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Manuscript title: Chemical Clogging of Granular Media under Acidic Groundwater Conditions-Experimental Simulation

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Abstract

Generation of acidic groundwater attributed to pyrite oxidation in low-lying acid sulfate soil causes substantial damage to the soil-water environment and civil infrastructure. The installation of Permeable Reactive Barrier (PRB) is a frontier technology in the field of acid neutralisation and for removing toxic heavy metal cations, e.g. soluble Fe and Al. This study aims to assess the potential of limestone (calcite) aggregates as the PRB's main reactive material in low-lying pyritic land. During long-term laboratory column experiments, a significant capacity of limestone for removing the contaminant chemical species was observed. Nevertheless, the formation of secondary mineral precipitates upon geochemical reactivity within the granular media in the PRB caused armouring and chemical clogging that diminished the rate of reactivity, i.e. the treatment capacity of calcite aggregates, mainly at the entrance zone of the porous media. Flow properties were altered due to blockage of pores; for instance, hydraulic conductivity was reduced by 25% at the inlet zone. Non-homogeneous clogging towards the outlet was analysed, and the time-dependent effect on longevity of a limestone column was studied and quantified.

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Introduction

Groundwater acidity resulting from Acid Mine Drainage (AMD) and pyrite (FeS_2) oxidation in

Acid Sulfate Soil (ASS) terrains are often responsible for catastrophic environmental impact in

most low-lying coastal regions of Australia (Blunden and Indraratna, 2001), South America and

Southeast Asia, as well as in some regions of Western Europe and Africa (Dent and Pons, 1995)

, encompassing about 12–14 million ha of acid sulfate (pyritic) soils (Shamshuddin et al., 2014).

Numerous field solutions have been implemented over decades for treating highly acidic

groundwater (Evangelou and Zhang, 1995, Indraratna et al., 2001, Mulligan et al., 2001,

Indraratna et al., 2005, Luke et al., 2017, Indraratna et al., 2017), but most of these techniques

that involve floodgates and weirs increase the risk of flooding, while excessive chemical (lime

and gypsum) treatment increase the alkalinity levels of the soil, which can affect aquaculture

farming. After numerous preliminary trials, Permeable Reactive Barriers (PRBs) have proven to

be one of the most cost-effective and efficient passive treatment methods of neutralising

groundwater acidity in low-lying pyritic floodplains and acid mine drainage in coal collieries

(Thiruvenkatachari et al., 2008, Indraratna et al., 2009, Regmi et al., 2010, Ekolu and Bitandi,

2018).

A PRB is an in-situ engineered geostructure which intercepts and filters a contaminant

plume; typically, it is a trench constructed as a subsurface treatment zone filled with a granular

material (Gavaskar, 1999). Nevertheless, chemical clogging of the PRB granular assembly

baffles the reactivity and treatability of filter grains due to encrustation of reactive media

surfaces and accumulation of secondary mineral precipitates within the voids. Even partial

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clogging by chemical precipitates affects the groundwater flow paths through the PRB, hence,

soil properties such as porosity and hydraulic conductivity are substantially reduced (Li and

Benson, 2005, Indraratna et al., 2014b, Pathirage and Indraratna, 2014). Moreover, the longevity

of the PRB is also decreased even before the desired treatment is achieved. In this regard, the

fundamental geochemical kinetics and the associated role of PRB aggregates need to be explored

further in a design point of view.

Clogging mechanisms differ from one PRB material to another based on their chemical

characteristics and influenced by the site-specific geo-hydraulic and geochemical conditions.

Therefore, distinctive methods of analysis should be followed to evaluate clogging of different

PRB materials. Zero valent iron (ZVI), carbonate minerals (calcite, dolomite, ankerite and their

mixtures), pea gravel, etc. are potential reactive fills used in PRBs for treating different

contaminants (Golab et al., 2006, Obiri-Nyarko et al., 2014).

Recycled concrete aggregates were used in a pilot scale PRB installed in a low-lying

sulfidic floodplain in Shoalhaven, Southeast Australia, for remediating acidic groundwater

(Indraratna et al., 2014a) as shown in Figure 1. According to a pilot-scale PRB study conducted

by Indraratna et al. (2014b), formation of iron and aluminium oxy/hydroxides resulted in at least

4%, 3% and 0.5% reductions in porosity at the entrance, middle and exit zones, respectively.

Apart from the general clogging of the granular assembly of the PRB, the authors of the current

study have observed that the performance of field instrumentation such as piezometers, as well

as observation and data logger wells were also influenced by precipitates causing flow barriers.

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For instance, when a number of vibrating wire and standpipe piezometer tips were extracted

from the field and tested microscopically, chemical clogging was obvious.

This study mainly focuses on chemical clogging of a limestone (calcite) PRB as a means

of remediating acidic mine drainage from coal mines in the Hunter Valley region of NSW,

Australia. While the role of biological clogging component in the overall reduction in porosity

and permeability is important (Cunningham et al., 1991; Seki and Miyazaki, 2001, Taylor et al,

1990), this aspect was not considered in this study as the chemical component likely governs

the overall clogging mechanisms. Underground mining creates tensile cracks of the overburden

soil layer overlying the pyrite layer, which then oxidises to produce sulfuric acid. During

subsequent rainfall events, acidic groundwater finds its way through rock joints into the stope

(Benner et al., 1999), damaging the adjoining ground areas and contaminating the nearby

waterways. With the objective of designing a PRB to mitigate the potential damage caused by

acid mine drainage, a preliminary experimental study was undertaken to explore the

geochemical kinetics of the proposed PRB material (i.e. calcite aggregates). For this purpose,

column experiments were carried out, simulating realistic flow and ground conditions to

identify and quantify the mechanisms of acid neutralisation, as well as the rates of heavy metal

removal and chemical clogging of limestone medium to facilitate reliable PRB design in the

field.

Materials and methods

The initial step of laboratory experiments was to conduct short-term batch tests for screening

the best material by testing their effectiveness in terms of acid neutralisation (Waybrant et al.,

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1998). Using batch tests, Golab et al. (2006) explored the short-term acid neutralising properties of limestone aggregates. In this study, a series of long-term column experiments were performed in order to further analyse the extended response of limestone in contact with acidic water, temporal reactivity reduction and changes of granular media properties over several months.

Column experiment setup

A one dimensional column experimental setup was used to study and quantitatively determine the effectiveness of contaminant removal and the extent of chemical precipitation of a column having limestone aggregates. A horizontal column shown in Figure 2b represents the groundwater flow along transects parallel to the width, and orthogonal to the length of the PRB. Since the PRB can be divided into a number of hypothetical slices along the length (in the direction of groundwater flow), understanding the flow characteristic along these sections is imperative (Figure 1).

As illustrated in Figure 2, laboratory testing was carried out in two identical acrylic columns, which were 0.65 m long with an internal diameter of 50 mm. The first column was prepared with sampling ports, while the second column was fitted with pressure transducers, along the length of the column. Pressure transducers which had a pressure range of 0-1bar with 0.5% full scale precision were connected to an automated data logger, which recorded the pore water pressure of the porous matrix. Two identical columns were used to eliminate the influence of sampling on pressure readings. Accuracy of pore water pressure measurements

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were vital, as these data were used to calculate the reduction in hydraulic conductivity, hence the temporal porosity reduction of the limestone assembly that influences its longevity.

Materials in the column

The limestone aggregates used in this study were obtained from a plant in Moss Vale, south of Wollongong City. Crystallised $CaCO_3$, rather than overburden limestone was selected. Materials consisted of 97.21% $CaCO_3$, indicating its obvious potential to generate considerable alkalinity for neutralising acidic groundwater. Also, $MgCO_3$ content was 1.22%, while the other secondary compounds of SiO_2, Al_2O_3, Fe_2O_3 were only 0.58%, 0.21% and 0.15%, respectively.

Particle size distribution of limestone used in column experiment is shown in Figure 3. The void ratio of limestone aggregates received from the plant was 0.57 and consisted of uniformly-graded gravel-sized particles (GP) according to the Unified Soil Classification System (ASTM D2487). Gravels were crushed and sieved to obtain 4-5 mm particles because, Indraratna and Vafai (1997) stated that for granular media, the width or diameter of the test chamber to maximum particle size ratio should exceed 8 to alleviate boundary effects. Since the diameter of the column was 50 mm, this ratio was well maintained above 8 by selecting this particular particle size.

Other than the limestone, inert silica sand was used at the inlet and outlet of the column. Particle size of the silica sand used was between 100 μm − 1000 μm and D10, D50 and D90 were 276 μm, 415 μm and 623 μm respectively.

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Synthetic groundwater

Having prepared the limestone columns, synthetic groundwater that mimics the field groundwater chemistry (Table 1) was pumped into the column. Due to weather changes and phreatic surface variations, concentrations of dissolved cations, anions, pH and alkalinity of actual groundwater in the site may become highly variable for small time intervals, thus creating difficulties in establishing common criteria to determine the essential hydraulic parameters and longevity of the porous media. After testing groundwater quality over the years, the water quality parameters of synthetic water were comparable to the average water chemistry at the site. According to Table 1, Fe concentration of water was much higher than that of other cations implying that nearby water bodies and infrastructure may have been affected by significant iron stains, apart from sulfate attack to concrete structures and corrosion of metal pipes usually encountered in acid mine drainage. Therefore, total iron was considered as the primary target contaminant to be treated by the PRB.

Test procedure

Materials were air dried before filling in to the columns. Each column was packed with 100 mm of inert silica sand at the inlet, followed by 500 mm of limestone and 50 mm of silica sand at the end of the column. Inert silica sand was used to ensure further filtration at inlet before flowing in to the limestone assembly, and at the exit outlet before treated water was pumped out. To avoid physical clogging within limestone aggregates by fine particles, sand was covered with a geotextile. During packing, columns were kept vertical, and the limestone

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aggregates were manually compacted in layers of 50 mm increments over a test specimen

height of 0.5 m. Aggregate mass which was required to obtain the bulk density of limestone

(1500 kg/m3) within a volume of 9.82 x 10^{-5} m^3 (i.e. layer thickness (50 mm) x area of column

cross section) was filled first. Then, materials were compacted using a steel rod (8mm

diameter), so that a layer height was 50mm, thus ensuring a relatively uniform density across

the column.

Column experiments were carried out at room temperature with a constant flow rate of

1.2 mL/min, which was applied using a Masterflex peristaltic pump. Before commencing the

experiments with acidic groundwater, the columns were rinsed with 5-6 pore volumes of

deionised water. Throughout this study, the initial void volume of the column is referred to as

the 'Pore Volume' (PV). It was determined by weighing the column filled with sand and

limestone when it was dry and fully saturated. The difference in weights was then used to

calculate the volume of water filling the voids, as this corresponded to an initial pore volume of

0.871 L. Synthetic groundwater was continuously pumped from right to left (see Figure 2).

Main effluents for chemical analyses were collected from both columns on a daily basis, while

water samples from the sampling ports were collected once a week. Six sampling points were

selected which were 100 mm apart (SP1 to SP6) and in line with the positions of pressure

transducers of the second column (PTC1 to PTC6). Soon after collecting the water samples,

their pH, Oxidation Reduction Potential (ORP) and Electrical conductivity were measured.

Subsequently, the water samples were filtered and other chemical analyses were performed to

obtain cation and anion concentrations, following the standard methods of water testing,

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namely, Inductively Coupled Plasma - Optical Emission Spectrometry(ICP-OES) for cation

analysis and Ion Chromatography (IC) for anion analysis (APHA, 1998). After six months,

limestone particles were found to be completely exhausted due to mineral fouling, and the

main effluent pH reached the same as that of the influent pH. Next, the columns were air dried

for two weeks before dismantling by keeping them vertical. Thereafter, internal limestone

particles were subjected to qualitative and quantitative analysis using Scanning Electron

Microscopy (SEM: JEOL JSM-6490LV) to further observe the mineral precipitates.

Results and discussion

Acid neutralisation properties of limestone

The pH variation of the main effluent with increasing number of pore volumes (i.e.

dimensionless time) pumped through the column are plotted in Figure 4a; it shows that the pH

profiles of both sampling column (SC) and pressure transducer column (PTC) follow a similar

trend, thus confirming the identical nature of these two columns.

When the columns were rinsed with deionised water prior to acidic water being pumped,

the pH of the effluent increased slightly, due to the dissolution of minor amounts of $CaCO_3$

from calcite. This increased alkalinity remained within the system until the acidic water was

pumped in, and this raised the initial pH of treated effluent to 8.78. The ORP in the columns

were 73 mV initially, indicating weak oxidising conditions under increased alkaline conditions

(Figure 4b). As soon as the virgin limestone was exposed to the original acidic influent, the

maximum discharge of Ca^{2+} with in first 21PV was observed near the inlet of the column (SP1),

as shown in Figure 5. Calcite dissolution was occurred according to Equations 1-4. Faster and

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inconsistent reactions occurred between fresh alkaline limestone and original acidic influent at

the commencement because initially the system was not in an equilibrium state. Thus, a strong

pH buffering could not be observed during first 21PVs, resulting in an accelerated pH drop

from 8.78 to 7.27 in the main effluent at approximately 5-10 PV shown in Figure 4a.

$$CaCO_3 + H^+ \quad \leftrightarrow \quad Ca^{2+} + HCO_3^- \tag{1}$$

$$CaCO_3 + H_2CO_3 \quad \leftrightarrow \quad Ca^{2+} + 2HCO_3^- \tag{2}$$

$$CaCO_3 \quad \leftrightarrow \quad Ca^{2+} + CO_3^{2-} \tag{3}$$

$$CaCO_3 + H_2O \quad \leftrightarrow \quad Ca^{2+} + HCO_3^- + OH^- \tag{4}$$

Subsequently, the column environment approached a stabilised chemical phase. After 21

PV the rate at which the Ca bearing minerals along the length of the column dissolved (From

SP1 to the effluent point in Figure 5) was slowly decreased until PV = 180, which was then

followed by a rapid reduction of the dissolved Ca concentration.   This implies the presence of

a strong and prolonged bicarbonate buffering zone (Regmi et al., 2010) during 21<PV <180.

Since Ca^{2+} was released slowly into the system during bicarbonate buffering stage, an elevated

alkalinity was maintained. Supporting the hypothesis of a stable reaction period, the treated

main effluent (Figure 4a) maintained a clear pH plateau from 21PV to 190 PV, in which the

main effluent acidity fluctuated slightly within the near neutral pH range of 6.75<pH<7.47.

Al et al. (2000) also noted the armouring of reactive carbonate minerals by secondary

mineral precipitates as the mine tailings rich in ferrous sulfide were neutralised. As a

consequence, the rate of mass transfer between primary minerals and pore water and the rates

of primary mineral dissolution were decreased. Similarly, the limestone crystals were gradually

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coated during bicarbonate buffering and reactivity decreased as the surface area decreased.

This led to a weaker treatability and a stagnated pH region.

Armouring was eventually accelerated, and the reactivity of limestone decreased rapidly

over a few PVs, which can be attributed to the swift pH drop at 190th PV in Figure 4a. The

system then stabilised in a second bicarbonate buffering zone that had lower rates of Ca

dissolution. Nonetheless, this rate was adequate to maintain successful buffering as per the

same reactions (Equations 1-4), albeit weaker than the first buffering zone. During this second

plateau, the pH of the main effluent decreased gradually from 6.56 to 5.92 over 200 PVs, and

the oxidising properties within the column were still insignificant (<370 mV). The pH variation

along the length of the column from SP1 to SP6 also indicated a similar gentle decline during

both bicarbonate buffering periods (Figure 6a). In contrast, the ORP within the limestone

assembly (Figure 6b) and of main effluent (Figure 4b) seem to increase gradually (< 275 mV),

which indicates the dominant influence of weak oxidising conditions.

The trend in temporal pH variations of effluent taken from six sampling ports (Figure 6a)

suggested that secondary mineral precipitates formed rapidly at the inlet of the column, but the

amount of mineral precipitates decreased towards the outlet. For instance, during the first pH

plateau, the SP1 effluent remained between 5.47< pH< 6.63 whereas near the outlet (SP6) the

range was 6.61< pH< 7.45. At the final stage of the experiment, SP1 effluent pH decreased to

4.03, which was even more acidic than the influent while SP6 still maintained a pH of 5.94.

Similarly influent Ca^{2+} concentration (625 mg/L) was reduced to 210 mg/l at the inlet, while it

remained 400 mg/L at the outlet (Figure 5), indicating that the acid neutralising capacity at the

inlet was expended faster due to the reduction in alkalinity.

With regard to removing contaminants from the site water, Fe^{2+} and Fe^{3+} (Total iron) are

the problematic ions that should be removed from the treatment process. Although the Total Fe

concentration of influent was 62.8 mg/L (see Table 1), as Figure 7 shows, this higher

concentration was significantly reduced in main effluent to 0.26 mg/L even at 400PV. This

proves that the limestone column can treat the main contaminant in the influent while

maintaining an almost neutral pH throughout that period. In SP1 and SP2 effluents, dissolved

total iron concentrations were increased after 150PV because, with fast alkalinity depletion at

the entrance, the ability of iron removal by means of precipitation was reduced. Although the

inlet zone was exhausted due to mineral coating, the outlet zone could still remove the

pollutants over a long period of time. These heterogeneous clogging aspects are elaborated in

the next sections.

Chemical clogging of porous media

Total iron in synthetic water encourages the formation of Fe oxides and hydroxides. OH^- and

CO_3^{2-} released in to the system (Equations 1-4) combine with Fe^{2+} and Fe^{3+} to form iron oxides,

hydroxides and carbonates in accordance with Equations 5-9. Since the total iron concentration

(62.8 mg/L) was much higher than the Al concentration (0.065 mg/L) in the influent, the

amount of Fe precipitates was greater than the amount of Al precipitates (Equation 10).

Therefore, Fe solids were indeed the major clogging component within the granular assembly

followed by aluminium hydroxide, as represented by the following chemical reactions.

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$$Fe^{2+} + 2(OH)^- \quad \leftrightarrow \quad Fe(OH)_2 \tag{5}$$

$$Fe^{2+} + CO_3^{2-} \quad \leftrightarrow \quad Fe(CO)_{3(s)} \tag{6}$$

$$Fe^{3+} + 3H_2O \quad \leftrightarrow \quad Fe(OH)_{3(s)} + 3H^+_{(aq)} \tag{7}$$

$$Fe^{3+} + 2H_2O \quad \leftrightarrow \quad Fe(OOH) + 3H^+_{(aq)} \tag{8}$$

$$2Fe^{3+} + 3H_2O \quad \leftrightarrow \quad Fe_2O_3 + 6H^+_{(aq)} \tag{9}$$

$$Al^{3+} + 3H_2O \quad \leftrightarrow \quad Al(OH)_{3(s)} + 3H^+_{(aq)} \tag{10}$$

The column was divided in to five imaginary zones to explain the clogging behaviour. Due to the higher reaction rates at the inlet zone at the commencement of synthetic water pumping, armouring and formation of precipitates had certainly initiated at this acid front. Figure 7 illustrates the total iron concentration dissolved in effluent water samples taken from six sampling ports. In zone 1, Fe contamination was partially removed by iron precipitates, and the excessive acidity was thereby removed to some extent. In the 1D flow occurring in the column, the treated effluent from zone1 then enters zone 2, and the limestone gravels in this second zone are then exposed to less acidity than the inlet zone which has already reacted with the original acidic influent. Therefore, as expected, the armouring of reactive particles and the formation of iron precipitates is quantitatively smaller in zone 2. This same trend had continued towards the outlet so the limestone in zone 5 was indeed exposed to the least acidity compared to the previous zones. Several past authors have also reported excessive clogging at the entrance, and its heterogeneous nature along the granular assembly (Kamolpornwijit et al., 2003, Li et al., 2005, Indraratna et al., 2014b).

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Furthermore, deterioration of reactive media after first bicarbonate buffering effect is evident in Figure 7. It can be observed that the dissolved iron concentrations at inlet slightly increased until 167th PV and began to increase sharply afterwards (i.e. during second buffering stage). When alkalinity was depleted at inlet, the intensity of precipitate formation was reduced during the second buffering stage, limiting the Fe removal by precipitation. Thus, dissolved Fe concentration was higher in first two zones while this concentration was still lower in the last three zones, which are still capable of Fe removal by precipitation.

Albeit the partial ceasing of precipitate formation in entrance zones, quantity of total accumulated precipitates was always higher in first two zones than the other regions. Fe precipitates are not redissolved until pH of a chemical system drops below 3. In the current experiments, pH within the column was always maintained above this buffering point of iron hydroxides (pH with in the column > 4), and hence the precipitates were not redissolved and continuously accumulated. This is very clear in the Figure 8 that shows the photo illustration of the sampling column at different pore volumes after dismantling.

Overall, the zonal clogging variations were conspicuous by the following observations.

(a) ICP-OES results proving a prominent rise of dissolved Fe concentrations at zones 1 and 2 after first bicarbonate buffering was depleted (Figure 7). This confirms the reduction in treatability capacity at the entrance (inlet zone).

(b) Orange precipitates formed within the column and then turned bright red with time (Figure 8a). Bright red/yellow coating of particles was also observed after dismantling the column (Figure 8b).

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(c) Clearly distinguishable Fe and Ca concentrations peak at the inlet, middle and exit zones in Energy-dispersive X-ray spectroscopy (EDS) spectra (Figure 9). The presence of considerable amounts of Ca minerals compared to other minerals in the selected limestone batch is evident from Figure 9a which shows the highest Ca peak. Nevertheless, Ca peak of fouled limestone extracted from the inlet (Figure 9b) has been considerably reduced proving the alkalinity depletion attributed to continuous exposure to the original acidic influent. In contrast, the maximum Fe peak occurs at the inlet compared to fresh limestone and other zones of the column, and this suggests the enhanced encrustation at entrance. As the intensity of armouring and clogging diminishes towards the outlet, the resulting Ca peaks increase and Fe peaks decrease, thereby supporting the concept of zonal clogging (Figures 9c and d).

Although the influent Al concentration was not excessive, it was vital to confirm if the Al concentration had increased in the effluent as a result of chemical reactions. Higher concentrations of Al should not be released in to the waterways as this can be fatal to aquatic flora and fauna (Sammut et al., 1996, White et al., 1997). As shown in Figure 10a, it was apparent that Al concentration was insignificant in the effluents taken along the length of the column (< 0.046 mg/L in main effluent). In addition, re-dissolution of Al hydroxides (Equation 10) could not take place, as testing was stopped before the effluent water could drop below the buffering point of Al hydroxides, i.e. pH = 4.

Concentrations of other cations Na^+, Mg^{2+}, K^+, and anions Cl^- and SO_4^{2-} in both influent and effluent were nearly constant throughout the experimental phase as illustrated in Figure 10b , which implies that they could not have contributed to the formation of precipitates.

Clogging effects on hydraulic properties

When the surfaces of particles are covered with secondary mineral precipitates their total surface area is gradually reduced, as are the pore spaces of the granular assembly, i.e. the bulk of these voids are taken over by accumulated precipitates. This loss of porous volume can alter the flow characteristics such as flow rates, residence times (reaction rates) and seepage velocities, while flow paths are inevitably reoriented within the granular fill (Li et al., 2005). For instance, even though a constant input rate was maintained (1.2 mL/min) at the inlet, outlet flow rate fluctuations were noticeable throughout the test as shown in Figure 11. Variations were minimal within first 150PV, which were subsequently deviated from the initial flow rate. This could be attributed to enhanced pore path blocking during clogging. Furthermore, Indraratna et al. (2014b) developed a numerical model which was capable of evaluating the time-dependent head variation and pore velocity at a point within the recycled concrete column, and then these parameters were used to calibrate the contaminant transport model applied to the laboratory column tests adopting the advection-reaction–dispersion equation.

The authors have further extended this model for limestone with corresponding reaction kinetics, and the model was calibrated with the current laboratory results. Changes in above hydraulic properties in turn can affect hydraulic conductivity of the porous media influencing

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the treatment provided by the limestone aggregates. This is why secondary mineral precipitation promotes the efficiency attenuation of a PRB (Indraratna et al., 2014b).

Porewater pressure measurements obtained from transducers were used to calculate the hydraulic conductivity along the granular assembly based on Darcy`s law. However since the outlet flowrate was maintained within the range of 0.98-1.23 mL/ min, it was assumed a constant flow rate along the column (1.2 mL/min which was given by peristaltic pump) for hydraulic conductivity calculations. The change in normalised hydraulic conductivity (i.e. the ratio between hydraulic conductivity at time t, and the initial hydraulic conductivity) of limestone assembly under constant flow conditions is illustrated in Figure 12. Initial permeability of the limestone column was measured to be 1.842×10^{-5} m/s. Due to excessive armouring and clogging, nearly 29% reduction in hydraulic conductivity was observed at the inlet, while it was only 6% at the outlet. Rate of change of hydraulic conductivity during the first bicarbonate buffering was higher than in the second buffering zone, and this can be attributed to the noticeable drop of hydraulic conductivity at around 150PV. This is due to the reduced rates of chemical reactions and precipitate formation during the latter stage as explained above.

From column tests to field conditions

Although the field flow (3D) might be different to simplified laboratory 1D column situation, the actual chemical reactions occurring in the laboratory and field are the same, albeit different rate kinetics related to flow rate and the contact areas of the aggregates. In essence, the reactions in the 1D column simulations are accelerated. Nevertheless, this time factor can be

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captured by the relevant rate kinetics for chemical species, hence, while experimental results show rapid clogging of columns within six months, in a prototype (real-life) field PRB this translates to several years when applied to field conditions using geochemical computational models incorporating the field dimensions. For instance, Pathirage and Indraratna (2014) found that the longevity of a pilot scale PRB (filled with recycled alkaline concrete aggregates) was greater than 15 years when transformed from 1D column dimensions to those of the field trial with a width of 1.2m. The Authors have modified the model for limestone, which was calibrated with the current data.

Clogging of PRB -field evidence

Indraratna et al. (2014a) reported excessive clogging of recycled concrete particles used in the pilot scale PRB installed in the Shoalhaven floodplain, located in the south of Wollongong City. During the EDS analysis, armouring of aggregates (i.e. encrusted surface of reactive grains- Figure 13) was characterised by higher Al and Fe peaks in relation to unused recycled concrete. This intense clogging raised the need of treating or replacing the granular fill. For instance, rejuvenation of affected material with alkaline irrigation water from an agricultural farm has been successfully demonstrated by Banasiak et. al. (2015). However, if the clogging is severe, material replacement will be necessary.

In addition to adversely affecting the performance of PRB, chemical clogging under acidic groundwater conditions may also affect the PRB monitoring network, which includes vibrating wire piezometers (VWP), observation and data logger wells. The clogging of VWP was identified by microscopic analysis that was carried out on a typical piezometer filter tip

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from a similar acid sulfate floodplain (Indraratna et al., 2018). The contrast in void spaces in

the fresh filter before clogging is distinct (Figure 14a), compared to the pores of the exhumed

filter accumulated with clogging material (Figure 14b). Previous studies by Houben (2001) and

Post and von Asmuth (2013) have also reported the potential for clogging of piezometers in

this manner, but without alluding to the geochemical reaction mechanisms.

Conclusions

This paper presented the results of laboratory column experiments conducted to examine the

potential of a limestone-based permeable reactive barrier for remediating groundwater acidity

derived from acid mine drainage. The results demonstrated that the calcite aggregates were

capable of maintaining a stepwise acid neutralisation capacity with two subsequent bicarbonate

buffering zones. While there was some variation in pH along the sampling points in the column,

the effluent maintained a near neutral pH range while 100% iron removal was achieved.

Iron was removed out of solution by means of iron precipitates (mainly Fe oxides and

hydroxides), which eventually coated the limestone aggregates and accumulated in the voids

between reactive particles affecting the treatment efficiency of the limestone fill. While the

inlet zone was vigorously clogged as a result of the precipitation process, the outlet zone was

still capable of providing the desired treatment. This resulted in inhomogeneous zonal clogging

along the column. For instance, at the inlet zone there was 65% reduction of Ca releasing rate

and 29% reduction of hydraulic conductivity, whereas at the outlet zone were only 30% and

6%, respectively. These observations were also consistent with the SEM and EDS analysis

performed on the limestone aggregates upon dismantling the column, e.g. sharp increase in Fe

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and reduction in Ca peaks at the entrance and middle section of the columns. Longevity of the granular assembly can be governed based on the rate of clogging which is indicated by hydraulic conductivity reduction and alkalinity depletion. Field evidence of chemical clogging was also found in instrument filters including piezometers and observation wells, which would in turn affect the performance monitoring of PRBs in the long term.

While this study enabled the quantification of the dominant chemical reactions between reactive media and typical acid mine drainage, the flow conditions through the field PRB are also influenced by the geometric scale effects. With this regard, although PRB design criteria can be initially established based on the chemical reaction rates and associated clogging aspects of the porous medium for 1D conditions (columns), appropriate numerical modelling strategies should be adopted to capture multi-directional water flow in a large scale PRB in the field. The authors are currently working on evaluating the scale effects applied to field conditions using an advanced mathematical models.

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Table 1. Water quality parameters of field water taken from Hunter valley collieries

Parameter	Results
pH	5.52
Redox (mV)	8.0
Acidity (to pH 7.0) (mg/L $CaCO_3$ equivalent)	240
Total Iron (mg/L)	62.8
Aluminium (mg/L)	0.065
Calcium (mg/L)	605
Magnesium (mg/L)	59
Potassium (mg/L)	8
Sodium (mg/L)	485
Chloride (mg/L)	217
Sulfate(mg/L)	2253

Figure 1. Pilot scale Permeable Reactive Barrier (PRB) in Shoalhaven, Southeast Australia (During laboratory tests, a 1D column simulates the flow along the transects marked)
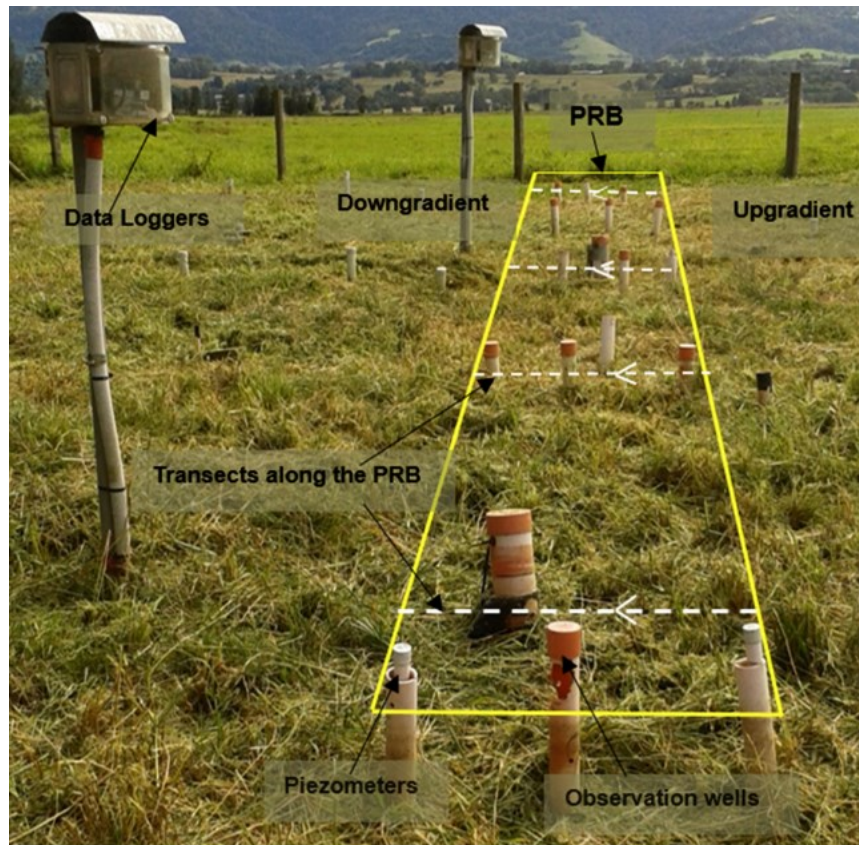
Figure 2. (a) Laboratory column experiment setup (b) schematic diagram of column arrangement (PT – Pressure Transducers, SP- Sampling points)
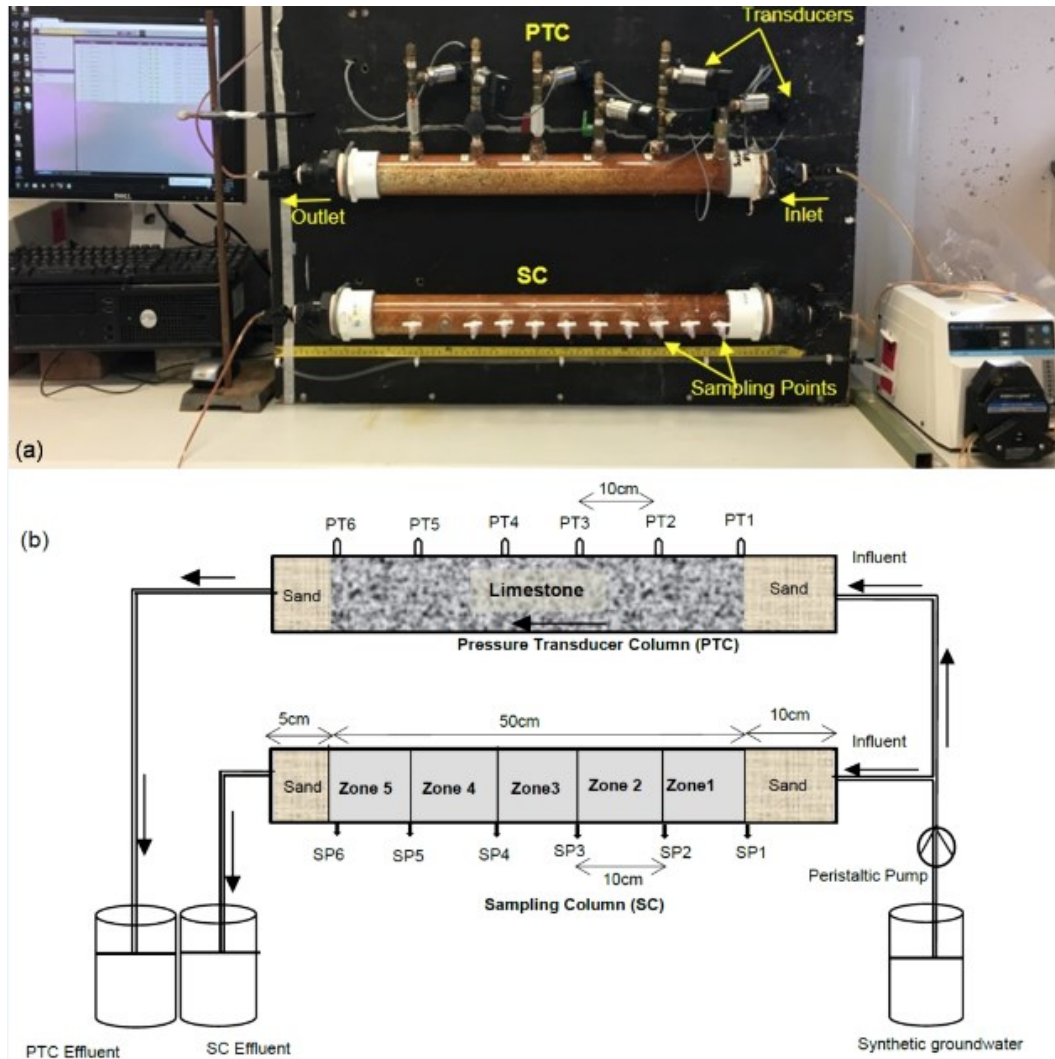
Figure 3. Particle size distribution of limestone used in column experiments

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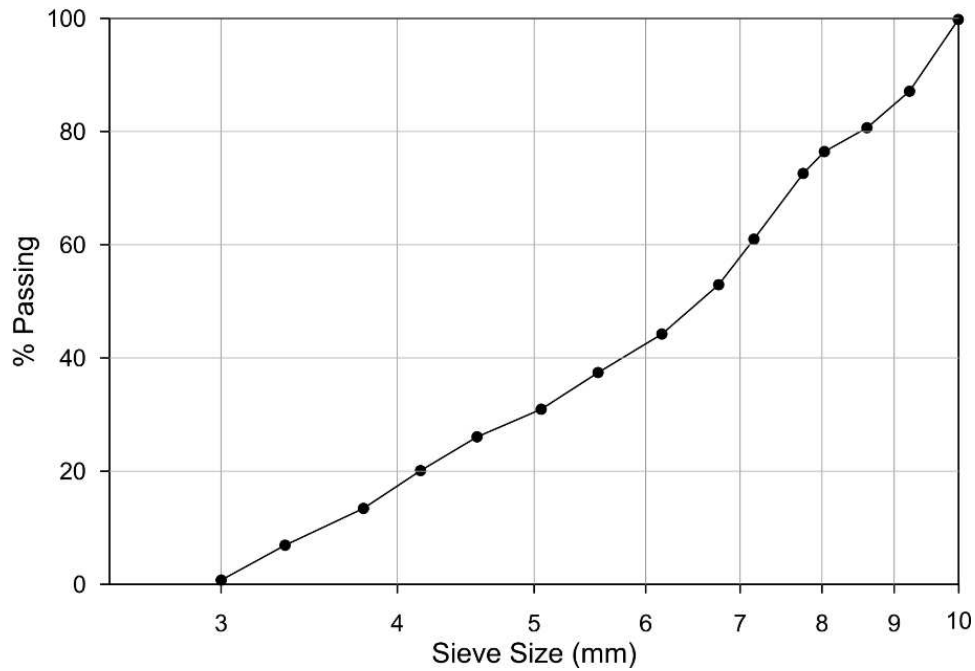
Figure 4. Variations in the main effluent parameters with number of pore volumes passing through the column (a) pH (b) Oxidation Reduction Potential (ORP)
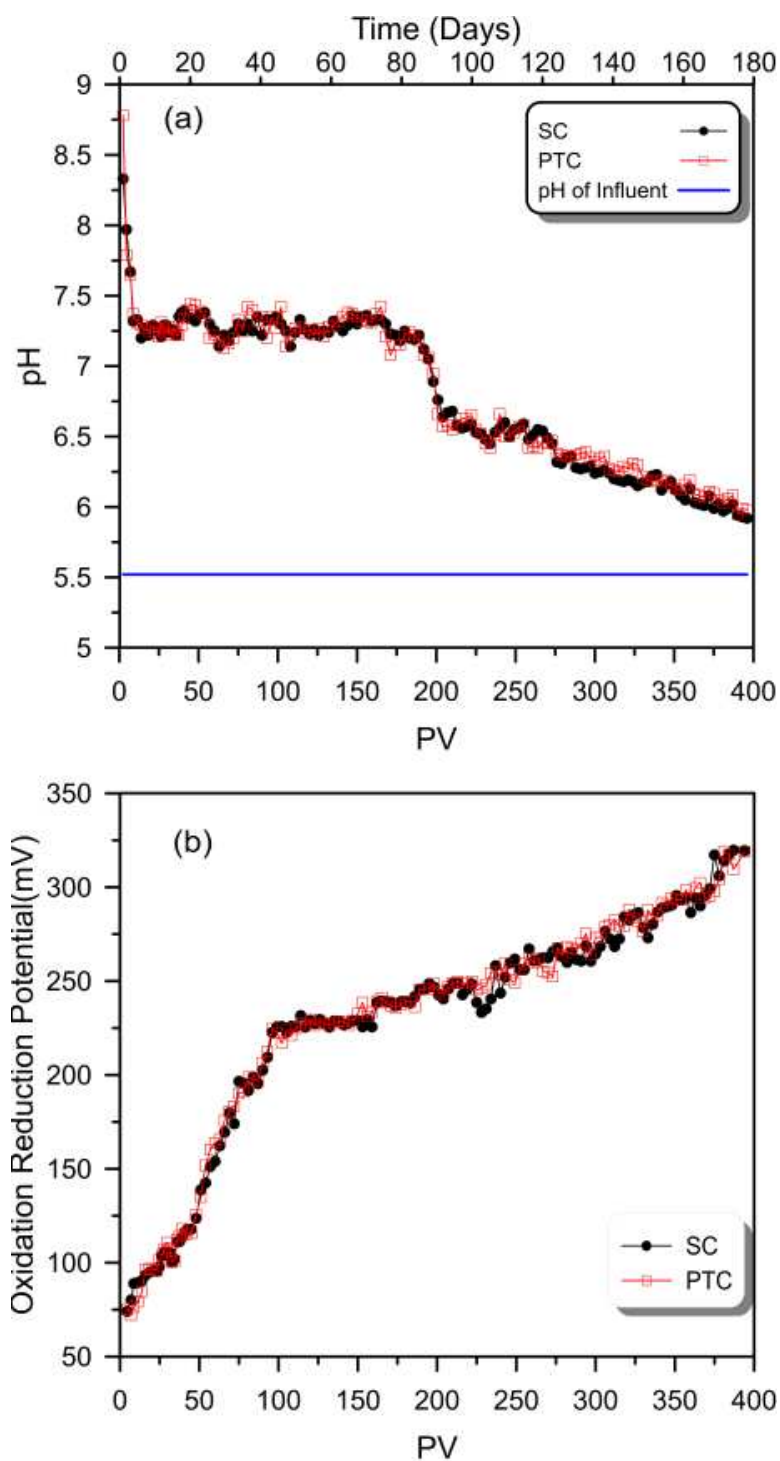
Figure 5. Dissolved Ca concentrations along the length of the column
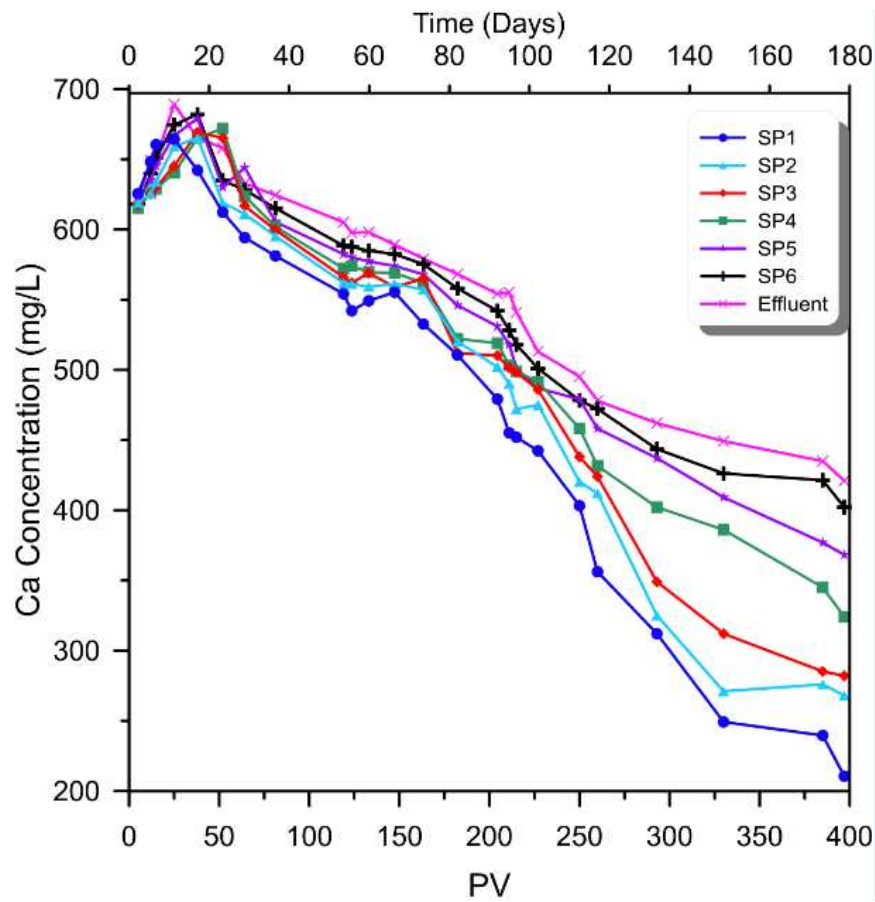
Figure 6. Effluent parameter variations of sampling ports along the length of the column (a) pH;

(b) Oxidation Reduction Potential (ORP)
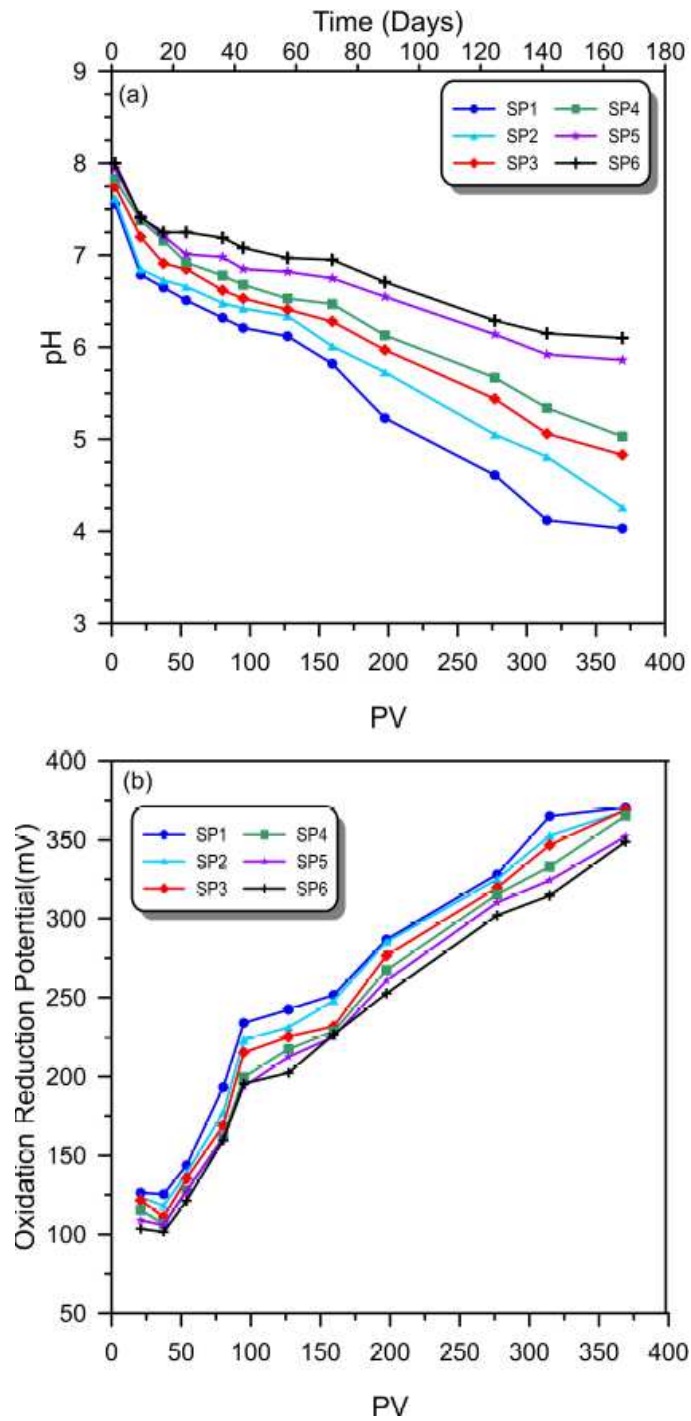
Figure 7. Dissolved total Fe concentrations along the length of the column
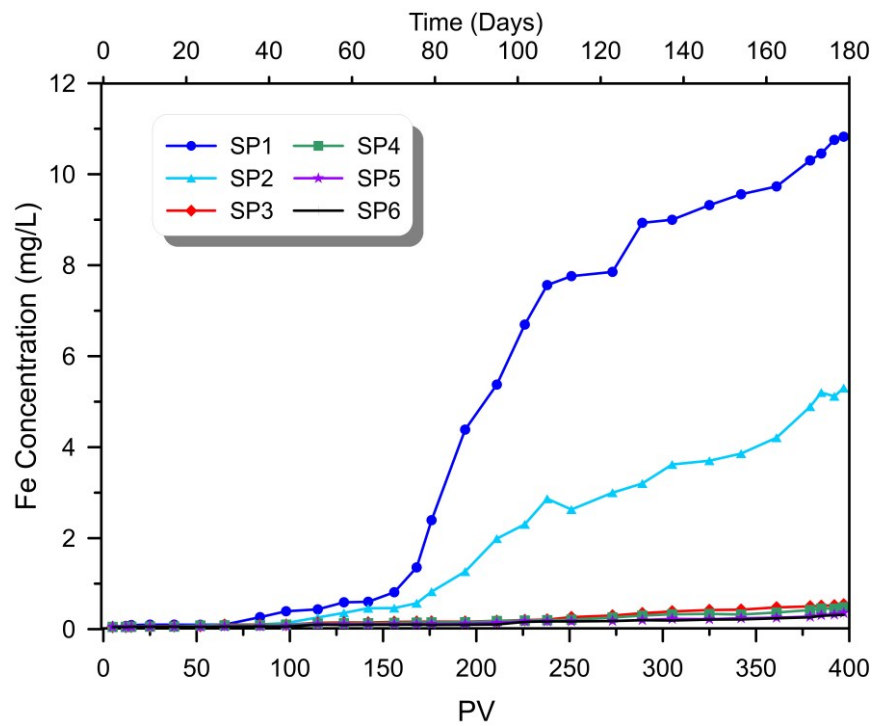
Figure 8. (a) Formations of iron oxides/hydroxides along the column with time (b) Granular coating of limestone inspected after dismantling the column
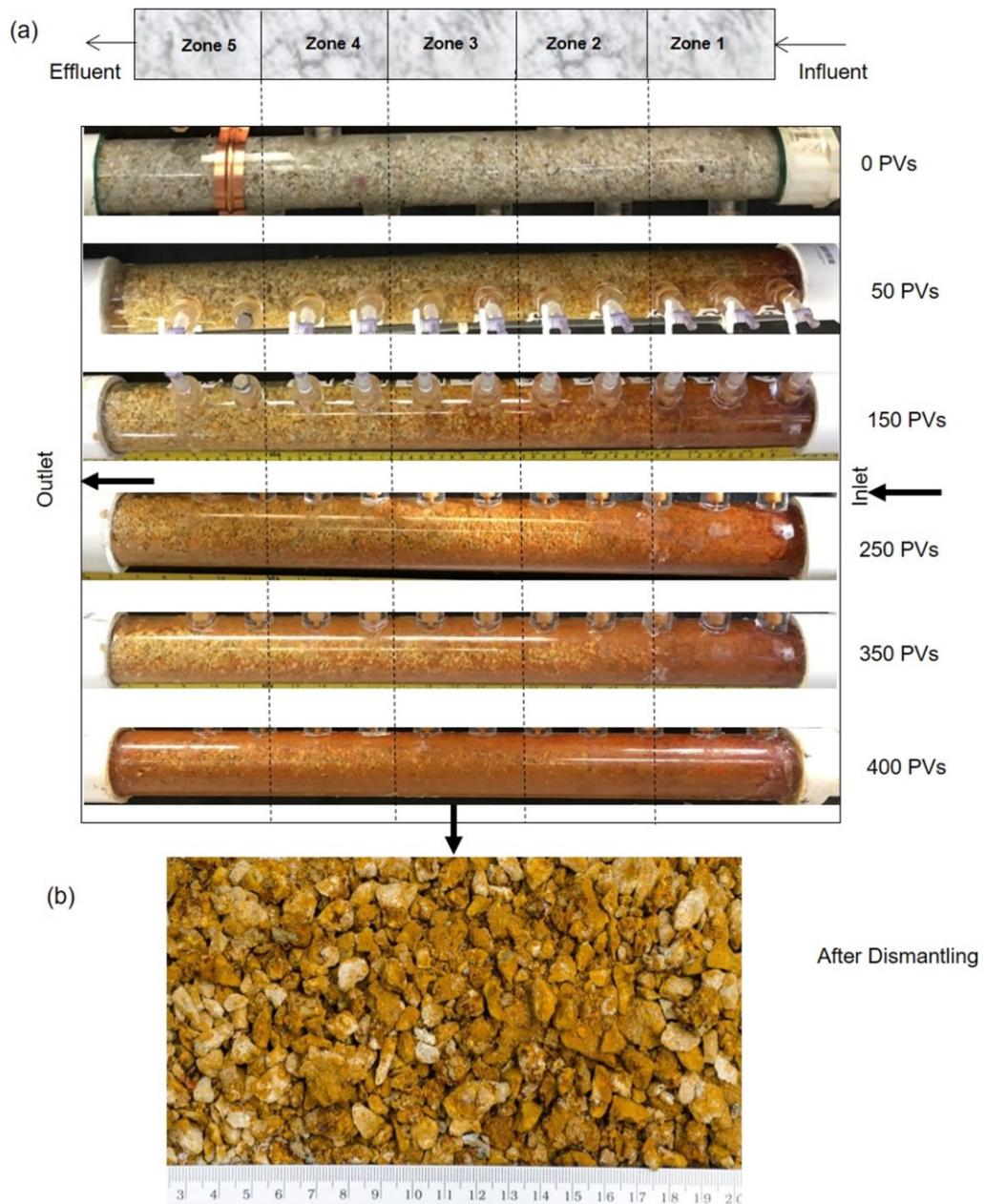
Figure 9. Comparison of the Energy-dispersive X-ray spectroscopy (EDS) spectra of fouled limestone particles (a) Virgin limestone (b) Entrance zone (c) Middle Zone (d) End zone

(a) Virgin limestone

(b) Entrance Zone

(c) Middle Zone

(d) End Zone
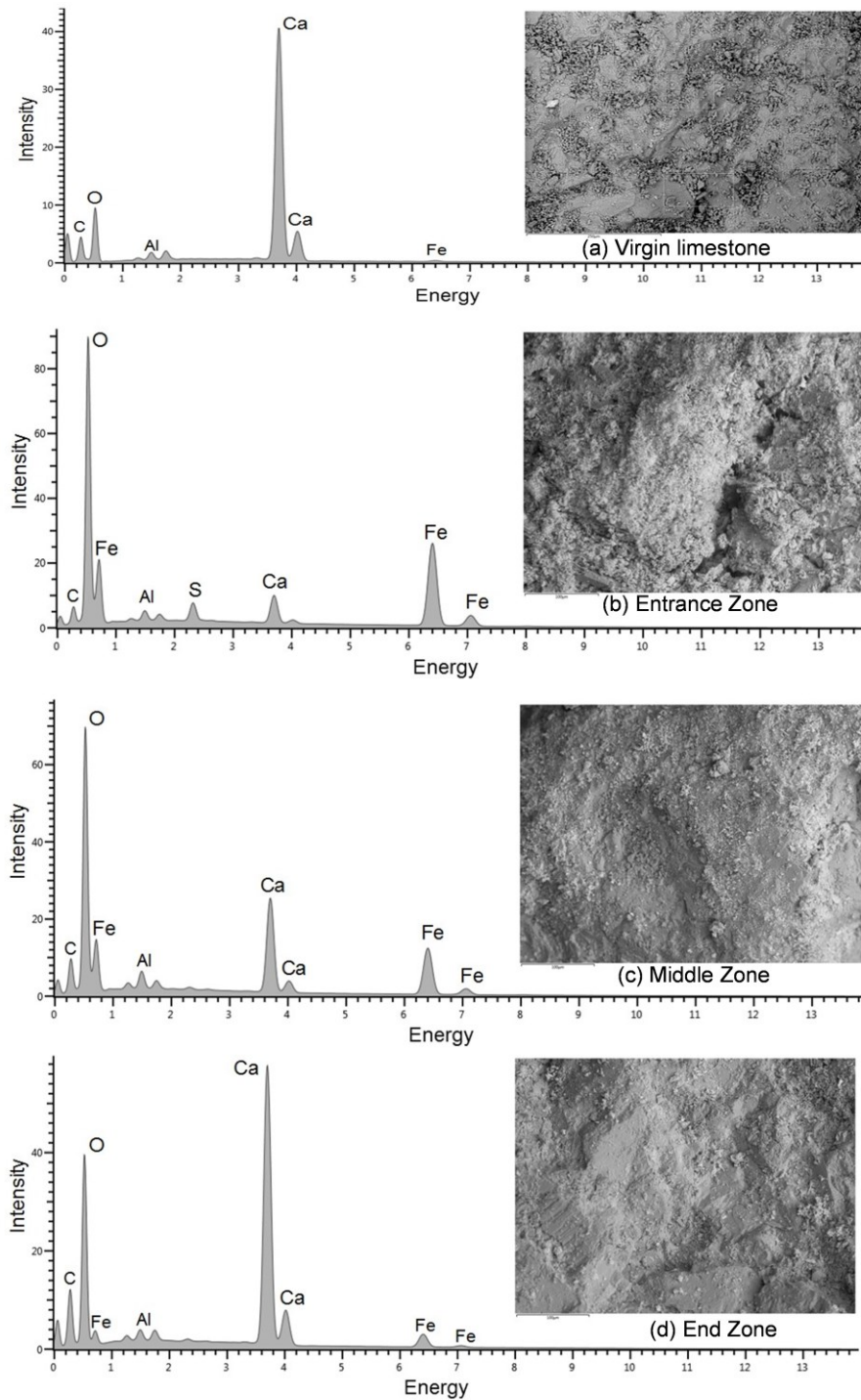
Figure 10. (a) Dissolved Al concentration along the length of the column (b) Other ions of influent and main effluent
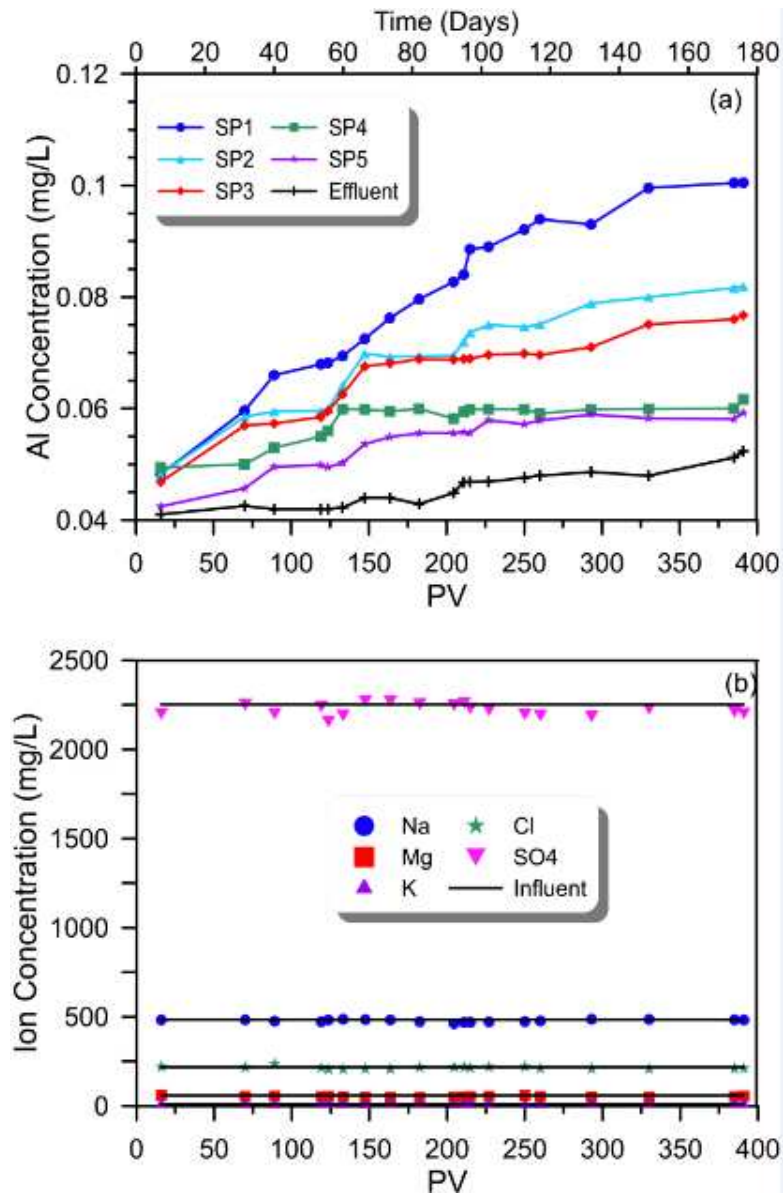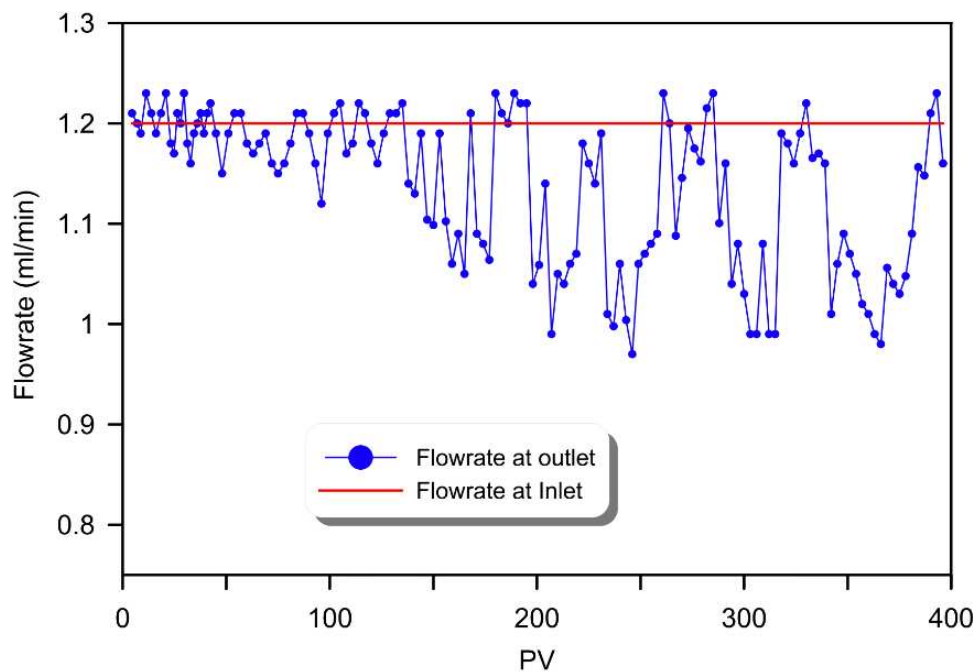
Figure 11. Flow rate at column inlet and outlet

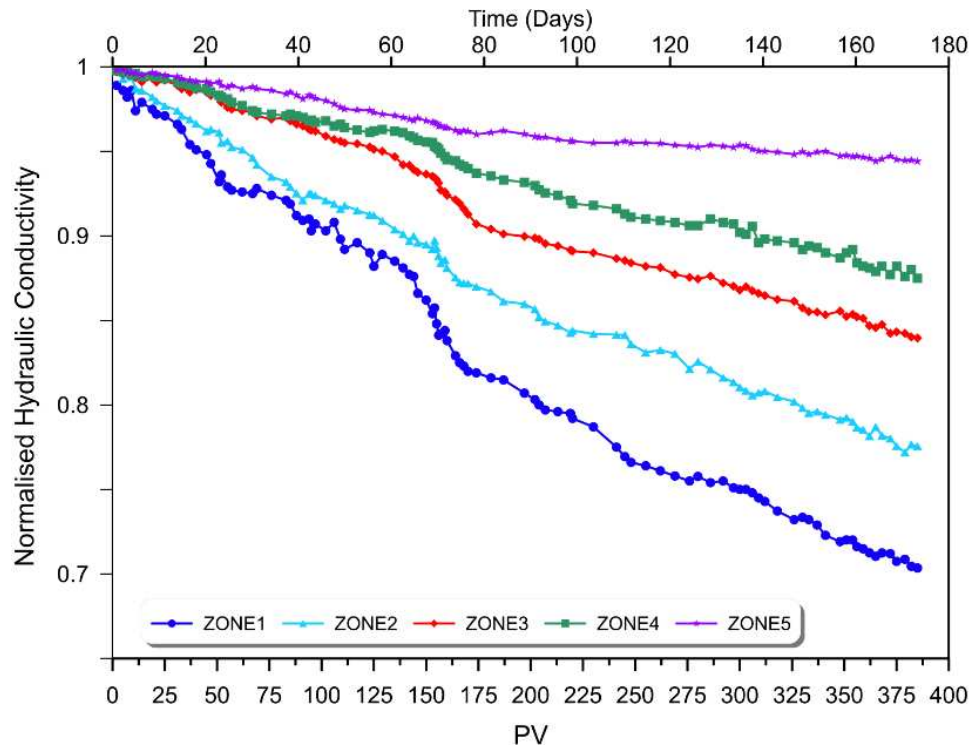**Figure 12.** Normalised hydraulic conductivity variation with number of pore volumes

Figure 13. Surface of armoured waste concrete particles taken out from the PRB site, Shoalhaven, Southeast Australia (Indraratna et al., 2014a)
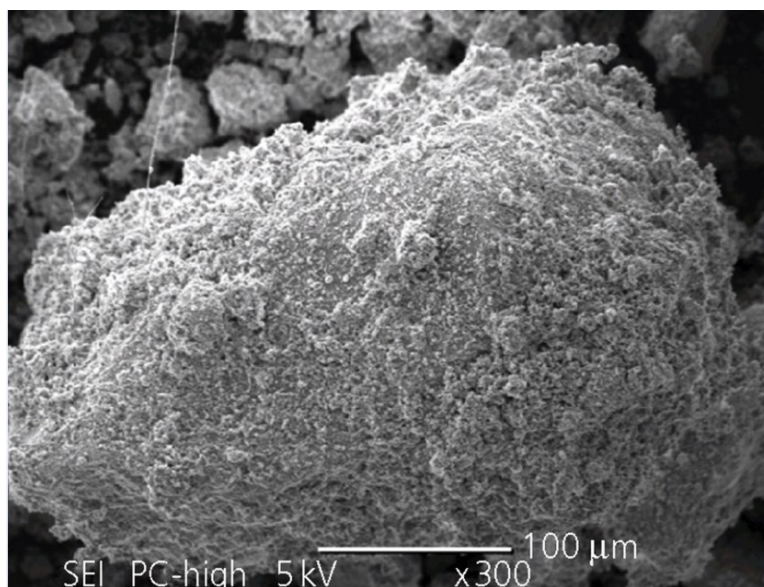
Figure 14. SEM micrographs of the piezometer filters (a) Clear filter tip before clogging (b) clogged filter tip due to chemical products accumulation in voids (Indraratna et al., 2018)

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