Acidic Flow-induced Clogging of Permeable Reactive Barriers in Pyritic Terrain Subhani Medawela, Ph.D.,¹ Buddhima Indraratna, Ph.D., CEng., CPEng, F.ASCE,² Senura Athuraliya, BEng³

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ABSTRACT

Column experiments were conducted to select a suitable reactive material for a permeable reactive barrier (PRB) installed in a low-lying acidic floodplain located 130 km south of Sydney, Australia. Limestone (98% CaCO₃) could neutralize the groundwater acidity while effectively removing excessive concentrations of Al and total Fe. A computational approach that captures coupled biochemical clogging of a granular limestone assembly was adapted to simulate the behavior of the PRB installed in the acidic terrain. At the end of bicarbonate buffering, the predicted reduction of hydraulic conductivity due to clogging at the inlet and outlet of this PRB was 45% and 33%, respectively. PRB monitoring framework was also affected by coupled clogging, which was evident from the electronic images and changes in piezometer and data logger readings.

INTRODUCTION

Natural soils that contain iron sulfides, such as pyrite (FeS₂), are prone to oxidize when they are open to the atmosphere. Sulfides oxidize to form sulfuric acid (H₂SO₄), which can acidify the soil to a pH as low as 3.5 (White et al. 1997). These soils are commonly known as acid sulfate soils. When the acidity of soil and excessive concentrations of metals (e.g. Fe and Al) leach into groundwater, it can result in harmful environmental conditions and damage infrastructure. (Sammut et al. 2010; Groeger et al. 2008). Thus, treating acidic groundwater in pyritic terrain is of paramount importance.

Shoalhaven floodplain, located 130 km south of Sydney, is a low-lying acidic terrain. Past researchers have tested the soil and water quality (Golab et al. 2006; Regmi et al. 2011; Pathirage & Indraratna 2015) of this floodplain and identified high levels of acidity (pH \sim 3.8) and unacceptable levels of total Fe (130 mg/L) and Al (54 mg/L). ANZECC (2000) guidelines prescribe the total Fe and Al concentrations in surface water bodies to be less than 0.5 mg/L and 0.54 mg/L, respectively.

Permeable Reactive Barrier (PRB) is an effective passive treatment method that removes groundwater acidity and dissolved metals (Benner et al. 1999; Indraratna et al. 2014a). A pilot-scale PRB was installed in the Shoalhaven floodplain in 2006 and extended longitudinally in 2019. This PRB is an underground granular filter filled with alkaline reactive media. When the acidic water passes through the PRB, chemical and biological reactions (Table 1) neutralize the acidity and remove metals by forming precipitates (oxides and hydroxides). However, these chemical

precipitates clog the porous media and reduce the hydraulic conductivity and porosity of the PRB (Li et al. 2006; Indraratna et al. 2014b). Also, iron-oxidizing bacteria (IOB), commonly found in Australian coastal acidic terrain (White et al. 1997), infiltrate the PRB and thrive within the granular assembly while catalyzing the formation of Fe precipitates, leading to a more significant porosity reduction. Thus coupled chemical and biological clogging of PRBs reduce their longevity (Indraratna et al. 2020).

This paper presents the experimental procedure for testing a suitable reactive material and the mathematical framework for simulating the coupled bio-geochemical clogging and longevity of a field PRB during the design stage. Moreover, evidence for the bio-geochemical clogging of the PRB monitoring network, including data loggers and piezometers, is also presented.

(Source: Medawera and Indraratha (2020))			
Reaction type	Dissolution/Precipitation Reaction	Kinetic rate coefficients (<i>k</i>)	
		molL ⁻¹ s ⁻¹	
		Laboratory	Field
Dissolution of Ca	$CaCO_3 + 2H^+ \leftrightarrow Ca^+ + H_2CO_3$	2.43E-07	7.21E-08
bearing minerals			
from limestone	$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$	2.43E-07	7.21E-08
Chemical/aerobic	$Fe_{(aq)}^{2+} + 1/4O_{2(aq)} + H_{(aq)}^{+} \rightarrow Fe_{(aq)}^{3+} + 1/2H_2O$	5.62E-08	1.97E-08
ferrous oxidation			
Microbial ferrous	$Fe_{t}^{2+} + \frac{1}{4} O_{0t} + H_{t}^{+} \xrightarrow{IOB} Fe_{t}^{3+} + \frac{1}{2} H O_{0t}$	3.09E-07	9.82E-08
oxidation	$r_{(aq)} + r_{(aq)} $		
Mineral	$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+_{(aq)}$	8.98E-08	2.81E-08
precipitates in	$Fe^{3+} + 2H_2O \rightarrow Fe(OOH) + 3H^+_{(aq)}$	8.49E-08	2.56E-08
granular	$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+_{(aq)}$	7.81E-08	2.62E-08
assembly	$Al^{3+} + 3H_20 \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)}$	3.03E-07	8.98E-08

Table 1: Chemical and biological interactions within the granular limestone assembly (Source: Medawela and Indraratna (2020))

MATERIALS AND EXPERIMENTAL METHODS

The most crucial step in PRB design is selecting a suitable reactive material that can successfully attenuate the targeted groundwater contaminants by physical, chemical and biological processes. Long-term column experiments are the conventional way of determining the decontaminating properties of a selected material. Calcitic limestone (98% CaCO₃), a highly alkaline granular material, was tested in the laboratory to determine its acid neutralization and metal removal capacity when used in a PRB installed in the Shoalhaven floodplain to treat acidic groundwater. The experiment was carried out following the procedure explained in Indraratna et al.(2020).

Two identical acrylic columns (length = 650 mm, diameter =50 mm), filled with 4-5 mm limestone particles, were used (Figure 1). The sampling column (SC) was used to collect water samples and analyze the spatial and temporal variations of acid neutralization and metal removal. The pressure transducer column (PTC) measured pore water pressure along the length of the column. Synthetic acidic groundwater that replicates the groundwater chemistry in the selected site (pH = 3.8, [Al³⁺] = 54 mg/L [total Fe] = 130 mg/L, [Cl^{-]} = 849 mg/L, [SO4^{2-]} = 1350 mg/L, [Ca²⁺] = 152 mg/L, [Mg²⁺] = 118 mg/ L, [Na⁺] = 504 mg/L, [K⁺] = 50 mg/L) was pumped through the columns (flow rate =1.2 ml/min). The column's initial void volume [also known as pore volume (PV)] was calculated from the difference between the column weights when it was dry and fully saturated. Initial values of PV for SC and PTC were 682 mL and 672 mL, respectively.



Figure 1: Column test setup

Once the pH at the column inlet dropped below 4, bacterial culture suspension (IOB) was pumped through the columns to simulate the biological growth inside the PRB. These acidophilic bacteria (*Acidithiobacillus ferrooxidans*) were cultured in the laboratory following the procedure explained by Indraratna et al. (2020).

Water samples were collected daily from the column outlet and weekly from the sampling ports (SP1 to SP6). The pH was measured immediately after collecting the samples using a multiparameter probe (Orion Star A325-ThermoFisher Scientific). A Helber counting grid and an optical microscope (Novel NMM-820) were used to observe the change in bacterial cell density of collected samples. Effluent samples were filtered, and the concentrations of cations were measured using inductively coupled plasma optical emission spectroscopy (Agilent, 700 series ICP-OES).

Besides understanding the chemical and biological processes that occur in groundwater treatment, the main objective of column experiments was to evaluate physical, chemical and biological clogging and hence the porosity reduction along the PRB centerline. A sand pack wrapped with geotextile was used at the inlet of the column (Figure 1) to avoid fine particles from entering the limestone assembly with groundwater. Hence physical clogging of limestone media was assumed to be negligible in the experiment. Porewater pressure variations along the horizontal flow path through the column were recorded by an automated data logger (Data Taker DT85, ThermoFisher Scientific) connected to six pressure transducers. Columns are divided into five zones for data interpretation (Figure 1).

RESULTS AND DISCUSSION

When the limestone is exposed to acidic water, H_2CO_3 is formed (Table 1) due to the rapid dissolution of Ca minerals [Figure 2(a)]. The increased alkalinity in the system neutralizes the excessive acidity of water at the inlet to a certain extent, increasing the pH at zone 1 [Figure 2(b)]. When this partially treated water in zone 1 enters zone 2, limestone particles in zone 2 are exposed to lesser acidity than the inlet aggregates. Thus, during the initial time steps, the dissolution of Ca in zone 2 is less than in zone 1 [Figure 2(a)]. Fe and Al ions are also partially removed from the acidic water in zone 1 before entering zone 2 because the chemical precipitation (see Table 1) was initiated at the inlet.

Al and Fe precipitates coat the reactive surfaces of limestone particles, known as armoring (Watzlaf et al. 2002), and gradually limit the Ca dissolution. Although Ca dissolution in zone-1

was highest before armoring started, the Ca concentration in zone-2 exceeded that in zone-1 after 150 PV because the armoring of zone-1 reduced the dissolution of Ca from inlet particles. The same treatment pattern continued from zone to zone between the column inlet and outlet. Because of these zonal variations of Ca dissolution, the pH of the water increased towards the column outlet and the effluent was neutralized [Figure 2(b)]. Thus, the non-homogenous treatment along the column resulted in the lowest alkalinity depletion at the outlet. For instance, the pH drop within 796 PVs for the inlet (SP1) was from 7.02 to 1.89, and 7.89 to 3.02 at SP6. Reduced dissolved Al and total Fe concentrations were also observed due to the precipitation, and the effluent ion concentrations met the relevant standards within the first 220PVs [Figures 2(c) and 2(d)].



Figure 2: Water quality of along the column (a) Ca²⁺ concentration (b) pH (c) Total Fe concentration (d) Al³⁺ concentration (Modified after Indraratna et. al (2020))

Three plateaus were observed in the pH profile of the column effluent [Figure 2(b)]. The first pH plateau maintained a near-neutral pH range (6.28 < pH < 6.60) from 80 PV until 220 PV, followed by a slow decrease in the pH (4.81 < pH < 6.28) until 550 PV. This pH drop corresponds to a gradual reduction of Ca dissolution at the column outlet from 220 PV onward. The equilibrium within the range 80 < PV < 220 PV could be attributed to the bicarbonate buffering of limestone when HCO₃⁻ ions are released due to CaCO₃ dissolution. At the end of the gradual pH reduction, the pH of the column dropped sharply, which can be attributed to a total depletion of alkalinity in the limestone assembly due to the continuous passage of acid. Although the concentrations of total Fe (Fe²⁺ and Fe³⁺) and Al were very high in influent synthetic water, they were almost completely removed (removal of 99% total Fe and 96% Al³⁺) from the column effluent during bicarbonate buffering [Figure 2(c) and 2(d)]. Thus, it is clear that the bicarbonate buffering is the most important phase of treatment by limestone aggregates because, while maintaining a near-neutral effluent, the target contaminants can be successfully removed during this time.

The second pH plateau was observed between 550 PV and 670 PV [Figure 2(b)]. During this time, the pH of column effluent remained stable in the proximity of 4, which corresponds to the buffering point for the re-dissolution of Al precipitates (Regmi et al. 2011). Due to the

continuous supply of acidic water, equilibrium attained by the re-dissolution of Al oxides and hydroxides could not continuously buffer the acidity of water, so the dissolved concentration of Al in the effluent increased up to 20 mg/L shortly after the value of pH dropped below 4 [Figure 2(d)]. The third plateau occurred when Ferric oxyhydroxides appeared to re-dissolve once the pH inside the columns decreased below 3 [Figure 2(c)]. Ferric hydroxides would maintain a pH \sim 3 when close to equilibrium, but the mass of Fe precipitates would not buffer the pH for an extended period; hence, the effluent pH could eventually reach that of the influent.

Darcy's law was applied to calculate the hydraulic conductivity using the pressure measurements obtained from PTC. The normalized hydraulic conductivity (i.e., the ratio between hydraulic conductivity at time t and the initial hydraulic conductivity, K/K_0) decreased with time (PV), as shown in Figure 3. The initial permeability of limestone was 1.8×10^{-5} m/s. At the end of the test, the hydraulic conductivity reduction at the inlet was 80%, while at the outlet, it was only 20%. This difference was caused by the non-homogenous armoring and clogging within the granular mass. However, of major concern is the point at which almost neutral pH of the column effluent is maintained within the bicarbonate buffering zone. The hydraulic conductivity at the inlet at the end of bicarbonate buffering (220 PV) decreased by 34%, but it was only about 6% at the outlet.



Figure 3: Variation of normalized hydraulic conductivity along the column (Data Source : Indraratna et al.(2020))

MATHEMATICAL MODELING FOR DESIGNING FIELD PRBs

Since the limestone (98% CaCO₃) aggregates were proven to be a suitable PRB material in the column experiments, they were used in a new pilot-scale PRB construction (18 m long, 1.2 m wide and 3 m deep) in the Shoalhaven floodplain in December 2019. PRB dimensions were determined based on the criteria suggested by Pathirage & Indraratna (2015) to determine the optimum width of a PRB. The flow occurs perpendicular to the 18 m length of the PRB (along 1.2 m width). Before constructing the PRB, its overall performance was simulated using a computational approach introduced by Medawela and Indraratna (2020). A summary of the model development is given in the subsequent sections.

Transient flow through a porous media can be modeled by Eq.1 (Harbaugh 2005):

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) + W = S_s \frac{\partial h}{\partial t}$$
(1)

where, K_{xx} , K_{yy} , and K_{zz} are the hydraulic conductivity along the *x*, *y*, and *z* coordinate axes, which are assumed to be parallel to the major axes of hydraulic conductivity (L/T); *h* is the hydraulic

head (L); W is the volumetric flux per unit volume representing sources and/or sinks of water, S_s is the specific storage of the porous material (L⁻¹); and t is time.

The one-dimensional formulation of Eq.1 can be solved by substituting Kozeny-Carmen relationship (Eq. 2) for K_{xx} .

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

where

$$\Delta n_t = (n_c + n_b) \tag{3}$$

 n_c is the porosity reduction due to chemical clogging and n_b is the porosity reduction due to biological clogging, whose mathematical expressions are given below.

$$n_c = \sum_{k=1}^{N_m} M_k R_k t \tag{4}$$

where M_k is the molar volume (m³mol⁻¹) of a mineral, *t* is the time, and $R_k = \sum_{n=1}^{N_m} r$ is the overall reaction rate for the mineral (molm⁻³S⁻¹) and *r* is the reaction rate of each reaction (molm⁻³S⁻¹);

$$r = -k\left(1 - \frac{IAP}{K_{eq}}\right) \tag{5}$$

where *IAP* is the ion activity product, K_{eq} is the solubility constant, and k is the kinetic rate coefficient (molm⁻³S⁻¹) for each reaction (Table 1). The value of *IAP/K_{eq}* can be directly calculated using the software PHREEQC Interactive V.3.3.12, in the form of saturation indices.

The concentration of biomass has been estimated using a logistic approach (Eq.6) developed based on Monod kinetics (Monod 1949).

$$n_b = \left[\frac{X_0 e^{k_c t}}{\rho_c \left(1 - \frac{X_0}{X_\infty} (1 - e^{k_c t})\right)}\right] \tag{6}$$

 X_0 is the initial bacterial cell concentration [ML⁻³], X_{∞} is the maximum bacterial cell concentration [ML⁻³], k_c is the carrying capacity coefficient [T⁻¹], and ρ_c is the solid phase biomass density [ML⁻³].

The final solution to the one-dimensional formulation of Eq. 1 can be obtained by substituting Eqs. 2, 3, 4, 5 and 6 as (Indraratna et al. 2020):

$$h(x,t) = F(x).e^{F(t)}$$
(7)

where,

$$F(x) = (C_1 sinCx + C_2 cosCx)$$
(8)

and,

$$F(t) = \frac{-C^2}{B} \left(-\frac{\sum_{k=1}^{Nm} M_k R_k t^2}{2} + \frac{X_{\infty}}{\rho_c K_c} ln \left[1 - \frac{X_0}{X_{\infty}} (1 - e^{k_c t}) \right] + (n_o + 2)t - 3ln [\Delta n_t - n_o + 1] + \frac{1}{3ln \left[\frac{X_0}{\rho_c} - n_o + 1 \right] + \frac{1}{\Delta n_t - n_o + 1} - \frac{1}{\left(\frac{X_0}{\rho_c} - n_o + 1 \right)}} \right)$$
(9)

In the above, B is a constant. C, C₁ and C₂ are integral constants.

Eq. 7 determines the hydraulic head at time t of a point located at a distance x from the inlet along the direction of groundwater flow. This solution captures the chemical precipitation and the twofold biological activity, i.e., the catalytic effect of bacteria on chemical precipitation and accumulated biomass.

Kinetic rate coefficients of chemical reactions listed in Table 1 were found by calibrating Eq.7 with the laboratory data obtained for the hydraulic head in the column experiments. Then the dimensional analysis was used to upscale these reaction rates from laboratory scale to field-scale (Medawela & Indraratna, 2020), as shown in Table 1. Using field-scale reaction rates, Eq. 7 was used to calculate the temporal variations of the hydraulic conductivity within the proposed PRB. Figure 4(a) shows the predicted hydraulic conductivity during the design stage of the PRB.

Medawela & Indraratna (2020) used commercially available groundwater modeling software (MODFLOW and RT3D) to develop a multi-component reactive transport capable of producing pH profile and ionic concentrations along the PRB as the model output. FORTRAN subroutines were used to introduce chemical and biological reactions in a granular limestone assembly when exposed to acidic groundwater at the Shoalhaven site. In this finite-difference model, the authors used Eq.7 to create an input data array of the hydraulic head at different time steps [Figure 4(a)]. This numerical model was a powerful tool that could simulate the overall performance of the PRB and its longevity. The model predicted the pH and metal concentrations of the PRB installed in the Shoalhaven acidic terrain is shown in Figure 4(b). According to the model simulations, successful acid neutralization will take place for more than 16 years. Removal of total Fe and Al will be up to the required standards until the 17th year of PRB operation. Thus, considering the removal of acidity and toxic cations, the longevity of the PRB was determined to be 16 years by this model.



Figure 4: Model predictions on PRB behavior (a) Normalized hydraulic conductivity (b) Water quality at the PRB outlet (Data Source: Medawela & Indraratna (2020))

After 16 years of operation, i.e. when the effluent pH is no longer neutral and Fe and Al concentrations are increased beyond the standards, the hydraulic conductivity at the inlet zone (0 m to 0.6 m along the groundwater flow path) was predicted to be reduced by 45%, whereas at the outlet, the reduction was 33 % (from 0.6 m to 1.2 m along the groundwater flow path) (Figure 4a). In the laboratory column experiments, when the outlet pH began to drop below 6.5 at 220 PV, i.e. at the end of the bicarbonate buffering, the hydraulic conductivity reduction at the inlet was 36% (Figure 3), which does not differ much from the predictions for the field PRB inlet (43%). However, the measured hydraulic conductivity reduction at the outlet of the columns after 220 PV was only 6%, while the model predicted value for the PRB was 33%. This is because instead of using different reaction rate kinetics for inlet, middle and outlet zones of the PRB, Medawela and Indraratna (2020) used upscaled rate kinetics calculated for the inlet along the entire flow path. It was to make the model conservative and determine the critical time at which the PRB would fail as clogging initiates at the PRB entrance, and the efficiency of the inlet aggregates decreased faster compared to the outlet. Therefore, the actual hydraulic conductivity reduction at

the PRB outlet would be less than 33%, and successful acid neutralization and metal removal would be greater than 16 years.

PIEZOMETER CLOGGING

The clogging due to the precipitation does not limit to the granular medium but can also be observed in monitoring instruments installed in acidic terrain. This can lead to malfunctioning of the monitoring network that is used to determine the performance and longevity of PRBs (Indraratna et al. 2020). There have been extensive studies of clogging reported in field drains, pumping wells and tailing dams (Bloomfield 1972; Houben 2003). However, there are limited studies on the bio-geochemical clogging of piezometers when installed in acid sulfate soils.





The clogging of piezometers can produce erroneous readings, particularly vibrating wire piezometers (VWPs), which cannot be flushed out, unlike the conventional standpipe piezometers (Indraratna et al. 2019). Some of the instrumentation that had malfunctioned over the years are shown in Figure 5; a deteriorated multiparameter sensor with iron oxide precipitates stained all over the sensor [Figure 5(a)], a clogged 'Casagrande' type filter tip of a standpipe [Figure 5(b)] and a clogged vibrating wire piezometer filter tip [Figure 5(c)]. Whilst the multiparameter sensor and standpipe filter tips were extracted from the Shoalhaven floodplain, and the VWP was exhumed from a trial embankment project in Ballina, which was also located in a similar low-lying pyritic floodplain (pH < 4 and relative organic content 4-6%). Given that standpipe piezometers after installation can be flushed out to minimize clogging potential, it is important to install both standpipe and vibrating wire piezometers in tandem to verify the field data against each other.

The VWP filter tip (low air entry, 50-micron pore diameter) was analyzed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) (JSM-6490LA) to determine the mineral clogging that takes place within the pores (Figure 6). The piezometer was extracted after 1.5 years of installation, and the excess pore water pressures did not dissipate even though major settlements were still occurring in the saturated clay foundation. The SEM images of the stainless steel filter tip show the accumulation of clogging material (darker contrast) within the pores of the filter material (lighter contrast). The clogging material was composed of Fe and Al bearing minerals that have precipitated at the filter tip after being exposed to contaminated acidic groundwater [Figure 6(b); spectrum -2]. Conversely, Figure 6(a) indicates the mineral

composition spectrum of the stainless steel filter material that corresponds to peaks in Cr, Ni and Fe.

CONCLUSIONS



Figure 6: SEM-EDS analysis of piezometer filter tip (a) filter material (spectrum-1); (b) clogging material (spectrum-2)

The research strategy applied for simulating the performance and treatment capacity of a pilotscale PRB (pH~3) located in a low-lying pyritic floodplain in Shoalhaven, NSW, Australia, was presented. Using synthetic acidic groundwater and acidophilic bacteria cultured in the laboratory as the column influent simulate more realistic field conditions during the column tests.

Laboratory trials confirmed the acid neutralizing and metal removal (dissolved Al and Fe) capacity of limestone (98% CaCO₃) to efficiently alleviate the adverse conditions produced by contaminated groundwater.

The optimum groundwater treatment by limestone was observed during the bicarbonate buffering period, i.e., during the first 25% of the column test duration. Based on predictions from a multi-component reactive transport model, optimum treatment of a pilot-scale PRB (18 m x 1.2 m x 3 m) installed in the Shoalhaven acidic terrain would be during the first 16 years. Eventually, the alkalinity of the limestone media is expected to deplete, and the associated hydraulic conductivity of the porous media can then reduce as a result of the coupled bio-geochemical clogging.

Significant biological and chemical clogging at the column inlet resulted in at least 70% reduction in the rate of Ca dissolution and 80% reduction in hydraulic conductivity at the end of the test, whereas, at the far outlet, the corresponding values were much lower at 55% and 20%, respectively. Therefore identifying the duration of bicarbonate buffering of a PRB via model simulations is essential, as it may be required to replace the inlet aggregates to revive the full performance of the alkaline granular assembly to extend the PRB longevity.

This study also verified that clogging in pyritic terrain would hinder the performance of piezometers and data loggers installed to monitor the condition of PRBs, which in turn could affect the maintenance frequency and the longevity of PRBs.

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