Development of Low Cost ARD Neutralisation Strategies for the Savage River Rehabilitation Project

Daniel J. Ray[1], Gary Hickman[2] Sophie Le Roux[3], Alison Hughes[3] and Jim Stefanoff[2]

[1]Aquatic Science, Bellerive, Tasmania, Australia, dray@aquaticscience.com.au
[2] CH2MHill,Corvallis , Oregon, USA, Gary.Hickman@CH2M.com
[3] EPA, Hobart, TAS, Australia, Sophie.LeRoux@environment.tas.gov.au

Note: Contact information should include affiliation, city, province or state (2-letter abbreviation), country and e-mail address
Authors should be listed in order of contribution to the paper.

Abstract

The Savage River Rehabilitation Project has investigated methodologies for the treatment of Acid Rock Drainage using carbonates, at the Savage River Mine, western Tasmania. The ARD sources include high dissolved aluminium and copper drainage from waste rock dumps, and high ferrous iron seepages from an old tailings dam. The paper discusses research undertaken over many years in an attempt to reduce the cost burden associated with long term treatment in isolated, high rainfall environments.
Currently the methodologies developed are being scaled up to full scale prototypes. Limestone with a grain size below 1.2 mm is used as the neutralising agent, primarily because it can be supplied to the mine site at a lower cost than alternative neutralisation reagents. Axial flow mixers have been developed as a method of contacting sufficient quantities of limestone with the ARD to enable effective neutralisation. The associated power costs are discussed. The importance of the conversion of ferrous iron to ferric iron has been found to be critical for the effective use of carbonates. The methodologies investigated for achieving this at full-scale, prior to reaction with carbonates are discussed.

Key Words: Acid Rock Drainage Treatment, Limestone, Carbonates, Ferrous and Ferric

Introduction

The Savage River Rehabilitation Project (SRRP) has been focused for several years on developing a low cost methodology for the treatment of acid rock drainage. The SRRP is currently in the process of scaling up a pilot scale neutralisation process to a full scale prototype. The cost of water treatment is a major consideration for the project as water treatment is expected to be required for decades as more passive mitigation measures are not currently viable. The SRRP has previously identified that if the average cost of reagent use could not be reduced to less than $350AUD per tonne ($CaCO_3$ equivalent), the duration or amount of ARD to be treated would have to be reduced (Kent et al., 2004).

Axial flow mixers are central to the treatment methodology being developed. The mixers are used to suspend carbonate material within the ARD being treated, to maximise contact and

attrition to keep surfaces active. Axial flow mixers are an effective methodology for suspending large amount of material, and are widely used in the minerals industry.

The project has investigated the use of different carbonates including limestone, dolomite and magnesite. It has been found that commercially crushed limestone with a sub 1.2mm particle size is the most viable reagent for the project for the following reasons:

- is a common mineral available from a local commercial supplier
- can be produced via a single stage crushing circuit without further milling which reduces the cost of production
- is of high purity reducing the build-up of benign material within the reactor

This paper gives a brief account of the methodology being developed by the SRRP, and the performance assessed during field trials. Reduction of hydraulic load was identified as key factor in reducing treatment cost. Poor treatment performance for the most concentrated acid drainage at Savage River (the Old Tailings Dam) occurred during pilot scale testing, with iron oxidation suspected as playing a major role in reducing the reactivity of carbonates. Other mechanism such as passivation by gypsum coating the carbonates may also have limited performance.

The main emphasis of this paper is subsequent laboratory trials to investigate the effect of iron oxidation on carbonate reactivity. Preliminary work on the oxidation of ferrous iron to ferric iron without the addition of alkali reagent is also discussed.

Methodologies

Field Trial Methodology

The central component of the water treatment system for the treatment of the acid rock drainage is presented in Figure 1 below. The axial flow mixer used was 170 L and was loaded with between 100 and 120 kg of limestone. The flow rate through the reactor varied with temperature as the carbonate reactivity declines in lower temperatures. The change in the limestone reactivity is described in Equation 1 (Ray *et al*. 2009). To compensate for this the process control system used a set flow rate at 10^0C (Q10) and adjusted the flow rate (Qt) according to the temperature of the water flowing from the reactor (t).

$$Q_t = Q_{10} * 0.5 * e^{(0.0693 * t)} \qquad \text{(Equation 1)}$$

Where: Q_t = Flow Rate for temperature t; Q_{10} = Flow Rate at 10°C; t = current temperature

The expected acidity load of the ARD was used to determine the optimal flow rate (Q_{10}) through the reactor.

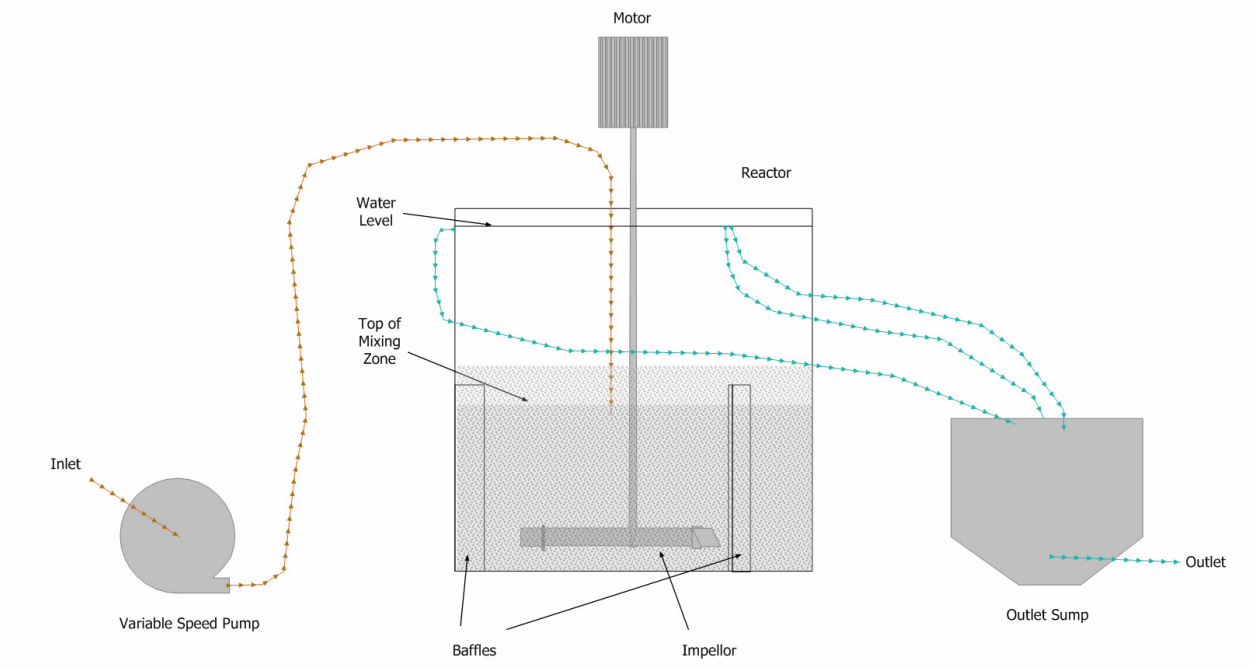

Figure 1. Schematic of axial flow mixer system used for the treatment of the Old Tailings Dam Seepage, and the Main Creek below B-Dump ARD.

The reactor was set up to treat the following streams:

- An aluminium and copper rich source of ARD flowing down Main Creek below B-Dump. Water was collected from a ponded portion of the creek.
- An iron rich source of ARD at the base of the Old Tailings Dam. Water was collected from ponds at the base of the dam, as well as from fresh seepage directly at the base of the dam.

The ARD sources were pumped with a variable speed peristaltic pump to the reactor.

Power Consumption

Using the data on the motor speed and load from the Old Tailings Dam trial, the torque per unit volume was calculated, and allowed an estimate to be made of the power consumption of a full scale plant at an assumed tank size of 11 m3 (Ray and Hughes, 2008). Using the data collected during the trial, and assuming a power loss of 20% in the gear and motor at full-scale, the power consumption was estimated to be 3.33 kW, or 80 kWh per day. Data obtained from the series of trials conducted suggest that an 11 m3 reactor may treat in the order of 0.44 t of acidity per day. Therefore, at a power cost of $0.15AUD per kWh, the power cost for treatment is estimated to be in the order of $27AUD per tonne of acidity treated, or $12AUD per day.

Laboratory mixing trial methodology

Sample collection

The focus of laboratory mixing trials was the iron rich ARD seepage fresh from the toe of the Old Tailings Dam. OTD seeps samples were collected in 10L plastic water bladders. In order to prevent oxidation of the ARD, the samples were purged on site using nitrogen gas until dissolved oxygen levels dropped to below 20% saturation. The water bladders were then transported to Hobart to perform the mixing tests.
Water from each bladder was mixed together to form a composite sample used for the oxidised and un-oxidised tests.

Oxidation of ARD seeps
A 9-litre sample of OTD seeps sub-sampled from the homogenised batch was oxidised using 225mL of 30% peroxide, at 70°C. A large volume of low density sludge was produced (about 33mL per litre of seeps). The sludge settled rapidly to leave a crystal clear supernatant which was used for testing and for the mixing experiments (Figure 2).

Figure 2. Oxidised iron sludge produced

Ferrous levels, measured by colorimetry (phenanthroline test), dropped from around 1450 mg/L to 260mg/L after oxidation. Table 1 shows the characteristics of the un-oxidised and oxidised water samples prior to limestone additions, as measured in the lab.

Table 1. Characteristics of the un-oxidised and oxidised ARD samples used in the mixing experiments

Parameters	**Un-oxidised ARD**	**Oxidised ARD**
Ferrous (mg/L)	1450	260
pH	2.8	2.1
Acidity (mg $CaCO_3$/L)	3460	2780
Conductivity (mS/cm)	6.2	7.5
DO (% saturation)	75	100

Limestone mixing experiments
The limestone used in the mixing experiments was sub 1.2mm limestone supplied by Unimin/Sibelco (Mole Creek). Limestone was added to oxidised and un-oxidised samples into 2-L mixing reactors, in 1x, 2x, 4x and 8x stoichiometric quantities (3.2, 6.4, 12.8 and 25.6 g/L $CaCO_3$ respectively). During mixing, the samples were analysed periodically for pH,

temperature, conductivity, dissolved oxygen, acidity and ferrous iron concentration. At the end of the mixing experiments (after about 24 hrs), the solutions were left to settle for approximately half an hour and the supernatant was sampled for the analysis of metals (copper, iron, aluminium, nickel, manganese and zinc), pH, acidity, acidity to pH 7, conductivity, sulphate and total suspended solids (TSS). The analyses were performed by Analytical Services Tasmania.

Figures 3 and 4 show the neat and oxidised ARD seeps in the mixing reactors before and after limestone addition. In both cases, the seeps went from crystal clear to orange-brown after adding limestone, as ferric iron precipitated into ferric hydroxide.

Figure 3. Un-oxidised ARD seeps in reactors before and after limestone addition (left to right 1x, 2x, 4x, and 8x stoichiometric quantities).

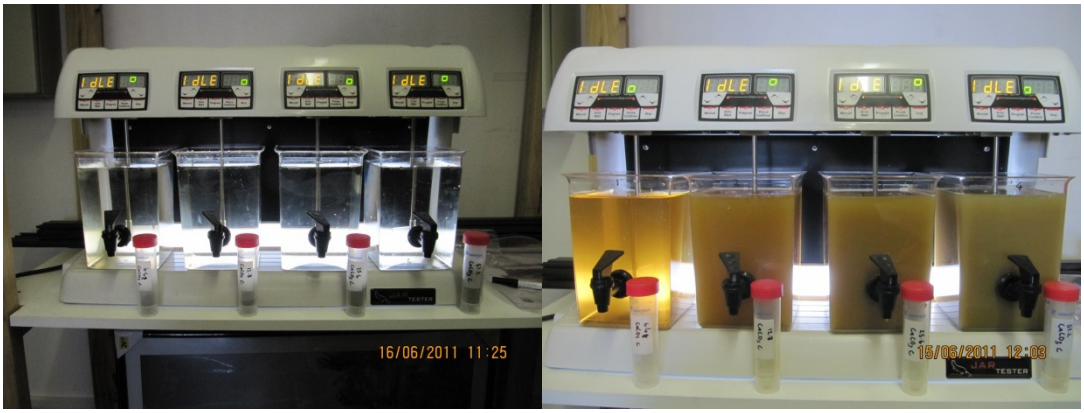

Figure 4. Oxidised ARD seeps (supernatant) in reactors before and after limestone addition (left to right 1x, 2x, 4x, and 8x stoichiometric quantities).

Acidity Method

Samples were titrated with 0.1N sodium hydroxide solution using phenolphthalein indicator as an endpoint (AWWA, 2005). The samples were titrated to the first appearance of the pink

endpoint then mixed vigorously. Precipitation of ferric hydroxide generates acid, lowering pH and reversing the pink colouration. Sodium hydroxide was added incrementally until the pink colour remained stable after 30 seconds agitation. The titre at this point was used to ascertain the acidity concentration. Blanks and duplicates were included in the analysis.

Ferrous Iron Determination

Ferrous iron was measured using a LaMotte Smart Spectrophotometer, a portable single beam spectrophotometer. The method used was the 1,10-Phenanthroline method – code 3668-sc without the use of the reducing reagent (which reduces ferric to ferrous for total iron determination).

Results and Discussion

Main Creek below B-Dump neutralisation (copper and aluminium source)

Inlet flows to the reactor during the Main Creek below B-Dump trial averaged 0.13 L/s at the start of the trial and was increased to 0.25 L/s after 2 weeks of consistently good performance. After a temperature correction is applied the average flow rate through the reactor at 10 ^{0}C was 0.19L/s. The acidity of the influent stream into the reactor was varied between 197 and 254 mg/L $CaCO_3$ eq (Figure 5). The acidity of the outlet water was <1 mg/L $CaCO_3$ eq for the entire trial, corresponding with a high level of metal removal.

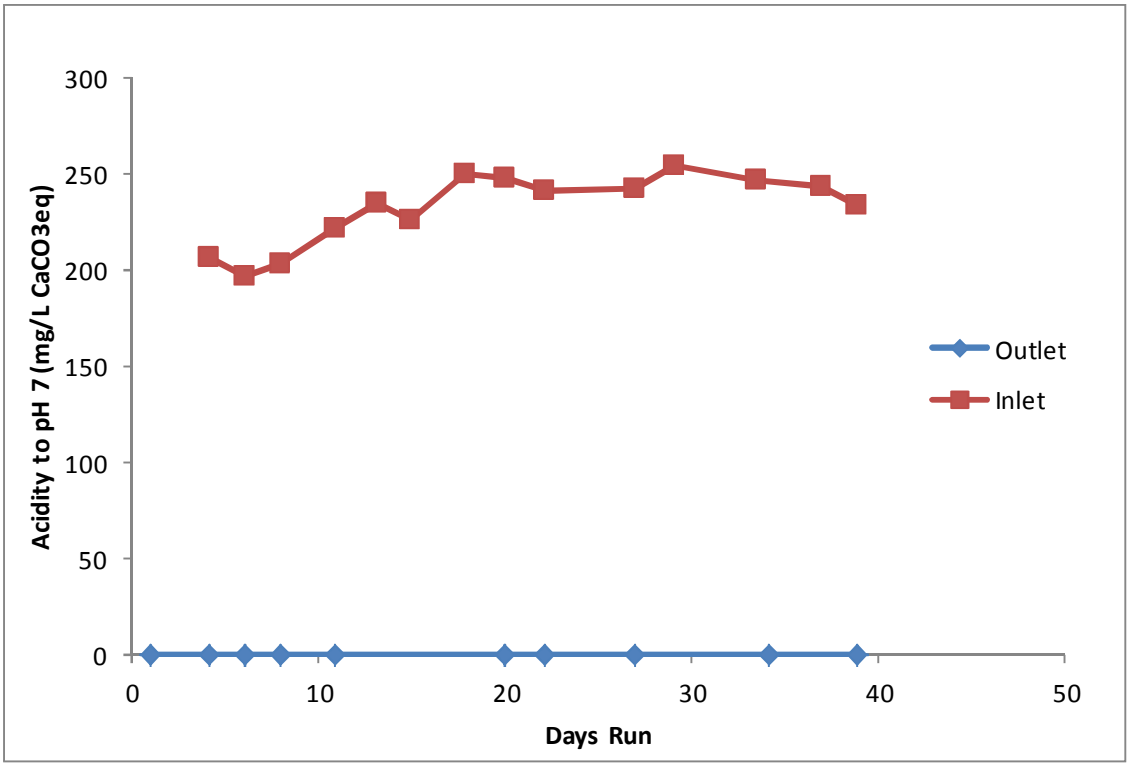

Figure 5. Main Creek below B-Dump water before and after the carbonate reactor with settlement.

Old Tailings Dam seepage neutralisation (iron source)

The first neutralisation trial was conducted on seepage collected from ponds at the base of the Old Tailings Dam. The flow rate into the plant for this phase of the trial was 0.098 L/s. On Day 41, the source of the water was changed to seepage emanating directly from the toe of the Old Tailings Dam, in order to collect a more concentrated ARD. This source of ARD water had minimal contact with the atmosphere and little dilution from catchment rainfall after flowing from the wall of the dam. The influent to the plant was therefore more concentrated (Figure 6) and had little opportunity to oxidise. The flow rate into the plant was reduced to 0.06 L/s to accommodate the anticipated increased acidity. The decrease in performance of the plant was immediate. The plant was then returned to the original configuration (Day 80), sourcing the water from the pond and performance improved.

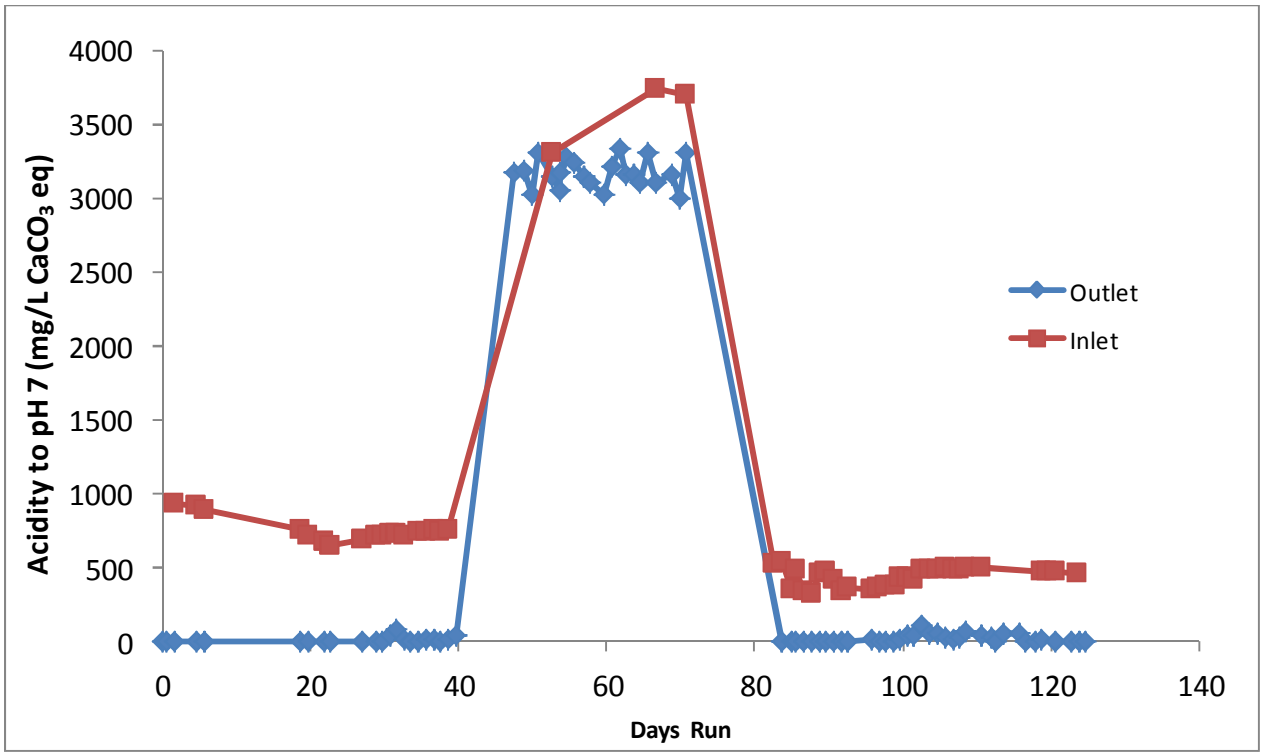

Figure 6. Acidity of inlet and outlet water, Old Tailings Dam seepage .

The reduced performance was suspected to be due to high levels of ferrous iron in the ARD sourced directly from the toe of the dam. Other factors such as the likely increased formation of gypsum (reducing performance by coating reactive surfaces) and the higher acidity load were identified as possible mechanisms for the reduced performance. The laboratory mixing trials were designed to directly test the effect of ferrous iron on carbonate reactivity.

Laboratory mixing trial

For both oxidised and un-oxidised OTD seeps, pH rose very rapidly after limestone additions (within half an hour, Figure 7). As expected, the higher the amount of limestone added, the greater the pH increase. For the un-oxidised seeps, pH initially rose rapidly then tended to plateau, whereas for the oxidised seeps the pH rise was more gradual for all four limestone additions. If pH alone was used as a measure of neutralisation success, the ARD that had not been oxidised may be considered better to treat with limestone, due to the rapid pH rise that occurred. As will be discussed, acidity is a more important measure of neutralisation success. .

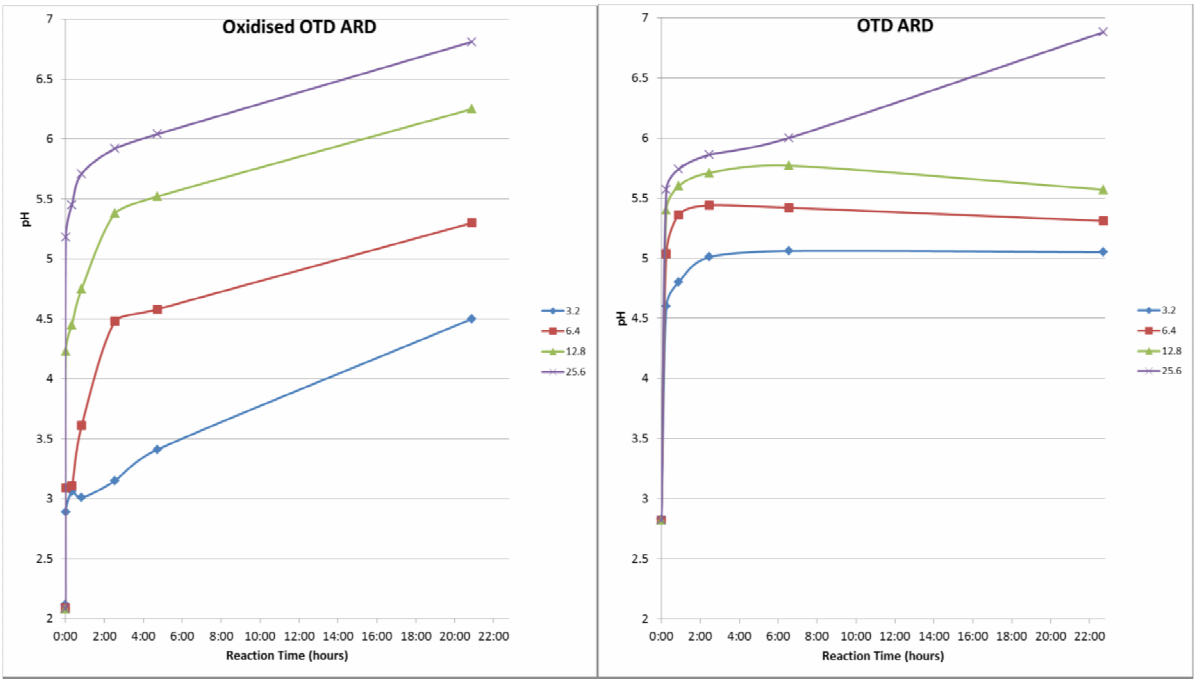

Figure 7. Change in pH for oxidised and un-oxidised OTD seeps during mixing experiments using various limestone concentrations (3.2, 6.4, 12.8 and 25.6 mg/L $CaCO_3$ eq)

In ARD, acidity is generated as a result of the oxidation and hydrolysis of dissolved metal ions, acting as Lewis acids. In an iron rich stream, acidity is mostly related to the concentration of ferric iron present. Therefore, acidity provides a better measure of treatment success than pH, since it reflects the reactivity of metal acids with limestone. The acidity plots show the value of pre-oxidising the seeps (Figures 8). For the oxidised seeps, the acidity dropped quickly after adding limestone and kept on decreasing, with both 4x and 8x stoichiometric quantities achieving full treatment. For the un-oxidised seeps, the measured acidity first increased slightly

in all four reactors and the cause of this is unknown. Despite this, the overall trend of lower acidity removal compared to the oxidised seeps is clearly evident. Complete neutralisation was only achieved for the highest concentration of limestone in the un-oxidised seeps. This was a result of sufficient abiotic ferrous oxidation, to convert all ferrous iron to ferric iron over the 22 hour period. The higher pH conditions that occurred in this reactor would have increased the reaction rate considerably (Stumm and Morgan 1996).

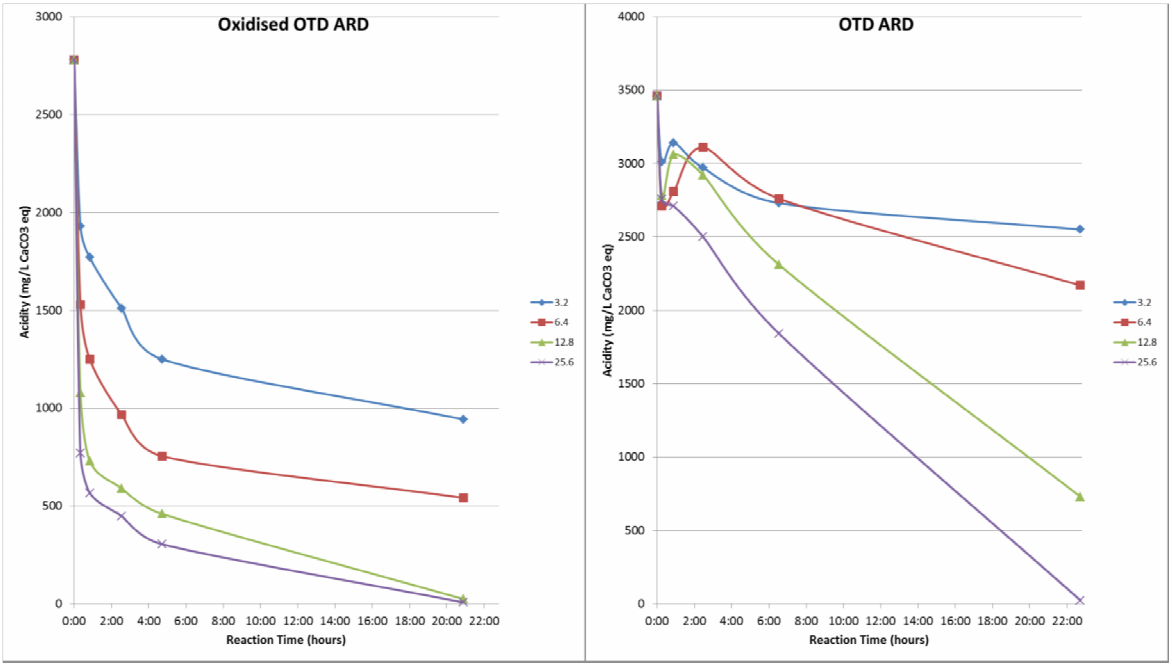

Figure 8. Change in acidity for oxidised and un-oxidised OTD seeps during mixing experiments using various limestone concentrations (3.2, 6.4, 12.8 and 25.6 mg/L $CaCO_3$ eq)

The dissolved oxygen was also monitored as seen in Figure 9. Reduction in DO levels were more pronounced in the unoxidised samples, especially for the higher limestone doses where the pH rise was greatest. DO levels did drop in the oxidised sample due to the ferrous iron that remained after oxidation.

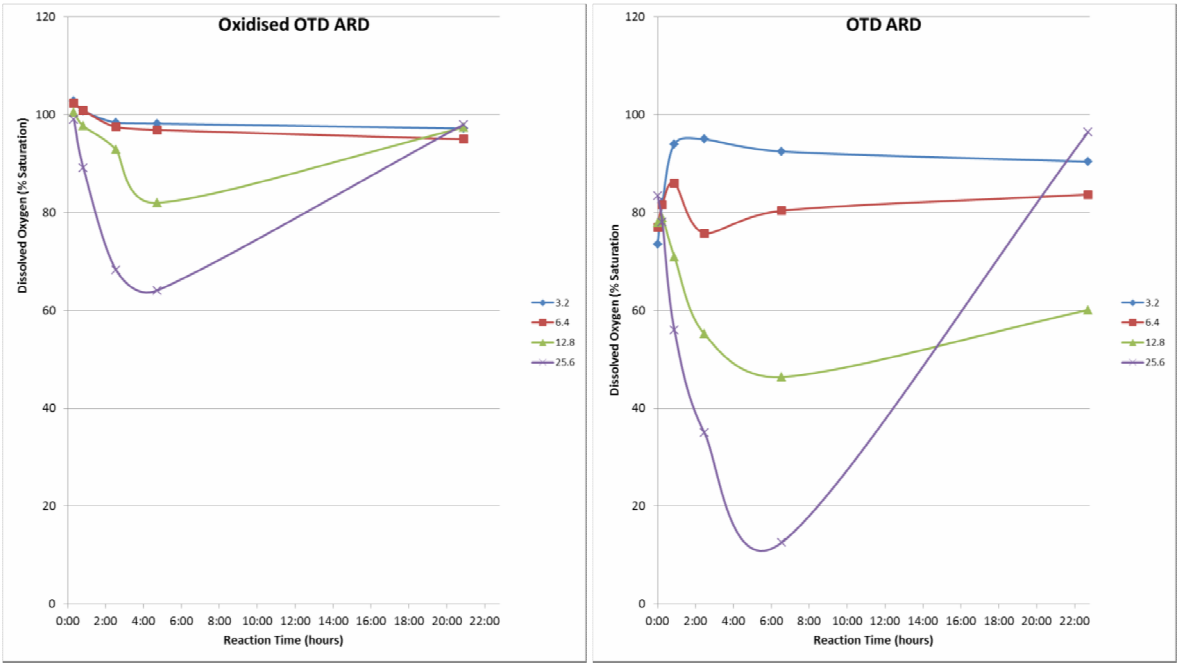

Figure 9. Evolution of dissolved oxygen for oxidised and un-oxidised OTD seeps during mixing experiments using various limestone concentrations (3.2, 6.4, 12.8 and 25.6 mg/L $CaCO_3$eq)

For the field trial undertaken at the Old Tailings Dam seepage the flow rate into the reactor when the seepage was sourced directly from the toe of the dam was 0.06 L/s. As the reactor volume is 170L this flow results in a hydraulic retention time of 47 minutes. Given the difference in the acidity neutralisation rates between oxidised and un-oxidised ARD a major reduction in reactor performance is expected if a ferrous rich ARD is not oxidised prior to being passed through the reactor.

A methodology to utilise a rock substrate and low energy aeration to oxidise ferrous rich water has been trialed in Tasmania. This process utilise bacterial oxidation process and did not require prior neutralisation. The methodology has been trialed on the OTD seepage at laboratory scale with complete conversion of ferrous to ferric iron. Given the above results the progression of these trial to a full scale prototype is also being progressed by the SRRP.

At the time of writing, the costs of the full-scale pilot plant were in development. It is estimated that the limestone reactor vessel itself, including the cost of the mixer, may cost in the order of $150 000 AUD. This does not include any costs associated with associated civil works, and associated pumps, pipes and other ancilliary equipment.

Conclusion

The carbonate reactor developed by the SRRP is currently being scaled up to a full scale prototype. The oxidation state of iron will be an important parameter to be understood prior to

the treatment of iron rich ARD sources. Further work is required into the effective oxidation of ferrous iron to ferric iron prior to treatment of many ARD sources with the carbonate reactor.

Acknowledgements

The research into utilisation of carbonates, of which this paper is part, has been made possible by the continued support of Grange Resources and the Tasmanian EPA. The work has been supported by many staff and contractors including, Stephen Kent (Caloundra Environmental), Bruce Hutchison, Tony Ferguson, Chris Hawkins (Grange Resources), Lois Koehnken (Technical Advice on Water), Rob Dineen, and Colleen Cole (EPA).

References

AWWA (2005) Standard Methods for the Examination of Water and Wastewater. American Water Works Association/American Public Works Association/Water Environment Federation, 21st Edition.

Kent, S., Ray, D., Hutchison, B., Dineen, R., (2004). Savage River rehabilitation project strategic plan. Minerals Council of Australia Inaugural Global Sustainable Development Conference, 25 – 29 October 2004. Melbourne.

Ray, D., Hughes, A. (2008) Pilot trial of an axial flow mixer to treat ARD using limestone at the Savage River Mine site, Joint Conference of the 6th International Acid Sulphate Soil Conference and the Acid Rock Drainage Symposium, 16 - 20 September 2008. Guangzhou.

Ray D., Clark M., Pitman T. (2009) Treatment of an Iron-rich ARD Using Waste Carbonate Rock: Bench-Scale Reactor Test Results. Mine Water and the Environment 28, 253-263.

Stumm W, Morgan JJ (1996) Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. (Wiley Interscience) rice WA (2009) Prediction Manual of Drainage Chemistry from Sulphidic Geologic Materials. MEND Report 1.20.1