

Hydro-geochemical Model for Treating Acidic Groundwater using a Permeable Reactive Barrier

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Abstract

This study couples geochemistry with geo-hydraulics to enable time-dependent modelling for the treatment of acidic groundwater using an alkaline permeable reactive barrier (PRB). This is the first such model developed for acidic groundwater generated from acid sulfate soil which is useful to address the adverse effects such as massive fish kills, corrosion of concrete and steel structures and unfavourable conditions for vegetation. The remediation process has been successful to date with a slight decrease in efficiency caused due to chemical clogging by secondary mineral precipitates, which reduces the porosity and hydraulic conductivity of the reactive medium. To predict these changes numerically, governing equations were incorporated into finite different codes, MODFLOW and RT3D. An original geochemical algorithm was developed for RT3D to simulate chemical reactions occurring in the PRB. The results and the model predictions are in agreement, confirming the hydraulic conductivity reduction due to mineral precipitation was only 3% at the entrance phase of PRB.

Keywords: Geochemical algorithm, Finite different modeling, Hydraulic conductivity reduction, Permeable reactive barrier, Acid sulfate soil

Introduction

The Australian coastal floodplains have been undergoing environmental and socio-economic problems due to the acid sulfate soils (ASS), which are spread over 3 million hectares of land (White et al., 1997). The oxidation of pyritic soil is increased due to the growing population and resulting changes in land use such as construction of deep flood mitigation drains which promote the generation of sulfuric acid. One of the injurious processes resulting is the leaching of heavy metals such as aluminium (Al) and iron (Fe) to adjacent water bodies. The acid sulfate soil research team at the University of Wollongong has been examining several engineering solutions such as weirs and floodgates, which have been mounted near Broughton Creek, Shoalhaven Floodplain, New South Wales (NSW) (Indraratna et al., 2001). These methods were capable to prevent pyrite oxidation, but were unable to treat prevailing acidity deposited in the soil (Indraratna et al., 2005). A noteworthy progress was achieved through a pilot-scale permeable reactive barrier (PRB) installed at Manildra Group's Environmental Farm in October 2006. Recycled concrete aggregates were utilised as the reactive material to neutralise the acidic groundwater (Golab et al., 2006). This PRB is a promising technique for sustaining a groundwater pH from alkaline to neutral (pH 10.0-7.2) and removing dissolved Al and total Fe below 2 and 0.5 mg/L, respectively inside the PRB. Even though the total performance was acceptable, a slight decrease in pH inside the PRB was seen

due to armouring of the reactive media by the Al- and Fe precipitates in the forms of oxy/hydroxide minerals. According to Regmi et al., (2011), laboratory column experiments have indicated a 50% reduction in the actual acid neutralisation capacity (ANC) of the recycled concrete compared to its theoretical ANC.

This study presents the model developed to couple geochemistry with geo-hydraulics in the remediation of acidic groundwater, which has not been carried out in the past, especially for time-dependent modeling and performance verification. The commercial numerical codes, MODFLOW and RT3D were used to couple groundwater flow with reaction kinetics. An original geochemical algorithm was developed to feed into RT3D which captures the geochemical reactions taking place in the PRB (Indraratna et al., 2014). This model is advantageous to practicing environmental engineers and scientists who have to work with the acid sulfate soil related problems.

Methodology

The pilot-scale PRB

In October 2006, the pilot-scale PRB (17.7 m long, 1.2 m wide and 3 m deep) was mounted at the study site, such that it intersects the region of maximum groundwater flow. Geo-textile material was used to shield the reactive media from physical clogging by soil and other fine debris inflowing the barrier. There are 36 observation wells and 15 piezometers installed inside, up-gradient and down-gradient of the PRB (Figure 1) to observe the phreatic surface variations, groundwater chemistry and hydraulic gradients.

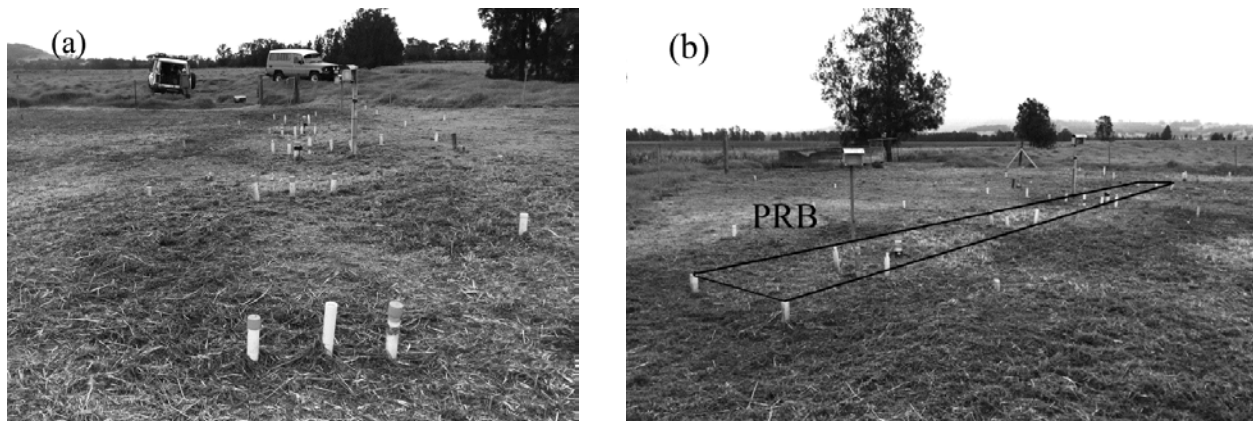


Figure 1. (a) and (b) Pilot-scale PRB and the observation wells and piezometers at study site (Pathirage et al., 2014)

Monthly field visits were carried out to monitor the water quality parameters in monitoring wells such as pH, ORP, and temperature and groundwater elevation in piezometers. These were directly measured onsite every month from the installation time to date. Groundwater samples were analysed according to APHA (1998) guidelines for acidic cations (total Fe, Al^{3+}), major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), anions (Cl^- and SO_4^{2-}), acidity and alkalinity. More elaborated details of the contents discussed in the paper can also be found in previous publications of the second Author and his research students in Computers and Geotechnics and ASCE Journals. Authors acknowledge Elsevier Publication for allowing permission to re-use some of technical content published in Computers and Geotechnics.

Mathematical model

The transition state theory (Eqn. 1) was used to develop the geochemical algorithm. This algorithm comprised of most leading reactions taking between acidic groundwater and the alkaline minerals existing in the recycled concrete.

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

where, r is the rate of mineral precipitation ($r > 0$) or dissolution ($r < 0$), k_{eff} is the effective rate coefficient, IAP is the ion activity product, and K_{eq} is the solubility constant for the reaction.

PRHEEQC software was used to calculate the saturation indices (SI) useful to compute the values for IAP/K_{eq} as shown in Equation 2. The effective rate coefficient (k_{eff}) for each substance in Equation 1 was a calibrated value and expected to be spatially invariant and time independent during the simulation (Table 1) (Indraratna et al., 2014).

$$SI = \log(IAP) - \log(K_{eq}) \quad (2)$$

Table 1. Calibrated k_{eff} values from the data provided by Regmi et al., (2011)

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

The precipitated secondary minerals which accumulate on the recycled concrete were assumed to be immobile. The pore space occupied by each mineral was calculated from their molar volume. Hence, the total volume change was calculated by the volume employed by mineral precipitates minus the volume gained by the dissolution of alkaline minerals in recycled concrete. The resulting porosity change was calculated using Equation 3 (Indraratna et al., 2014).

$$n_t = n_0 - \sum_{k=1}^{N_m} M_k R_k t \quad (3)$$

where, n_0 , n_t are the porosities initially and at time t respectively, M_k is the mineral molar volume, R_k is the overall reaction rate of the mineral, N_m is the number of minerals from 1 to k .

The associated change in hydraulic conductivity was calculated by the normalised Kozeny Carmen equation (Eqn. 4) (Pathirage et al., 2012, Li et al., 2006).

$$K = K_0 \left[\frac{n_0 - \Delta n_t}{n_0} \right]^3 / \left[\frac{1 - n_0 + \Delta n_t}{1 - n_0} \right]^2 \quad (4)$$

where, K_0 and K are hydraulic conductivities initially and at time t , Δn_t is the change in porosity at time t .

The finite different numerical codes: MODFLOW and RT3D were coupled to simulate the transport of the main cations in the field. MODFLOW did not update the associated change in hydraulic conductivity due to mineral precipitation/dissolution at each time step. In order to enable that, a

mathematical model was established to capture the changing hydraulic conductivity via the change in head (h) (Eqn. 5). The methodology for obtaining Equation 5 is elaborated in Indraratna et al., (2014).

$$h = \left(\exp \left[- \frac{\mu^2 b K_0}{S \sum_{k=1}^{N_m} M_k R_k} \frac{(1-n_0)^2}{n_0^3} \left\{ \alpha^2 \left(1.5 + \frac{1}{\beta} \right) \right\} \right] \right) \cdot (C \sin \mu x + D \cos \mu x) \quad (5.a)$$

$$\alpha = n_0 + \sum_{k=1}^{N_m} M_k R_k t \quad (5.b)$$

$$\beta = 1 - n_0 - \sum_{k=1}^{N_m} M_k R_k t \quad (5.c)$$

where, b is the aquifer thickness, S is the storage co-efficient, and μ , C , D are integral constants.

It was important to update the porosity and hydraulic conductivity changes at each time step due to the changes in volume fractions of precipitated and dissolved minerals. For instance, when the simulation was carried out for the 1st time step, the resulting porosity and hydraulic conductivity should be updated for the 2nd time step. This was capable through Equation 5 which determines the resulting head as that was a vital input for MODFLOW to carry on the simulation for subsequent time steps. The developed geochemical algorithm fed into RT3D was coupled with MODFLOW by the advection, diffusion and dispersion equation (Eqn. 6). MODFLOW and RT3D were run contemporarily to obtain the concentrations of reactants at each time step. In this study, dissolution/precipitation reactions were taken into account by replacing λ with, r in Equation 1 multiplied by M .

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 [C]}{\partial x^2} - v \frac{\partial [C]}{\partial x} - \lambda C \quad (6)$$

where, R is the retardation coefficient, C is the aqueous species concentration, D is the hydrodynamic dispersion coefficient, v is the seepage velocity and λ is the first-order decay constant.

Model application to PRB

The reactive transport analysis was carried out along the centreline of the PRB representing the whole PRB. The width of the PRB (1.2 m) was discretised into 0.1 m intervals (Figure 2). The acidic groundwater inflowing the PRB was expected to be in chemical equilibrium. The flow domain was a fully saturated system with specified head boundaries and a mean hydraulic gradient of 0.006, observed according to the field data from 2006 to 2012. The top, bottom and lateral faces of the flow domain were no-flow boundaries.

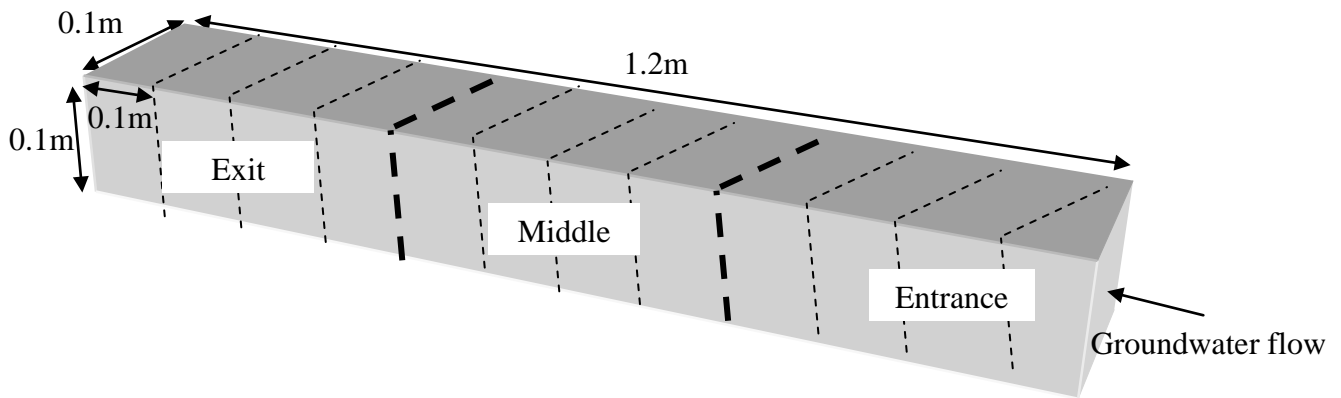


Figure 2. Discretisation of the centreline of the PRB

Results and Discussion

The model output presented the profiles of pH, Al and total Fe concentrations. Figure 3 shows the favourable comparisons found between the model predictions and field measurements for pH, Al and total Fe concentrations for 2012, which is after 6 years of installation of the PRB. In 2012, the up-gradient groundwater pH fluctuated between 3.2 and 4.1 with an average of 3.6, while the pH inside the PRB was neutral, ranging from 6.7 to 7.4 with an average of 7. It is obvious from both field measurements and simulation results that the pH at the entrance zone of the PRB is lower than that of at the middle and exit zones. This is possibly because of the exhaustion of alkaline material of the reactive media during the neutralisation of acidic groundwater. Additionally, the armouring and clogging of the reactive media due to the secondary mineral precipitation is also accountable for the small decrease in pH at the entrance of the PRB.

The highest Al^{3+} concentration detected up-gradient of the PRB was 32 mg/L for 2012. Both field monitoring results and simulation results show that the Al^{3+} reduced promptly within the PRB to less than 1 mg/L. Similarly, high concentrations of total Fe in the up-gradient of the PRB were also detected with a rapid decrease to less than 0.5 mg/L within the PRB. The rapid decrease in Al and total Fe shows that they are precipitated in their oxy/hydroxide forms.

The porosity and hydraulic conductivity would be decreased as a disadvantage of the secondary minerals precipitation inside the PRB. Nevertheless, the computed decrease in hydraulic conductivity for last six years was only 3%, which is not substantial because of the granular sized recycled concrete aggregates ($d_{50}=40$ mm) used in the PRB. Moreover, this slight decrease is supported by the detected stable piezometric heads within the PRB over the last 6 year monitoring period, which shows no risk of clogging prolong to failure of the PRB (Figure 4).

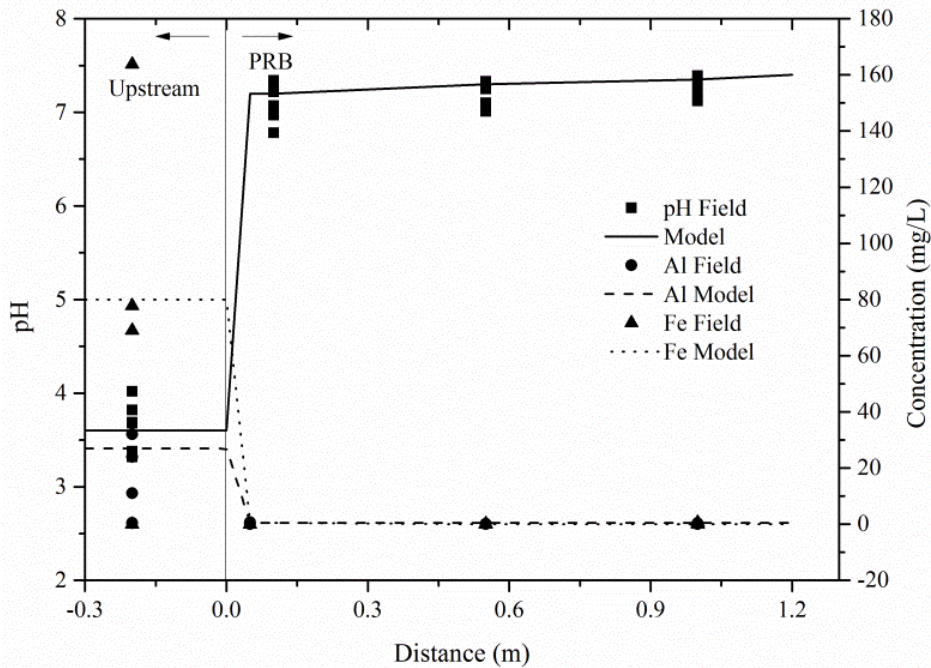


Figure 3. Field observed results and model predictions of pH, Al and Fe concentrations in the upstream and PRBn for 2012

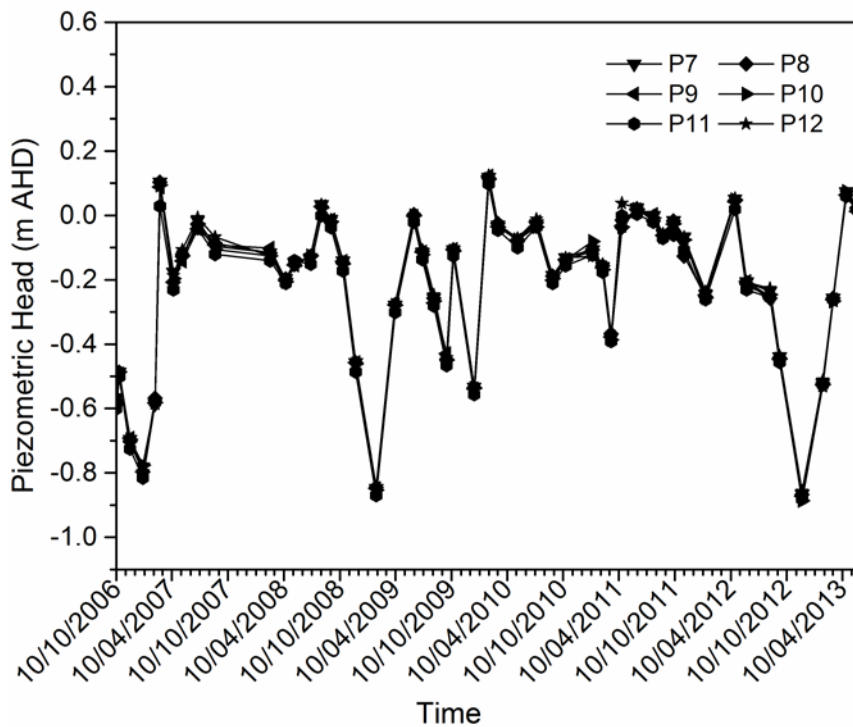


Figure 4. Groundwater elevations inside the PRB with respect to time (P7-P12 are the six piezometers inside the PRB) (updated after Regmi 2012)

Conclusion

MODFLOW and RT3D were run simultaneously to simulate flow and the reactive transport of dominant mineral components. The simulated pH and the Al^{3+} and total Fe concentrations were in good agreement with the observed field data. The developed mathematical model captures the

change in hydraulic conductivity due to mineral precipitation/dissolution. The associated hydraulic conductivity reduction after six years of operation is only 3% in the PRB. Moreover, this is confirmed by the steady piezometric heads inside the PRB. 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.

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References

- APHA 1998. *Standard Methods for the Examination of Water and Wastewater*, Washington, 20th Edition, American Public Health Association.
- Indraratna, B., Glamore, W., Blunden, B., Downey, J. & Tularam, A. 2001. 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. & Lawson, E. M. 2006. Modeling porosity reductions caused by mineral fouling in continuous-wall permeable reactive barriers. *Journal of Contaminants Hydrology*, 83, 89-121.
- Pathirage, P. U., Indraratna, B., Nghiem, L. D., Banasiak, L. & Regmi, G. 2012. Armouring by precipitates and the associated reduction in hydraulic conductivity of recycled concrete aggregates used in a novel PRB for the treatment of acidic groundwater. 11th Australia - New Zealand Conference on Geomechanics: Ground Engineering in a Changing World (pp. 828-833). ANZ Geomechanics. Melbourne, Australia.
- Pathirage, P. U., Indraratna, B., McIntosh, G. & Banasiak, L. 2014. Modeling of mineral fouling in an alkaline permeable reactive barrier in Australia. 14th International Conference of the International Association for Computer Methods and Advances in Geomechanics. Kyoto, Japan. (Accepted)
- 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.
- Regmi, G. 2012. Performance Validation of a Permeable Reactive Barrier (PRB) for Treating Acidic Groundwater. Degree of Doctor of Philosophy, University of Wollongong.
- 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.