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MODELING OF ACID GENERATION IN PYRITIC ESTUARINE SOILS

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ABSTRACT

The effective management of acid sulfate or pyritic soils is a major issue for many coastal regions in Australia. Drainage and subsequent aeration of potential acid sulfate soils often leads to pyrite oxidation and the acidification of the soil and groundwater. A numerical model has been developed to calculate the rate and magnitude of pyrite oxidation in acid sulfate soils, and the distribution of oxidation products such as H^+ , SO_4^{2-} and Fe^{3+} within the soil profile. The pyrite oxidation model includes vertical diffusion of oxygen from the atmosphere through soil macropores, lateral diffusion of dissolved oxygen from the macropores into the soil matrix, and the consumption of dissolved oxygen in the acid sulfate soil layers by pyrite oxidation. The model developed by the authors is used in conjunction with a commercially available water flow model which is used to simulate the groundwater and soil moisture regime in a three dimensional space. The model can be used to assess the effectiveness of different acid sulfate soils management strategies. The acidity generated by various drain management strategies is demonstrated.

INTRODUCTION

The amount of acidic pyrite oxidation products generated at a site, or the effectiveness of potential acid sulfate soil management techniques that rely on better management of the groundwater table, can be assessed by using simulation models that consider the groundwater hydrology at a site and its relationship to oxidation of pyrite. Considerable effort has been placed into the development of analytical and numerical solutions for modeling the oxidation of pyrite or other similar sulfidic minerals (eg. Wunderly *et al.*, 1996). Development of these models has been mainly focused on better understanding of the generation of acidic leachate from waste rock dumps and tailings lagoons associated with discard from sulfidic mineral mining activities, and as such, are only partly applicable to the study of sulfidic soils. Only one pyrite oxidation model has been designed specifically for the simulation of acid generation and transport in sulfidic soils (Bronswijk *et al.*, 1993). However, this model only simulates oxygen transport and pyrite oxidation in one dimension.

Blunden and Indraratna (2000) show that the magnitude and distribution of pyrite oxidation in land underlain by acid sulfate soil is not spatially or temporally uniform. In order to assess the effectiveness of groundwater management strategies at the appropriate spatial scale (eg. paddock or sub-catchment), the authors recommend that modeling of pyrite oxidation and the subsequent generation of sulfuric acid should be carried out in two or three dimensional space. This enables the magnitude and distribution of pyrite oxidation to be assessed over a site with reference to changes in the groundwater regime that are influenced by deep flood mitigation drains.

A three dimensional pyrite oxidation numerical model suitable for the assessment of acid sulfate soil management strategies at the paddock scale is described in this paper. The value of assessing pyrite oxidation across the site is shown with reference to the simulation of a drained site (i.e. existing deep flood

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mitigation drains with flap valve floodgates) and three alternative management options with elevated drain water levels.

THEORETICAL FORMULATION OF THE PYRITE OXIDATION MODEL

Oxygen transport down macropores

The oxidation of pyrite in acid sulfate soils is largely determined by the concentration of oxygen in the soil. The concentration of oxygen at a particular depth in the soil determines the rate of pyrite oxidation at that depth. Where a steady state oxygen concentration profile forms quickly, say within minutes or hours, this relationship between oxygen concentration, supply and consumption can be described as:

$$\frac{\partial}{\partial x} \left(D_s(\epsilon_g) \frac{\partial C_a(x)}{\partial x} \right) = \alpha_v \quad (1)$$

where; $C_a(x)$ is the concentration of oxygen in air-filled pores (m^3 per unit volume of soil), D_s is the diffusion coefficient of oxygen in air-filled pores ($\text{m}^2 \text{d}^{-1}$), t is time (d), x is distance (m), ϵ_g is air-filled porosity, and α_v is the volumetric consumption rate of oxygen per day.

The physical structure of the acid sulfate and the overlying soil layers largely determines D_s . For the acid sulfate soils encountered at the authors' field site, the most outstanding structural feature of the soil is the presence of large (2-10 mm diameter), continuous and straight macropores created by previous plant root activity. These macropores are surrounded by a tightly packed clayey matrix with massive structure. Oxygen diffuses vertically from the atmosphere into the soil through the air-filled macropores. The oxygen in the macropores is dissolved into the soil solution at the macropore walls, where it can diffuse into the soil matrix. This is shown in Figure 1. The dissolved oxygen is then consumed by pyrite oxidation.

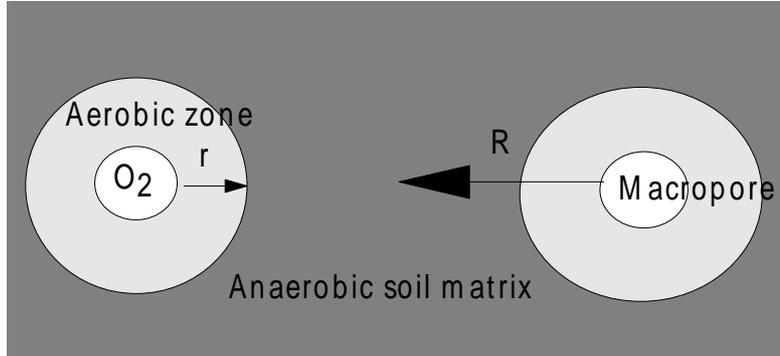


Figure 1 Plan view of the soil structure and oxygen transport in the pyrite oxidation model. R is the radius of the soil aggregates, r is the radius of the anaerobic zone.

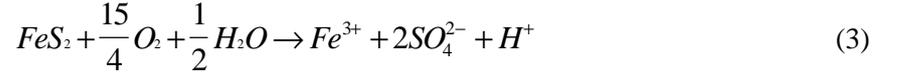
Pyrite oxidation in the aerobic soil matrix

The oxidation of pyrite is based on the “spherical reduction” concept that is adopted by many processed based numerical models of pyrite oxidation subsequently. Using this technique, the consumption of pyrite crystals by oxidation is calculated by (Blunden, 2000):

$$\frac{\partial m}{\partial t} = \frac{0.311 C_{FeS_2}}{\rho d} \sqrt{C_p} + C_{om} \times \frac{0.311 C_{FeS_2}}{2\sqrt{C_p}} \quad (2)$$

where: A is the surface area of pyrite crystals (m^2), K is the rate constant ($kg\ m^{-2}\ d^{-1}$), m is the mass of pyrite (kg), t is time (d), N is the number of pyrite crystals per $1\ m^3$ of acid sulfate soil, d is the diameter of the pyrite crystals (m), C_{FeS_2} is the pyrite content ($kg\ m^{-3}$), and ρ is the density of pyrite ($kg\ m^{-3}$).

In pyritic soil, the concentration of dissolved oxygen ($kg\ m^{-3}$) in water (C_w) can be partitioned such that $C_w = C_p + C_{om}$, where C_p and C_{om} are the concentrations of oxygen consumed by pyrite and other factors such as organic matter decomposition, respectively. $\frac{\partial m}{\partial t}$ now represents the rate of disappearance of pyrite crystals as a result of oxidation by oxygen from the atmosphere, and by the oxidation of organic substances in the soil. The stoichiometric reaction equation for pyrite oxidation by diffused oxygen is:



Therefore, in aerobic conditions, 1 mole of pyrite consumes 3.75 moles of oxygen during complete oxidation, which is equal to 1 kg of pyrite consuming 1 kg of oxygen during complete oxidation. Thus, Equation (2) may also be expressed as the mass oxygen consumption rate, α_m , by pyrite oxidation within the soil matrix, where:

$$\alpha_m = \frac{0.311C_{FeS_2}}{\rho d} \sqrt{C_p + OM} \quad (4)$$

OM can be regarded as a small constant used to account for the consumption of oxygen by sources other than pyrite in the soil. The oxygen consumption term α_m in Eqn (4) is equal to $\frac{\partial m}{\partial t}$ from Eqn (2).

Solving Eqn (4) yields the dissolved oxygen concentration profile $C_p(x)$ and the thickness of the anaerobic zone inside the soil matrix. The total oxygen consumption (ϕ_T) is calculated by integrating $\alpha_m(x)$ over the thickness of the aerobic zone (Blunden and Indraratna, 2000), which gives:

$$\phi_T = \left(\left[\frac{A' C_b + OM'}{\sqrt{\beta}} \right] \tanh \sqrt{\beta}(R-r) \right) \times S_o \quad (5)$$

where: A' is a constant and OM' is the intercept of a linear approximation of the oxygen consumption rate, C_b is the oxygen concentration at the boundary of the soil matrix and the macropore, and $\beta = \frac{A'}{D_w}$. S_o is defined as the specific surface area of the soil through which oxygen diffusion takes place in $1\ m^3$ of soil or a measure of the soil structure. In this model, the soil structure within the matrix is assumed to be a plate structure, hence, $S_o = 1/R$ (Blunden, 2000).

The calculation of the amount of oxygen consumption by organic mater (ϕ_{OM}) is simple because it is assumed to be at a constant rate in the aerobic fraction of the soil matrix, $(R-r)/R$, whereby:

$$\phi_{OM} = \frac{OM'(R-r)}{R} \quad (6)$$

Thus, the steady state amount of oxygen consumed by pyrite oxidation is calculated by:

$$\phi_{FeS_2} = \phi_T - \phi_{OM} \quad (7)$$

From the amount of oxygen consumed by pyrite (Eqn. 7), the amount of pyrite oxidised is calculated, and the production of Fe^{3+} , H^+ and SO_4^{2-} is determined accordingly. The numerical scheme was developed into a FORTRAN 77 program, ASS3D, that is used in conjunction with the volumetric soil moisture content output file from simulations of the groundwater regime using FEMWATER (Lin *et al.*, 1997), a 3D finite element model for simulating flow in variably saturated media.

APPLICATION OF THE ASS3D MODEL

The effectiveness of manipulating the water level in deep flood mitigation drains to reduce groundwater drawdown that enables to the oxidation of pyrite in acid sulfate soil was investigated using the ASS3D-FEMWATER model. Three drain management alternatives were simulated, namely the existing drained state, maintenance of elevated drain water levels at -0.5 and -0.3 m AHD through the installation of weirs at these elevations. The groundwater regime at the study site was simulated using FEMWATER by constructing a finite element mesh 150 m long (the length of a piezometer transect at the study site), 5m deep and 40 m wide (the width of a field), assigning material properties and applying appropriate boundary conditions. The atmospheric and drain water level boundaries were determined from field data collected between July 1997-98. The atmospheric boundary was defined as a transient variable flux at the nodes at the top of the finite element mesh. A severe drought period that was experienced on the South Coast of NSW during the 1997-98 summer, that caused the groundwater table to fall below the pyritic layer for the existing drained state, was included in the groundwater simulation. For the existing drain simulation, the drain water level was defined as a variable head at the elements across the drain-soil interface. For the weir simulations, the drain water level was defined as a constant head. The drain water level boundary conditions are shown in Figure 2 and were applied at one end of the 3D mesh.

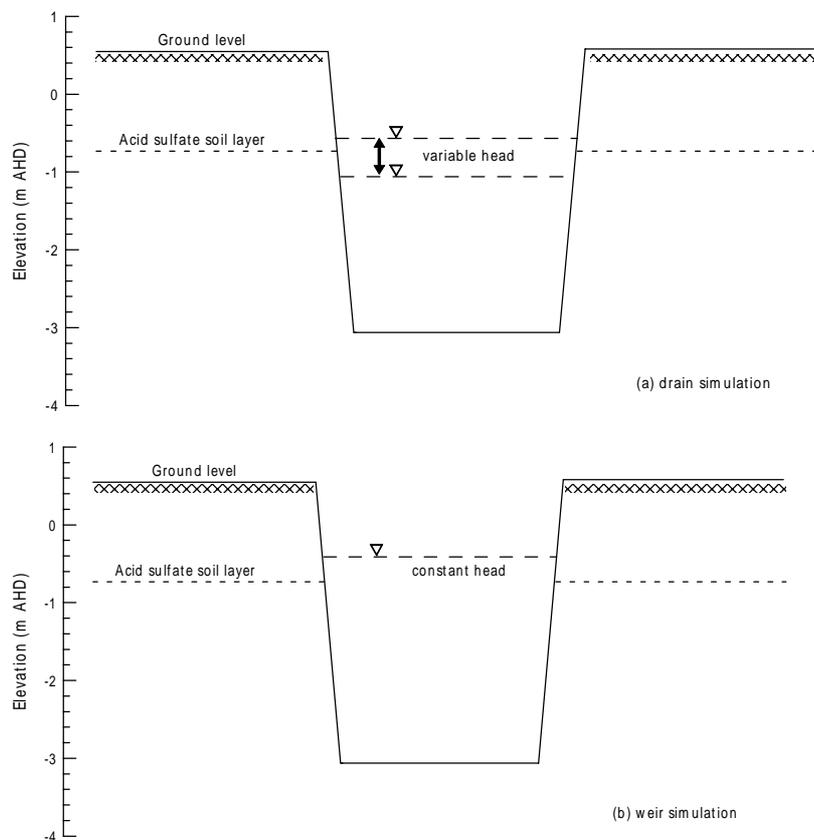


Figure 2 Simulated head boundaries for drain water levels, a) drain simulation using variable head; b) weir simulation using constant head.

FEMWATER simulations - groundwater elevation

Manipulation of the drain-soil boundary conditions had a significant influence on the elevation on the simulated groundwater table across the 3D mesh. The groundwater elevation at 10 m and 90 m distance from the drain is shown in Figure 3 for the existing drain and weirs at -0.5 and -0.3 m AHD. A substantial increase in the elevation of groundwater level was achieved by maintaining a constant, elevated water level in the drain by the weirs. During the worst part of the drought period (day 250) where groundwater levels fell well below the elevation of the pyritic soil layer, maintenance of the drain water level at -0.5 m AHD resulted in the groundwater at 10 and 90 m from the drain being 0.35 m and 0.49 m higher than under the existing drained conditions, respectively. Maintenance of the water level in the drain at -0.3 m AHD resulted in the groundwater at 10 m and 90 m from the drain being 0.64 m and 0.84 m higher than under the existing conditions, respectively.

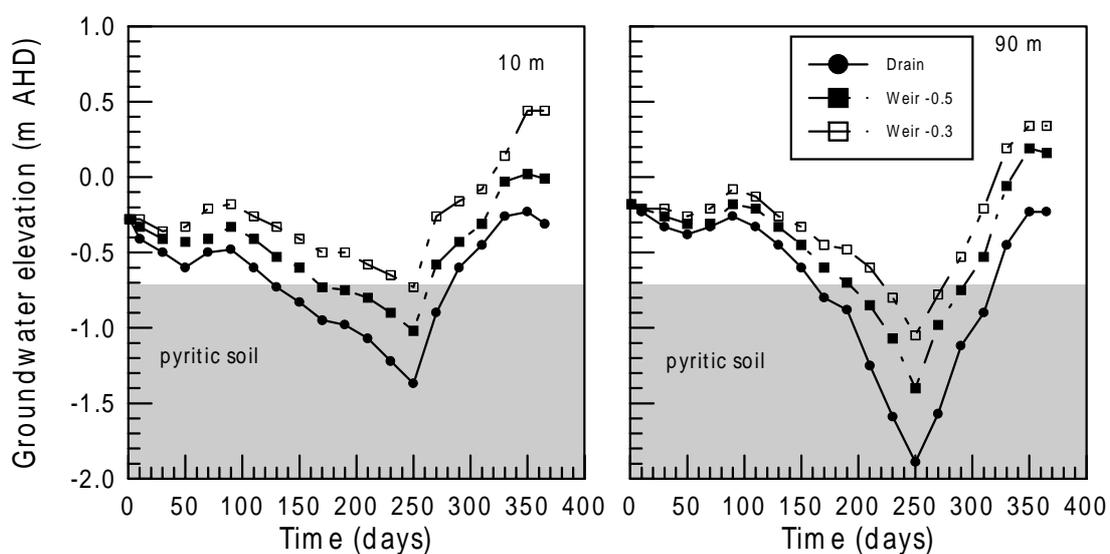


Figure 3 Simulated groundwater elevations for various drain management options.

ASS3 simulations - sulfate production from pyrite oxidation

The generation of sulfate and the consumption of pyrite by oxidation was, as expected, greatest in the existing drained state. For the period simulated, the existing drained conditions produced 91×10^3 mol sulfate from the oxidation of pyrite over the 6000 m^2 mesh area (i.e., $40 \text{ m} \times 150 \text{ m}$). The amount of sulfate produced with respect to the various drain management options simulated is shown in Figure 4. Maintenance of the drain water level at -0.3 m AHD resulted in 12.5×10^3 mol sulfate being generated, whereas maintenance of the drain water level at -0.5 m AHD resulted in 42×10^3 mol sulfate being generated.

The pyrite concentration of the sulfidic soil at elevations of -0.7, -1.0 and -1.5 m AHD was determined from samples collected at 90 m distance from the drain at the end of the simulation period. The pyrite concentration was measured at these depths at both the start and end of the simulation period, and compared against the predicted pyrite concentration made by ASS3D at the end of the simulation. The computed pyrite concentration in the soil profile after 365-days for the drain simulation correspond well with the measured pyrite concentration from the field. The amount of pyrite consumed during oxidation was slightly underestimated (by 0.09 %) at the -0.7 m AHD depth node relative to the pyrite concentration measured on field samples. At -1.0 m AHD, a very small overestimate (0.01%) of the amount of pyrite oxidized was calculated by ASS3D. Given the likely variability in the pyrite concentration of the sulfidic soil, the calculation of pyrite concentration by ASS3D is in good agreement with field data, thereby confirming the validity of the simulation model (Blunden, 2000).

The implementation of relatively inexpensive weirs within the flood mitigation drains can give rise to a substantial reduction in the amount of pyrite oxidation products generated. This suggests that maintenance of higher drain water levels, possibly in conjunction with allowing ingress of some tidal water through modified floodgates, may improve groundwater quality in areas affected by drainage induced pyrite oxidation. Simulation of the groundwater regime caused by the installation of a weir in the drain to maintain a drain water level of -0.5 m AHD resulted in a reduction of 54% of the amount of pyrite oxidised relative to the drained state. Sulfate production occurred between days 215-281 which corresponds with the worst part of the drought period. Raising the elevation of the drain water level to -0.3 m AHD resulted in even less pyrite being oxidised (14% relative to the drained state). For the -0.3 m AHD weir simulation, the oxidation of pyrite was confined to the time between days 240-268. This shows that implementation of the weir strategy delays the onset of oxidising conditions in the pyritic soil. The onset of pyrite oxidation was delayed by 35 days for the -0.5 m AHD weir and by 70 days for the -0.3 m AHD weir, respectively. Under 'normal' climatic conditions, it is envisaged that elevated drain water levels would maintain groundwater levels above the pyritic soil horizon all of the time. The effectiveness of raising groundwater tables above the pyritic layer using weirs has been confirmed in field trials (Blunden, 2000).

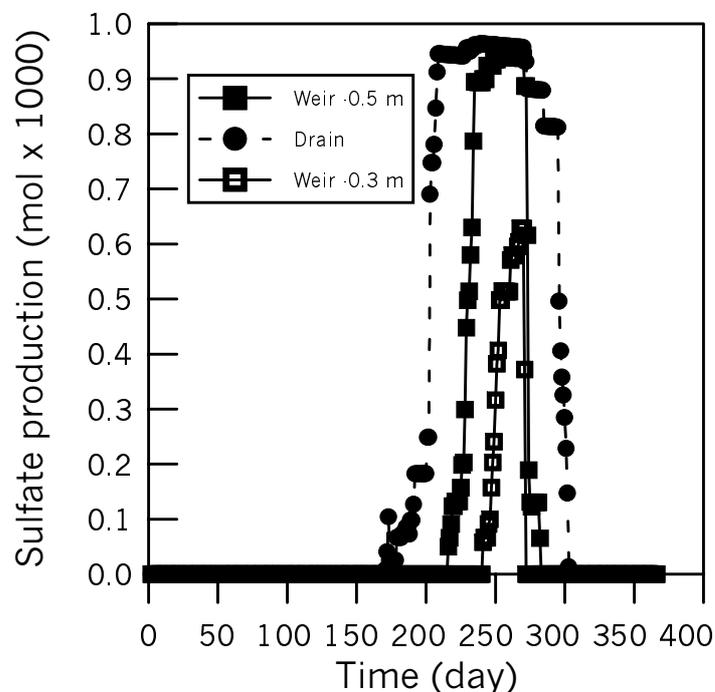


Figure 4 Sulfate production for the ASS3D simulation of drain management options

CONCLUSION

A numerical scheme for the simulation of pyrite oxidation, and the generation of acidic oxidation products, in acid sulfate soil that have a macropore dominated structure has been derived. This numerical scheme was developed into a simulation model, ASS3D, which in conjunction with a commercially available groundwater flow model, can be used to assess various acid sulfate soil management options. Application of ASS3D showed that substantial reduction in the generation of pyrite oxidation products could be achieved by the installation of weirs that maintain high water levels in drains.

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