Effective remediation of groundwater in acid sulphate soil terrain

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Acidic groundwater, generated from acid sulphate soil (ASS) is a major geo-environmental problem in Australia. Manipulation of groundwater through the use of weirs and gates in the nearby creeks and drains of ASS, which is being practised right now for preventing pyrite oxidation, are not effective in low land floodplains due to the risk of flooding. The application of permeable reactive barrier (PRB) can be a novel alternative for remediation of acidic groundwater in such floodplains. Laboratory column experiments were carried out prior to installation of the PRB for examining the efficiency of the material. Results of these experiments have shown that recycled concrete could effectively neutralise the acidic water for longer period with complete removal of aluminium (Al) and iron (Fe). Despite the reduction of the efficiency of the recycled concrete due to armouring by accumulated precipitates of Al and Fe, excellent performance of the recycled concrete was observed for an extended period under controlled laboratory condition. Following these results, a pilot PRB was installed in the Broughton Creek flood plains in southeast NSW to observe its performance under varying natural conditions of the field. The PRB has been maintaining near neutral pH with complete removal of Al and Fe from the groundwater of ASS matching with the results of column test. The promising performance of the pilot PRB for last three years shows that PRB can be used as one of the cost effective and environmental friendly alternative to the recently utilised other techniques in ASS.

Key Words: Acid sulphate soil, armouring, column tests, permeable reactive barrier (PRB), recycled concrete.

1 INTRODUCTION

The release of acidic water often containing high concentration of toxic metals from acid sulphate soil (ASS) is an environmental problem of significant international importance. Changes in land use pattern (e.g.: deep flood mitigation drain) and hydrological systems (e.g: drought period) can promote the oxidation of pyrite in shallow zone of acid sulphate soils with a concomitant generation of sulphuric acid in soil, which, in turns, mobilise the toxic metals (Al and Fe) from the soil (Dent, 1992, White et al., 1997). Transportation of acidic water with high concentration of dissolved Al and Fe towards the water body either by infiltration into the aquifers or by discharging into nearby drains after the rainfall events have significantly degraded coastal environment of Australia. Massive killing of fish and oysters by highly acidic water rich in Al in the nearby creeks, unsuitability of land and groundwater for agriculture, corrosion of concrete infrastructures such as bridge and culverts are the major socio-environmental problems in southeast coast of NSW, Australia. Although the research has been conducted on investigation of causes of acidic water, extensively for more than five decades in Australia (Singer and Stumm, 1970, White et al., 1997), very limited studies have been conducted for their remediation.

From last decade, techniques that either prevent pyrite oxidation or remediate the resultant surface water coming from the ASS have been studied (Blowes et al., 2003, Indraratna et al., 2005). Ground manipulation technique, which has been successfully utilised in the acid rock drainage for decreasing the oxidation of tailings by complete inundation of acid producing materials, can also control the pyrite oxidation in acid sulphate soils (Blunden et al., 1997). Blunden and Indraratna (2001) found that restoration of the groundwater table of nearby area by fixed level weirs installed in flood mitigation drains would control the pyrite oxidation, preventing the pyrite from oxidation. As an advance, modification of such weirs to two-way floodgates in coastal areas allowed entry of tidal ingress of brackish creek water which could improve the drain water quality by buffering action of carbonate/bicarbonates present in the seawater (Glamore and Indraratna 2004). Even though such weirs work best in areas with fast drainage and groundwater table not too close to the surface, they can elevate the risk of flooding for low lying areas with poor drainage. In addition, other techniques such as direct addition of lime into the soil, pump-and-treat methods are not suitable in such large areas because of high operating costs (Komnitsas et al., 2004).

The aim of the current research is to develop a remediation technique suitable for low-lying areas where the conventionally utilised techniques are not feasible. Permeable reactive barrier can be a cost effective alternative technique in such areas, which has not been implemented elsewhere for remediating ASS problems. A number of successful field implementations backed by laboratory experiments and small- scale field tests have indicated the potential of PRBs as a promising technology for groundwater treatment (Blowes et al., 2000, Gu et al., 2002, Waybrant et al., 2002). Although PRBs have been used worldwide for the remediation of contaminated sites, their application for
curbing ASS problems is very limited to date, except for one trial Limestone drain as reported by Waite et al. (2002) which contained limestone under oxidising conditions. Selection of the suitable reactive material for PRB is also an important factor for the design of the PRB (Gavaskar, 1999) because of the possibility of fast exhaustion of the materials as well as reduction in efficiency by excessive fouling of precipitates during chemical reaction. This study investigates the efficiency of the recycled concrete for remediating acidic groundwater by a series of laboratory tests and by examining the performance of a pilot PRB installed in Acid Sulphate Soil terrain.

2 COLUMN TEST

2.1 MATERIALS AND METHOD

Selection of the reactive material for treating acidic groundwater is of paramount importance for the design of a PRB in ASS terrain with reference to its reactivity and metals removal capacity. Screening tests on 23 different alkaline materials were previously conducted in the laboratory with the drain water collected from the Acid Sulphate Soil affected area in southeast of NSW, as reported by Golab et al. (2006) (Figure 1). The work carried out by Golab et al., (2006) shows that recycled concrete can be a suitable reactive media over other alkaline materials because of its high pH retaining capacity and being easily available waste material (refer to Golab et al., 2006 for details). Following on these results, recycled concrete was selected for further investigation of its efficiency to treat the acidic groundwater. The recycled concrete used in this experiment was a waste material discarded after the demolishing of old concrete structure. The chemical composition of the elements present in the crushed powdered recycled concrete used for column experiment was same as that presented by Regmi et al., (2009) since the same batch of material was used for this study. Effects of particle size distribution and flow rates are not considered for this column experiment as the objective was to study the long- term performance of the material. Therefore, uniformly graded particle size (Cu = 3.1, Cc = 1.63) and constant flow rates (2.4 mL/min) were taken for this study. The input solution for column experiment was the synthetic acidic water (Table 1), comparable in characteristics to the average groundwater from ASS terrain in southeast of NSW, Australia presented by Regmi et al., (2009).

![Figure 1. Change of pH with respect to time for selected reactive materials among the 23 alkaline materials that were batch tested with acidic drain (after Golab et al., 2006)](image)

![Figure 2. (A) Schematic Diagram and (B) Picture of Laboratory column set-up for treating simulated acidic water](image)

Laboratory column experiment was carried out in a 650 mm long and 50 mm inner diameter acrylic column at room temperature as shown in Figure 2. Recycled concrete was filled in the middle section of the column between a 100 mm silica sand layer at bottom and 50 mm layer at the top. Sampling ports were located at 25, 50, 100, 200, 300, 500 and 600 mm (outlet) from the zone of intersection of bottom sand and aggregate along the length of the column. pH and Oxidation Reduction Potential (ORP) were immediately measured after collecting the samples. Acid Neutralization Capacity (ANC) of the material was analysed following the Acid Sulphate Soil Laboratory Method Guidelines 2004 (Ahern et al., 2004) and all the remaining chemical analyses (acidity, alkalinity, major cations and anions) were performed according to the standard method for water and wastewater examination (APHA, 1998).

The geochemical speciation/mass transfer computer code PHREEQC V 2.15 (Parkhurst and Appelo, 1999) with MINTEQ database was used to calculate the Saturation Index (S.I.) of minerals based on effluent water quality data. Saturation indices of different minerals at different pore volumes are compared for predicting the minerals which were responsible for precipitation during the period of experiment. After completion of the experiment, precipitates were
collected from the column; air dried, carbon coated with carbon sputter coat and then examined with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) to characterize the precipitates.

Table 1. Water Chemistry of the influent solution prepared for column experiment simulating the water chemistry of the acidic groundwater in ASS terrain presented in Regmi et al., 2009.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>ORP</th>
<th>Acidity*</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Al³⁺</th>
<th>Fe³⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>-</td>
<td>mV</td>
<td>mmol eq/L</td>
<td>19.14</td>
<td>1.07</td>
<td>2.84</td>
<td>3.7</td>
<td>1.5</td>
<td>1.5</td>
<td>23.0</td>
<td>12.10</td>
</tr>
<tr>
<td>Values</td>
<td>2.67</td>
<td>610</td>
<td>6.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Acidity was measured equivalent with respect to CaCO₃.

2.2 RESULTS

In order to study the reaction potential of the recycled concrete, water quality parameters such as pH, ORP, release of Calcium, metal removal rate (Fe and Al) were studied with respect to number of pore volumes of the acid passed through the column during the experiment. Saturation indices and mineralogical analysis were performed to confirm the types of the minerals precipitation inside the column. Efficiency of the material was studied with respect to its potential to neutralise the acidic water to near neutral pH.

Initially, the pH of the effluent with deionised water was very high (~ pH 12) with respect to which oxidation reduction potential (ORP) was low (50 mV) indicating that the reduction condition was favoured inside the column. The most abundant alkalinity generating compound in the recycled concrete responsible for maintaining the nearly neutral pH of the effluent is the cement present in the concrete which mainly consists of calcium oxides. Significant amount of carbonate/bicarbonate alkalinity is generated when calcium oxides from the concrete starts to dissolve with water in presence of CO₂ (Indraratna et al., 2008). When contacted with acidic influent having high amount of dissolved metals under highly oxidised condition, the pH started to decrease and ORP increased due to the rapid depletion of carbonate alkalinity. After reaching PV 40, pH was stabilised to near neutral value (Figure 3a) for long period (PV 250) until the bicarbonate alkalinity was generated from concrete into the system because pH value of 8.3 is the point from where the alkaline system will generate bicarbonate alkalinity to buffer the acidic water in addition to converting the remaining carbonate alkalinity to bicarbonate one, which maintains the near neutral stable pH. Over the near neutral pH period, the ORP remained at low values and varied between 200-250 mV, indicating that poor oxidation conditions prevailed within that period. However, Figure 3b shows rapid drop in pH at bottom zones of the column within a few pore volumes. For example: pH dropped dramatically from higher value to lower values (below pH 4) at PVs 169, 240, 466, 524 for sampling ports at distance of 50 mm, 200 mm, 500 mm and 600 mm respectively. The fast drop in pH at bottom zone and growth of this falling pattern of pH towards the top of the column with respect to increasing pore volumes indicates that either the alkalinity of material at the bottom zone was completely exhausted or its efficiency was lost due to the armouring effects because of the fouling of precipitates on the surface of the material.

Nevertheless, the maintenance of the plateau pH of the effluent at near neutral range (pH 7.5- 6.5) for long period illustrates that although the lower part of the materials which were in first contact with acid water lost its efficiency in the early phase, the alkalinity generated in the upper part of the system maintained the plateau of the effluent at near neutral pH for longer period. These results show that the recycled concrete did not show any sign of early diminishing neutralising capacity despite large amount of acidic water was passed continuously through the column, proving its high potential for neutralising acidic groundwater.

Fe and Al were completely removed from the acidic water passed through the column until near neutral pH was maintained into the system after which its removal capacity decreased (Figure 3c). This indicates that the observed decrease in Al and Fe removal capacity corresponds to complete depletion of alkalinity where abrupt decrease in pH was observed (Figure 3).

Saturation indices of the minerals based on the effluent’s water chemistry for different pore volumes were calculated using PHREEQC, and compared to determine which minerals were saturated during the length of the experiment (Table 2). The results from PHREEQC show that Al and Fe were the main elements which would have precipitated out while the system maintained nearly neutral pH. The effluent water was highly supersaturated with respect to Al minerals (gibbsite, boehmite and diasporo) and Fe minerals (hematite, maghemite, goethite, lepidocrocite, ferrihydrite) justifying a tendency for precipitation of Al and Fe. After the completion of the experiment, the precipitates from the column were collected and air dried. Some researches (e.g.: Furukawa et al., 2002) have found that it is difficult to detect the elements present in amorphous precipitates by X-ray Diffraction test (XRD). Therefore, the samples were analysed with SEM/EDS to confirm the types of minerals precipitated inside the column. Several peaks of Fe, Al, O observed in EDS results of the precipitates observed by SEM (Figure 4) confirm the major precipitation by Fe and Al as their oxides, oxyhydroxides, hydroxides as predicted by saturation indices (Peak of C observed in the beginning was the presence of carbon coat).
Figure 3. Water quality parameters as a function of number of pore volumes of acidic groundwater passed through the test column

Table 2. Saturation indices of different minerals calculated using PHREEQC 2.15, an equilibrium model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Chemical Formula</th>
<th>5 PV</th>
<th>70 PV</th>
<th>152 PV</th>
<th>273 PV</th>
<th>466 PV</th>
<th>558 PV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diaspore</td>
<td>AlOOH</td>
<td>-0.28</td>
<td>2.85</td>
<td>3.3</td>
<td>2.55</td>
<td>0.99</td>
<td>1.04</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al(OH)₃</td>
<td>-2.17</td>
<td>0.96</td>
<td>1.41</td>
<td>0.66</td>
<td>-0.89</td>
<td>-0.85</td>
</tr>
<tr>
<td>Boehmite</td>
<td>AlOOH</td>
<td>-2</td>
<td>1.13</td>
<td>1.57</td>
<td>0.83</td>
<td>-0.73</td>
<td>-0.68</td>
</tr>
<tr>
<td><strong>Fe minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>13.42</td>
<td>18.17</td>
<td>18.12</td>
<td>4.5</td>
<td>4.08</td>
<td>4.02</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeOOH</td>
<td>4.21</td>
<td>6.59</td>
<td>6.56</td>
<td>0.5</td>
<td>0.54</td>
<td>-0.49</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>-10.6</td>
<td>-1.52</td>
<td>-1.36</td>
<td>-4.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferihydrite</td>
<td>Fe(OH)₃</td>
<td>-0.11</td>
<td>2.27</td>
<td>2.24</td>
<td>-4.57</td>
<td>-3.78</td>
<td>-4.81</td>
</tr>
<tr>
<td><strong>Ca minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>-0.11</td>
<td>-0.12</td>
<td>-0.13</td>
<td>-0.1</td>
<td>-0.29</td>
<td>-0.41</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
<td>-0.34</td>
<td>-0.35</td>
<td>-0.36</td>
<td>-0.33</td>
<td>-0.52</td>
<td>-0.64</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>1.49</td>
<td>0.6</td>
<td>0.85</td>
<td>-3.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Within the first 250 PVs, almost 100% removal of Fe and Al indicates that large amount of precipitates might have been formed inside the column by buffering action of carbonate/bicarbonate alkalinity. However, rapid drop in pH towards the bottom of the column at short period indicates that 100% removal of Fe and Al could not be achieved at the bottom of the column because Al and Fe can precipitate at pH > 4.5 and 3.5 respectively (for details, refer to Indraratna et al
Nevertheless, the amounts of Fe and Al which could not be removed by the concrete at the bottom zones, precipitated out again when travelling towards top before reaching outlet. This was due to the reaction of these Al and Fe ions with alkalinity generated by fresh concrete in the upper part of the column, therefore, the column could remove Fe and Al completely in the effluent till PV 250. This hypothesis is supported by the release of calcium by the column for long period (Figure 3d). Figure 3d also shows that release of Ca at the bottom zone reached peak in short period and dropped down quickly to smaller values when compared with the upper part. In addition, continuous release of small amount of Ca in effluent for longer period confirms that complete exhaustion of the alkalinity was not favoured in the system.

Furthermore, although the concrete had theoretical capacity to treat the given acidic water until 510 PVs (based on the acid neutralisation capacity and mass of the concrete used in the column), the observed performance of concrete for neutralisation of acidic water with 100% removal of these metals was only for 250 PVs. This clearly indicates that armouring by Al and Fe precipitates could significantly reduce efficiency of the concrete. As an evidence of armouring, white and orange precipitates coating on the surface of the concrete and filling on the voids were visibly seen inside the columns which were growing from bottom of the column towards the top slowly with respect to time. Despite the reduction in efficiency, the concrete could remove 100% Al and Fe for large pore volumes until near neutral pH was maintained in the system.

![Figure 4. SEM-EDS Analysis of the precipitate from column experiment (EDS results presented for the precipitates within the rectangle in SEM image)](image)

**3 PERFORMANCE OF PILOT PRB IN ACID SULPHATE SOIL**

Based on the promising result of the recycled concrete for its capacity to neutralise acidic groundwater as well as to remove Al and Fe completely as observed in column test after short listed by batch test, it was decided to use recycled concrete for the remediation of groundwater in acid sulphate soil terrain. To the knowledge of the authors, not a single PRB under reducing condition is reported to be installed for treating acidic water from Acid Sulphate Soil although several laboratory scaled research have been performed for study of efficiency of the materials (Golab et al., 2006, Komnitsas et al., 2004, Waybrant et al., 2002). Therefore as an initial step, a pilot scaled PRB (17.7 m × 1.2 m × 3.0 m) as shown in Figure 5 was installed in the acid sulphate soil terrain located in Bombaderry, southeast of NSW, Australia.

The performance of the PRB has been monitored continuously for nearly three years from the water quality parameters by data loggers installed inside the PRB and monitoring wells installed up-gradient and down-gradient to PRB. Figure 6 shows the performance of the recycled concrete for neutralising acidic water in acid sulphate soil. Upgradient to the PRB, the groundwater was acidic (pH ranges 3 to 4.5). Spatial and temporal variation was obvious due to heterogeneity of available pyritic material in the soil and variation in weather condition. Initially the pH of the barrier increased to reach a peak value because the concrete was not fully saturated during installation. Therefore, that period was considered as unstable period. Once the material was fully saturated, the pH started to decrease rapidly reaching to ~ pH 8 by the depletion of carbonate alkalinity matching with the column test results. After which, it was stabilised at near neutral pH. The PRB has been maintaining near neutral pH (~7.5-7.0) even after nearly three years of its installation period and the current results show that it will continue maintaining this near neutral pH for more period as expected from the column test results. However, the observed pH in the monitoring wells of the area downgradient to PRB at distance of 5 m and 10 m from the data loggers (inside the PRB) was lower than pH inside the barrier, but significantly higher than pH observed in upgradient to the barrier. Possible reasons for such smaller values are: (i) production and mixing of acid from soil as the downgradient areas also contained huge amounts of pyrite in soil (ii) possibility of mixing the acid (which was generated in the upgradient) from the sides of the barrier because the size of the PRB was small). However, the rise in pH after the installation of PRB even in 10 m downgradient area to nearly 6 and above shows significant improvement in water quality of downgradient even the pilot scaled PRB was small in size.
These results predict that if such pilot scaled PRBs are installed in series, groundwater quality can be significantly improved and the benefit of using recycled concrete is that it minimises the cost of material being easily available waste material. Furthermore, Fe and Al of the wells inside the barriers measured frequently in every three months after installation of the PRB inside the barrier were negligible (0-2 mg/L) confirming the column test results. Since the Al and Fe removal capacity observed during this study period has not decreased till date, the results are not presented here. The concentrations of both the Al and Fe inside the PRB are expected to increase when there is a drop in pH from neutral range. Thus, the result of the pH for nearly three years shows that performance of the barrier is promising similar with that obtained from the column test. However, the longevity of the PRB is still undetermined because ultimately the barrier will become ineffective due to armouring by precipitates of iron and aluminium as demonstrated by the column test.

Figure 5. Pilot Scale PRB in acid sulphate soil of Broughton Creek Flood plain in Southeast of NSW, Australia

Figure 6. Groundwater pH measured hourly inside the Barrier (DL1 and DL2) by two data-loggers, monthly in upgradient to barrier and downgradient to barrier from the observation wells at 5 and 10 m from the permeable reactive barrier

4 CONCLUSIONS

A laboratory column test was conducted to study the efficiency of the materials for treating acidic water from Acid Sulphate soils. The results of the water quality parameters, equilibrium modelling of minerals and mineralogical analysis have confirmed that buffering capacity of the material has been controlled by dissolution of carbonate/bicarbonate minerals and precipitation of Al and Fe. Performance of the recycled concrete under the accelerated flow in column for maintaining near neutral pH and removing all the dissolved Al and Fe from simulated acidic water for long duration confirms its suitability for remediating acidic water from acid sulphate soil. However, the precipitation of the Fe and Al minerals during the neutralization reaction period have significantly reduced the efficiency of the materials which might have a significant threat on the performance of the barrier by reducing its longevity if large amounts of Fe and Al are generated continuously for a longer period.

The performance of the PRB has been monitored in the field for last three years. Monitoring data indicate that the pilot scaled PRB is operating very effectively for maintaining the pH to nearly neutral level with complete removal of dissolved iron and aluminium from the groundwater, thus re-confirming column test results. However, the longevity of the PRB depends on the rate of acidity production in the soil as well as the amount of dissolved iron and aluminium in the groundwater. Because of continuous precipitation of the iron and aluminium inside the PRB, it is therefore most likely that armouring effect may be the limiting factor on the performance of the barrier as shown by column test. Further monitoring is needed to evaluate the longevity of the PRB as performance has been decreasing slowly. Nevertheless, as the material has shown impressive performance both in the laboratory test and small scale field study, PRB with recycled concrete can be a suitable environmental friendly and cost effective alternative to the conventionally utilised other techniques for spot treatment of acidic water in acid sulphate soil.

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