

A Kinetic Approach to Assessing the Risk of Groundwater Acidification from Sulfidic Soils

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ABSTRACT

To assess potential impacts to groundwater from the disturbance of acid sulfate soils at a large construction project in coastal Victoria, Australia, an extensive program of fieldwork was undertaken to provide geological, meteorological and hydrogeological inputs into a site conceptual model to assess source, pathway and receptor linkages at the site. Soils were geochemically and geotechnically characterised from both background and disturbed areas, and free draining kinetic columns were constructed using local rainwater as the leachant.

The results of a ten month kinetic leach program were used to assess the potential long term risk posed to the receiving environment from insitu and stockpiled soils and assist in the development of groundwater management measures and improved water management at the constructed facility.

Keywords: Kinetic leach trial, acid sulfate soils

INTRODUCTION

The site is located in an area comprising gentle undulating terrace sand covered plains and alluvial floodplains and swamps (Rosengren and Boyd, 2008) of the early to mid Holocene, affected by both periods of drought (during 2007-2009) and flooding (during the winter of 2013). The groundwater level within the overburden groundwater aquifer at the site was reported to seasonally fluctuate by up to 1.5 m. Soils comprising acid sulfate soils (ASS) are present above and below the groundwater level, across the site, with soils with the highest potential to generate acidity present within the low lying swampy areas.

During the development of the site, ASS had been excavated and placed in stockpiles to represent artificial dunes, while in other areas, insitu ASS was dewatered due to construction activities. Concerns were raised about long term risks presented by ASS oxidation. In response, an extensive program of work was undertaken to evaluate the potential impact of ASS at the site on the surrounding environment.

To assess the risk associated with the release of acid from the disturbed soils a probabilistic statistical assessment of the sulfidic soils sampled at the site was conducted (Barker and Wallis, 2014). A GoldSim model was constructed to undertake a preliminary assessment of fate and transport of non-attenuated solute (i.e. acidic leachate) migrating off-site. In particular, the time it could take for a non-attenuated solute to migrate towards key environmental receptors was conservatively estimated. Two potential receptors; the Powlett River, situated approximately 1100 m east/northeast from the site and a tributary of the Powlett River, situated approximately 500 m from the site were identified.

The results demonstrated that there was a 50% probability that (a non-attenuated) leachate could reach the Powlett River in 12 years and the tributary in 4 years. There was a 5% probability that the leachate would reach the River in less than 2 years. Given the potential for impacts to the surrounding environment, an intensive investigation was undertaken to better understand the acid loads and timing of acidification.

Characterisation of the site conditions comprising assessment for the presence of ASS (using Suspension Peroxide Oxidation Combined Acidity & Sulfur (SPOCAS) analysis) combined with kinetic geochemical characterisation methods was undertaken. Groundwater quality at the site was monitored at a high frequency, through a network of groundwater wells within the overburden material, with a view to capturing local variations to groundwater quality from the construction activities that were ongoing (Dannatt and Wallis, 2014).

The kinetic methods employed were those typically used for mine-related acid drainage projects, this was one of the few construction projects known in Australia where kinetic techniques have been employed in any assessment. The free draining leach column method was modified from the standard methodology (with respect to leachate volumes and frequency of leach events) to reflect the site conditions encountered and the material properties (adapted from McElnea and Ahern (2000)).

The specific objectives of this geochemical leach assessment were to quantify the acid load released from each of the insitu and exsitu areas and provide an indication of the length of time that active management practices would be required.

METHODOLOGY

Sample Collection

Sample locations were selected based on the ASS test results obtained from previous soil investigations. The purpose was to obtain a range of different soil types with varying acidity regimes which would represent typical insitu and exsitu soil conditions. Approximately 4 kg of soil sample was collected from each location using a Geoprobe® drill rig with a push tube system. The soil samples were logged using the Unified Soil Classification System.

Sample Analysis

Samples were submitted to a National Analytical Testing Authority (NATA) accredited laboratory for static geochemical analytical work. A sub-sample of approximately 500 g was sent to Golder geotechnical laboratory for geomechanical testing. Soil samples were analysed for the parameters listed in Table 1.

Table 1 Soil and groundwater analysis methods and parameters

	Standard Parameters	Limit of Reporting
Soil		
Geomechanical	Atterberg Limits	1% and (0.5% for Linear Shrinkage)
pH/Electrical Conductivity	pH (1:5)	0.1 pH units
	EC (1:5)	1 µS/cm
Static Acid Base Account	SPOCAS Suite	pH unit, 2 mole H+/T, 0.02%S
Multi-Elements in Solids	Total Metals (Al, As, Ba, Be, Cd Cr, Co, Cu, Fe, Pb, Mn, Ni, V, Zn)	1-50 mg/kg
	Hg	0.1 mg/kg
	Sulfate	50 mg/kg
	Chloride (Cl-)	10 mg/kg
	Soluble Major Cations (Ca, Mg, Na, K)	10 mg/kg
Multi- Elements in water	Leachable Metals (Al, As, Ba, Be, Cd Cr, Co, Cu, Fe, Pb, Mn, Ni, V, Zn, Hg)	0.0001-0.01 mg/L
Soil Parameters	Cation Exchange Capacity (CEC), Organic Matter, Moisture Content,	0.1 meq/100 g, 0.5%, 1%
X-Ray Fluorescence (XRF)	Fused disc XRF	SiO ₂ – 0.05%, Cr ₂ O ₃ , MnO, P ₂ O ₅ – 0.005%: Others: 0.01%

X-Ray Defraction (XRD)	XRD and Siroquant Analysis	Generally 0.1%
Leachate		
Acidity	Acidity	1 mg/L
Dissolved Major Anions and Cations	Cl, SO ₄ , Alkalinity and Ca, Mg, K and Na	1 mg/L
Dissolved Metals	As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, Fe, Al and Hg	Al – 0.01 mg/L, Cd-0.0001 mg/L, Zn-0.005 mg/L, V/Fe-0.05 mg/L Others:0.001 mg/L

Kinetic Leach Column Testing

Two procedures for kinetic testing of solid mine waste materials; the Free Draining Leach Test, described in Appendix E of the AMIRA International ARD Test Handbook (2002) developed in Australia and the ASTM Designation: D 5744 – 96 (Reapproved 2001) accelerated weathering test method developed in the USA. Modifications to the above methods have been made based on available refereed literature describing ASS studies that have utilised column experiments. Further modifications, described below, were made during the running of the leach experiments.

Rainfall collected at the site was used as the leachant. The volume of rainwater used per leach event was initially based on the Bureau of Meteorology’s monthly climate statistics for the Wonthaggi Weather Station obtained during the period 1981 to 2010. The aim was to leach the columns with the same amount of water as that which falls on the site in a 20 year period. Based on an average monthly rainfall of 79.2 mm (and taking into account total annual actual evapotranspiration), the volume of rainwater required to be leached through the columns over a 10 month period (to simulate a 20 year period), was 3.4 litres per week (total of 136 L).

Approximately 2.5 kg of ‘as received’ soil (i.e. no drying or grinding), was placed in each column (C01-C09) except for columns C05 and duplicate column C06 where approximately 1.8 kg of soil was used in the column. The sample weight was corrected to ‘dry weight’ using the soil moisture content test results.

Four columns comprised soil samples collected from the stockpiled soil (C01, C03, C04, C05) and two columns comprised soil samples collected from the insitu, expected dewatered zone, (C07 and C09). Three duplicate columns (C02 duplicate of C01, C06 duplicate of C05 and C08 duplicate of C07) were also included in the program.

A total of 20 leach events were undertaken for all columns except C05 and C06, where the experiments were terminated early due to the dispersive nature of the material (only 14 and 12 leach events were completed respectively). Samples of leachate are then collected and analysed (presented in Table 1).

During the first one to two leaching events, it was attempted to leach 3.4 Litres through the soil samples, however, due to low the permeability of the soil the method required modification; the frequency of leach events and the volume of leachant had to be reduced. The frequency of leaching

events was reduced from weekly to approximately every 2 weeks and the volume of leachant was reduced to approximately 1.7 litres per sampling event. In addition, following the first leach event, a vacuum pump was employed to assist in the collection of samples as insufficient sample was leaching by free drainage.

For four of the columns (C02, C03, C05 and C06), the volume of leachant had to be further reduced due to the highly dispersive nature of the fines. These challenges provide useful information regarding the soil behaviour and aided the development of the site conceptual hydrogeological model. The total volume of leachant added to each column over the leach events was between 20.1 and 37.4 Litres. This volume is equivalent to that which would be received at the site over a 3 to 5.5 year period.

RESULTS AND DISCUSSION

Pre leached Static

Soils sampled for this study comprised medium plasticity soft silty clay overlying low to medium dense silty sand. The organic matter content ranged from less than 0.5 %, in C09, to 2.1 %, in C07.

The pH (1:5 soil:water) of the exsitu samples range from 5.4 to 6.9 pH units. The pH of the insitu samples ranged from 4.9 to 5.5 pH units with samples from C07 returning the lowest pH values of 4.9 and 5.1 pH units. The EC values of the exsitu samples ranged from 325 to 718 $\mu\text{S}/\text{cm}$ and are higher than the EC of the two insitu samples which are 147 $\mu\text{S}/\text{cm}$ and 207 $\mu\text{S}/\text{cm}$. The titratable actual acidity (TAA) test results of the exsitu samples ranged from 6 to 13 moles H^+/t and were generally lower than the TAA results for the insitu samples which range from 5 to 59 moles H^+/t . Insitu soil samples from C07 exhibited the highest TAA test results compared to other samples.

The potential sulfidic acidity (S_{POS}) test results of the exsitu samples ranged from <10 to 47 moles H^+/t although the majority of the samples had S_{POS} test results between 12 and 24 moles H^+/t . Only one sample (from C04) returned a S_{POS} value of 47 moles H^+/t . The S_{POS} test results of the exsitu samples are generally lower than the S_{POS} test results of the insitu samples which ranged from <10 to 178 moles H^+/t . Test results from insitu soil samples from C09 were considerably higher than test results from other soil samples.

Nine of the 12 samples returned S_{POS} values above the laboratory limit of reporting. None of the exsitu or insitu samples contained any retained acidity. None of the exsitu or insitu samples contained acid neutralising capacity (ANC), as measured by acid reacted magnesium or acid reacted calcium. The 'net acidity' values of the exsitu samples ranged from <10 to 54 moles H^+/t and were generally, lower than the 'net acidity' value of the insitu samples which ranged from 24 to 183 moles H^+/t .

Post-Leach Testing

The concentration of metals within the leachate, over the course of the project is presented in Figure 1. The pH (1:5 soil:water) of all post-leach samples remained comparable to the pre-leach test results except for samples from C01, which returned a higher pH, and samples from C04, C05 and its duplicate C06, and C09 which returned a lower pH. The sample in C01 was the only sample that was leached of all its actual acidity and it is likely that the pH of the post-leach soil was influenced by the pH of rainfall more so that the samples in the other columns. Columns C04 and C09

generated the most amount of acidity via oxidation of sulfides whilst C05 and C06 could not be leached for the full extent of the monitoring program and may have retained some acidity.

Based on the S_{POS} test results of the leached soil, the entire measureable pyrite content of the soil placed within the columns had oxidised during the 10 month leaching program except at C01 and C09 where S_{POS} results of 18 moles H^+/t were recorded post the leach program. At C01, the post-leach S_{POS} result exceeded the pre-leach S_{POS} result (by 4 H^+ mole/tonne) which was likely due to the sample heterogeneity. As C09, the post-leach S_{POS} results was significantly less than the pre-leach S_{POS} result (i.e. reduced by 150 moles H^+/t) however, some potential acidity remained.

The TAA test results are above the laboratory limit of reporting for all samples except C01. This is inferred to indicate that all leached soils, apart from that at C01, contain some actual acidity which has the potential to be leached in the future; moderate levels of TAA (~30 moles H^+/t) were recorded in columns C04, C07 and C08 whilst low levels (<15 moles H^+/t) were recorded in the remaining columns.

Leachate Quality

In general, leachate from C04 (exsitu soil) and C09 (insitu soil) contained the highest concentrations of metals (Figure 1). At C09, the concentrations of metals in the leachate rose until leach event 4 to 5 after which the dissolved metal concentrations in the leachate began to decline. This trend is consistent with the trends in decreasing pH and increasing sulfate (Figure 2). A second increase in dissolved Al, As, Fe and Zn concentrations was observed in the leachate from C09, following leach event 10. This trend is consistent with a second rise in sulfate concentration and drop in pH post leach event 10 (Figure 2 (iii)).

The trend in dissolved metal concentrations (i.e. decrease following initial leach events) was similar for all metals except Cu where the concentration generally increased during the testing period. Based on this trend, the dissolved Cu test results suggest that Cu in the soil in column C09 is more strongly attenuated than other metals tested and the rate of Cu release increases when the pH drops to below approximately 2.6 pH units. Low levels of dissolved Al and Fe were detected in the leachate which was expected given the static test results for these metals.

Dissolved Al is likely present due to the dissolution of aluminosilicate clay minerals following the drop in pH whilst the dissolved Fe is likely present due to the dissociation of pyrite within the samples.

Leachate results were compared to groundwater quality at the site. Groundwater quality was found to be relatively stable when the whole site was considered. Localised variability was recorded, but these impacts could be correlated to the construction activities in close proximity to the monitoring point, thus impact from the acidic run off were not identified. Nevertheless, as a precautionary measure, run off from the stockpiles at the site is collected in a network of drains and treated.

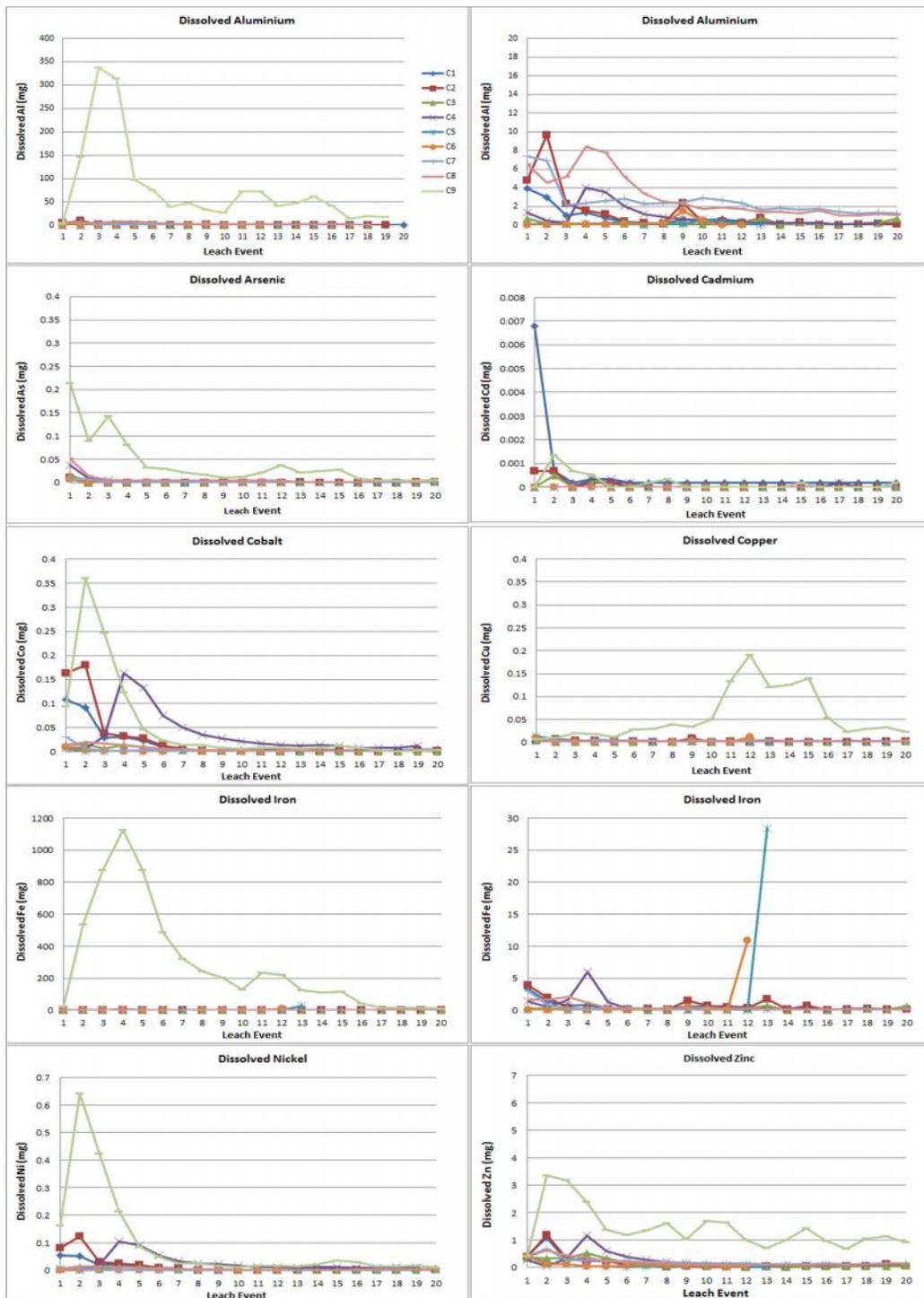


Figure 1 Comparison of dissolved metal concentrations in leachate.

XRF/XRD Analysis

Based on the results of the XRF analysis, the leached samples predominantly comprised silica (SiO₂) with lesser amounts of Aluminium Oxide (Al₂O₃; up to 9.55%), Iron Oxide (Fe₂O₃; up to 2.42%) and Potassium Oxide (K₂O; up to 1.46%).

Secondary iron minerals, such as jarosite and schwertmannite which commonly precipitate from iron-sulfate rich waters, were not identifiable within samples via XRD. This may be because they are only a minor component of the sample matrix (i.e. newly formed minerals). Alternatively they lack sufficient crystallinity to be detected. Freshly precipitated secondary minerals are likely to be highly amorphous and lack a regular crystalline structure.

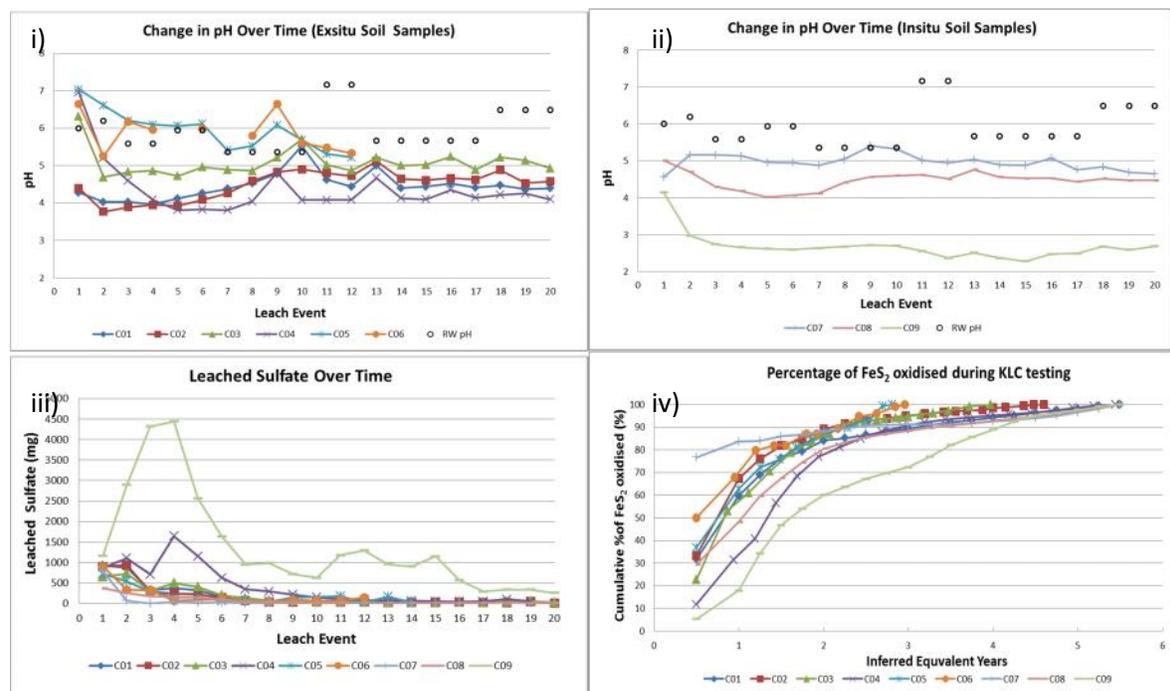


Figure 2 Change in pH over the leaching period for exsitu (i) and insitu (ii) samples. Rainwater pH (RW pH) also shown, iii) Sulfate export from the columns, iv) rate of sulfate generation / pyrite oxidation, assumes 100% of sulfate was leached during experiment.

Pyrite Oxidation Rates

Preliminary pyrite oxidation rates were calculated using the static and kinetic leach testing results. The assumptions used during this assessment are summarised as follows: (i) the samples are representative of the material in the constructed dunes; (ii) total pyrite content is calculated from the sum of sulfate in the leachate; (iii) the role of Fe(III) in the pyrite oxidation is limited given the low Fe concentration in waters at the site; (iv) by leach event 20, all of the pyrite has oxidised.

The cumulative percentage of FeS₂ oxidised over the course of the experiment was calculated through measurement of the sulfate generation over time and assuming oxygen as the primary oxidant. The rate of pyrite oxidation was plotted against the inferred equivalent field time (based on volume of leachant), as shown in Figure 2 (iii) and (iv).

It was noted that the oxidation rate decreased at approximately the 2.5 year mark, thus the assessment of acid loads to the environment two rates were used: within the first 2.5 years of oxidation, and following 2.5 years of oxidation. The oxidation rates for soil collected from the site are summarised as follows; oxidation rate within 2.5 years of disturbance, was estimated to range between 2×10^{-7} to 1.3×10^{-6} % pyrite oxidised per second. Oxidation rate following 2.5 years of disturbance, was estimated to range between 1×10^{-7} to 3.6×10^{-7} % pyrite/ sec. These rates are within the range reported in the literature (1×10^{-7} to 2×10^{-4} % pyrite/ sec, (Hipsey and Salmon, 2008).

CONCLUSION

Based on the pyrite oxidation rates estimated during these works, the risks to groundwater from the oxidation of pyrite (within insitu and exsitu ASS) was most significant during the first and second year of soil disturbance and dewatering (2009 and 2010). However, based on groundwater monitoring (Dannatt and Wallis, 2014), the acid load released to groundwater during this time may not have caused acidic conditions to form; the construction period being as long as the acid generation period. Thus, the significant amount of high alkalinity construction materials (i.e. concrete) used at the site to potentially buffered the groundwater pH.

As the acid formation from the insitu and exsitu ASS is likely to reduce with time, as the rate of oxidation of pyrite stabilises and the potential acid load is significantly depleted, the long term risks to groundwater (i.e. following 2013) are likely to be limited. As a response to this, groundwater monitoring frequency has been reduced to quarterly events.

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