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Permeable reactive barrier rejuvenation by alkaline wastewater

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Abstract
Chemical armouring of recycled concrete in a permeable reactive barrier (PRB) used for the neutralisation of acidic groundwater in acid sulfate soil terrain significantly decreases its acid neutralising capacity (ANC) by approximately 50% compared with its theoretical ANC. A long-term column test was conducted under simulated field groundwater conditions to assess the re-conditioning of armoured recycled concrete aggregates with alkaline wastewater, with the aim to restore and enhance the ANC and longevity of the PRB. The benefits of alkaline wastewater injection included sharp but short enhancement of the recycled concretes' ANC, as indicated by an increase in effluent pH (pH 3 to 7·7) and alkalinity (0 to 21·6 mM CaCO3) and a reduction in oxidation reduction potential (ORP, 530 to 160-200 mV). While the results showed that the alkaline wastewater did not significantly reduce chemical armouring, it aided in the liberation of lodged mineral precipitates between concrete aggregates, reducing the severity of chemical and physical clogging. Batch tests demonstrated that, when exposed to acidic water, the ANC of recycled concrete pre-conditioned with alkaline wastewater was enhanced as indicated by higher pH, lower ORP and greater release of calcium (Ca2+) and alkalinity, compared to non-pre-conditioned concrete.

Keywords
geotechnical engineering, groundwater, recycling, reuse of materials

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Abstract

Chemical armouring of recycled concrete in a permeable reactive barrier (PRB) used for the neutralisation of acidic groundwater in acid sulphate soil (ASS) terrain significantly decreases its acid neutralising capacity (ANC) by approximately 50% compared with its theoretical ANC. A long-term column test was conducted under simulated field groundwater conditions to assess the re-conditioning of armoured recycled concrete aggregates with alkaline wastewater, with the aim to restore and enhance the ANC and longevity of the PRB. Benefits of the alkaline wastewater injection included sharp but short enhancement of the recycled concretes' ANC as indicated by an increase in effluent pH (pH 3 to 7.7) and alkalinity (0 to 21.6 mM $CaCO_3$), and a reduction in oxidation reduction potential (ORP, 530 mV to 160-200 mV). While results showed that the alkaline wastewater did not significantly reduce chemical armouring, it aided in the liberation of lodged mineral precipitates between concrete aggregates, reducing the severity of chemical and physical clogging. Batch tests demonstrated that, when exposed to acidic water, the ANC of recycled concrete pre-conditioned with alkaline wastewater was enhanced as indicated by higher pH, lower ORP and greater release of calcium (Ca^{2+}) and alkalinity, compared to non-preconditioned concrete.

Keywords chosen from ICE Publishing list
Keyword 1; Groundwater 2; Recycling & reuse of materials 3; Geotechnical engineering

List of notation

K	hydraulic conductivity of column at time (t)
K_0	initial hydraulic conductivity
n_0	initial porosity of the column
n_t	porosity of column at time (t)
Δn_t	change in column porosity at time (t)
V_P	volume occupied by precipitated mineral
V_T	volume of column

1. Introduction

Acid sulphate soils (ASS) affect over 3 million hectares of coastal floodplains and estuaries in Australia (White *et al.*, 1997). Increased population and resulting changes in land use (e.g. construction of deep flood mitigation drains) during the 1960s promoted the oxidation of pyritic soil, the generation of sulphuric acid and the mobilisation of toxic metals such as aluminium (Al) and iron (Fe) to nearby waterways. Consequently, severe, periodic discharges of acidic water attack concrete and steel infrastructure, clog waterways with Fe flocculates, kill aquatic ecology and produce large acid scalds that render land unusable for agricultural purposes.

Engineering solutions such as weirs and modified floodgates have been installed near Broughton Creek, Shoalhaven Floodplain, New South Wales (NSW) (Indraratna *et al.*, 2001; Glamore and Indraratna, 2004). While these approaches were successful in preventing further pyrite oxidation, they were unable to remediate existing acidity stored in the soil (Indraratna *et al.*, 2005). In addition, they are not feasible in very low-lying areas due to enhanced flooding risk. The installation of a subsurface horizontal lime-fly ash barrier was able to control pyrite oxidation and improve groundwater quality within close proximity to the barrier (Indraratna *et al.*, 2006). However, this was only a short-term remediation option. A significant advancement was achieved through the installation of a pilot-scale permeable reactive barrier (PRB) (17.7 m length, 1.2 m width, 3.0 m depth) containing recycled concrete as the reactive media (Golab *et al.*, 2009; Golab *et al.*, 2006) at Manildra Group's Environmental Farm in October 2006.

While long-term monitoring has revealed that the PRB has maintained a groundwater pH from alkaline to neutral (pH 10.0-7.2) and Al and total Fe below average concentrations of 2 and 0.5 mg/L respectively inside the barrier, a slow decrease in performance due to armouring of the recycled concrete caused by the precipitation of Al- and Fe-oxy/hydroxide minerals has been observed (Indraratna *et al.*, 2010). Laboratory column experiments and geochemical modelling showed a reduction of 50% in the actual ANC of the reactive media compared to its theoretical ANC (Regmi *et al.*, 2011b). Over time, precipitates occupy the pore spaces between the recycled concrete within the PRB, reducing its porosity and hydraulic conductivity. However, field observations and modelling have shown that in many cases this loss of porosity and hydraulic conductivity occurs at relatively low rates (ITRC, 2011), which is the case for the pilot-scale PRB as currently indicated by steady piezometric head (Indraratna *et al.*, 2010).

While removal and replacement of the recycled concrete is one management option for restoring the performance of the PRB, this represents a significant operation and maintenance cost. Rule-of-thumb criteria have been used for economic analysis at previous sites, including maintenance cost estimates assuming 25% of reactive material will be replaced every 10 years at sites with low precipitation potential, and every 5 years for sites with high precipitation potential (Gavaskar *et al.*, 1998). The pilot-scale PRB has been in operation for 7 years and is still performing relatively well. Thus, an alternative to material replacement is needed to

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increase the long-term performance of the recycled concrete for remediating the acidic groundwater.

The Manildra Group has a Water Recovery Plant, which recycles approximately two thirds of their wastewater. The novel approach of this project is to evaluate the application of this reject alkaline wastewater to the PRB to improve its performance by increasing alkalinity and reacting with the acidic groundwater in its flow-path. A long-term column experiment replicating field conditions was carried out to examine the effectiveness of injecting alkaline wastewater through the PRB for increasing the efficiency of the recycled concrete aggregates. In addition, batch tests were undertaken to investigate how pre-conditioning of the recycled concrete with alkaline wastewater enhances its ANC and longevity.

2. Materials and Methods
2.1 Reactive material
The large concrete fragments, which were sourced from a refuse depot handling 25 year old concrete elements from road expansion works in rural NSW, were crushed into smaller size aggregates such that what passes through a 4.75 mm sieve and what retains in a 3.35 mm sieve was used in order to ensure a uniform particle size in the column. This was the same batch of recycled concrete used in the pilot-scale PRB. The major cations in the recycled concrete are predominantly calcium (Ca, 57.3%), Fe (21.4%), Al (9.85%), magnesium (Mg, 5.27%), silica (Si, 3.06%) and others (3.04%) (Regmi *et al.*, 2009).

2.2 Synthetic acidic groundwater and alkaline wastewater
The influent for the column experiment (Table 1) was a synthetic acidic solution prepared with the concentration of all major constituents matching average values in groundwater from ASS terrain on the Shoalhaven Floodplain measured continuously for 1.5 years (Regmi *et al.*, 2009). The alkaline wastewater from Manildra Group's Water Recovery Plant was collected from Effluent Storage Pond 5 on Manildra Group's Environmental Farm. The purpose of this pond is to allow the storage of the reject wastewater that is blended for irrigation on the farm. The utilisation of the unused wastewater assists in reducing the salt load applied to the irrigated cropping area. Constituents of a sample of this alkaline water are shown in Table 1. Slight fluctuations in these parameters may transpire due to the total storage time of the effluent wastewater.

2.3 Experimental protocol
The alkaline injection column apparatus was constructed similar to previous column design (Regmi *et al.*, 2009). The design was initially modified to replicate the alkaline injection strategies that can be adopted at the pilot-scale PRB field site for rejuvenation by means of downwards infiltration i.e. by way of a horizontal column as opposed to a vertical column used previously. However, the closed system resulted in the synthetic acidic water rising into the

alkaline injection port resisting the flow path of the alkaline wastewater injection regardless of the flow rate provided by the peristaltic pump. The revised injection process of pumping the alkaline wastewater through the inlet valve proved effective. This method allowed the alkaline wastewater to pass through the entire column and enabled it to act in regions of concentrated chemical armouring i.e. column inlet zone. The transparent acrylic column of 1.5 L capacity (L = 65 cm, I.D. = 5 cm) (Figure 1) contained a 10 cm silica sand ball after the influent point followed by 50 cm of crushed recycled concrete aggregate and another 5 cm silica sand ball. A geosynthetic membrane separated the sand zones from the inlet and outlet to prevent physical clogging by the sand. Table 2 summarises the physical parameters of the column.

The synthetic acidic water was passed through the column at a constant flow rate (1.2 mL/min) using a Masterflex peristaltic pump. This was higher than the field groundwater flow rate in order to demonstrate the acid neutralisation behaviour of the recycled concrete in a short period in the laboratory. Based on this flow rate, the retention time for one pore volume (PV, void volume of column) is 9.62 hours, which is 10 times smaller than the retention time for a groundwater flow rate of 30 cm/day at the field site. The column was flushed with 4-5 PVs of deionised water before commencing the experiment at room temperature.

Seven sampling ports (SP1-SP7) were located at 2.5, 5.0, 10, 20, 30, 40 and 50 cm distance along the column from left (influent point) to right (effluent point). The sampling ports were fitted with a leur adaptor, to allow vacuum sampling during the experiment. Effluent and water from the sampling ports were analysed immediately after the samples were collected for pH, electrical conductivity (EC), oxidation reduction potential (ORP) and temperature. Samples were filtered through 0.45 μm cellulose acetate filter paper, and both acidified and non-acidified samples were collected and stored in a refrigerator at 4°C before analysis. Alkalinity measurement and all other chemical analyses were performed following standard methods for the examination of water and wastewater (APHA, 1998). Total Fe concentrations were measured using atomic absorption spectroscopy (AAS) and Al^{3+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} concentrations were measured using inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-optical emission spectrometry (ICP-OES) (Southern Cross University Environmental Analysis Laboratory).

After the ANC of the recycled concrete was significantly reduced (when the effluent pH reached approximately pH 3), the column was injected with the alkaline wastewater. Three trial injections were undertaken: (T1) 10 PVs at 20 mL/min; (T2) 10 PVs at 10 mL/min to increase reaction time between the alkaline wastewater and precipitates formed on the concrete aggregates and within the pores; (T3) 20 PVs at 10 mL/min to investigate the effects of increased alkaline wastewater volume. A comparison of the effluent composition pre- and post-injection was used to determine the effectiveness of the alkaline wastewater in rejuvenating the recycled concrete.

In addition, a batch test was undertaken to evaluate if pre-conditioning of the recycled concrete with alkaline wastewater improves its ANC. Recycled concrete aggregates (100 g, same size employed in column test) were placed into glass bottles, which were then filled with 800 mL deionised water (control test) and alkaline wastewater (pre-conditioned test). The recycled concrete was allowed to react with the alkaline wastewater for 131 days to allow equilibrium to take place prior to exposure to synthetic acidic water i.e. until pH, EC and ORP measurements of the supernatant were relatively stable. The control and pre-conditioned recycled concrete was then exposed to the synthetic acidic water for an extended period of time (approximately 120 days) to determine the effectiveness of the recycled concrete in neutralising acidity and removing contaminants. The supernatant of each bottle were analysed for the first 6 hours of the experiment and then at 1, 4, 7, 14, 32, 68, 131, 132, 138, 146, 159 and 251 days for pH, EC, ORP, alkalinity and temperature. Following each reading, the bottles were turned end-over-end to ensure complete mixing of the deionised water and alkaline wastewater with the recycled concrete aggregates. In addition, 60 mL samples were collected for the analysis of Al^{3+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} following the same methods used to analyse samples from the column experiment.

2.4 Changes in porosity and hydraulic conductivity

To calculate changes in porosity within the column due to the precipitation of Al- and Fe-bearing minerals, the influent and influent concentration of Al and total Fe throughout the column experiment was plotted. As a constant influent concentration was employed, the volume of Al^{3+} and total Fe retained within the column was obtained through subtraction of the integrated data of the influent curve (computed using OriginPro 8.5) from the integrated data of the effluent curve. This was then multiplied by the pore volume of the column (0.6924 L) to give the mass (mg) of Al^{3+} and total Fe precipitated. Using the molar volume of the predominant Al- and Fe-bearing precipitates formed within the column (gibbsite $Al(OH)_3$ 31.97 cm^3/mole; goethite $FeOOH$ 20.33 cm^3/mole), the volume occupied by each mineral (V_P) was calculated. The porosity within the column (n_t) at different PVs with the change of precipitated minerals with time was calculated using Equation 1:

$$n_t = n_0 - \left(\frac{V_P}{V_T} \right)$$

1.

The normalised Kozeny-Carmen equation (Equation 2) was used to estimate the hydraulic conductivity (K) at different PVs with the change of precipitated minerals with time (Pathirage *et al.*, 2012; Li *et al.*, 2006; Indraratna *et al.*, 2014):

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

2.

3. Results

3.1 Acid neutralisation behaviour during pre-alkaline injection period

A step-wise decrease in pH due to a reduction in ANC of the recycled concrete was observed in the pre-alkaline injection period (Figure 2(a). While this is consistent with results from previous long-term column experiments (Regmi *et al.*, 2011b), the rate at which a reduction in effluent pH occurred was quicker decreasing to appoximately pH 2.8 within 312 PVs compared to a pH of 2.7 within 500 PVs observed by Regmi *et al.* (2011b). This can be explained by the larger porosity of the column (0.71) and slower flow rate (1.2 mL) used in this study compared to that reported in Regmi *et al.* (2011b) (0.53, 2.4 mL). The larger porosity allows for a greater surface area of recycled concrete exposed to the acidic influent; thus a greater ANC. The distinct plateaus in pH can be attributed to three stages of buffering: (Stage 1) Dissolution of carbonate/bicarbonate alkalinity from the recycled concrete as indicated by the near-neutral plateau at pH 8.00-7.02; (Stage 2) Precipitation/dissolution of Al hydroxide minerals at approximately pH 4.2; (Stage 3) Precipitation/dissolution of Fe oxyhydroxide minerals at pH 3.4.

The high initial effluent pH (9.56-8.63) can be attributed to the dissolution of soluble Ca-bearing minerals portlandite ($Ca(OH)_2$) and ettringite ($(CaO)_6(Al_2O_3)(SO_3)_3.32H_2O$) from the recycled concrete and the release of alkalinity. However, as the recycled concrete contains a negligible amount of portlandite (0.3% weight, Regmi *et al.* (2011a)) and the fact that ettringite undergoes dissolution between pH 10.7 and 9.5 (Álvarez-Ayuso and Nugteren, 2005), this high pH was only maintained for 9 PVs. Following this the effluent pH decreased from pH 8.63 to pH 8 and was maintained near-neutral (pH 8-7.02) until 130 PVs (Day 51). This is due to the dissolution of calcium aluminate hydrated compounds (C-A-H) such as anorthite ($CaAl_2Si_2O_8$) within the concrete (Regmi *et al.*, 2011a). The pH then dropped abruptly to pH 4.2, which continued until 212 PVs followed by a slow decrease to pH 3.4. The pH at the different sample points decreased in the lower parts of the column with increasing PV of acidic influent flow through the column.

ORP (see Figure 2(b)) demonstrated several distinguishable trends similar to previous column experiments (Regmi *et al.*, 2011b) in relation to the observed neutralisation reactions and column responses to chemical armouring. Low initial ORP for the effluent and SP1-SP3 (351-231 mV) indicates weak oxidising conditions inside the column. The ORP increased sharply in Stage 1 for SP1-SP3, which was caused by a fast depletion of alkalinity at the advancing acid influent front within the column corresponding to sharp decreases in pH. The effluent ORP increased to 500 mV between Stage 2 and Stage 3, indicating oxidising conditions throughout the column.

The EC of the column effluent typically fluctuated between 4.5-5.8 mS/cm concluding the steep increase in EC occurring in the first 10 PVs of acidic influent passed through the column (Figure

3). The low initial effluent EC (0.63 mS/cm) is due to flushing of the column with deionised water. Concluding the release of calcium carbonate ($CaCO_3$) from the concrete, there was little variation in EC in response to trends of Al^{3+} and total Fe precipitate armouring around the concrete aggregates. Slight variations in effluent EC over the duration of the column experiment are a result of slight variations in the batches (60 L) of acidic influent made up throughout the experiment.

Alkalinity of the column effluent is related to the release of alkaline minerals from the recycled concrete aggregates and, in addition, the chemistry of the acidic influent. Before the depletion of alkalinity at 130 PVs (see Figure 4(a)), the pH was relatively stable and near-neutral (pH 7.2-7.3). Following this there was a significant drop in the amount of Ca^{2+} released from the recycled concrete as indicated by the decrease in Ca^{2+} in the effluent from 466 mg/L at 130 PVs to 345 mg/L at 142 PVs (see Figure 4(b)). The growth of white and orange precipitates inside the column (see Figure 5)) decreased the reactivity of the recycled concrete and corresponds to the drop in alkalinity and Ca^{2+} released from the concrete. These white and orange precipitates, attributed to the Al and Fe oxy/hydroxides, respectively, initially formed near the column inlet and then further along the column as the flow of acidic influent continued.

3.2 Metal removal capacity during pre-alkaline injection period
The performance of recycled concrete for the removal of Al^{3+} and total Fe from the synthetic acidic influent is shown in Figure 6(a). Removal of Al^{3+} was approximately100% until 130 PVs, whereby removal significantly decreased to 38.1% (142 PVs, 56 days). This coincides with the depletion of alkalinity within the column effluent, the decrease in pH from pH 7 to pH 4.2. Removal of Al^{3+} was due to the precipitation of Al in hydroxide form (gibbsite ($Al(OH)_3$) and boehmite($AlOOH$)) as confirmed by analysis of the precipitates formed on the recycled concrete during previous column experiments (Regmi *et al.*, 2011a) and similarly reported by studies of field PRBs and column tests for acid mine drainage and other groundwater contamination (Blowes *et al.*, 2003; Jurjovec *et al.*, 2002; Phillips *et al.*, 2000). Total Fe removal was 99.6% throughout the experiment until 212 PVs (93 days), after which it decreased to 89.8% just prior to the alkaline injection trial. Fe precipitated as Fe oxyhydroxide (goethite ($FeOOH$)). The flow of acidic influent through the column was stopped at 312 PVs (Day 128) when the effluent pH reached 2.83. The saturation index (SI) of minerals dissolving (SI<0) and precipitating (SI>0) was calculated using geochemical speciation/mass transfer computer code PHREEQC V2.15 (Parkhurst and Appelo, 1999) with MINTEQA database with the input parameters Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cl^-, SO_4^{2-} in the influent water and alkalinity, pH and temperature. The effluent was saturated (SI>0) with respect to Al (gibbsite and alunite) and Fe minerals (hematite, goethite, jarosite-K) during the pre-alkaline injection period (Figure 7).

The concentration of Na^+, Cl^-, Mg^{2+}, K^+ and SO_4^{2-} in the effluent remained relatively constant throughout the experiment prior to alkaline injection (see Figure 6(b)), indicating that they are

not affected by the neutralisation reactions occurring within the column, except for K^+ as some K-jarosite precipitated out of solution. However, the overall change in K^+ was also not significant, as seen in Figure 6(b). Slightly higher concentrations of ions compared to their concentration in the influent can be attributed to the minor leaching of these minerals from the recycled concrete. This was similarly observed in previous column experiments (Regmi *et al.*, 2011b).

3.3 Mineral precipitation and changes in physical properties

Chemical armouring of the recycled concrete by precipitates was studied by monitoring the change in physical parameters i.e. porosity and hydraulic conductivity with respect to the number of PVs of acid passed through the column, as shown in Figure 8. The change in porosity and hydraulic conductivity due to mineral precipitation was calculated using Equation 1. The reduction in hydraulic conductivity in the column due to mineral precipitation and dissolution were calculated from Equation 2. Chemical armouring of the recycled concrete from the beginning of the column experiment until the alkalinity was exhausted (212 PVs) reduced the porosity of the column, which is similarly observed in several laboratory column and field studies on PRBs (Li *et al.*, 2006; Kamolpornwijit *et al.*, 2003; Furukawa *et al.*, 2002; Wilkin *et al.*, 2003). The porosity decreased gradually from 0.710 to 0.703 (0.97% reduction) and the hydraulic conductivity decreased from 0.880 to 0.856 m/d (2.75%). However, the pores in the column were large enough that complete clogging of the pores did not occur and, thus, flow through the column was maintained throughout the experiment.

3.4 Alkaline wastewater injection

Approximately 400 L of acidic synthetic influent was passed through the column before alkaline injection was attempted. Following each successive alkaline injection trial noticeable trends were observed in effluent pH (Figure 2(a)). These include: a distinctive sharp but short increase in effluent pH (Injection 1 at 310 PV: pH 2.8-7.2, Injection 2 at 343 PV: pH 3.0-7.1, Injection 3 at 364 PV: pH 3.2-6.7) indicating an increase in the recycled concretes' neutralisation capacity; and a steady reduction in effluent pH to values typical during pre-injection period 10 PVs after alkaline injection. This indicates the short-term temporary nature of the alkaline rejuvenation after significant chemical armouring of the recycled concrete aggregates has occurred. The maximum effluent pH observed during the post-alkaline injection period (8.04) was very similar to the maximum effluent pH observed during the pre-injection period (8.00).

In comparison with the effluent pH, within 3-10 PVs following alkaline injection weak oxidising conditions were dominant within the column, as represented by the reduction in effluent ORP (T1: 530-226 mV, T2: 501-167 mV, T3: 385-258 mV, Figure 2(b)). These are ideal ORP values where the neutralisation of acidic groundwater and precipitation of Al and Fe can occur. There was a return to strong oxidising conditions within the column concluding the passing of 10-18 PVs of acidic influent through the column. However, the neutralisation capacity of the recycled

concrete benefited from multiple alkaline injection trials. Each successive rejuvenation attempt produced a slight reduction in the effluent ORP, as denoted by the steady reduction of peak ORP values from 537 mV after T1 to 311 mV after the third injection trial.

There was little variation in the EC of the effluent during the post-alkaline injection period (Figure 3). The range in the effluent EC during the pre-injection period was 4.35-5.81 mS/cm, which was similar to that observed during the post-injection period (4.10-5.11 mS/cm). In addition, the EC of the alkaline wastewater (5.5-6 mS/cm) was very similar to the EC of the acidic influent and effluent during the pre-injection period.

The increase in alkalinity of the column effluent during the post-injection period is due to chemistry of the alkaline wastewater i.e. alkalinity provided by the wastewater (2460 mg/L as $CaCO_3$) and not due to the release of alkaline minerals from the concrete. Effluent alkalinity increased significantly 2-3 PVs after the injections trials (T1: 0-2044 mg/L $CaCO_3$, T2: 0-2274 mg/L $CaCO_3$, T3: 2192 mg/L $CaCO_3$) and decreased rapidly within 3-6 PVs. (Figure 4(a)). There was no significant difference in the concentration of Ca^{2+} released from the concrete before and after alkaline injection. Ca^{2+} released from the concrete decreased following injection and returned to the pre-injection concentration of 200 mg/L within 4-7 PVs (Figure 4(b)).

The increase in effluent pH and decrease in ORP following each alkaline injection trial led to the precipitation of Al- and Fe-bearing minerals from the acidic influent, as shown by the decrease in concentration of Al and Fe in the effluent (T1: 90.4-0 mg/L, T2: 103.2-0 mg/L, T3: 80.9-0 mg/L, Figure 6(a)). This could be clearly seen by Figure 7 where positive SI values were significantly increased for the Al and Fe minerals which were precipitating. When the ORP returned to values of 315-500 mV, the re-dissolution of Al and Fe precipitates occurred, as indicated by the increase in Al and total Fe concentration after 9-11 PVs.

While there was variation in the response of other ions following the alkaline injection trials, the alkaline injection did not appear to have a lasting effect on their concentration post-injection with most returning to their pre-injection concentration. The concentration of Mg^{2+} increased significantly post-alkaline injection (T1: 109-388 mg/L; T2: 122-600 mg/L, T3: 112-400 mg/L) due to the higher concentration of Mg^{2+} in the alkaline wastewater (364 mg/L) compared to that of the acidic influent (110 mg/L). However, the concentration of Mg^{2+} in the effluent returned to the pre-injection concentration (110-120) within 12 PVs. Similarly, Cl^- and SO_4^{2-} also decreased post-injection (Cl^-: T1 872-691 mg/L, T2 944-388 mg/L, T3 854-367 mg/L; SO_4^{2-}: T1 1482-1107 mg/L, T2 1611-270 mg/L, T3 1413-270 mg/L), which can be attributed to the lower concentration of Cl^- and SO_4^{2-} in the alkaline wastewater (428 mg/L and <1 mg/L, respectively) compared to their concentration in the acidic influent (850 mg/L and 1500 mg/L, respectively). The concentration of Cl^- and SO_4^{2-} returned the pre-injection concentration in the post-injection period (Cl^-: 940 mg/L, SO_4^{2-}: 1500-1600 mg/L). The concentration of K^+ in the effluent

decreased slightly following the alkaline injection (T1: 48-40 mg/L, T2: 53-40 mg/L, T3: 49-37 mg/L) and increased to a concentration (52-55 mg/L) slightly higher than that observed pre-injection (45-50 mg/L).

With the precipitation of Al and Fe-bearing minerals caused by the alkaline injection, the porosity and hydraulic conductivity of the column marginally decreased (Figure 8). However, due to the liberation of lodged precipitates within the pores in the column during the first alkaline injection trial, as indicated by collected precipitates in the effluent container, and the re-dissolution of Al and Fe minerals, porosity and hydraulic conductivity increased again as obstructions preventing the influent flow path were removed. Importantly the removal of isolated clogging within the pores removes undesired flow path impedance allowing aggregate materials to react with the synthetic acidic influent.

3.5 Pre-conditioning of recycled concrete with alkaline wastewater
Changes in pH and ORP during the batch tests are shown in Figure 9. Prior to exposure to acidic water the pH of the supernatant in the control test (exposed to deionised water) was observed to increase to a plateau of pH 10.1, due to the release of Ca^{2+} and alkalinity from the recycled concrete (Figure 10), after which it decreased again to pH 8.37. This release is less likely to occur in the pre-conditioned test due to the already high concentration of Ca^{2+} (40 mg/L) and alkalinity (2460 mg/L as $CaCO_3$) of the alkaline wastewater compared to that of the deionised water. Therefore, the pH of supernatant in the pre-conditioned test was relatively stable at pH 8.4 until 68 days where it increased to a pH of 9.38. Following exposure to the acidic water, the pH achieved by the control and pre-conditioned test increased significantly from 4.96 to pH 7 within 7 days. It is hypothesised that the alkaline wastewater is retained within the pores of the recycled concrete aggregates and also as a coating on the surface of the concrete, which enhances chemical reactions between the concrete and the acidic water, thereby slowing the reduction in neutralisation capacity of the aggregates. The pH in the control test at 250 days (pH 7.86) was lower than the pH in the pre-conditioned test (pH 8.19), thus indicating the influence of excess alkalinity and Ca^{2+} released from the pre-conditioned recycled concrete (100 mg/L as $CaCO_3$ and 320 mg/L Ca^{2+}, respectively) compared to that released in the control test (18 mg/L as $CaCO_3$ and 846 mg/L Ca^{2+}, respectively). The average ORP of the supernatant for the pre-conditioned test (201.8 mV) was greater than the control test (179.7 mV) prior to exposure to acidic water, due to the presence of more reducing agents within the alkaline wastewater. Following the addition of the acidic water, the ORP of the supernatant increased for both the control (77.9-219.3 mV) and pre-conditioned concrete (77.9-214.3 mV), indicating slightly enhanced oxidising conditions for the control compared to the pre-conditioned concrete.

The concrete in the control test released Na^+ (6-16 mg/L), K^+ (4-10 mg/L), Mg^{2+}, (3-11 mg/L), Cl^- (49-60 mg/L) and SO_4^{2-} (20-38 mg/L) and trace amounts of Al^{3+} (0.035-0.185 mg/L) and total Fe

(0.004-0.013 mg/L) into solution prior to exposure to acidic water (Figure 11(a), (b)). Similarly, these ions were also found in the supernatant in the pre-conditioned test prior to exposure to acidic water (Figure 11(c), (d)). However, they generally decreased with time indicating their coating of the concrete aggregates and movement within the pores of the concrete. The concentration of these ions did not significantly change with only a slight increase observed in both the control and pre-conditioned test after the addition of acidic water, as a result of leaching of these ions from the recycled concrete, as was also observed during the column experiment.

3.6 Implications for pilot-scale permeable reactive barrier

This study illustrates that the reuse of alkaline wastewater has practical relevance and potential as a management tool for PRB technology in ASS terrain. Due to the porous nature of the recycled concrete aggregate, pre-conditioning of the concrete before placement in a PRB could be beneficial to allow for enhanced neutralisation and removal of Al and total Fe from the acidic groundwater. It is evident that future rejuvenation attempts via injection of alkaline wastewater into a PRB should trial injection at the initial stages of notable decreases in effluent pH, most suitably during the distinguished plateaus of neutralisation (Stage 1) prior to exhaustion of carbonate/bicarbonate buffering. Further injection of the alkaline wastewater in Stage 2 could promote further alkaline buffering within the PRB. While it is perceived that increasing alkalinity within the column in the initial stages of treatment may present a noticeable reduction in downstream pH levels for the PRB, enhanced precipitation of Al and Fe-bearing minerals may increase the extent of chemical armouring, as indicated by the decrease in porosity and hydraulic conductivity following the alkaline injection trials, and hasten the reduction in ANC of the recycled concrete aggregates. However, due to the larger particle size used in the current pilot-scale PRB (d_{50}=40 mm) compared to that used in the column test, and the fact that the decrease in porosity and hydraulic conductivity within the column was marginal any enhancement of chemical armouring is not expected to be significant prior to exhaustion of the ANC of the concrete.

4. Conclusions

This paper presents the study of the rejuvenation of recycled concrete as reactive media in a PRB for the treatment of acidic groundwater from ASS terrain in coastal Australia. A long-term laboratory column test was conducted to simulate the treatment of acidic water from ASS under simulated field groundwater conditions. The column experiment showed that recycled concrete was able to maintain a near-neutral pH for a long period and removed 100% of the Al^{3+} and total Fe during this period due to the release of carbonate/bicarbonate alkalinity and the precipitation of Al and Fe oxy/hydroxide minerals. Injection of alkaline wastewater through the column was undertaken to assess the re-conditioning of armoured recycled concrete aggregates with alkaline wastewater. The concentrations of Al^{3+} in the effluent increased after 130 PVs and that of total Fe after 212 PVs. Distinctive sharp but short bursts in the neutralisation capacity of the

recycled concrete (3-4 PVs) as indicated by an increase in effluent pH and a reduction in the columns ORP after each alkaline injection demonstrated the short- term benefits of alkaline rejuvenation. Typically, the columns increase in pH was restricted to 10-18 PVs after trialled injections and demonstrated the inability of the column to maintain a steady release of alkalinity and Ca^{2+} concluding each injection. Results from batch tests shows that due to the porous nature of the concrete aggregates, pre-conditioning of concrete by the alkaline wastewater enhances its ANC and ability to remove Al^{3+} and total Fe from acidic water.

Should this potential PRB management tool receive the necessary government approval for field trials, a proposal will be developed for Manildra Group's Water Recovery Plant for the recycling of its alkaline wastewater, for the remediation of local acidic groundwater. This would allow the complete rejuvenation process to be conducted 'on site', using waste material resources contained within Manildra Group's Environmental Farm. The experimental data contributes to knowledge, providing insight to PRB rejuvenation and enhancement of longevity using alkaline wastewaters and the study gains a valuable insight into the suitability of waste alkaline rejuvenation for future PRB installations, and additionally what this means for future PRB design and PRB technology.

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Table captions

Table 1. Column influent solution chemistry simulating groundwater in ASS terrain (Regmi *et al.*, 2009) and alkaline wastewater chemistry (courtesy of Manildra Group)

Table 2. Physical parameters of the column

Figure captions

Figure 1. Schematic diagram of the laboratory column setup

Figure 2. pH (a), oxidation reduction potential (b) of effluent and at sample points along the column as a function of pore volume and time. Alkaline injection points indicated by (1), (2) and (3)

Figure 3. Electrical conductivity (mS/cm) of the effluent and at sample points along the column as a function of pore volume and time. Alkaline injection points indicated by (1), (2) and (3)

Figure 4. Alkalinity (a), calcium released from the recycled concrete (b) along the column as a function of pore volume and time. Alkaline injection points indicated by (1), (2) and (3)

Figure 5. Al- and Fe-bearing precipitates formed within column prior to alkaline injection (230 PVs)

Figure 6. Concentration of Al^{3+} and total Fe (a) other ions (b) in effluent and influent as a function of pore volume and time. Alkaline injection points indicated by (1), (2) and (3)

Figure 7. Saturation index (SI) of minerals calculated using PHREEQC as a function of pore volume and time. Alkaline injection points indicated by (1), (2) and (3)

Figure 8. Normalised porosity (n_t/n_0) and hydraulic conductivity (K/K_0) within the column

Figure 9. pH (a), oxidation reduction potential (b) of the supernatant during the batch tests as a function of time

Figure 10. Alkalinity (a), calcium released from the recycled concrete (b) during the batch tests as a function of time

Figure 11. Concentration of Al^{3+} and total Fe (a) other ions (b) in the supernatant during the batch tests as a function of time