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Reducing the risk of acidic groundwater through modelling the performance of a permeable reactive barrier in Shoalhaven Floodplain

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ABSTRACT

Acidic groundwater generated from acid sulfate soil (ASS) usually carries high concentrations of aluminium (Al) and iron (Fe), which create unfavourable conditions to living habitat. ASS research team at the University of Wollongong, Australia implemented an innovative geotechnical engineering technique for the remediation of acidic groundwater through a permeable reactive barrier (PRB) using recycled concrete aggregates as the reactive material. This PRB was installed at the Shoalhaven Floodplain, southeast New South Wales (NSW), Australia in October 2006 and has proved effective in neutralisation of groundwater by increasing the pH from 3.6 to 7 and removing 99% of Al and Fe from groundwater to date. Dissolved Al and Fe were removed through continuous precipitation which would clog the pore spaces of reactive medium by secondary mineral precipitation. This paper provides a complete evaluation of the performance of the PRB through field work and groundwater flow modelling coupled with geochemistry. The developed model (using finite difference codes: MODFLOW and RT3D) describes the chemical clogging due to mineral precipitates and the associated reductions in porosity and hydraulic conductivity of the reactive medium. The results obtained from numerical modelling, groundwater samples analysis and mineralogical analysis of barrier specimens confirm that the current PRB has performed well since the last seven years. Only a smaller amount of clogging was evident at the entrance of PRB with only a 3% reduction of hydraulic conductivity. This model would be beneficial for the environmental scientists and geotechnical engineers who have to deal with the ASS problems, especially in coastal Australia.

Keywords: acid sulfate soils, permeable reactive barrier, groundwater flow modelling, geochemistry

1   INTRODUCTION

In-situ remediation of acidic groundwater through permeable reactive barriers (PRB) has been practiced throughout the world. Different types of alkaline materials were adopted in the remediation process. Zero valent iron (ZVI) is one of the common reactive materials used for acidic water remediation. Gillham and O'Hannesin, (1994), Blowes et al., (2000), Phillips et al., (2000) and Li and Benson, (2005) reported the effective performance of ZVI PRBs and their longevity predictions. Some of the other reactive materials used for acidic groundwater remediation were organic carbon-rich material (wood chips, municipal compost and paper mill pulp) (Waybrant et al., 1998; Benner et al., 2000), carbonate minerals (calcite, dolomite, ankerite) (Blowes et al., 1997; Jurjovec et al., 2002) and limestone (Amos and Younger, 2003).

In the current study, recycled concrete has been utilised as a promising alkalinity generating material to reduce the risk of acidic groundwater after experimenting over more than twenty materials (Golab et al., 2006). Acidic groundwater generated from acid sulfate soils (mainly pyrite) has low pH plus high concentrations of soluble Al and Fe. Figure 1 shows the geological structure at the study site. These heavy metals create unfavourable conditions for living beings in water and corrode concrete and steel infrastructure. Thus it is vital to reduce the risk of acid sulfate soils and come up with a promising and long-term treatment methodology. Acid sulfate soils research team at the University of Wollongong installed a PRB in the Shoalhaven Floodplain, South of Sydney, Australia in 2006. The performance of this PRB has being monitored to date. This paper presents the evaluation of performance through numerical modelling and verification of the developed model using field data.
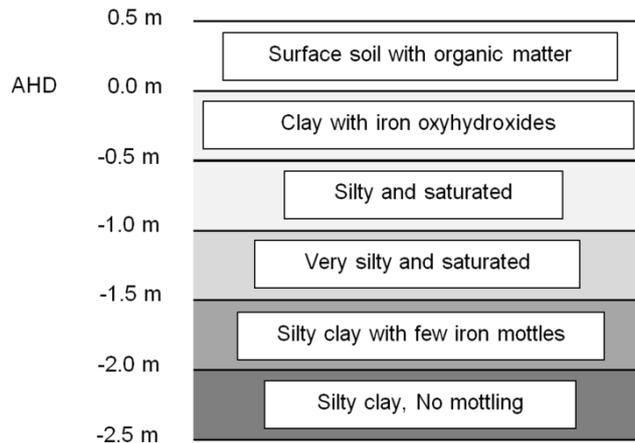
Figure 1. Geological structure at the PRB site (AHD: Australian Height Datum) (after Indraratna et al., 2014a)

MODFLOW and RT3D finite difference codes were used to simulate the coupled groundwater flow and contaminant transport. A mathematical model was developed to find the pressure head solution for MODFLOW which captured the change in porosity and hydraulic conductivity due to dissolution of alkaline minerals and precipitation of secondary minerals. A novel geochemical algorithm introduced by Indraratna et al. (2014b) was used in RT3D. The mineralogical analysis carried out for barrier specimens are presented.

2   MATERIALS AND METHODS

2.1   Permeable reactive barrier

The study site is located in the Lower Shoalhaven Floodplain (34°49'S, 150°39'E), south-eastern NSW, Australia. The PRB is installed in a farming land (1000 ha) on Manildra Group's Environmental Farm, next to a flood mitigation drain which flows into Broughton Creek, which is a left bank tributary of the Shoalhaven river. The low-lying study area is prone to flood in heavy rainfall events with an elevation fluctuating from 0 to 1.25 m AHD (Australia height datum). In early October 2006, a pilot-scale PRB (17.7 m long x 1.2 m wide x 3 m deep) was installed by cut and fill method, parallel and 15 m from the flood mitigation drain to intersect the zone of maximum groundwater flow. The PRB was designed to maximise the groundwater residence time within the barrier and to minimise bypassing of the barrier. A geotextile fabric was stretched above the trench and was backfilled with the crushed recycled concrete (d_{50} = 40 mm). This geotextile fabric was used to guard the reactive media (recycled concrete aggregates) from physical clogging by tiny soil particles and other fine debris entering the barrier.

Observation wells and data loggers were installed to obtain the water quality parameters in a timely manner to monitor the performance of the PRB. In total, 10 observation wells (50 mm in diameter), two wells for data loggers (100 mm in diameter) and six piezometers were initially planted inside the PRB length of five transects approximately parallel to the groundwater flow as indicated in Figure 2. Two multi-parameter automated data loggers were placed to the data logger wells such that the tip of every data logger was about 300 mm from the well bottom, to make sure that the data logger probes were immersed in groundwater, even during intense drought situations. Each data logger was calibrated and set to record pH, dissolved oxygen (DO), temperature and water pressure hourly. In addition, there are 20 extra observation wells (2 m deep and 50 mm external diameter) installed up and down-gradient of the PRB. Overall, there are 36 observation wells and 15 piezometers installed up-gradient, down-gradient and inside of the PRB to observe hydraulic gradients, phreatic surface variations, hydraulic conductivity and groundwater chemistry.
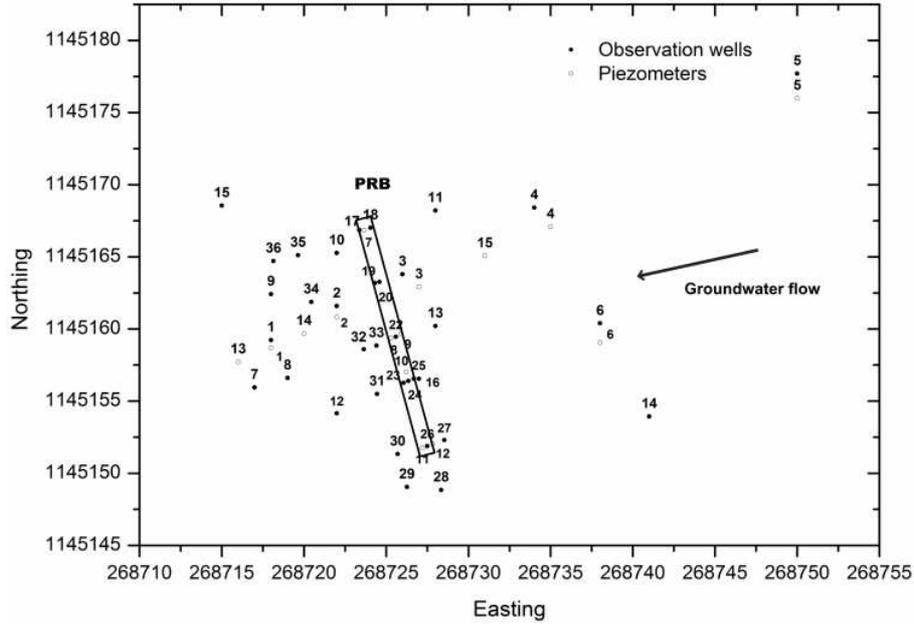
Figure 2. Monitoring network around the PRB at study site (after Indraratna et al., (2014a)

2.2 Performance monitoring in the PRB

Temporal and spatial distribution of water quality parameters like groundwater pH and different concentrations of dominant ions after installation of the PRB were assessed to monitor the performance of field PRB. Groundwater quality parameters up-gradient, down-gradient and inside of the PRB were compared. Groundwater samples were collected monthly from the observation wells in acid flushed polyethylene plastic bottles and analysed for basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), acidic cations (Al^{3+} and total Fe), anions (Cl^- and SO_4^{2-}), acidity and alkalinity. Ca and Al were analysed using inductively coupled plasma – mass spectrometry (ICP-MS) and Fe was analysed using atomic absorption spectroscopy (AAS). All chemical analyses were conducted according to the standard process for water and wastewater (APHA, 1998). Results from column experiments (Indraratna et al., 2010; 2014b) confirmed that Ca^{2+}, Al^{3+} and total Fe were the main importance in the acid neutralisation procedure taking between recycled concrete and the acidic groundwater. Hence, these three dominant ions were monthly measured for the field samples. The other ions had no significant change, and were therefore measured quarterly each year.

2.3 Numerical modelling

In this study, remediation was through dissolution of alkalinity generating material and through precipitation of Al and Fe out of acidic solution. Indraratna et al. (2014b) developed a geochemical model coupling transient groundwater flows. The transport profiles of contaminants through the PRB were simulated whilst calculating the reduction in porosity (*n*) and hydraulic conductivity (*K*) due to mineral precipitation. MODFLOW and RT3D software codes were used for this numerical study. Reaction kinetics for dissolution of Ca-bearing minerals and precipitation of secondary minerals were calculated using the Transition State theory (Equation 1).

$$r = -k_r \left(1 - \frac{IAP}{k_{eq}} \right) \tag{1}$$

where, *r* is the reaction rate, k_r is the effective rate coefficient, *IAP* is the ion activity product, k_{eq} is the equilibrium solubility constant. In Equation 1, the value of IAP/k_{eq} was calculated using saturation indices (*SI*) (Equation 2). In this study, saturation indices for chemical reactions were calculated from PHREEQC software once the influent parameters were given.

$$SI = \log(IAP) - \log(k_{eq}) \tag{2}$$

The details of the geochemical algorithm previously developed by Indraratna et al. (2014), shows the relationship between the reaction rate for a substance (*r*) and the overall reaction rate for a specific ion (*R*).The porosity reductions due to secondary mineral precipitation were calculated using Equations 3 and 4, as given below.

$$\frac{\partial \phi_k}{\partial t} = M_k R_k \tag{3}$$

$$n_t = n_0 - \sum_{k=1}^{N_m} M_k R_k t \tag{4}$$

where, ϕ_k is the volume fraction of precipitated mineral, M_k is the molar volume of mineral and R_k is the total reaction rate for a particular substance, N_m is the number of minerals and n_0 and n_t are the initial porosity and porosity at time *t*, respectively. The associated change in hydraulic conductivity was calculated using normalised Kozeny Carmen equation (Equation 5). Hence,

$$K = K_0 \left[\frac{n_0 - \Delta n_t}{n_0} \right]^3 \bigg/ \left[\frac{1 - n_0 + \Delta n_t}{1 - n_0} \right]^2 \tag{5}$$

where, K_0 is the initial hydraulic conductivity and Δn_t is the difference in porosity at two consecutive time intervals.

MODFLOW and RT3D were used to simulate the groundwater flow and contaminant transport through the centreline of the PRB. The width of the PRB (1.2 m) was discretised into a mesh of 12 squares (1.2 m x 0.1 m) as shown in Figure 3.
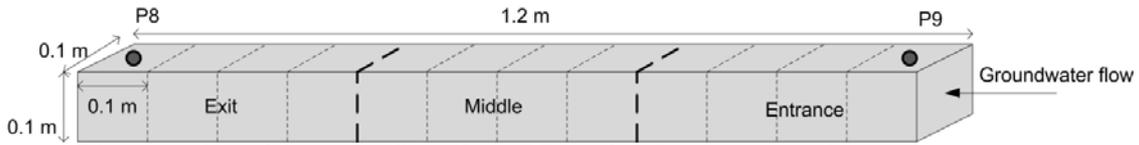

Figure 3. Discretisation of the centreline of the PRB (after Pathirage and Indraratna 2014)

One dimensional flow through PRB was considered. Piezometers located at the PRB entrance zone (P9) and exit zone (P8) are indicated in Figure 3.

MODFLOW does not update the change in porosity and hydraulic conductivity due to secondary mineral precipitation. Thus, a mathematical solution was introduced by Indraratna et al. (2014b) to calculate the head solution (*h*) in every time step (Equation 6). The pressure head for the starting block (P9) calculated using Equation 6 was fed into MODFLOW to simulate the pressure head at P8 for each time step.

$$h = \left(\exp \left[-\frac{\mu^2 B K_0}{S \sum_{k=1}^{N_m} M_k R_k} \frac{(1-n_0)^2}{n_0^3} \left\{ \alpha^2 \left(1.5 + \frac{1}{\beta} \right) - 3(\alpha + \ln \beta) \right\} \right] \right) \cdot (C \sin \mu x + D \cos \mu x) \tag{6}$$

where, *B* is aquifer thickness, *S* is storage co-efficient, μ, *C* and *D* are constants. The parameters α and β are given by:

$$\alpha = n_0 + \sum_{k=1}^{N_m} M_k R_k t \tag{6a}$$

$$\beta = 1 - n_0 - \sum_{k=1}^{N_m} M_k R_k t \tag{6b}$$

Therefore, the new groundwater flow velocity (u_b) for each time step was calculated using Equation 7. Hence,

$$u_b = -\frac{K}{n}\frac{\partial h}{\partial x} \tag{7}$$

RT3D was adopted to simulate the flow and transport of contaminants using the advection, dispersion and reaction equation (Equation 8). RT3D comprises of seven pre-defined reaction components and a user-defined component which can be used to accommodate customized reactions. In this study, a user-defined module was adopted with the developed geochemical algorithm fed through the reaction component ($R_k M_k C$) in Equation 8.

$$R_e \frac{\partial C}{\partial t} = D\frac{\partial^2 [C]}{\partial x^2} - u_b \frac{\partial [C]}{\partial x} - R_k M_k C \tag{8}$$

where, C is the concentration of the contaminant, R_e is the retardation coefficient (R_e = 1 because sorption was ignored in the model) and D is the dispersion coefficient with a longitudinal dispersivity of 0.3 m and a mean groundwater flow velocity of 0.05 m/day (approximate porosity of the PRB was 50%) was assumed in the model.

3   RESULTS

The groundwater pH along the centreline shows significant improvement in groundwater inside and down-gradient of the PRB (Figure 4). This clearly shows the capability of recycled concrete's alkalinity generation to improve the down-gradient water quality. The groundwater pH in the observation wells varied greatly from 4.2 to 7.5 which are 4-12 m away from PRB (Figure 4). This is lesser than the groundwater pH inside PRB, but certainly higher than the acidic pH up-gradient of the PRB. The reason for getting a lower pH reading in the down-gradient than inside the PRB is probably because of: (i) dilution of the effluent coming out from the PRB and (ii) irregular mixing of acidic groundwater created in the pyritic layers (because PRB is not capable of minimising the pyrite oxidation process).

High concentrations of Al and Fe were observed up-gradient of PRB ranging from 1.5-60 mg/L and 2-290 mg/L, respectively (Figure 5). The results obtained during the 7 years monitoring period in the PRB showed that most of the Al^{3+} and Fe enclosed in the groundwater precipitated quickly when Ca-bearing alkaline minerals in recycled concrete started to dissolve and thereby increased the groundwater pH. A rapid decrease in Al^{3+} and Total Fe can be seen inside the PRB and most importantly has been consistently less than 2 and 0.5 mg/L, respectively (Figure 5). The concentrations of Al and Fe in the down-gradient increased with distance away from the PRB. This is possibly due to the currently available and continuing oxidation of pyrite in soil, which generates fresh acid, and releasing toxic metals from the soil. Moreover, there is a possibility for the remediated groundwater from the PRB would blend with the in-situ acidic groundwater in heavy rainfalls, thus increasing Al and Fe concentrations and decreasing the pH. Furthermore, there is a chance that some amount of untreated groundwater from above, below and from the sides of the PRB flows approaching the down-gradient monitoring zone. Although, the down-gradient concentrations were larger than those inside the PRB, they were still less than the up-gradient acidic groundwater.

The model outputs are in favourable agreement with the field data obtained through the centreline of the PRB. Table 1 shows simulation results and field data for pH, Al and total Fe concentrations for 2013 that is after 7 years of operation. The averaged pH of the up-gradient groundwater was 3.6, while the averaged pH inside the PRB was 7. Field monitoring showed that the concentrations of Al^{3+} and total Fe reduced abruptly inside the PRB, in agreement with the model results.
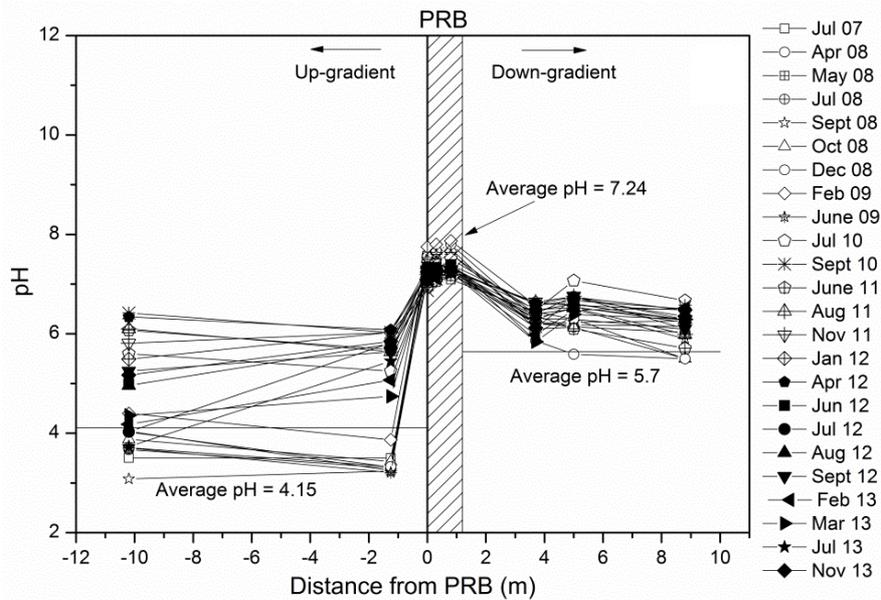
Figure 4. Average groundwater pH up-gradient, inside and down-gradient of the PRB (after Indraratna et al., 2014a)
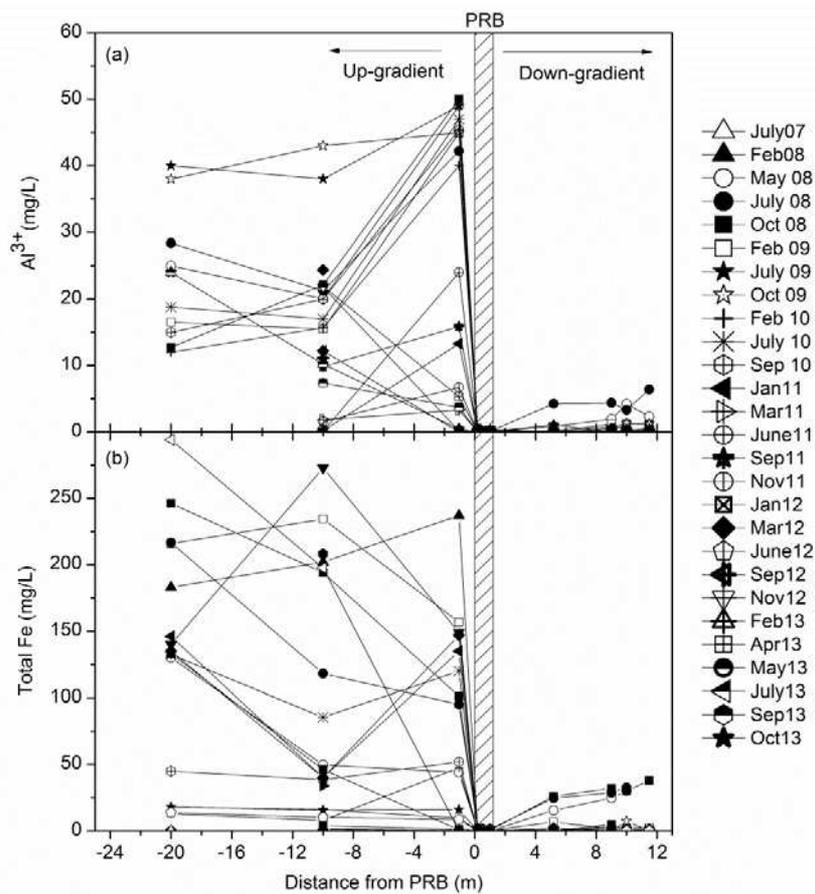

Figure 5. (a) Al and (b) total Fe concentrations up-gradient, PRB and down-gradient (after Indraratna et al., 2014a)

The depletion of dissolved Al and Fe indicate that they precipitated inside the PRB decreasing the porosity and hydraulic conductivity. Although this pilot-scale PRB has been treating acidic groundwater for more than 7 years, the calculated reduction in hydraulic conductivity was as small as 3% at the entrance zone, and almost insignificant at the middle and exit zones. The slight decrease in hydraulic conductivity was probably due to the larger sized recycled concrete aggregates (d_{50}=40 mm)

installed in the PRB which delay extreme clogging. Same behaviour was identified by Li et al. (2005) and Bilek, (2006) where the clogging was a maximum at the entrance zone, because the secondary minerals did not distribute evenly throughout the barrier.

Table 1:   Model predicted and measured values in the field PRB (after Indraratna et al., 2014b)

	Input values	Averaged measured values inside the field PRB	Averaged model predicted values inside the field PRB
pH	3.6	7	7.3
[Al] (mg/L)	27	1	0.5
[Total Fe] (mg/L)	80	1	0

The PRB was excavated near observation well 22 (Figure 2), to obtain a recycled concrete sample in October 2013. X-ray florescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy/ energy dispersive spectroscopy (SEM/EDS) analyses were undertaken to determine precipitation of the secondary minerals. These analyses gave quantitative and qualitative measures of the precipitates. Orange and white precipitates were visible on the specimens collected from the PRB, indicating that chemical armouring on reactive surfaces has taken place. XRD and XRF analysis confirmed that Ca-bearing minerals provided the needed alkalinity, while Al and Fe oxy/hydroxides were the main precipitates. SEM-EDS analysis confirmed that Al and Fe had higher peaks in the armoured concrete, compared to that in virgin concrete (Figure 6). This further confirms that the precipitates were dominantly Al and Fe-bearing minerals. From XRD results, the precipitated secondary minerals of Al- and Fe had a mass ratio of 41:59.
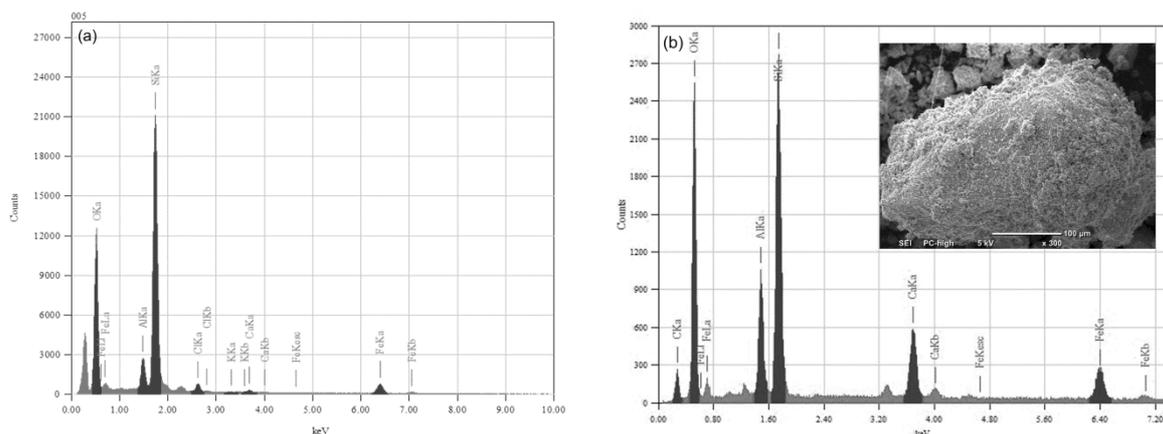

Figure 6. EDS analysis (a) fresh recycled concrete and (b) armoured recycled concrete collected from the PRB. SEM image (included inside (b)) shows the analysed area (after Indraratna et al., 2014a)

4   LONGEVITY

The acid neutralisation capacity (ANC) and the longevity of this PRB depletes with time while the neutralisation process takes place. Pathirage and Indraratna (2014), mentioned that ANC was reduced by 54% due to the secondary mineral precipitation. The pilot-scale PRB discussed in this study was placed with 80 tonnes of recycled concrete (porosity of approximately 50%). ANC of recycled concrete was 146 g/kg, thus, 80 tonnes contained 11.7 tonnes of acid neutralisation capacity (Pathirage and Indraratna, 2014). Assuming a typical groundwater flow velocity of 0.05 m/day at this study site, there would be 4.85×10^5 L of acid transported through PRB per year. The usual acidity measured at the up-gradient was 565 mg/L (equivalent to $CaCO_3$), which corresponds to a usage of 0.274 tonnes of reactive material per year. Therefore, it would take 42.7 years to utilize all the alkaline material. If the 54% depletion of ANC due to secondary minerals precipitation was considered, the predicted longevity of the PRB would be 19.5 years (with a mean groundwater velocity of 0.05 m/day).

5   CONCLUSION

Field monitoring data of the pilot scale PRB to reduce the risk of acidic groundwater generated from acid sulfate soils is reported in this paper. Recycled concrete has the ability to sustain a near-neutral

pH over a considerable period, meanwhile removing toxic heavy metals from groundwater. Chemical armouring/clogging reduced the ANC of recycled concrete. Field data from the centreline of the PRB was used to validate the simulation. The predicted values from MODFLOW and RT3D simulations for pH, concentrations of Al^{3+} and total Fe are found to be in favourable agreement with the observed field data for 2013. The average pH was 7 within the PRB. The pH of the PRB has been declining gradually, attributed to depletion of alkalinity generating materials in recycled concrete and also because of armouring/clogging by precipitates on the reactive surfaces. Clogging, and associated reduction in porosity and hydraulic conductivity was most prominent where the groundwater entered the PRB. From October 2006 to October 2013, the calculated decrease in hydraulic conductivity at the entrance zone was only 3%, which is acceptable, because of the coarse grained recycled concrete aggregates (d_{50}=40 mm) used in the PRB that delays total clogging.

5   ACKNOWLEDGEMENTS

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