# Do acid sulfate soils need to be ring-mill ground to ensure an accurate Acid Base Account?

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## Abstract

Australian Standard acid sulfate soil methods require the grinding of soil to <0.075 mm. This necessitates the use of a ring-mill or similar apparatus, which is expensive and time-consuming. We investigate whether ring-mill grinding is needed for accurate and reproducible acid-base accounting, or if conventional fine-grinding (i.e. <0.5 mm) is sufficient to obtain acceptable results. Preliminary unreplicated experiments provided valuable information used to formulate the final experimental work. Following these initial experiments, five soils from an ASS survey in coastal central Queensland were selected for further investigation. These soils were chosen to reflect the range of chemical properties found in acid sulfate soils. Soils from the two treatments were analysed in quintuplicate by Chromium and SPOCAS suite analyses (Ahern *et al.* 2004). While individual analytes did show significant differences between treatments in some soils, there was no significant difference in the net acidity between ring-mill grinding and conventional grinding for soils without acid neutralising capacity (ANC). For the self-neutralising soils, conventional grinding gave significantly lower ANC results compared to the ring mill. It is uncertain whether ring-mill grinding gives a true reflection of the ANC available in the natural environment, as commercially-available agricultural lime ($CaCO_3$) is usually >0.075 mm diameter.

## Key Words

Acid sulfate soils, analysis, soil grinding, ring-mill, acid-base account.

## Introduction

With rising world population and with that growing coastal development, increasingly ‘the nastiest soils in the world’ (Dent 1986) are being disturbed. Without proper management, these acid-producing soils have the potential to cause serious/severe environmental harm, degrade expensive infrastructure (bridges, roads, pipelines) as well as impact upon human health. With the advent of a regulatory and best-practice management framework for acid sulfate soils in many Australian states, the disturbance and subsequent development of often environmentally sensitive coastal areas are now subject to much greater scrutiny. In Queensland, the State Planning Policy SPP2/02 (supplemented by the Queensland ASS Technical Manual) compels developers and Councils to follow set protocols for the sampling, chemical analysis, confirmation testing and management of acid sulfate soils (ASS). Consequently, soil testing laboratories that traditionally had an agricultural focus, along with new testing facilities, are now gearing up for ASS testing.

The chemistry of ASS is complex, as can be the chemical analysis and interpretation of test results. As with all soil analysis, appropriate sample preparation is fundamental to obtaining accurate, precise and representative results. Protocols must be such that a suitably ground, well-mixed sub-sample is produced that is representative of the soil collected in the field. Guidelines for the analysis of ASS (Ahern *et al.* 2004) and a recent Australian Standard (AS4969.1—2008 Analysis of acid sulfate soil—Dried samples—Methods of test, Method 1: Pre-treatment of samples) call for grinding of soils to less than 0.075 mm to ensure sample homogeneity and greater reactivity. Maher *et al.* (2004) used 4 soils to compare the chromium reducible sulfur ($S_{CR}$) and water soluble sulfate results obtained following 2 grinding treatments, 1) gently hand grinding to pass a 1 mm sieve and 2) ring-mill grinding for various grinding times from 1–30 minutes. The authors reported higher levels of $S_{CR}$ for the ring mill ground soil compared to the hand-ground sample and only minor differences for water soluble sulfate between the 2 grinding treatments. Higher recovery of $S_{CR}$ was attributed to abrading coatings of pyrite grains as a result of more aggressive grinding.

Gently hand grinding before sieving is not a recommended procedure in the Australian soil testing industry. It is unlikely that a representative sub-sample could be achieved for samples dominated by coarse sand and organic matter. In the Australian Laboratory handbook of Soil and Water Chemical Methods (Rayment and Higginson 1992) and its soon to be released revision (Rayment and Lyons, In Press), three soil grinding specifications are recommended. Coarse grinding to pass a 2 mm sieve is recommended for 'plant available' soil tests. For organic carbon and total nitrogen, generally smaller sample weights are required and fine grinding to pass a 0.5 mm sieve is recommended for homogeneity. The third specification <0.05 mm (ultra-fine grinding) involves the use of ring-mill systems. However such ultra-fine grinding is only recommended for XRF spectroscopy to avoid random scattering of fluorescent light from the surface of the sample pellet.

To date, no systematic comparison between regular fine grinding (<0.5 mm) and ring-mill grinding has been reported for ASS. This study compares five soils prepared by fine grinding to <0.5 mm (hereafter called 'conventional fine grinding vs ring mill grinding for the ASS tests comprising the Chromium and SPOCAS suites.

## Methods

### *Soil grinding mills*

After fan-forced drying of soil at 85ºC, the entire sample was ground to pass a 2 mm sieve. Those soils high in clay content that set hard were first fractured using a wooden mallet as shown in Figure 1. The coarse-ground sample was thoroughly mixed before the entire sample was finely ground to pass a 0.5 mm sieve (Figure 2). After this fine grinding samples were thoroughly mixed. Figure 2 shows the ring mill system used to grind a 30–50 g sub-sample of fine ground soil, for 2–3 minutes grinding time using the steel rings shown.

**Figure 1. Soil preparation equipment and coarse grinder (<2 mm) used in this study. Fine textured soils can dry very hard and need to be disaggregated up using either a mallet or device such as a vice before coarse grinding.**

**Figure 2. Soil grinding equipment used for fine grinding to <0.5 mm (left) or <0.05 mm using a ring mill grinder (right). Both fuzed zirconia rings and steel rings are shown.**

### *Chemical analysis*

The five soil samples were analysed in quintuplicate following the methods described in Laboratory Methods Guidelines (Ahern *et al*. 2004). These tests include: $S_{CR}$ (chromium reducible sulfur – Sullivan *et al*. 2000), $S_P$ (peroxide sulfur), $S_{KCl}$ (KCl-extractable S), $S_{RAS}$ (residual acid-soluble sulfur), TAA (titratable actual acidity), TPA (titratable peroxide acidity), $ANC_E$ (excess ANC), $pH_{KCl}$ (pH of suspension 1:40 1M KCl extract) and $pH_{OX}$ (pH of 1M KCl suspension after initial peroxide digestion). Calculations derived from tests including $S_{POS}$ (peroxide oxidisable sulfur) are also compared for the two grinding treatments.

## Results and Findings

Data in Figure 3 and Table 1 indicate that fine-grinding of soils is just as effective as ring-mill grinding in recovering chromium reducible sulfur ($S_{CR}$) for acid sulfate soils. Whilst the average standard deviation of results for ring-mill grinding is slightly less than for fine-grinding, on average fine-grinding produces a slightly higher result than ring-milling. Maher *et al*. (2004) surmised that grinding (they only looked at ring-mil ground soil) was necessary to abrade coatings on sulfide grains to maximise recovery, but for the 5 soils studied here it appears that conventional fine-grinding is also capable of ensuring adequate sulfide recovery.

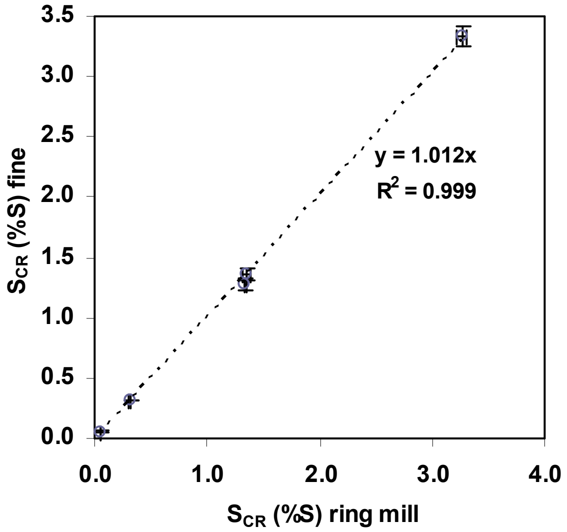

**Figure 3. Effect of grinding treatment on chromium reducible sulfur ($S_{CR}$). (Means shown, error bars represent ±1 s.d. for 5 replicates).**

For environmental management/risk assessment purposes the quantity 'net acidity' is of principal importance, as it represents a worst-case scenario of the amount of acidity that a soil may generate if it is allowed to fully oxidise and release its entire store of acidity. In the acid-base accounting (ABA) equation, the net acidity represents the sum of the potential sulfidic acidity (i.e. $S_{CR}$ or $S_{POS}$), actual acidity (TAA) and retained acidity ($S_{RAS}$ or $S_{NAS}$), minus soil ANC (moderated by an empirical fineness factor, to allow for the surface area of carbonates in the sample). It is apparent for the three soils (in Figure 4 and Table 1) not containing ANC, that there is no statistical difference in net acidity calculated from the SPOCAS suite between fine-grinding and ring-mill grinding treatments.

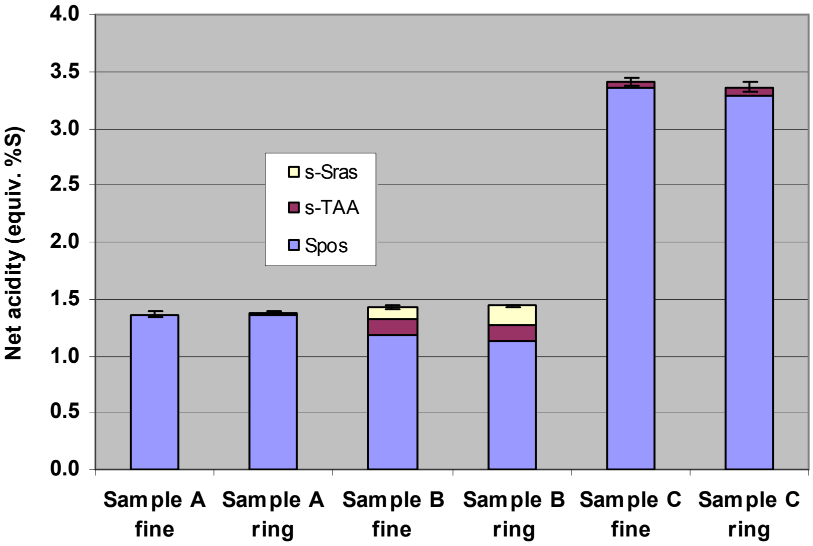

**Figure 4. Effect of grinding treatment on net acidity by the SPOCAS suite for 3 soils without ANC (Means shown, error bars represent ±1 s.d. for 5 replicates).**

However, individual analytes do show differences for some soils. For instance, $S_{KCl}$ shows a general trend to increasing values for the more vigorous ring mill grinding. This could represent oxidation of sulfide and its conversion to sulfate during the grinding process, or simply greater exposure of soil mineral surfaces hence more effective extraction of sulfate by 1M KCl. If the former were the case, then a commensurate increase in TAA might be expected, compensated by a proportionate decrease in $S_{POS}$. This appears to be the case for samples B and C (Table 1), though the increase in TAA does not exactly tally with the decrease in $S_{POS}$. For sample A there is little discernible effect. The increase in the TAA may simply be a consequence of the increased surface area and exposure of fresh mineral surfaces for titration. Conventional fine grinding did however yield substantially lower (i.e. 15–18%) $ANC_E$ results compared to ring-milling. This is not unexpected, since the determination involved a slow titration with dilute acid whose kinetics are controlled by surface area. The neutralisation reactions are also surface-controlled in the field. The ring mill grinding of shells and other carbonates that contribute to the lab ANC may be an overestimate of field ANC. It is uncertain whether ring-mill grinding gives a true reflection of the ANC available in the natural environment, or for lime-treated ASS, as shells and commercially-available agricultural lime ($CaCO_3$) are usually >0.075 mm in diameter.

**Table 1. Comparison between fine grinding and ring mill grinding for a range of ASS analytes (Means shown, italicised data represents the s.d. of 5 replicates of the preceding analyte. A fineness factor of 1.5 for ANC was used in net acidity calculations).**

| **Soil** | **A** | | **B** | | **C** | | **D** | | **E** | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Analyte** | **Fine** | **Ring** | **Fine** | **Ring** | **Fine** | **Ring** | **Fine** | **Ring** | **Fine** | **Ring** |
| **$S_{CR}$** | 1.366 | 1.352 | 1.282 | 1.340 | 3.336 | 3.266 | 0.058 | 0.056 | 0.318 | 0.314 |
| ***(%S)*** | *0.048* | *0.028* | *0.049* | *0.012* | *0.080* | *0.049* | *0.0044* | *0.005* | *0.004* | *0.009* |
| **$S_{POS}$** | 1.353 | 1.357 | 1.180 | 1.124 | 3.354 | 3.291 | 0.067 | 0.042 | 0.319 | 0.280 |
| ***(%S)*** | *0.029* | *0.013* | *0.018* | *0.011* | *0.030* | *0.046* | *0.004* | *0.002* | *0.005* | *0.008* |
| **$pH_{KCl}$** | 5.10 | 5.42 | 3.60 | 4.10 | 5.22 | 5.30 | 9.20 | 9.26 | 8.80 | 8.88 |
| | *0.00* | *0.04* | *0.00* | *0.00* | *0.04* | *0.00* | *0.04* | *0.05* | *0.00* | *0.04* |
| **s-TAA** | 0.012 | 0.016 | 0.134 | 0.146 | 0.052 | 0.073 | n/a | n/a | n/a | n/a |
| ***(%S)*** | *0.001* | *0.000* | *0.003* | *0.003* | *0.001* | *0.001* | *n/a* | *n/a* | *n/a* | *n/a* |
| **$pH_{OX}$** | 2.16 | 2.15 | 2.10 | 2.08 | 1.88 | 1.90 | 7.08 | 7.40 | 6.98 | 6.98 |
| | *0.05* | *0.06* | *0.00* | *0.04* | *0.04* | *0.00* | *0.04* | *0.07* | *0.04* | *0.04* |
| **s-TPA** | 1.343 | 1.342 | 1.337 | 1.278 | 3.872 | 3.808 | n/a | n/a | n/a | n/a |
| ***(%S)*** | *0.015* | *0.010* | *0.018* | *0.017* | *0.021* | *0.054* | - | - | - | - |
| **$ANC_E$** | n/a | n/a | n/a | n/a | n/a | n/a | 9.88 | 11.64 | 5.26 | 6.42 |
| ***(%$CaCO_3$)*** | - | - | - | - | - | - | *0.33* | *0.11* | *0.11* | *0.04* |
| **$S_{KCl}$** | 0.151 | 0.161 | 0.288 | 0.286 | 0.394 | 0.411 | 0.012 | 0.037 | 0.038 | 0.077 |
| ***(%S)*** | *0.001* | *0.002* | *0.005* | *0.006* | *0.012* | *0.010* | *0.000* | *0.002* | *0.000* | *0.006* |
| **$S_{RAS}$** | n/a | n/a | 0.154 | 0.222 | n/a | n/a | n/a | n/a | n/a | n/a |
| ***(%S)*** | - | - | *0.012* | *0.011* | - | - | - | - | - | - |
| **Net acidity** | 1.365 | 1.373 | 1.430 | 1.436 | 3.406 | 3.364 | -2.088 | -2.472 | -1.017 | -1.278 |
| **SPOCAS** | *0.029* | *0.015* | *0.021* | *0.014* | *0.030* | *0.046* | *0.07* | *0.025* | *0.025* | *0.013* |

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