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Abstract

Acidic groundwater generation from acid sulfate soil is a severe environmental and socio-economic problem in coastal Australia. A novel permeable reactive barrier (PRB) utilising recycled concrete aggregates as the reactive media was installed in the Shoalhaven Floodplain, south of Wollongong in Australia. The performance of the PRB has been monitored to study the acid neutralisation behaviour of recycled concrete and its potential to remove high concentrations of Al and Fe, which are threatening to living habitat. This study aims to couple geochemistry with geo-hydraulics in the remediation of acidic groundwater generated in acid sulfate soil terrain, which has not been addressed in the past (especially using recycled concrete aggregates), in view of time-dependent modelling and performance verification. Coupling includes complex geochemical reaction kinetics with transient groundwater flows. Moreover, chemical clogging due to mineral precipitates has rarely been quantified. Deposition of precipitated minerals in void spaces within the PRB reduces the porosity and hydraulic conductivity of the reactive medium, which in turn effects the reorientation of flow paths and changes in reaction times. The commercial numerical codes, MODFLOW and RT3D were used to couple the groundwater flow with reaction kinetics. A systematic algorithm was developed for RT3D to simulate geochemical reactions occurring in the PRB. The field results show good agreement with the model predictions. The hydraulic conductivity reductions occur near the entrance of the PRB due to the high amount of mineral precipitation. Compared to the entrance, hydraulic conductivity reductions were negligible midway and at the effluent end of the PRB.

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A Novel Hydro-geochemical Model for Treating Acidic Groundwater Utilising a Permeable Reactive Barrier

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ABSTRACT

Acidic groundwater generation from acid sulfate soil is a severe environmental and socio-economic problem in coastal Australia. A novel permeable reactive barrier (PRB) utilising recycled concrete aggregates as the reactive media was installed in the Shoalhaven Floodplain, south of Wollongong in Australia. The performance of the PRB has been monitored to study the acid neutralisation behaviour of recycled concrete and its potential to remove high concentrations of Al and Fe, which are threatening to living habitat. This study aims to couple geochemistry with geo-hydraulics in the remediation of acidic groundwater generated in acid sulfate soil terrain, which has not been addressed in the past (especially using recycled concrete aggregates), in view of time-dependent modelling and performance verification. Coupling includes complex geochemical reaction kinetics with transient groundwater flows. Moreover, chemical clogging due to mineral precipitates has rarely been quantified. Deposition of precipitated minerals in void spaces within the PRB reduces the porosity and hydraulic conductivity of the reactive medium, which in turn effects the reorientation of flow paths and changes in reaction times. The commercial numerical codes, MODFLOW and RT3D were used to couple the groundwater flow with reaction kinetics. A systematic algorithm was developed for RT3D to simulate geochemical reactions occurring in the PRB. The field results show good agreement with the model predictions. The hydraulic conductivity reductions occur near the entrance of the PRB due to the high amount of mineral precipitation. Compared to the entrance, hydraulic conductivity reductions were negligible midway and at the effluent end of the PRB.

Keywords: acid sulfate soil, permeable reactive barrier, groundwater flow modelling, geochemistry, hydraulic conductivity

1 INTRODUCTION

The coastal floodplains and estuaries have been undergoing environmental and economic problems due to the presence of acid sulfate soils (ASS), which are spread over 3 million hectares of Australian land (White et al., 1997). As long as the ASS is undisturbed, there is no prolonging harm. The increasing population and resulting changes in land use patterns such as construction of deep flood mitigation drains promote the oxidation of pyritic soil, thus generate sulfuric acid. One of the harmful processes involved is the mobilisation of toxic metals such as aluminium (Al) and iron (Fe) to nearby waterways. Subsequently, severe discharges of acidic water attack steel and concrete infrastructure, clog waterways with Fe flocculates, kill aquatic ecology and produce large acid scalds which makes the land unusable for agricultural purposes.

The acid sulfate soil research team at the University of Wollongong has been researching several engineering solutions such as weirs and modified floodgates, which have been installed near Broughton Creek, Shoalhaven Floodplain, New South Wales (NSW) (Indraratna et al., 2001). These methods were successful in preventing further pyrite oxidation, but they were unable to remediate existing acidity stored in the soil (Indraratna et al., 2005). Furthermore, they are not applicable in very low-lying areas as they increase the risk of flooding. A significant improvement was attained through the installation of a pilot-scale permeable reactive barrier (PRB) at Manildra Group's Environmental Farm in October 2006. Recycled concrete aggregates ($d_{50} = 40$ mm) were used as the reactive

medium to neutralise the acidic groundwater (Golab et al., 2006). This PRB has proven to be a promising technique for maintaining a groundwater pH from alkaline to neutral (pH 10.0-7.2) and removing Al and total Fe below average concentrations of 2 and 0.5 mg/L, respectively inside the barrier. Although the overall performance was satisfactory, a slow decrease in pH inside the PRB was observed due to armouring of the recycled concrete by the precipitation of Al- and Fe-oxy/hydroxide minerals. Laboratory column experiments showed a reduction of 50% in the actual acid neutralisation capacity (ANC) of the reactive media compared to its theoretical ANC (Regmi et al., 2011).

This study aims to model the performance of the PRB through coupling the geochemistry with groundwater flow modelling. To achieve that, a comprehensive geochemical algorithm was developed capturing the most dominant reactions and coupled to a transient groundwater flow model. Commercial numerical codes, MODFLOW and RT3D were used for this purpose. With time, secondary mineral precipitates occupy the pore spaces between the recycled concrete aggregates within the PRB, reducing its porosity and hydraulic conductivity. However, field observations and modelling results have shown that, this loss of porosity and hydraulic conductivity occurs at relatively low rates, thus the effect is not significant. This model will be useful for practising engineers and environmental scientists who have to deal with ASS problems, especially in coastal Australia.

2 MATERIALS AND METHODS

2.1 Permeable reactive barrier

The investigated site where the pilot-scale PRB is installed is located in farming land situated in the Lower Shoalhaven Floodplain area, near Bombaderry, south eastern NSW, Australia. The study site is next to a flood mitigation drain that flows into Broughton Creek, a left bank tributary of the Shoalhaven River. The site has the following properties in accordance for the installation of the PRB: the site is low-lying (0-1 m AHD) and, therefore, not suitable for weirs or two-way floodgates because of the risk of flooding; the groundwater is acidic with high Al (≤ 70 mg/L) and Total Fe (≤ 450 mg/L) concentrations; a drain is in close proximity for the treated groundwater to flow into; and there are no man-made structures present at the site, therefore, the barrier would not disturb any structures and allows access for excavators and other heavy equipment.

On the 5th of October 2006, the pilot-scale PRB (17.7 m long, 1.2 m wide and 3 m deep) was installed at the study site, parallel and 15 m from the drain such that it intersects the zone of maximum groundwater flow. The PRB was designed to maximise the groundwater residence time within the barrier and minimise the bypassing of the barrier. Geo-textile fabric was used to support the PRB and to protect the reactive media (i.e. recycled concrete) from physical clogging by soil and other fine particles entering the barrier. A total of 36 observation wells and 12 piezometers were installed inside, up-gradient and down-gradient of the PRB (Figure 1) to monitor phreatic surface variations, hydraulic gradients and groundwater chemistry.

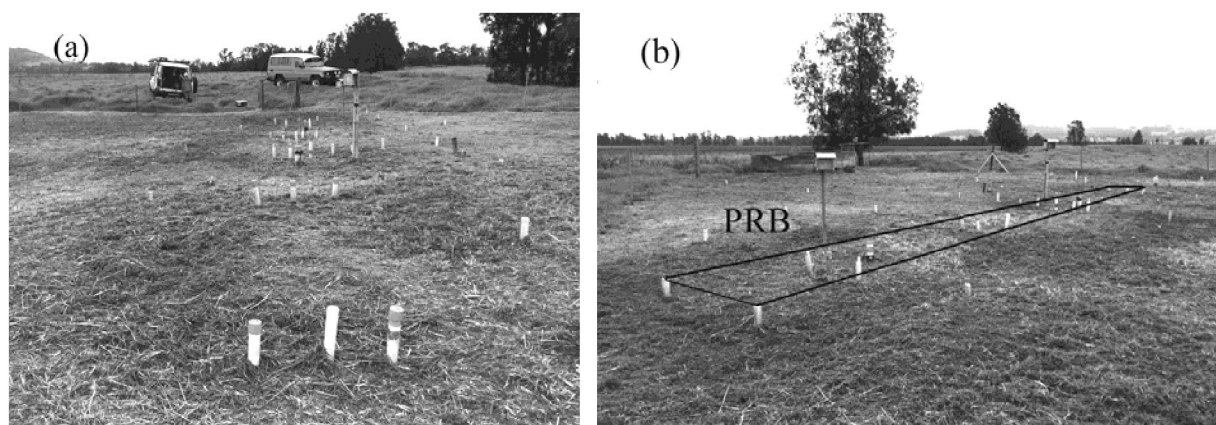


Figure 1 (a) and (b) Pilot-scale PRB and monitoring network at study site

Groundwater elevation in piezometers and water quality parameters such as pH, ORP, and temperature in monitoring wells were directly measured in the field every month from October 2006 to

date. Groundwater samples were analysed for total Fe, Al^{3+} , major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), anions (Cl^- and SO_4^{2-}), acidity and alkalinity. All chemical analyses were performed following the standard method for water and wastewater examination (APHA, 1998).

2.2 Model development

Commercially available software, MODFLOW and RT3D (finite different methods) were used to couple the groundwater flow and contaminant transport. MODFLOW does not have a way of automatically changing the porosity or the hydraulic conductivity unless they are manually entered. In this study, it was vital to correlate the change in porosity and hydraulic conductivity due to secondary mineral precipitates. In order to quantitatively assess the impact of clogging behaviour on porosity and hydraulic conductivity, a comprehensive mathematical model was developed (Indraratna et al., 2014). This model (Equation 1) captures the change in head in conjunction with change in hydraulic conductivity due to fine particles accumulation on the pore spaces. Therefore, Equation 1 was helpful to calculate the starting head for MODFLOW at every time step.

$$h = \left(\exp \left[- \frac{\mu^2 b K_0}{S \sum_{k=1}^{N_m} M_k R_k} \frac{(1 - n_0)^2}{n_0^3} \left\{ \alpha^2 \left(1.5 + \frac{1}{\beta} \right) - 3(\alpha + \ln \beta) \right\} \right] \right) \cdot (C \sin \mu x + D \cos \mu x) \quad (1.a)$$

$$\text{where, } \alpha = n_0 + \sum_{k=1}^{N_m} M_k R_k t \quad (1.a)$$

$$\beta = 1 - n_0 - \sum_{k=1}^{N_m} M_k R_k t \quad (1.a)$$

where, h is head, b is aquifer thickness, K_0 is initial hydraulic conductivity, n_0 is initial porosity, M_k is mineral molar volume, R_k is overall reaction rate for the mineral, S is storage co-efficient, N_m is number of minerals, t is time, μ , C and D are integral constants. The step by step procedure for obtaining Equation 1 is illustrated in Indraratna et al. (2014).

An original geochemical algorithm was developed using the transition state theory (Equation 2) proposed by Li and Benson (2005) and Yabusaki (2001). This is the first such geochemical algorithm developed which captures the reactions between acidic groundwater and recycled concrete. There are thirteen primary mineral dissolution-precipitation reactions as shown in Indraratna et al., (2014). For the benefit of the reader and to ensure standalone clarity of this paper, the developed geochemical algorithm previously demonstrated by Indraratna et al., (2014), is given in Appendix.

$$r = -k_{eff} \left(1 - \frac{IAP}{K_{eq}} \right) \quad (2)$$

where, r is reaction rate, k_{eff} is effective rate co-efficient, IAP is ion activity product and K_{eq} is solubility constant. Advective-dispersive-reactive transport of aqueous and solid phase species are solved through RT3D, which is a three-dimensional multi-component transport model used in saturated groundwater flow systems (Clement, 1997). RT3D consists of seven pre-defined reaction modules, and a "user-defined" reaction module. The latter was used in this study to feed the geochemical algorithm in to the system. Then MODFLOW and RT3D were run simultaneously to get the concentrations of reactants at every time step. The concentration of each species was calculated for each cell in the finite difference grid during each time step. Kinetic reaction rate coefficients (k_{eff}) used for mineral precipitation/dissolution are given in Table 1.

Table 1: Kinetic reaction rate coefficients (k_{eff}) for the mineral dissolution/precipitation

Mineral phase	k_{eff} (mol/L.s)
Ca^{2+}	2.27×10^{-7}
Al^{3+}	6.86×10^{-8}
Total Fe (Fe^{2+} and Fe^{3+})	5.87×10^{-8}

2.3 Model application to PRB

The authors decided to carry out a reactive transport analysis along the centreline of the PRB, assuming the centreline represents the whole PRB. The total width of the PRB (1.2 m) was discretised into intervals of 0.1 m in the horizontal direction (Figure 2). The first one third of the domain was considered as the entrance zone, the next one third was the middle zone and the last one third was the exit zone of the PRB. The acidic groundwater entering the PRB was assumed to be in chemical equilibrium. The flow domain was simulated as a fully saturated system. The specified head boundaries were applied and a mean hydraulic gradient of 0.006, observed on the basis of field data from 2006 to 2012 was used to represent realistic field conditions. The lateral, top and bottom faces of the domain were considered as no-flow boundaries.

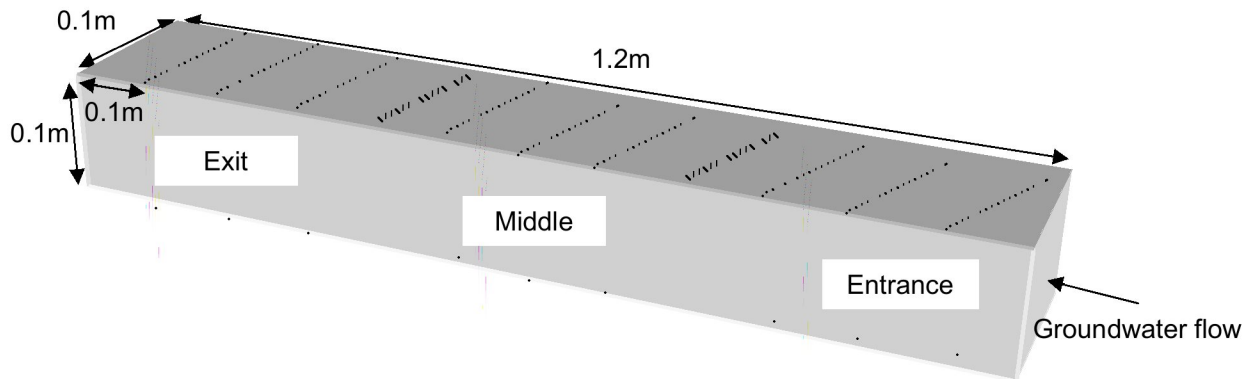


Figure 2 Discretisation of the centreline of the PRB

3 RESULTS AND DISCUSSION

The model outputs gave the profiles of pH, Al and total Fe concentrations. Figures 3, 4 and 5 show the favourable comparisons obtained between the predictions and field measurements for pH, Al and total Fe concentrations, respectively for 2012, that is after 6 years of operation. In 2012, the groundwater pH up-gradient of the PRB varied between 3.2 and 4.1 with an average of 3.6, while the pH inside the PRB was higher and varied from 6.7 to 7.4 with an average of 7. The model predicted pH values match with the rapid increase in pH from up-gradient to PRB and the near-neutral plateau inside the PRB. It is evident from both field measurements and model predictions that the pH at the entrance zone is lower than that of at the middle and exit zones. This is probably due to the exhaustion of reactive material during the neutralisation process. Furthermore, the effect of armouring and clogging of the reactive media from the secondary mineral precipitation is also responsible for the slight decrease in pH at the entrance zone of the PRB.

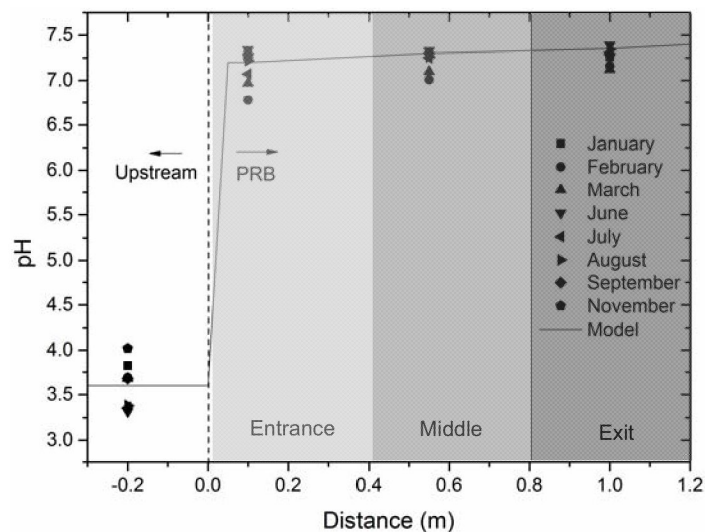


Figure 3 Measured and predicted pH values for field PRB for 2012

The highest Al concentration observed up-gradient of the PRB for 2012 was 32 mg/L. Both field monitoring results and model predictions indicate that the concentrations of Al^{3+} reduced rapidly within the PRB to very low levels ($< 1 \text{ mg/L}$). Similar to that, high concentrations of total Fe up-gradient of the barrier were also observed with a sharp decrease ($< 0.5 \text{ mg/L}$) at the entrance of the PRB. The rapid decrease in Al and total Fe indicates that they have been precipitated in the forms of oxy/hydroxides.

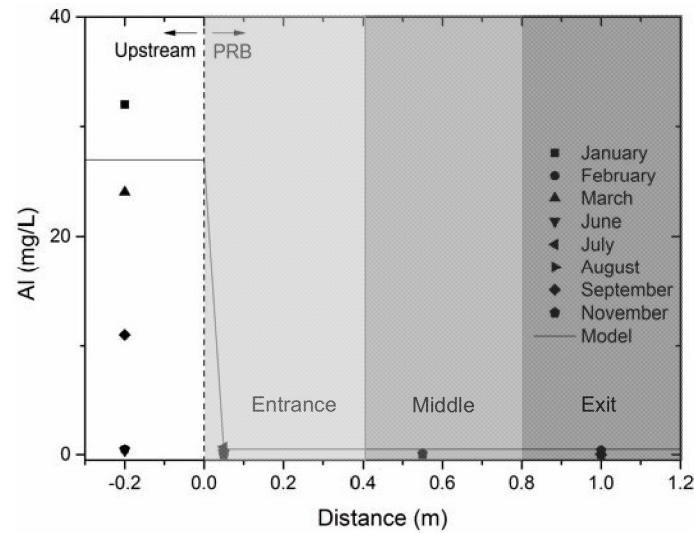


Figure 4 Measured and predicted Al concentrations for field PRB for 2012

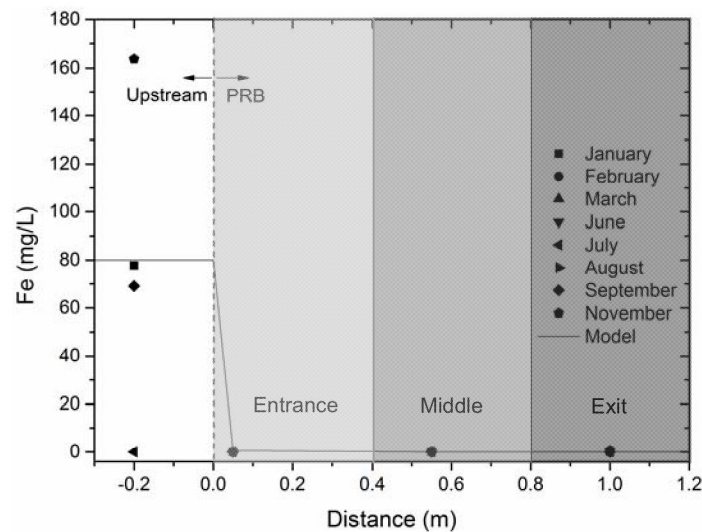


Figure 5 Measured and predicted Fe concentrations for field PRB for 2012

As an adverse effect of the secondary minerals precipitation inside the PRB, the porosity and hydraulic conductivity would be decreased. However, the calculated decrease in hydraulic conductivity during operation of the PRB for six years was only 3%, which is not significant because of the larger sized recycled concrete aggregates ($d_{50}=40 \text{ mm}$) used in the PRB. Furthermore, this is evident from the observed steady piezometric head within the PRB over the 6 year monitoring period, which indicates no threat of failure of the PRB from clogging (Figure 6).

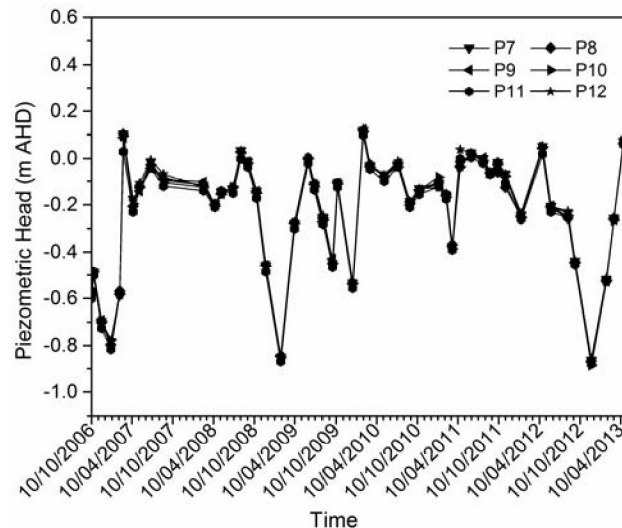


Figure 6 Groundwater elevations inside the PRB with respect to time (P7-P12 are the six piezometers inside the PRB)

4 CONCLUSION

A novel geochemical algorithm was developed to capture all the dominant reactions and this was used for the input of RT3D. MODFLOW and RT3D were run in tandem to simulate flow and the reactive transport of mineral components. The model predicted pH and the concentrations of Al^{3+} and total Fe were acceptable with the observed field values. The performance of the PRB for the last six years confirms that recycled concrete is a low cost suitable reactive material for using in PRBs for the remediation of acidic groundwater in typical acid sulfate soil terrain. The average pH within the PRB was around 7. The pH of the entrance zone of the PRB has been decreasing slowly, compared to that of the middle and exit zones. This is attributed to hindrance of the alkalinity generating materials in recycled concrete as well as by secondary mineral precipitates accumulating on the reactive surface and in pore spaces of the materials. The associated hydraulic conductivity reduction after six years of operation is only 3% at the entrance zone of the PRB with negligible reductions at the middle and exit zones of PRB.

5 ACKNOWLEDGEMENTS

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REFERENCES

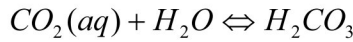
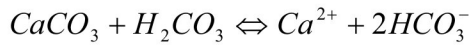
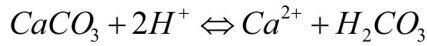
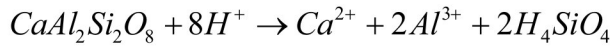
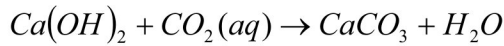
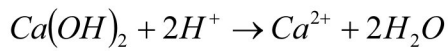
- APHA 1998. *Standard Methods for the Examination of Water and Wastewater*, Washington, 20th Edition, American Public Health Association.
- Clement, T. P. 1997. RT3D: A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers, PNNL-SA-11720 In: Laboratory, P. N. N. (ed.). Richland, Washington.
- Golab, A. N., Peterson, M. A. & Indraratna, B. 2006. Selection of potential reactive materials for a permeable reactive barrier for remediating acidic groundwater in acid sulphate soil terrains. *Quarterly Journal of Engineering Geology and Hydrogeology*, 39, 209-223.
- Indraratna, B., Glamore, W., Blunden, B., Downey, J. & Tularam, A. Year. Engineering strategies for controlling problems of acid sulphate soils in low-lying coastal areas. In: Smith, D. W., Fityus, S. G. & Allman, M. A., eds. *Proc. 2nd Australia and New Zealand Conference on Environmental Geotechnics*, 2001 Newcastle, Australia. Not Collected: Australian Geomechanics Society Inc., 133-146.
- Indraratna, B., Golab, A. & Glamore, W. 2005. Acid sulphate soil remediation techniques on the Shoalhaven River Floodplain, Australia. *Quarterly Journal of Engineering Geology and Hydrogeology*, 38, 129-142.

- Indraratna, B., Pathirage, P. U., Kerry, R. & Banasiak, L. 2014. Coupled hydro-geochemical modelling of a permeable reactive barrier for treating acidic groundwater. *Computers and Geotechnics Journal*, 55, 429-439.
- Li, L. & Benson, C. H. 2005. Impact of fouling on the long-term hydraulic behaviour of permeable reactive barriers. *IAHS-AISH Publication*, 23-31.
- Regmi, G., Indraratna, B., Nghiem, L. D. & Golab, A. N. 2011. Treatment of Acidic Groundwater in Acid Sulphate Soil Terrain Using Recycled Concrete: Column Experiments *Journal of Environmental Engineering, ASCE*, 137, 433-443.
- White, I., Melville, M. D., Wilson, B. P. & Sammut, J. 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management*, 5, 55-72.
- Yabusaki, S. 2001. Multicomponent reactive transport in an in situ zero-valent iron cell. *Environmental Science and Technology*, 35, 1493-1503.

APPENDIX

Geochemical algorithm

Bicarbonate buffering (maintenance of an almost neutral pH) and complete removal of Al and Fe from the solution:



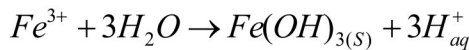
Dissolution of Ca bearing minerals and precipitation of secondary minerals were assumed to follow the transition state theory with the following expressions:

$$\frac{d[m_{Ca(OH)_2}]}{dt} = \frac{1}{2} \frac{d[H^+]}{dt} = -\frac{d[Ca^{2+}]}{dt} = r_1[Ca^{2+}] = k_{[Ca^{2+}]} \left[\frac{a_{Ca^{2+}} a_{OH^-}^2}{K_{eq, Ca^{2+}, OH^-}} - 1 \right]$$

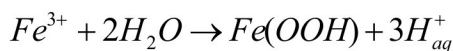
$$\frac{d[m_{CaAl_2Si_2O_8}]}{dt} = \frac{1}{8} \frac{d[H^+]}{dt} = -\frac{d[Ca^{2+}]}{dt} = -\frac{1}{2} \frac{d[Al^{3+}]}{dt} = r_{[Ca^{2+} Al^{3+}]} = k_{[Ca^{2+} Al^{3+}]} \left[\frac{a_{Ca^{2+}} a_{Al^{3+}}^2}{K_{eq, Ca^{2+} Al^{3+}}} - 1 \right]$$

$$\frac{d[m_{CaCO_3}]}{dt} = \frac{1}{2} \frac{d[H^+]}{dt} = -\frac{d[Ca^{2+}]}{dt} = -\frac{d[H_2CO_3]}{dt} = r_2[Ca^{2+}] = k_{[Ca^{2+}]} \left[\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{eq, Ca^{2+}, CO_3^{2-}}} - 1 \right]$$

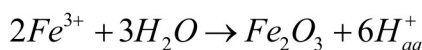
$$\frac{d[m_{CaCO_3}]}{dt} = \frac{d[H_2CO_3]}{dt} = -\frac{d[Ca^{2+}]}{dt} = -\frac{1}{2} \frac{d[HCO_3^-]}{dt} = r_3[Ca^{2+}] = k_{[Ca^{2+}]} \left[\frac{a_{Ca^{2+}} a_{HCO_3^-}}{K_{eq, Ca^{2+}, HCO_3^-}} - 1 \right]$$



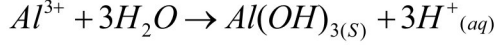
$$\frac{d[Fe^{3+}]}{dt} = -\frac{d[m_{Fe(OH)_3}]}{dt} = -\frac{1}{3} \frac{d[H^+]}{dt} = r_1[Fe^{3+}] = k_{[Fe^{3+}]} \left[\frac{a_{Fe^{3+}} a_{OH^-}^3}{K_{eq, Fe^{3+}, OH^-}} - 1 \right]$$



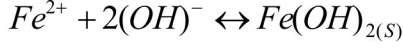
$$\frac{d[Fe^{3+}]}{dt} = -\frac{d[m_{Fe(OOH)}]}{dt} = -\frac{1}{3} \frac{d[H^+]}{dt} = r_2[Fe^{3+}] = k_{[Fe^{3+}]} \left[\frac{a_{Fe^{3+}} a_{OOH^{3-}}}{K_{eq, Fe^{3+}, OOH^{3-}}} - 1 \right]$$



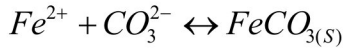
$$\frac{1}{2} \frac{d[Fe^{3+}]}{dt} = -\frac{d[m_{Fe_2O_3}]}{dt} = -\frac{1}{6} \frac{d[H^+]}{dt} = r_3[Fe^{3+}] = k_{[Fe^{3+}]} \left[\frac{a_{Fe^{3+}}^2 a_{O^{2-}}^3}{K_{eq, Fe^{3+}, O^{2-}}} - 1 \right]$$



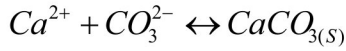
$$\frac{d[Al^{3+}]}{dt} = -\frac{d[m_{Al(OH)_3}]}{dt} = -\frac{1}{3} \frac{d[H^+]}{dt} = r_{[Al^{3+}]} = k_{[Al^{3+}]} \left[\frac{a_{Al^{3+}} a_{OH^-}^3}{K_{eq, Al^{3+}, OH^-}} - 1 \right]$$



$$\frac{d[Fe^{2+}]}{dt} = \frac{1}{2} \frac{d[OH^-]}{dt} = -\frac{d[m_{Fe(OH)_2}]}{dt} = r_1[Fe^{2+}] = k_{[Fe^{2+}]} \left[\frac{a_{Fe^{2+}} a_{OH^-}^2}{K_{eq, Fe^{2+}, OH^-}} - 1 \right]$$



$$\frac{d[Fe^{2+}]}{dt} = \frac{d[CO_3^{2-}]}{dt} = -\frac{d[m_{FeCO_3}]}{dt} = r_2[Fe^{2+}] = k_{[Fe^{2+}]} \left[\frac{a_{Fe^{2+}} a_{CO_3^{2-}}}{K_{eq, Fe^{2+}, CO_3^{2-}}} - 1 \right]$$



$$\frac{d[Ca^{2+}]}{dt} = \frac{d[CO_3^{2-}]}{dt} = -\frac{d[m_{CaCO_3}]}{dt} = r_4[Ca^{2+}] = k_{[Ca^{2+}]} \left[\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{eq, Ca^{2+}, CO_3^{2-}}} - 1 \right]$$

The overall reactive kinetics for each species in the algorithm are listed as:

$$\frac{d[Ca^{2+}]}{dt} = -r_1[Ca^{2+}] - r_{[Ca^{2+} Al^{3+}]} - r_2[Ca^{2+}] - r_3[Ca^{2+}] + r_4[Ca^{2+}]$$

$$\frac{d[Fe^{3+}]}{dt} = r_1[Fe^{3+}] + r_2[Fe^{3+}] + 2r_3[Fe^{3+}]$$

$$\frac{d[Fe^{2+}]}{dt} = r_1[Fe^{2+}] + r_2[Fe^{2+}]$$

$$\frac{d[Al^{3+}]}{dt} = r_{[Al^{3+}]} - 2r_{[Ca^{2+} Al^{3+}]}$$

$$\frac{d[H^+]}{dt} = 2r_1[Ca^{2+}] + 8r_{[Ca^{2+} Al^{3+}]} + 2r_2[Ca^{2+}] - 3r_1[Fe^{3+}] - 3r_2[Fe^{3+}] - 6r_3[Fe^{3+}] - 3r_{[Al^{3+}]}$$

$$\frac{d[HCO_3^-]}{dt} = -r_2[Ca^{2+}] - 2r_3[Ca^{2+}] + r_2[Fe^{2+}] + r_4[Ca^{2+}]$$