text{fineness factor}^7.$$

The components on the right hand side of the **Net Acidity** expression (or various combinations of these components) are determined using appropriate analytical methods (see Section 7.2.2).

### 7.2.2 SPOCAS Suite and Chromium Reducible Sulfur Suite

Laboratory methods suitable for analysis of acid sulfate soils are fully described in the *Acid Sulfate Soils Laboratory Methods Guidelines* produced by the Queensland Department of Natural Resources, Mines and Energy, Queensland (Ahern *et al.*, 2004). These guidelines are available at <http://acidsulfatesoils.environment.wa.gov.au>.

The net acidity of soil samples collected in ASS investigations should be analysed using at least one of the two recommended standard analytical suites for ASS analysis – SPOCAS Suite and Chromium Reducible Sulfur Suite.

- **SPOCAS Suite**

Suspension Peroxide Oxidation Combined Acidity and Sulfate (SPOCAS) method is a self-contained acid base accounting test. It provides a measurement of the maximum oxidisable sulfur, Titratable Actual Acidity (TAA) and Titratable Peroxide Acidity (TPA) and the potential Acid Neutralising Capacity (ANC) present in the soil sample. 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 calculated Titratable Sulfidic Acidity (TSA) is the difference between TPA and TAA. The peroxide oxidisable sulfur content ( $S_{\text{POS}}$ ) provides a measure of the maximum amount of potentially oxidisable sulfur in the soil sample and represents the sulfur trail.  $S_{\text{POS}}$  values can overestimate the potential sulfidic acidity in soils where appreciable organic sulfur is present and is oxidised by the peroxide (e.g. soil layers rich in organic matter).

- **Chromium Reducible Sulfur Suite**

The chromium reducible sulfur 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. The initial step in the chromium reducible sulfur suite is to measure the reduced inorganic sulfur content (by the Chromium Reducible Sulfur ( $S_{\text{CR}}$ ) method) to estimate the potential sulfidic acidity. Measurements of existing acidity and ANC are also made.

The chromium suite is not subject to significant interferences from sulfur, either in organic matter or sulfate minerals (e.g. gypsum; Sullivan *et al.* 1999). The inorganic sulfur compounds measured by this method are: i) pyrite and other iron disulfides; ii)  $S_{\text{E}}$ , elemental sulfur; iii) thiosulfate, tetrathionate, polythionites; and iv)  $S_{\text{AV}}$ , acid volatile sulfides (e.g. greigite, mackinawite, amorphous FeS) provided these have not been lost during sample transport and preparation. On wet samples, the chromium reduction method can

<sup>6</sup> Due to the particular characteristics of the soil and groundwater regime in Western Australia, the DoE will only recognise the validity of ANC values if they are derived using the techniques outlined in Section 7.2.3.

<sup>7</sup> When ameliorating ASS by mixing it well with finely divided pure agricultural lime, a safety factor of 1.5 must be applied. Equally, a minimum safety factor of 1.5 should be applied to any naturally occurring ANC that is present in the soil.

be made specific to the iron disulphide 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 (e.g. 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.

For soils 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 provides a better estimate of the soil's sulfide content. Whenever there is a variation between the sulfur measurement results from various sulfur methods used to predict sulfidic acidity (e.g.  $S_{CR}$ ,  $S_{POS}$ ), then the  $S_{CR}$  result should take precedence for use in the acid-base account.

*Note: If there is no obvious reason (e.g. a highly organic/peaty sample) for a substantial variation (between  $S_{CR}$  and  $S_{POS}$ ), then the first step is to conduct a repeat analysis to confirm the analytical results.*

A combination of analyses may be required if more detailed knowledge of the soil chemistry is necessary e.g. to determine the most appropriate neutralising agent or management technique.

A full Acid Base Accounting (ABA) calculation should be completed when using the Chromium or SPOCAS suites.

Samples should be submitted to a laboratory that is NATA accredited for all of the analyses to be undertaken for all media.

### 7.2.3 Acid Neutralising Capacity (ANC)

Acid neutralising capacity (ANC) is a measure of a soil's inherent ability to buffer acidity and resist the lowering of the soil pH. Acid buffering in the soil may be provided by dissolution of calcium and/or magnesium carbonates (e.g. shell or limestone), cation exchange reactions, and by reaction with the organic and clay fractions. The effectiveness of these buffering components in maintaining soil pH at acceptable levels (eg. pH 6.5–9.0) will depend on the types and quantities of clay minerals in the soil, and on the type, amount and particle size of the carbonates or other minerals present.

Further information on ANC can be obtained from *Acid Sulfate Soils Laboratory Methods Guidelines* Queensland Department of Natural Resources, Mines and Water, Queensland (Ahern *et al.*, 2004).

The DoE has recent experience with a number of projects in Western Australia where the level of ASS management undertaken was reduced, because laboratory soil analyses indicated that the ASS materials in question had sufficient ANC to render them self-neutralising. However, it was found that under real field conditions, disturbance of the soil profile did in fact result in the generation of significant acidity, with resultant environmental damage including release of heavy metals into groundwater and surface waters. Once this mobilisation of acidity and metals has occurred, it is very difficult, if not impossible, to reverse.

To minimise the risk of further environmental harm, the DoE has subsequently modified its policy position in relation to ANC. The paragraphs below provide an expanded discussion on factors affecting ANC and the application of ANC in the interpretation of results.

The net acidity leached to the environment upon disturbance of ASS, 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. The actual amount of neutralising capacity available under real field conditions is influenced by the following factors:

- **Particle size or fineness of acid neutralising material**

The larger the particle size of a material, the lower the surface area to volume ratio, and thus the lower the reactivity which in turn reduces the effective acid neutralising capacity. Titratable Sulfidic Acidity (TSA) results and ANC results often underestimate the potential risk of acid leakage to the environment as it is likely that not all of the shell/carbonate materials within the soils would be available for immediate neutralisation of acid because of low unit surface area, and the likelihood of the formation of insoluble coatings on the shell surfaces. In particular, shell fragments >2 mm diameter cannot be relied upon to provide any real neutralisation value. "Utilisation factors" recognise the difference in reactivity of different particle sizes. Estimates of utilisation factors for limestone of various particle sizes are listed in Table 5. Utilisation factors for shell fragments of comparable sizes would be expected to be lower than these values due to stronger chemical binding of calcium carbonate within shell bodies.

Table 5: Utilisation factors for limestone of various particle size (adapted from NSW ASSMAC guidelines)

Particle size	Utilisation Factor
>0.850 mm	10%
0.300 – 0.850 mm	60%
<0.300 mm	100%

For example limestone with a particle size of 0.500 mm has a utilisation factor equivalent to 60% of the neutralising value of finer grade limestone of particle size <0.300 mm.

- **Armouring**

Shells found in ASS commonly have a coating (or 'armouring') of insoluble or sparingly soluble gypsum, silica or iron compounds, rendering much of their carbonate content unavailable for neutralisation.

- **Reaction kinetics**

Neutralising materials present in the soil profile may not be able to react quickly enough to counteract developing acidity. In this case, there may be a net export of acid.

- **Laboratory methods**

Standard laboratory methods for ASS involve the removal of coarse shell fragments and sieving of the sample to <2 mm prior to grinding and analysis. Potential neutralising materials in the fraction <2 mm remain in the sample and are very finely ground, greatly increasing their reactivity. Those potential neutralising materials in the particle size fraction 0.3 mm to 2 mm would not be 100% available under real field conditions (see Table 5), with the results that analysis of the finely-ground sample may yield an analytical ANC in excess of what would normally be available from the soil *in-situ*.

For all of the above reasons the DoE considers that utilisation of ANC values without confirmatory field kinetic testing or modified laboratory methods cannot be used as an argument to reduce the level of management required for the disturbance of ASS.

*Note: Given the sensitivity of groundwater resources in Western Australia, and the uncertainty surrounding reaction kinetics, an ASS Dewatering Management Plan should still be developed for sites with potential sulfidic acidity in excess of Texture-Based Action Criteria (see Table 6), regardless of the outcome of the ANC testing. Further guidance on management measures for acid sulfate soils, including dewatering management, can be obtained from the document entitled Treatment and management of acid sulfate soil disturbance. (Insert reference when new management guideline is finalised)*

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## 8 Step 4: Reporting Results

Good reporting is the outcome of a consistent methodology for acid sulfate soil identification and investigation and the effective transfer of information. Analytical results should be compared to the correct assessment criteria and all ASS investigation reports should include measures to ensure the quality and reproducibility of all sampling methods used at the site.

Reports prepared for acid sulfate soil investigations should contain the information discussed in this section.

### 8.1 Assessment Criteria

The assessment criteria adopted for ASS in Western Australia are the *Texture-based ASS Action Criteria* as developed by QASSIT and outlined in the *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils in Queensland 1998* available at <http://acidsulfatesoils.environment.wa.gov.au> (see Table 6).

The *Action Criteria* are based on **Net Acidity** (Section 7.2.1) where:

$$\text{Net Acidity} = \text{Potential Sulfidic Acidity} + \text{Existing Acidity} - \text{Acid Neutralising Capacity (ANC)}$$

calculated as equivalent sulfur (e.g. s-TAA + S<sub>CR</sub> in %S units) or equivalent acidity (e.g. TAA + a-S<sub>CR</sub> in mol H<sup>+</sup>/tonne). The highest laboratory result(s) should be always used to assess against the action criteria.

As clay content tends to influence a soil's natural pH buffering capacity, the action criteria are grouped by three broad texture categories – coarse, medium and fine (refer to Table 6).

Table 6: Texture-based acid sulfate soils 'action criteria'.

Type of material		Net Acidity Action Criteria			
		<1000 tonnes of materials is disturbed		>1000 tonnes of materials is disturbed	
Texture range McDonald et al. (1990)	Approx. clay content (%)	Equivalent sulfur (%S) (oven-dry basis)	Equivalent Acidity (mol H+/tonne) (oven-dry basis)	Equivalent sulfur (%S) (oven-dry basis)	Equivalent Acidity (mol H+/ tonne) (oven-dry basis)
Coarse Texture Sands to Loamy sands	< 5	0.03	18.7	0.03	18.7
Medium Texture Sandy Loams to Light Clays	5 – 40	0.06	37.4	0.03	18.7
Fine Texture Medium to Heavy Clays and Silty Clays	> 40	0.1	64.8	0.03	18.7

The action criteria refer to Net Acidity for a given volume of ASS.

The highest result(s) should always be used to assess if the relevant action criteria level has been exceeded; using the average or mean of a range of results is not considered appropriate.

For further information refer to *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland* (Ahern et al., 1998).

If the *Texture-based ASS Action Criteria* are exceeded by any sample results, an Acid Sulfate Soil Management Plan (ASSMP) will need to be developed and implemented for disturbance of ASS at a site.

## 8.2 Quality Assurance/Quality Control (QA/QC)

ASS investigations should include measures to ensure the quality and reproducibility of all sampling methods used at the site. Accurate QA/QC is required to ensure that the samples collected are of the highest quality and integrity, and that analysis is completed with the highest accuracy. Where results are produced with inadequate QA/QC procedures, they cannot be accepted as being accurate or representative of the site conditions.

QA/QC measures are required regardless of the number of samples taken.

### 8.2.1 Field QA/QC

The minimum field QA/QC procedures that should be performed are:

- collection of field duplicates as quality control samples;
- use of standardised field sampling forms (including Chains of Custody) and methods; and
- documenting calibration and use of field instruments.

Field duplicate samples (also known as blind replicates) are used to identify the variation in analyte concentration between samples collected from the same sampling point and also the repeatability of the laboratory's analysis. Field duplicates should be collected at the rate of one field duplicate for every 20 investigative samples. The field duplicate sample and investigative sample from the same sample location should be submitted to the laboratory as two individual samples without any indication to the laboratory that they have been duplicated.

### 8.2.2 Laboratory QA/QC

Analysis of samples should be completed by laboratories which hold National Association of Testing Authorities (NATA) accreditation for the particular parameters and methodologies required. Information on QA/QC methods should be obtained from the designated laboratory prior to sampling to ensure that they meet acceptable standards.

The laboratory report should be a NATA endorsed report and include the results of the analysis, sample numbers, laboratory numbers, a statement about the condition of the samples when they were received (e.g. on ice, cold, ambient, etc.), date and time of receipt, dates and times of extraction and analysis of samples, quality control results and a report on sampling and extraction holding times.

### 8.2.3 Data Review

Following receipt of field and/or laboratory data, a detailed review of the data should be completed to determine their accuracy and validity, prior to them being used to make any decisions. Analytical data should be reviewed against field data and field observations to identify any spurious results inconsistent with field findings. Where inconsistencies are identified, re-sampling or re-analysis may be required.

## 8.3 Reporting

The following information should be provided in relation to all ASS investigation reports:

- a completed Site Summary Form (Acid Sulfate Soils Assessment), available from the DoE website <http://acidsulfatesoils.environment.wa.gov.au>;
- the exact location of each borehole shown on an appropriately scaled map;
- a brief description of the equipment and/or methods used to retrieve the samples;
- site photographs, showing general site conditions and the soil profile, identifying each stratum;
- a summary table with observations and data, similar to Table 7, including:
  - the full grid reference of each borehole using Australian Metric Grid;
  - an exact description of the vertical dimensions of the borehole relative to existing surface height in both metres below ground level (mBGL) and metres above AHD;
  - soil texture, grain size, roundness, sorting and sphericity using the Australian Soil and Land Survey Field Handbook (McDonald *et al.*, 1990) as a guide;
  - colour using a Munsell colour chart;

- mottling, organic matter, moisture content, watertable level and other diagnostic features (e.g. jarosite, shell);
- results from field soil  $\text{pH}_F$  and  $\text{pH}_{\text{FOX}}$  tests, including the pH of water and peroxide used (where conducted);
- tabulated summary of results of laboratory analyses in %S units;
- calibration certificates or calibration results;
- cross-sections of the soil profile beneath the study area;
- copies of original laboratory result certificates including NATA accreditation details;
- discussion of any discrepancy between field observations and laboratory analyses results;
- discussion of field and laboratory QA/QC;
- discussion of the potential risk of environmental harm associated with disturbance of the site; and
- recommendations as to whether or not an ASSMP will be required.

If the DoE receives a report where any of the above have been omitted, the proponent will be requested to re-submit the report with the missing data included. This will increase the time taken for the DoE to provide review and comment on the report.

Further information in relation to the content, compilation and presentation of site investigations can be found in the DoE guideline *Reporting on Site Assessments* (December 2001), which is part of the *Contaminated Sites Management Series*. This guideline is available at <http://contaminatedsites.environment.wa.gov.au>.

As acid generating potential is related to geological strata, acid sulfate soil investigations should aim to clearly focus on characterising each geological unit beneath the site. With this in mind, for clarity and to expedite the review process, soil test results, including laboratory results, should be reported in tables and figures which clearly show the corresponding geological description so that the characteristics of each soil horizon can be identified more easily. Table 7 sets out how results should be provided.

Table 7: Example of combined field description and ASS data presentation table.

Field Observations			Field Test					Lab pH		SPOCAS					S <sub>CR</sub> Suite			Action Criteria																						
Sample ID	Depth/mBGL		Soil Description	Depth to Water	pH	pHFOX	pH - pHFOX	Reaction Rate	Temperature	pH KCl	pH OX	TAA	TPA	TSA	S <sub>POS</sub>	AN <sub>CE</sub>	Net Acidity	pH KCl	TAA	S <sub>CR</sub>	Net Acidity* (SPOCAS)	Net Acidity* (S <sub>CR</sub> )																		
				mBGL																			pH units	pH units	LMHX V	°C	pH units	pH units	%S	%S	%S	%S	%S	%S	%S	%S				
Assessment Criteria																						-	4	4	1	NV	NV	NV	NV	0.03	0.03	NV	0.03	NV	NV	NV	0.03	0.03	0.03	0.03

DOE1: 395565.32mE / 6390725.45mN

DOE1	0	0.2	Sandy Silt. Grass root zone. Sand component mostly fine grained, well sorted, very angular. Munsell colour 7.5YR 3/2 dark brown.		5.85	3.14	2.71	L	-	4.7	4.1	0.036	0.000	-0.036	0.03	-	0.06	4.3	0	0.02	0.03	0.02
DOE1	0.2	0.5	Peaty Silty Clay. Roots (fine fibrous). Munsell colour 7.5YR 2.5/1 black.	0.35	4.76	2.37	2.39	M	42	5.2	4.2	0.033	0.000	-0.033	0.01	-	0.04	4.4	0	0	0.01	0.00
DOE1	0.5	0.7	Clayey Sand. Minor root matter. Greyish brown sand very fine to fine grained, angular, moderately sorted. Munsell colour 2.5Y 5/1 grey.		3.92	2.10	1.82	V	85	3.9	3.4	0.034	0.000	-0.034	0.05	-	0.08	4.2	0	0.01	0.05	0.01
DOE1	0.7	0.85	Sand. Very fine to coarse grained, angular, poorly sorted quartz. Munsell colour 5Y 8/1 white.		5.40	2.73	2.67	M	37	5.1	4.1	0.072	0.072	0.000	0.02	-	0.1	5.3	0	0.01	0.02	0.01
DOE1	0.85	0.95	Sand. Very fine to coarse grained, angular, poorly sorted quartz (with some grains Fe stained). Intensely mottled yellow orange. Munsell colour 10YR 7/8 yellow.		5.55	2.67	2.88	M	46	5.0	3.0	0.034	0.000	-0.034	0.04	-	0.07	5.2	0	0.01	0.04	0.01
DOE1	0.95	1.1	Sand. Fine to medium grained, angular, moderately sorted. End of mottled zone. Predominantly. Munsell colour 10YR 8/1 white with Munsell colour 10YR 7/8 yellow.		5.62	2.28	3.34	H	72	4.9	4.5	0.046	0.000	-0.046	0.04	-	0.09	4.8	0	0.02	0.04	0.02
DOE1	1.1	1.25	Sand. Fine grained, angular, well sorted. White light grey. Munsell colour 10YR 8/1 white.		5.70	2.77	2.93	H	75	5.6	3.4	0.036	0.072	0.036	0.07	-	0.1	5.3	0	0.02	0.07	0.02
DOE1	1.25	1.5	Sand. Fine grained, angular, well sorted. Munsell colour GLEY#2 10B 4/1 dark bluish grey.		5.97	3.78	2.19	X	82	6.2	2.8	0.033	0.222	0.190	0.16	-	0.19	5.5	0	0.02	0.16	0.02

DOE2: 395357.21mE / 6390310.82mN

DOE2	0.5	1.1	Peat. Black, fibric to hemic peat with fine fibrous roots. No sediment - all organic matter. Munsell colour GLEY#1 N 2.5/ black.		5.20	2.80	2.40	X	64	6.3	3.5	0.255	1.406	1.151	0.52	-	0.78	6.0	0	0.15	0.52	0.15
DOE2	1.1	1.45	Peat. Dark red brown fibric peat. Fibrous roots upto 2mm thick. Increased root content when compared to above interval. All organic - no sediment. Munsell colour 2.5YR 2.5/3 dark reddish brown.	1.2	3.97	3.00	0.97	X	68	5.2	3.4	0.114	0.278	0.164	0.08	-	0.2	5.4	0	0.03	0.08	0.03
DOE2	1.45	1.6	Peat. Dusky red sapric peat. Fibrous roots as above, but decreased content. No sediment - organic matter almost gelatinous. Munsell colour 2.5YR 3/2 dusky red.		5.32	1.83	3.49	V	90	6.0	3.1	0.036	0.425	0.389	0.45	-	0.49	4.9	0	0.39	0.45	0.39
DOE2	1.6	2.1	Peat. Black sapric peat (very little root matter preserved). Munsell colour GLEY#2 5PB 2.5/1 bluish black.		6.12	2.98	3.14	M	53	5.5	3.8	0.131	0.981	0.850	0.44	-	0.57	4.6	0	0.11	0.44	0.11
DOE2	2.1	2.3	Peat. Black peat becoming sandy with depth. Sand fraction very fine to fine grained, rounded to angular.		6.09	1.90	4.19	X	83	5.8	4.5	0.082	0.752	0.670	0.63	-	0.71	4.8	0	0.46	0.63	0.46
DOE2	2.3	2.8	Sand. Brown black sand comprised of fine grained, well rounded, well sorted predominantly quartz with high sphericity. Minor pea and some carbonate fragments. Munsell colour 2.5Y 3/2 very dark greyish brown.		6.44	2.67	3.77	M	53	5.7	4.9	0.082	1.635	1.553	0.36	-	0.44	5.7	0	0.07	0.36	0.07
DOE2	2.8	4	Sand. Cream sand comprised of quartz and carbonate. Munsell colour 2.5Y 6/3 light yellowish brown. Quartz fraction well rounded, well sorted, fine grained with high sphericity. Carbonate fraction - off-white, well sorted, well rounded, fine grained, moderate sphericity. Some shell material present as evidenced by laminated fragments.		6.20	2.13	4.07	H	70	5.9	5.3	0.079	0.324	0.245	0.21	-	0.29	5.9	0	0.13	0.28	0.13

Notes: BGL = below ground level; Net Acidity\* = TAA + SPOCAS or S<sub>CR</sub>

## 9 Further Intrusive Investigations to Support Management Plan for the Disturbance of ASS

In some cases, especially where dewatering is required, the initial soil sampling and analysis program may not provide sufficient information upon which to base a comprehensive and effective management plan. In these instances additional investigations will be required before an appropriate management plan can be developed.

The amount and type of further information required will vary dependent upon the nature of sulfide distribution at the site and upon the nature of the proposed development. It may include the following:

- groundwater quality assessment to determine appropriate management options for groundwater;
- site specific hydrogeological investigations and modelling to predict the extent of the dewatering draw-down cone;
- ASS investigation of area of the dewatering draw-down cone;
- in-fill characterisation if required – e.g. in areas with highly variable sulfide distribution;
- analysis of arsenic and other metals; and/or
- soil/sediment contamination assessment/ metal analysis to determine appropriate disposal options.

In such instances, management plans will not be approved by the DoE until sufficient further investigations have been undertaken.

Supplemental guidance on the requirements for further intrusive investigations to support ASSMPs for the disturbance of ASS can be obtained from the document entitled *Treatment and management of acid sulfate soil disturbance*. (Insert reference when new management guideline is finalised)

## 10 Further Information

Further information in relation to acid sulfate soils can be obtained from guidelines and manuals developed by the New South Wales and Queensland State governments, in particular:

- *Acid Sulfate Soils Laboratory Methods Guidelines*. In *Queensland Acid Sulfate Soils Manual 2004*. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.
- *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998*, Queensland Acid Sulfate Soils Investigation Team;
- *New South Wales Acid Sulfate Soil Manual 1998*, Acid Sulfate Soil Advisory Committee; and
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# APPENDIX 1: Performing and Interpreting Soil Field pH Tests

It is important to note that whilst a useful exploratory tool, soil field pH tests are indicative only, are definitely not quantitative and cannot be used as a substitute for laboratory analysis to determine the presence or absence of ASS. Laboratory analysis is needed to quantify the amount of existing, plus potential, acidity. This Appendix provides information on how to perform field pH tests and interpret the results from them. For further information on how to conduct and interpret these tests, consult the *Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998* (Ahern et al., 1998).

Field pH tests should be conducted using a field pH meter calibrated according to the manufacturer's instructions. All results ( $\text{pH}_F$  and  $\text{pH}_{\text{FOX}}$  values, peroxide reaction) should be tabulated and reported.

## A1 Suggested Equipment for Field Tests

It is important that prior to conducting the field tests, the appropriate testing equipment is obtained. For a basic set up the following items would be required:

1. pH meter and electrode – charged and calibrated
2. at least 2 buffer solutions – eg. pH 4.0 and pH 7.0
3. test tubes or beakers – wide, unbreakable, heat resistant, and clear eg. Falcon 50ml polypropylene ( $\text{pH}_F$  test tubes are ideally shallow to facilitate cleaning eg. cut the top of a 50ml tube at about 10ml)
4. test tube rack or jar rack marked with depths – use a separate rack for  $\text{pH}_F$  tests and  $\text{pH}_{\text{FOX}}$  tests in case they bubble over
5. skewers or stirrers – wooden, for test tubes
6. 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) pH adjusted to 4.5–5.5
7. storage bottle for  $\text{H}_2\text{O}_2$
8. sodium Hydroxide (NaOH) – to raise pH of peroxide to 4.5–5.5 (pH 5.5 ideal)
9. deionised (DI) water
10. squirt bottle for DI water
11. tissues
12. gloves and safety glasses
13. protective clothing
14. bucket – to tip used soil and hydrogen peroxide into
15. bucket and brush – to rinse tubes out in ready for next site
16. recording sheets
17. excess water for rinsing
18. first aid kit – especially eye wash solutions
19. 1M hydrochloric (HCl) acid – to test for shell presence

## A2 Conducting Field Tests – Some Considerations

When the analytical results are reported, the field test results (when accompanied by good soil profile descriptions) will help increase the understanding of profile processes with respect to acidity.

When performing field tests, the soil samples must not be left in the open air in the test tubes or beakers for an extended period of time before conducting the tests. If sulfides are present, there is a risk that they will oxidise, and this will substantially affect the end pH result by lowering the  $\text{pH}_F$ .

This will give a misleading result that the soil profile is more acid than it really is. It would be preferable (and more efficient) to prepare the field pH test tubes with the soil:water pastes and the soil:peroxide mixtures and commence the soil profile descriptions while the reactions are occurring. This way, the soils are given time to react and there is no time wasted waiting for them to cool. It is important though, to keep an eye on the reactions as some may be vigorous and overflow, and result in contamination of nearby soil samples.

When conducting the  $\text{pH}_{\text{FOX}}$  test, it is important to allow enough time for the reaction to occur, especially if low strength (ie. <30%) hydrogen peroxide is used.

The field  $\text{pH}_{\text{F}}$  and  $\text{pH}_{\text{FOX}}$  tests can be made more consistent if a fixed volume of soil (using a small scoop) is used, a consistent volume of peroxide is added, left to react for at least an hour (at a secure location, the  $\text{pH}_{\text{FOX}}$  can be left overnight), then the sample moistened with deionised water before reading  $\text{pH}_{\text{F}}$  and  $\text{pH}_{\text{FOX}}$ .

Field tests should preferably be performed on-site, however there are many areas (eg. wetlands) where performing field tests can prove difficult (eg. too wet, mosquito problems). In this situation, samples must be placed on dry ice and taken to a suitable location for conducting field tests. These tests should be performed ideally within 24 hours. As some samples may contain large amounts of organic matter (especially in wetland situations) and may also contain monosulfides, any delay in performing field tests could result in misleading  $\text{pH}_{\text{F}}$  results.

### A3 On-site Chemical and Material Safety Precautions

#### A3.1 Hydrogen peroxide

Care needs to be taken when using hydrogen peroxide in the field. Peroxide ( $\text{H}_2\text{O}_2$ ) (30%) is used as the primary reagent in the  $\text{pH}_{\text{FOX}}$  test. The concentration is 10 times stronger than the peroxide commonly found in household medicine cabinets. The reaction of peroxide with soil containing iron sulfides may produce sulfurous gases, as well as giving off heat in excess of  $90^\circ\text{C}$ .

Caution: 30% Hydrogen Peroxide is a strong oxidising agent and should be handled carefully with appropriate eye and skin protection. **This test is suitable for experienced operators only.** Even the less concentrated 6% peroxide (which some operators are using) should be used with caution.

The peroxide when first received may have a pH of 3.5 or lower. Chemical companies commonly put stabilisers in the peroxide to prevent it from decomposing and releasing oxygen by keeping the pH low. The pH required for the field pH peroxide test is pH 4.5–5.5. This may be obtained by adding sodium hydroxide (pH 14) to the peroxide. Since both of these chemicals are highly corrosive, and many of the long-term side effects are not fully known, it is recommended that the following precautions are taken when performing field tests.

Always:

1. Use gloves, glasses, lab coat or protective clothes;
2. Conduct pH peroxide test in a well ventilated area;
3. Use test tubes capable of withstanding rapid heat changes and high temperatures;
4. Avoid skin and eye contact with peroxide; and
5. Label all peroxide bottles with safety data information.

#### A3.2 Other chemicals

Several other chemicals are used in the field when sampling for ASS. Buffering solutions and potassium chloride (KCl) solutions are used to calibrate and maintain pH meters and care should be exercised when using these substances. Follow safety directions on Material Safety Data Sheets (MSDS).

Hydrochloric acid (HCl) is used when performing tests to assess the presence of carbonates in soil material. HCl is strongly acidic and is very corrosive to skin and caution needs to be taken when using it. Again, follow directions on MSDS. Store HCl separate from buffer solutions as HCl gas may slowly diffuse through the plastic bottles and alter the buffer solutions.

#### **A4 Field pH Test (pH<sub>F</sub>)**

The pH<sub>F</sub> test measures the existing acidity of a soil:water paste, and is therefore used to help identify if ASS are present. If the measured pH of the soil paste is pH<sub>F</sub> < 4, oxidation of sulfides has probably occurred in the past, indicating the presence of AASS. Highly organic soils or heavily fertilised soils may also return a pH<sub>F</sub> close to 4. A pH<sub>F</sub> >4 but ≤5 indicates an acid soil, but the cause of the acidity will need to be further investigated by laboratory analysis. The pH<sub>F</sub> test does not detect any unoxidised sulfides (i.e. PASS). For this reason, this test must be used in conjunction with the pH<sub>FOX</sub> test.

##### **A4.1 Soil:water mixtures and soil pastes**

Standard field soil pH tests have been conducted using a 1:5 soil:water mixture. This is quite successful where sands are concerned (as they breakdown readily), however in a field situation it is often difficult to get all soil into solution by shaking only for a brief period of time. In particular, where wet clays are present, it becomes very difficult in the field to shake the mixture to suspend all the clay particles in solution. It is more likely that the clay will stay in a ball and while some fine particles previously attached to the edge of the clay bolus are suspended, the remainder sticks to the bottom of the test tube. This means that the soil:liquid ratio is widened substantially and the pH of the mixture will have a higher reading, so that it will not give a true and accurate measurement of the pH of the soil. In the laboratory, this sample would be dried, ground, mixed, and shaken mechanically for hours allowing substantial time for the clay to be broken down—in the field, this option is not practical. Further, it is not practical to weigh out soils in the field to obtain a perfect 1:5 soil:water mixture, and so any solutions made up are usually done on a volumetric basis assisted by graduated test tubes, flasks, or beakers.

Making a soil:water paste is more practical for field situations and is recommended for ASS field pH (pH<sub>F</sub>) tests. This is detailed in the procedure below. It is recommended that short test tubes are used for pH<sub>F</sub> tests as they are easy to clean. Further, the paste must be stirred using a stirring implement (eg. skewer or strong toothpicks). Stirring the paste well will enhance the accuracy of the pH result as the electrode will get good contact with the soil.

##### **A4.2 Field pH test procedure**

Procedural outline – field pH<sub>F</sub> test

1. Calibrate battery powered field pH meter.
2. Prepare the test tubes in the test tube rack. Make sure the rack is marked with the depths so there is no confusion about the top and bottom of the profile. Use of separate racks for the pH<sub>F</sub> and pH<sub>FOX</sub> tests is recommended as contamination may occur when the pH<sub>FOX</sub> reactions are violent.
3. Conduct tests at intervals on the soil profile of 0.25 m or at least one test per horizon whichever is lesser.
4. Remove approximately 1 teaspoon of soil from the profile. Place approximately ½ teaspoon of the soil into the pH<sub>F</sub> test tube and place ½ teaspoon of the soil into the pH<sub>FOX</sub> test tube for the corresponding depth test. It is important that these 2 sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0–0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
5. Place enough deionised water (pH 5.5) in the pH<sub>F</sub> test tube to make a paste similar to ‘grout mix’ or ‘white sauce’, stirring with a skewer or similar to ensure all soil ‘lumps’ are removed. Do not leave the soil samples in the test tubes without water for more than 10 minutes. This

will reduce the risk of sulfide oxidation—the  $pH_F$  is designed to measure existing acidity, any oxidation subsequent to the soil's removal from the ground will not reflect the true situation. In some instances, in less than 5 minutes, monosulfidic material may start to oxidise and substantially affect the  $pH_F$  results.

6. Immediately place the spear point electrode (preferred method) into the test tube, ensuring that the spear point is totally submerged in the soil:water paste. Never stir the paste with the electrode. This will damage the semi-permeable glass membrane.
7. Measure the  $pH_F$  using a pH meter with spear point electrode.
8. Wait for the reading to stabilise and record the pH measurement. All measurements and pH calibration should be recorded on a data sheet.

TABLE A1: Results – field pH test

pH value	Result	Comments
$pH_F \leq 4$	Actual acid sulfate soils (AASS) indicating oxidation of sulfides	This is generally <u>not</u> conclusive because highly organic soils such as peats and occasionally heavily fertilised soils may also give $pH_F \leq 4$ .
$pH_F \leq 3.7$	Expected if jarosite exists in the sample	This is also an AASS. Jarosite needs a pH of at least 3.7 to form. Horizons containing some jarosite and some other mottling (iron, grey) may have a pH $>3.7$ if the sample contains a mixture of jarosite and higher pH soil. This depends on the level of oxidation and the ability of the soil to 'hold' the acid.
$pH_F > 7$	Expected in waterlogged, unoxidised, or poorly drained soils	Marine muds commonly have a pH $>7$ and this reflects seawater (pH 8.2) influence. May be a PASS after oxidation with $H_2O_2$ .
$4 < pH_F \leq 5.5$	An acid soil	Investigate further for possible ASS link, e.g. AASS with shell presence.

### A5 Field pH Peroxide Test ( $pH_{FOX}$ )

The  $pH_{FOX}$  test is used to indicate the presence of iron sulfides or PASS. This test involves adding 30% hydrogen peroxide (pH adjusted to 4.5–5.5) to a sample of soil. If sulfides are present a reaction will occur. The reaction can be influenced by the amount of sulfides present in the sample, the presence of organic matter, or the presence of manganese. Once the reaction has occurred, the pH is measured.

Adding hydrogen peroxide, which is a strong oxidising agent, 'mimics' what would naturally occur if the soil is exposed to air. In a natural environment, if left exposed, soils may take from 2 hours for sands, possibly through to many decades for heavy marine clays, for some or all of the oxidation reactions to take place. Obviously it is not practical to wait for this long for a reaction to occur.

It should be noted that although the iron sulfides are oxidised and acid is produced over a shorter amount of time than would occur naturally, the amount of acid produced is the same. It is important to assess first the likely presence (through field tests) and secondly the level of iron sulfides present (through laboratory analyses) so that management can prevent any undesirable impacts.

The  $pH_{FOX}$  test is purely qualitative. Further, no calculations can be performed to give an accurate account of the levels of sulfides present in the sample—but rather, the test gives an indication whether sulfides may occur (or another form of compound that is contributing to acidity). This

means that it CANNOT give an accurate measurement of how much lime should be added to the soil.

The sample of soil must be taken from the same depth increment (sub-sample) as the  $pH_F$  was measured. It is important that the  $pH_{FOX}$  is performed on a separate sub-sample, and NOT on the soil:water paste that was prepared for the  $pH_F$  test. This will ensure that the minimal degree of dilution occurs during the oxidation phase, and that the resulting  $pH_{FOX}$  measurement is as accurate as possible indication of the potential for oxidation of that particular sub-sample of soil.

A combination of three factors is considered in arriving at a 'positive field sulfide identification':

- a reaction with hydrogen peroxide - the strength of the reaction with peroxide is a useful indicator but cannot be used alone. Organic matter, coffee rock and other soil constituents such as manganese oxides can also cause a reaction. Care should be exercised in interpreting a reaction on surface soils and high organic matter soils such as peats and coffee rock, and some mangrove/estuarine muds and marine clays. This reaction should be rated, e.g. L = Low reaction, M = Medium reaction, H = High reaction, X = Extreme reaction, V = volcanic reaction.
- The actual value of  $pH_{FOX}$ . - If  $pH_{FOX} < 3$ , and a significant reaction occurred, then it strongly indicates a PASS. The more the  $pH_{FOX}$  drops below 3, the more positive the presence of inorganic sulfides.
- A much lower  $pH_{FOX}$  than field  $pH_F$  - The lower the final  $pH_{FOX}$  value and the greater the difference between the  $pH_{FOX}$  compared to the  $pH_F$ , the more indicative the presence of PASS. This difference may not be as great if starting with an already very acid  $pH_F$  (close to 4), but if the starting pH is neutral or alkaline then a larger change in pH should be expected. Where fine shell, coral or carbonate is present the change in pH may not be as large due to buffering. The 'fizz test' (effervescence with 1 M HCl) should be used to test for carbonates and shell.

Of these three factors, the final  $pH_{FOX}$  value is the most conclusive indicator, and the lower the final  $pH_{FOX}$ , the more confident one can be that PASS may be present.

#### A5.1 Strength and pH of peroxide

The pH and strength of peroxide used is important. The pH of the peroxide should be pH 4.5–5.5 (ideally pH 5.5). This ensures that the result measured is a reflection of the oxidation of the soil (if any) and not of the existing pH of the peroxide. When peroxide is purchased often the stabilisers added by the chemical companies will result in a pH of approximately 3.5. This pH can be raised by adding small amounts of sodium hydroxide (NaOH)—failure to adjust the pH can lead to false field results.

Analytical grade peroxide (30%) is most suitable for field  $pH_{FOX}$  tests as an oxidation agent that is highly effective and 'quick' to react with any iron sulfides in a soil sample. This strength of peroxide is highly corrosive, slightly unstable, and highly reactive on hands, etc. As such, a high level of safety precautions is required. However, there is no reason why a well-trained officer cannot safely and responsibly conduct field tests with 30% hydrogen peroxide.

#### A5.2 Field pH peroxide test procedure

Procedural outline – Field pH peroxide test

1. Adjust and record the pH of the hydrogen peroxide before going into the field. This can be done by adding a few drops of NaOH at a time, checking the pH with the electrode regularly. NaOH is highly caustic so safety precautions must be exercised. Also, NaOH will raise the pH quickly so the pH needs to be monitored. Do NOT buffer a large quantity of hydrogen peroxide at one time. Only buffer the amount to be used in the field. Usually a couple of

months supply is adequate. This must be kept in a fridge, well labelled with only small quantities to be taken into the field at one time. This will ensure the longevity of the peroxide. Further, over time, the pH of the peroxide that has already been buffered may change. It is important to check the pH of the peroxide in the morning before departing to the field. Having a small quantity of NaOH in the field kit is recommended so the peroxide can be buffered if required.

2. Calibrate battery powered field pH meter.
3. Prepare the test tubes in the test tube rack as for pH<sub>F</sub> test. Make sure the rack is marked with the depths so there is not confusion about the top and bottom of the profile. Use of separate racks for the pH<sub>F</sub> and pH<sub>FOX</sub> tests is recommended as contamination may occur when the pH<sub>FOX</sub> reactions are violent.
4. Conduct pH<sub>F</sub> tests at intervals on the soil profile of 0.25 m or at least one per horizon whichever is lesser.
5. Remove approximately 1 teaspoon of soil from the profile. Place approximately ½ teaspoon of that soil into the pH<sub>F</sub> test tube and place ½ teaspoon of soil into the pH<sub>FOX</sub> test tube for the corresponding depth test. It is important that these 2 sub-samples come from the same depth and that they are similar in characteristics. For example, DO NOT take ½ teaspoon of soil from the 0-0.25m depth that is grey mud, while selecting ½ teaspoon from the same depth that is a yellow mottled sample. These will obviously give different results independent of the type of test conducted.
6. Add a few drops of 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 4.5–5.5 to the soil in a heat-resistant test tube and stir the mixture. Do NOT add the peroxide to the test tube in which the pH<sub>F</sub> test was conducted, that is, the pH<sub>FOX</sub> test tube should not have any deionised water in it. Beakers can be used however when multiple tests are being conducted it is difficult to handle the large beaker size efficiently. Do NOT add more than a few drops at a time. This will prevent overflow and wastage of peroxide. A day's supply of peroxide should be allowed to reach room temperature prior to use (cold peroxide from the fridge may be too slow to react).
7. Ideally, allow approximately 20 minutes for any reactions to occur. If substantial sulfides are present, the reaction will be vigorous and may occur almost instantly. In this case, it may not be necessary to stir the mixture. Careful watch will be needed in the early stages to ensure that there is no cross contamination of samples in the test tube rack. If the reaction is violent and the soil/peroxide mix is escaping from the test tube, a small amount of deionised water can be added to cool and calm the reaction. Usually this controls overflow. Do NOT add too much deionised water as this may dilute the mixture and affect the pH value. It is important to only use a small amount of soil otherwise violent reactions will overflow and the sample will be lost.
8. Steps 6 and 7 may be repeated until the soil/peroxide mixture reaction has slowed. This will ensure that most of the sulfides have reacted. In the lab this procedure would be repeated until no further reaction occurs, however in the field, best judgement is recommended.
9. If there is no initial reaction, individual test tubes containing the soil/peroxide mixture can be placed into a cup of hot water (especially in cooler weather) or in direct sunlight. This will encourage the initial reaction to occur. When the sample starts to 'bubble', remove the test tube immediately from the cup and replace into test tube rack.
10. Wait for the soil/peroxide mixture to cool (may take up to 10 minutes). The reactions often exceed 90°C. Placing an electrode into these high temperature situations may result in physical damage and inaccurate readings as most pH meters are set to record a result for an ambient temperature of approximately 25°C.
11. Use an electronic pH meter (preferred method) to measure the pH<sub>FOX</sub>. Place a spear point electrode into the test tube, ensuring that the spear point is totally submerged in the soil/peroxide mixture. Ensure that the plastic soil sleeve that exposes the spear point totally is used on the end of the electrode in preference to the protective pronged sleeve that almost totally conceals the spear point. This will ensure good contact with the soil. Never stir the mixture with the electrode. This will damage the semi-permeable glass membrane.
12. Rate the reaction using a LMHXV scale (Section A5).

13. Wait for the reading to stabilise and record the  $pH_{FOX}$  measurement.
14. All measurements and pH calibration measurements should be recorded on a data sheet.

TABLE A2: Results – field  $pH_{FOX}$  test.

pH value and reaction	Result	Comments
A strong reaction of soil with peroxide – X or V	A useful indicator but cannot be used alone.	Organic matter, coffee rock, and other soil constituents such as manganese oxides can also cause a reaction. Care must be exercised in interpreting a reaction on surface soils and high organic matter soils such as peats and coffee rocks, and some mangrove/estuarine muds and marine clays.
$pH_{FOX}$ value at least one unit below field $pH_F$ and reaction to peroxide	May indicate PASS but depends on the initial and resultant pH	The greater the difference between the two measurements ( $\Delta pH$ ), the more indicative the value is of a PASS. The lower the final $pH_{FOX}$ , the better the indication of a positive result (eg. a 1 unit change from pH 8 to 7 would not indicate PASS, however a 1 unit change from pH 3.5 to 2.5 would be indicative).
$pH_{FOX} < 3$ , strong reaction with peroxide, and large $\Delta pH$	Strongly indicates PASS – potential for the soil to produce sulfidic acid upon oxidation	The lower the $pH_{FOX}$ below 3, the more positive the likely presence of sulfides. A combination of all three parameters (reaction strength, unit pH change, and final $pH_{FOX}$ result) is most confirmatory.
A $pH_{FOX}$ 3–4 and reaction to peroxide	The test is less positive and is a borderline result	Sulfides may be present however organic matter may also be responsible for the decrease in pH. Laboratory analyses are required to confirm if sulfides are present.
$pH_{FOX}$ 4–5	The test is neither positive nor negative	Sulfides may be present either in small quantities and be poorly reactive under quick test field conditions, or the sample may contain shell/carbonate, which neutralises some or all acid produced by oxidation. Equally the $pH_{FOX}$ value may be due to the production of organic acids and there may be no sulfides present in this situation. In such cases, the chromium reducible sulfur method would be best to check for the presence of iron sulfides.
$pH_{FOX} > 5$ and little or no drop in pH from $pH_F$ but reaction to peroxide	Little net acidifying ability is indicated	On soils with neutral to alkaline field pH and shell or white concretions present, the fizz test with 1M HCl should be used to test for carbonates. The SPOCAS method should be used to check for any oxidisable sulfides and the presence of self-neutralising ability.

### A6 Field Test Results Interpretation

Field test results are dependant on many factors including accuracy of pH meters, strength of reagents, and operator skill. The reactions and results obtained from the field pH peroxide test can be further influenced by additional factors such as soil type, moisture content, ambient air temperature, presence of organic matter, or bicarbonate as shell or seawater in the soil sample. Some of these reactions are listed in Table A3 together with explanatory comments.

TABLE A3: Some common field test results.

pH <sub>F</sub>	pH <sub>FOX</sub> (at completion of reaction)	Δ pH	Reaction rate	Result (eg. **PASS or ***AASS)	Comments / Possible explanation
3.5	3.3	0.2	L	AASS present	Oxidation has occurred and sulfuric acid has formed in the past. This soil may not have much more potential to oxidise further as the pH <sub>F</sub> and pH <sub>FOX</sub> are similar.
3.7	1.4	2.3	X or V	AASS present; PASS – strong indication	Oxidation has occurred in the past. This soil has the potential to oxidise further indicated by the strong reaction, appreciable pH unit difference (pH <sub>FOX</sub> is significantly lower than the pH <sub>F</sub> ) and the very low final pH <sub>FOX</sub> .
6.5	2.1 (1.9)*	4.4	X or V	No AASS; PASS – strong indication	This soil is not yet oxidised but has the ability to produce sulfuric acid if exposed. Little buffering capacity in the soil. Laboratory analysis using SPOCAS could confirm this.
8.5	3.0 (3.2)*	5.5	H	No AASS; PASS – likely	The initial pH may be reflecting a strong seawater influence (pH 8.2) or some form of dissolved carbonates. The large ΔpH indicates a strong likelihood of PASS even though the pH <sub>FOX</sub> is borderline. Here, the ΔpH and the reaction gives strength to the argument. Laboratory analysis using SPOCAS and reacted calcium (Ca <sub>A</sub> ) could confirm this (see Ahern & McElnea (1999)).
8.0	2.0 (6.0)*	?	H	No AASS; PASS – strong indication; Considerable buffering capacity	The initial alkaline pH <sub>F</sub> indicates a seawater influence. The initial large decrease in pH indicates the soil is likely to contain sulfides. The pH measured after 20 minutes may indicate a large % of shell dissolving into solution as the acid contacts it (a small amount of HCl added to a sample of soil could confirm its presence). Laboratory analysis using SPOCAS and Ca <sub>A</sub> could confirm this (see Ahern & McElnea (1999)).
5.5	5.4 (5.3)*	0.2	X or V	No AASS; PASS – unlikely	The strong reaction is probably due to the presence of manganese in the soil sample.
5.5	3.8 (3.5)*	2.0	H (slow froth)	No AASS; PASS – possible	The strength of the reaction indicates possible organic matter. There may be some sulfides present also. Laboratory analysis using the S <sub>CR</sub> could confirm this.

\* pH<sub>FOX</sub> after 20 minutes (or overnight)

\*\* PASS – Potential Acid Sulfate Soils

\*\*\* AASS – Actual Acid Sulfate Soils

## APPENDIX 2: Glossary

**(Acid) Fizz test:** The field test used for soils to test for the presence of carbonate minerals, whereby dilute hydrochloric acid is added to the soil. An effervescent fizzing reaction indicates the presence of carbonate minerals.

**Acid Base Accounting (ABA):** The process by which the various acid-producing components of the soil are compared with the acid neutralising components so that the soil's net acidity can be calculated.

**Action criteria:** The critical net acidity values (expressed in units of equivalent % pyrite sulfur, or equivalent mol H<sup>+</sup>/t) for different soil texture groups and sizes of soil disturbance that trigger the need for ASS management.

**Actual Acidity:** A component of existing acidity. 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. It is measured in the laboratory using the TAA method. It does not include the less soluble acidity (ie. retained acidity) held in hydroxy-sulfate minerals such as jarosite.

**ANC:** Acid neutralising capacity. A measure of a soil's inherent ability to buffer acidity and resist the lowering of the soil pH.

**ANC<sub>BT</sub>:** Acid neutralising capacity by back titration. Acid neutralising capacity measured by acid digest followed by back titration of the acid that has not been consumed.

**ANC<sub>E</sub>:** Excess acid neutralising capacity. Found in soils with acid neutralising capacity in excess of that needed to neutralise the acidity generated by oxidation of sulfides. The soil is oxidised with peroxide, then a titration is performed with dilute hydrochloric acid to a pH of 4, followed by a second peroxide digestion. If a soil has a positive ANC<sub>E</sub> result then the TPA result is zero and vice versa.

**Ca<sub>HCl</sub>:** Calcium soluble in 4 M HCl, which includes soluble and exchangeable calcium as well as calcium found in certain carbonate minerals (eg. dolomite, calcite, aragonite).

**Ca<sub>KCl</sub>:** Potassium chloride extractable calcium measured following the TAA analysis, which includes soluble and exchangeable calcium as well as calcium from gypsum.

**Ca<sub>NAS</sub>:** Net acid soluble calcium. The calcium soluble in 4 M HCl that is not soluble in 1 M KCl. (Ca<sub>HCl</sub> – Ca<sub>KCl</sub>). It can be used (in combination with Mg<sub>NAS</sub>) to provide an estimate of the soil carbonate content, but may be an overestimate if calcium is dissolved from non-carbonate or non-acid-neutralising minerals.

**Ca<sub>P</sub>:** Peroxide calcium. Calcium measured following the TPA analysis, which includes soluble and exchangeable calcium, calcium from gypsum, as well as calcium (eg. from carbonates) dissolved as a result of acid produced due to oxidation of sulfides by peroxide.

**Chromium Suite:** The acid base accounting approach used to calculate net acidity which uses the chromium reducible sulfur method to determine potential sulfidic acidity. A decision tree approach based on the pH<sub>KCl</sub> result is then used to determine the other components of the acid base account.

**C<sub>IN</sub>**: Inorganic carbon. ( $C_T - C_{TO}$ ). It is used to estimate the carbonate content of the soil.

**CRS**: The acronym often given to the Chromium Reducible Sulfur method.

**C<sub>T</sub>**: Total carbon. A measure of the total carbon content of the soil, encompassing both organic and inorganic forms.

**C<sub>TO</sub>**: Total organic carbon. The carbon in sample measured following a sulfurous acid digestion procedure used to remove carbonate carbon.

**Existing Acidity**: The acidity already present in acid sulfate soils, usually as a result of oxidation of sulfides, but which can also be from organic material or acidic cations. It can be further sub-divided into actual and retained acidity, ie. Existing Acidity = Actual Acidity + Retained Acidity.

**Fineness factor**: A factor applied to the acid neutralising capacity result in the acid base account to allow for the poor reactivity of coarser carbonate or other acid neutralising material. The minimum factor is 1.5 for finely divided pure agricultural lime, but may be as high as 3.0 for coarser shell material.

**Jarosite**: Jarosite is a characteristic pale yellow mineral deposit that can precipitate as pore fillings and coatings on fissures. Where there is a fluctuating watertable, jarosite may be found along cracks and root channels in the soil. However, jarosite is not always found in AASS.

**Mg<sub>A</sub>**: Reacted magnesium. The magnesium soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. ( $Mg_P - Mg_{KCl}$ ). It can be used (in combination with Ca<sub>A</sub>) to provide an estimate of the soil carbonate content, but may be an underestimate if the HCl-titration to pH 4 has not been performed as part of the TPA/ANC<sub>E</sub> procedure.

**Mg<sub>HCl</sub>**: Magnesium soluble in 4 M HCl, which includes soluble and exchangeable magnesium as well as magnesium found in certain carbonate minerals (eg. dolomite, magnesite).

**Mg<sub>KCl</sub>**: Potassium chloride extractable magnesium measured following the TAA analysis, which includes soluble and exchangeable magnesium.

**Mg<sub>NAS</sub>**: Net acid soluble magnesium. The calcium soluble in 4 M HCl that is not soluble in 1 M KCl. ( $Mg_{HCl} - Mg_{KCl}$ ). It can be used (in combination with Ca<sub>NAS</sub>) to provide an estimate of the soil carbonate content, but may be an overestimate if magnesium is dissolved from non-carbonate or non-acid-neutralising minerals.

**Mg<sub>P</sub>**: Peroxide magnesium. Magnesium measured following the TPA analysis, which includes soluble and exchangeable magnesium, as well as magnesium (eg. from carbonates) dissolved as a result of acid produced due to oxidation of sulfides by peroxide.

**Monosulfides**: The term given to the highly reactive iron sulfide minerals found in ASS that have the approximate formula 'FeS' and which are soluble in hydrochloric acid (as opposed to iron disulfides such as pyrite that are not appreciably soluble in hydrochloric acid).

**Net Acidity**: The result obtained when the values for various components of soil acidity and acid neutralising capacity are substituted into the Acid Base Accounting equation. Calculated as:  
 Net Acidity = Potential sulfidic Acidity + Existing Acidity - (Acid Neutralising Capacity/Fineness Factor)

**pH<sub>F</sub>:** Field pH. Field determination of pH in a soil:water paste.

**pH<sub>FOX</sub>:** Field peroxide pH. Field determination of pH in a soil:water mixture following reaction with hydrogen peroxide.

**pH<sub>KCl</sub>:** Potassium chloride pH. pH in a 1:40 (W/V) suspension of soil in a solution of 1 M potassium chloride measured prior to TAA titration.

**pH<sub>OX</sub>:** Peroxide oxidised pH. pH in a suspension of soil in a solution after hydrogen peroxide digestion in the SPOCAS method.

**POCAS:** An acronym standing for Peroxide Oxidation Combined Acidity and Sulfate method (Method Code 21). This method has been superseded by the SPOCAS method.

**POCASm:** An acronym standing for the modified Peroxide Oxidation Combined Acidity and Sulfate method. This method has been superseded by the SPOCAS method.

**Potential (sulfidic) acidity:** The latent acidity in ASS that will be released if the sulfide minerals they contain (eg. pyrite) are fully oxidised. It can be estimated by titration (ie. TSA) if no acid neutralising material is present, or calculated from  $S_{POS}$  or  $S_{CR}$  results.

**Retained Acidity:** The 'less available' fraction of the existing acidity (not measured by the TAA) that may be released slowly into the environment by hydrolysis of relatively insoluble sulfate salts (such as jarosite, natrojarosite, and other iron and aluminium hydroxy-sulfate minerals).

**S<sub>CR</sub>:** The symbol given to the result from the Chromium Reducible Sulfur method (Method 22B). The  $S_{CR}$  method provides a measure of reduced inorganic sulfide content using iodometric titration after an acidic chromous chloride reduction. This method is not subject to interferences from organic sulfur.

**S<sub>HCl</sub>:** Sulfur soluble in 4 M HCl which includes soluble and adsorbed sulfate, sulfate from gypsum, as well as sulfate from hydroxy-sulfate minerals such as jarosite and natrojarosite.

**S<sub>KCl</sub>:** Potassium chloride extractable sulfur measured following the TAA analysis, which includes soluble and adsorbed sulfate as well as sulfate from gypsum.

**S<sub>NAS</sub>:** Net acid soluble sulfur. ( $S_{HCl} - S_{KCl}$ ). The sulfur soluble in 4 M HCl that is not soluble in 1 M KCl. It provides an estimate of the sulfate contained in jarosite and similar low solubility hydroxy-sulfate minerals (and can be used to estimate retained acidity).

**S<sub>P</sub>:** Peroxide sulfur. Sulfur measured following the TPA analysis, which includes soluble and exchangeable sulfate, sulfate from gypsum, as well as sulfide converted to sulfate and that released from organic matter as a result of peroxide oxidation.

**S<sub>POS</sub>:** Peroxide oxidisable sulfur from the SPOCAS method. The sulfur soluble after the peroxide digest and TPA titration that was not soluble following KCl-extraction and TAA titration. ( $S_P - S_{KCl}$ ). It provides an estimate of the soil sulfide content, but is affected by the presence of organic sulfur.

**S<sub>RAS</sub>:** Residual acid soluble sulfur. The sulfur measured by 4 M HCl extraction on the soil residue remaining after peroxide digestion and TPA titration of the SPOCAS method. It provides an estimate of the sulfate contained in jarosite and similar low solubility hydroxy-sulfate minerals (and can be used to estimate retained acidity).

**S<sub>T</sub>:** Total sulfur. A measure of the total sulfur content of the soil, encompassing both organic and inorganic forms.

**S<sub>TOS</sub>:** Total oxidisable sulfur. An estimate of soil oxidisable sulfur made from determining the sulfur not soluble in 4 M HCl. ( $S_T - S_{HCl}$ ). It tends to provide an overestimate of soil sulfide content.

**Self-neutralising soils:** This term is given to ASS where there is sufficient acid neutralising capacity (with the relevant safety factor applied) to neutralise the potential sulfidic acidity held in the soil (ie. the net acidity from the Acid Base Account is zero or negative). Soils may be 'self-neutralising' due to an abundance of naturally occurring calcium or magnesium carbonates (eg. crushed shells, marine animal exoskeletons, coral) or other acid-neutralising material.

**SPOCAS:** An acronym standing for Suspension Peroxide Oxidation Combined Acidity and Sulfur method (Method Code 23), the peroxide-based method that supersedes the previous POCAS and POCASm methods.

**SPOCAS Suite:** The acid base accounting approach used to calculate net acidity based on the Suspension Peroxide Oxidation Combined Acidity and Sulfur method. A decision tree approach based on the values of  $pH_{KCl}$  and  $pH_{OX}$  is used to decide what analytical path is followed in order to allow calculation of net acidity.

**TAA:** Titratable actual acidity. The acidity measured by titration with dilute NaOH following extraction with KCl-solution in the SPOCAS method. Previously referred to as Total Actual Acidity in the POCAS and POCASm methods.

**TPA:** Titratable peroxide acidity. The acidity measured by titration with dilute NaOH following peroxide digestion in the SPOCAS method. Previously referred to as Total Potential Acidity in the POCAS and POCASm methods.

**TSA:** Titratable sulfidic acidity. The difference in acidity measured by titration with dilute NaOH following extraction with KCl-solution and the acidity titrated following peroxide digestion in the SPOCAS method. ( $TPA - TAA$ ). Previously referred to as Total Sulfidic Acidity in the POCAS and POCASm methods.

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*How can it be improved?*

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