

The Feasibility of Treatment of Acid Mine Drainage with Seawater

Devin Sapsford, Lawrence de Leeuw, James Phillips and Peter Brabham
Cardiff University, United Kingdom

ABSTRACT

This paper presents results from an experimental study on the interaction of acid mine drainage from the abandoned Parys Mountain mine site (UK) and seawater with a focus on its potential use as a reagent in mine water treatment. Parys Mountain is a former copper mine, the acid mine drainage discharge measured during the study was pH 2.1 – 2.4 with elevated iron concentrations (up to 490 mg/L) and a range of other elevated metal concentrations including copper (34 mg/L), zinc (11 mg/L), lead (109 µg/L) aluminium (57 mg/L), and cadmium (135 µg/L). Currently the discharge (circa 10 L/s) flows via the Afon Goch for approximately 2 km to discharge to the Irish Sea. Remediation options have been considered for the site and include active and hybrid active-passive treatments with active treatment being favoured given the challenging AMD chemistry. Because active treatment is costly, alternative remediation strategies would be favourable. Considering that seawater has alkalinity due to the presence principally of dissolved carbonates and borates, this study looks at the feasibility of using seawater as a reagent to treat the mine drainage. Field titrations were performed using seawater to titrate the acidic mine drainage whilst pH was monitored and samples withdrawn for analyses of dissolved species. It was determined that mixing of mine water with seawater in ratio 1:1 was found to give the following removals (quoted as load removal with residual metal concentration in parentheses): Cd 77% (16 µg/L); Zn 77% (1.3 mg/L); Cu 74% (4.5 mg/L); Al 68% (9.2 mg/L) and Fe 36% (58 mg/L), thought to be due to precipitation of K-jarosite. The load removal is reasonably good at simple mixing ratio of 1:1 but the residual concentrations are relatively high. Clearly if stringent concentration-based discharge consents were imposed then mixing (1:1) with seawater would not satisfy these consents (mixing at higher ratios might), however, if the aim is to reduce metals loading to the coastal water for as low a cost as possible, then seawater mixing and removal of precipitated metals may be a promising avenue to explore further.

Keywords: Neutralization; metals removal; remediation

INTRODUCTION

Acid mine drainage is a widespread problem for mining operations around the world, both for active sites and former mine sites. One such legacy site is Parys Mountain, Anglesey, UK where AMD currently pollutes local water courses and the near-shore environment. This study focusses on AMD from the Dyffryn Adda adit discharge which enters the Afon Goch Amlwch watercourse, which then flows through the town of Amlwch and into the Irish Sea. Parys Mountain is an Ordovician/Silurian volcanogenic massive sulphide ore deposit (Barrett et al. 2001). The “mountain” lies approximately three kilometres from the north Anglesey coast in North Wales, and reaches a peak height of < 150 m above ordnance datum. The ore bodies’ occurrences comprise both massive and banded polymetallic sulphide lenses, hosting copper, zinc, lead, silver, and gold. Despite the range of metals in the ore, the mountain has been predominantly mined for copper. Archaeological evidence suggests that mining activity has been present on the site for approximately 4000 years, and around the time of the industrial revolution, circa 1750, it was Britain’s and one of the World’s primary sources of copper. A range of treatment technologies for the principal Parys Mountain discharge have been reviewed including active treatment using standard chemical precipitation of metals and long sea outfall without treatment. The regulatory framework to achieve compliance is detailed by the requirements of the European Water Framework Directive. The CAPEX and OPEX associated with conventional lime treatment and uncertainty about the success of passive treatment drives the research and development of novel approaches to treating problematic discharges without excessive cost.

Aims

The key aims of the present study were to (i) examine the interaction of mine water with seawater (ii) to determine whether this presents a viable potential treatment method for removing dissolved metals. There is a paucity of studies that examine the interaction of mine water with seawater, exceptions include Braungardt et al. (2003) and Achterberg et al. (2003) who studied AMD / seawater interactions in estuary systems. There is also no mention of seawater as a reagent in water treatment with the exception of the study by Muraviev et al. (1997) which examined the use of seawater as a reagent to regenerate ion exchange resins used in mine water treatment.



Figure 1 Parys Mountain mine site, Anglesey, UK

METHODOLOGY

Field experiments were undertaken to determine the ratio of sea water to mine water required to raise the pH to 7 and determine any concurrent removal of dissolved metals. Mine water neutralization experiments were carried out using water directly from the Dyffryn Adda Adit. Each ratio of mine water to seawater mixing (1:1 to 1:90) was conducted as a separate experiment rather than sequentially adding seawater. pH, DO, Redox potential (presented corrected to v. SHE) were measured in the field using a Hanna HI 9828 Multiparameter probe throughout the process and water samples for dissolved metals analyses were taken at the different stages. Acidity/Alkalinity and anion determination ion (using IC) were carried out in the laboratory. In a second round and third round of neutralization experiments, air was bubbled through each mine water/seawater mixture (using a 12V air compressor) for 10 minutes. In addition to aeration, in the 3rd round of neutralization experiments the seawater was reacted with limestone chippings (4 – 10 mm) for 24 hours prior to the mixing experiments. All water samples for metals analyses were filtered (0.45 µm) and acidified with 1ml of 10% nitric acid, diluted x 10 and analysed by ICP-MS.

RESULTS AND DISCUSSION

Mine water neutralization

The water quality parameters of the Parys Mountain mine water were as follows on the two sampling occasions: pH 2.37, Eh 419 mV, pH 2.10, Eh 402 mV and acidity 1786 mg/L. Corresponding data for the seawater used was as follows, pH 8.14, Eh 300 mV. The seawater used in the aeration experiment was pH 7.50, Eh 290mV and a third batch of seawater attained a pH of 8.26 and Eh of 215 mV on 24 hour contact with limestone chips. Fig 2 shows the results of mixing 1 part mine water with increasing amounts of seawater. It can be seen that neutralization to pH 7 requires 90 parts seawater to 1 part Parys Mountain mine water when simply mixed. If the mixture is aerated for 10 minutes after the seawater addition a reduction can be seen in the volume of seawater required to bring the pH to 7 (MW:SW of 1:40). This is probably due to stripping of dissolved CO₂ from the mixture as it is formed during the reaction of HCO₃⁻ in the seawater with H⁺ in the mine water. The increase in alkalinity (116 to 182 mg/L as CaCO₃) imparted to the seawater by soaking it in limestone for 24 hours explains the reduction in the volume of this pretreated seawater required to reach pH 7 (MW:SW of 1:25). The mine water flow at Parys Mountain is circa 10 L/s. An upper estimate of a viable seawater mixing ratio for use in treatment is 1:10 (MW:SW) which would result in a combined flow of 110L/s (comparable to some of the larger coal mine drainage treatment flows in the UK). It can be seen that at 1:10 ratio that the pH values are 4.9, 5.33 and 5.79 respectively.

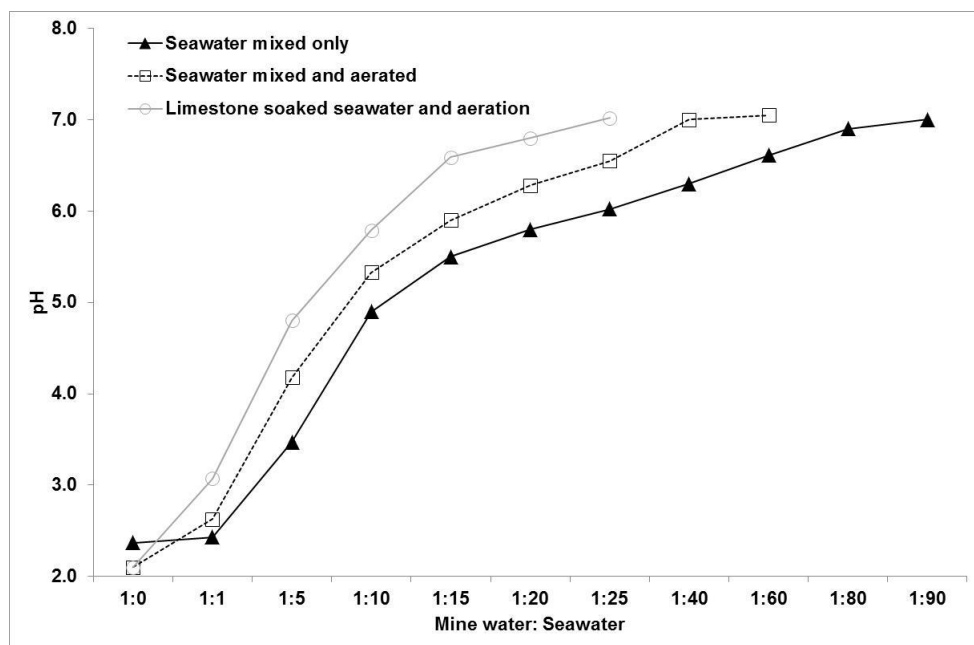


Figure 2 pH of mine water and seawater mixtures

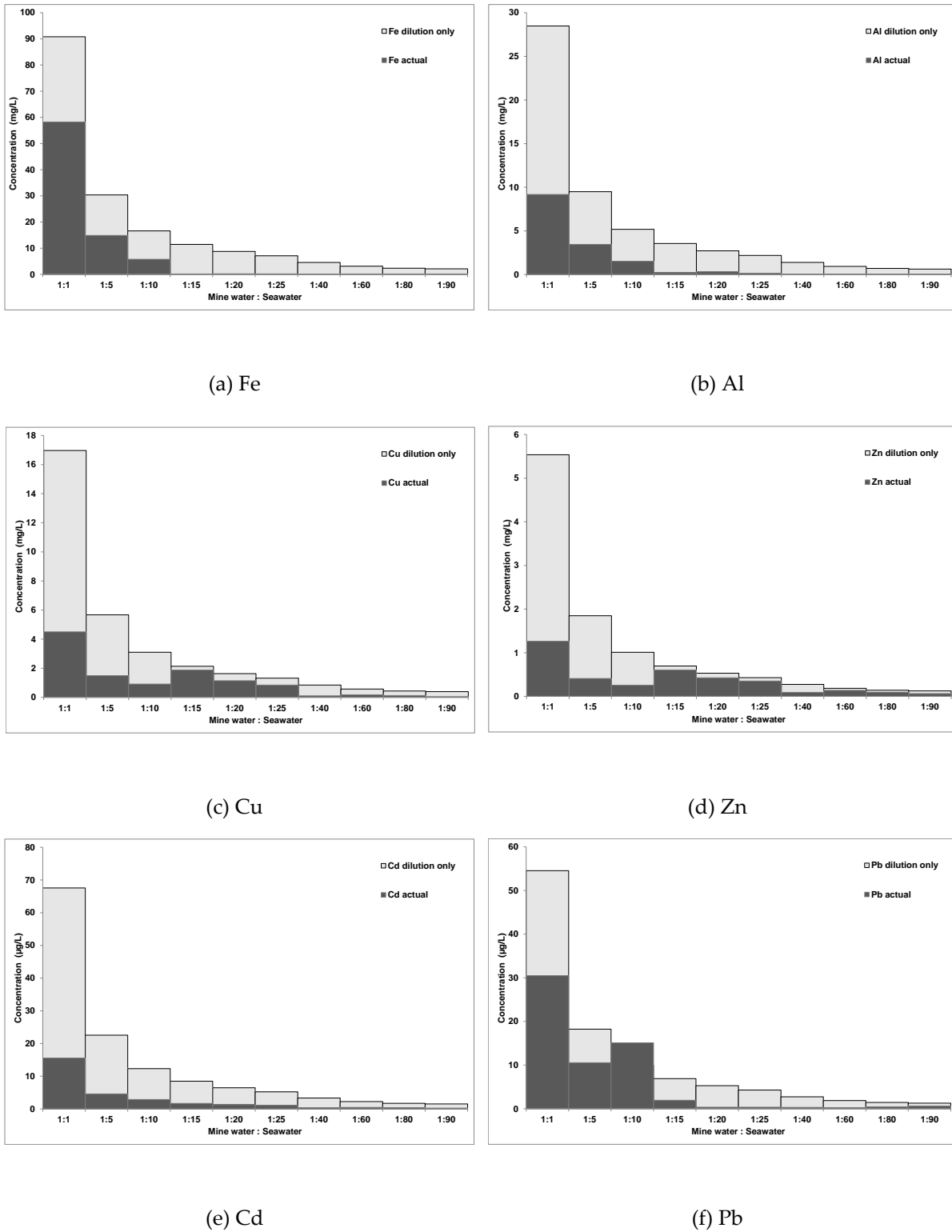


Figure 3 Residual dissolved metals after mixing with seawater at different ratios. Shown are concentrations predicted from dilution of mine water and actual measured concentrations.

Metals removal

Mixing of the mine water with equal parts seawater led to an instantaneous colour change from colourless to orange indicative of precipitation of iron, with higher proportions of seawater the orange colour was less detectable due to the high volume of seawater. As the pH increased, metals began to precipitate out and form a layer on the bottom of the mixing container. The resultant settled sludge can be seen in Fig 4 at the base of the reaction vessel. Fig 3 shows the concentrations of residual dissolved Fe, Al, Cu, Zn, Pb and Cd in solution after mixing with various amounts of seawater. Since when creating mine water and seawater mixtures the high concentrations of metals in the mine water are diluted, each graph also shows the decrease in concentration expected by dilution alone. It can be seen that in all cases (except for Pb at a ratio of 1:10) at all dilution ratios, the residual dissolved metals concentrations are considerably lower than by simple dilution indicating that metals have been removed from solution during mixing with seawater. For Fe (Fig 5) it can be seen that 36% of the dissolved Fe is removed by simple mixing 1:1 with seawater, this indicates (also suggested by the observed colour change) that an Fe(III)-bearing precipitate formed, which also buffered the pH (only a small change in pH observed (see Fig 2). 92 – 99% of Fe is removed at ratio of 1:15 and above. 68 % of the Al is removed by mixing 1:1 with seawater, with 88 – 99 % of the Al removed above 1:15 (where the pH < 5.5) as expected from the solubility of Al. The removal of Fe and Al at 1:1 ratio whilst the pH is low suggests the precipitation of an Fe-Al mineral, possibly jarosite-alunite. PHREEQC modelling with the mine and seawater compositions demonstrates that precipitation of K-jarosite can account for the observed decrease in Fe concentration.



Figure 4 Precipitate formed from mixture of mine water with seawater can clearly be seen at the bottom of the reaction vessel.

74% of Cu (Fig 4 (c) and Fig 5) was removed from solution by mixing 1:1 with seawater. Of note is the variable Cu removal; a high removal at 1:1 through to 1:10, very low removal of 12% at 1:15 though to a maximum Cu removal observed for MW:SW ratio of 1:40. This behaviour is also observed with Zn, with 77% being removed at 1:1, and the highest removal between mixing values of 1:1 and 1:10, whilst lows of 13% removal occurred at 1:15, and removals did not recovering above this ratio. This behaviour is indicative of complex adsorption behaviour, whilst there is an abundance of Fe/Al precipitates to sorb to, it is likely that at the pH reached 5 and above that

competitive sorption by the swamping excess of ions in the seawater outcompete Cu and Zn for sorption sites on these precipitates. Achterberg et al (2003) found that AMD source metals remain in the dissolved phase in an estuary (albeit at much lower concentrations). 77% of the dissolved Cd is removed by mixing 1:1 with seawater and removal thereafter remains reasonably constant with a high of 88% removal at ratio of 1:40. Why Cd behaviour is different to Zn and Cu is unknown but note the difference in magnitude of the starting concentrations. The removal of Cu, Zn and Cd at low pH at low mixing ratios may be due to the suspected jarosite-alunite precipitation. Cu, Zn, and Cd are known to be able to substitute into the jarosite-alunite structure.

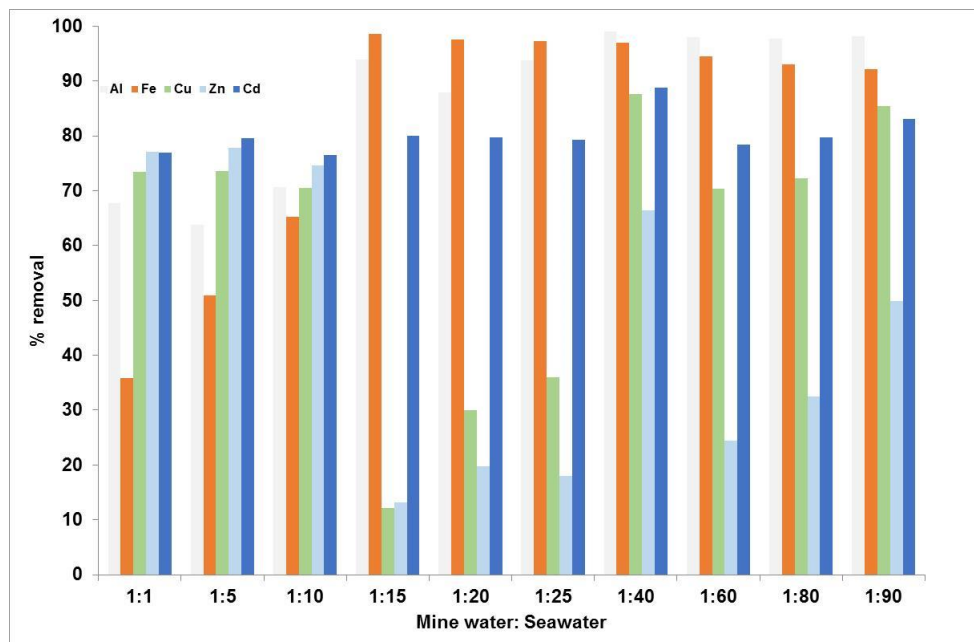


Figure 5 % removal of metals from solution upon mixing with different ratio of seawater

CONCLUSION

Mixing seawater with Parys Mountain AMD at ratios between 1:1 to 1:90 results in the removal of dissolved metals Fe, Al, Cu, Pb, Zn and Cd from solution. Cu and Zn showed decreased removal at certain ratios thought to be due to competitive sorption between Cu and Zn and seawater cations such as Mg²⁺. This may have significant implications for the fate and transport modelling for AMD releases to sea. Neutralization of the AMD occurs as the mixing ratio is increased. Incorporating aeration, and contacting the seawater with limestone chips decreases the amount of seawater required to raise the pH of the mine water/seawater mixtures. Mixing of mine water with seawater in ratio 1:1 was found to give the following quoted as load removal with residual metal concentration in parentheses: Cd 77% (16 µg/L); Zn 77% (1.3 mg/L); Cu 74% (4.5 mg/L); Al 68% (9.2 mg/L) and Fe 36% (58 mg/L). Clearly the load removal is reasonably good at simple mixing ratio of 1:1 but the residual concentrations are relatively high.

Feasibility of use for AMD treatment at Parys Mountain

Treatment of Parys Mountain mine water (or other similar discharges close to the sea) is likely to comprise mine water capture, treatment and final discharge to the sea. The feasibility of using seawater as a reagent in mine water treatment would depend upon the regulatory framework for the discharge. Clearly if stringent concentration-based discharge consents were imposed then mixing (1:1) with seawater will not satisfy these consents (mixing at higher ratios might), however if the aim is to reduce metals loading to the coastal water for as low a cost as possible then seawater mixing and removal of precipitated metals may be a promising avenue to explore further. It should be noted that the mixing with seawater removes metals from solution, for full treatment a suitable liquid/solid separation would be required in the treatment train. For example settling ponds, VFRs (Sapsford et al., these Proceedings; Sapsford et al., 2007) or reedbeds. Thus a full system would comprise a pump and piping for seawater abstraction, a mixing chamber for seawater (perhaps contacted with limestone in a limestone drain to boost alkalinity) and mine water followed by the selected settling/filtration system. If pumping of seawater was not an option, there might be scope for a tidally driven mixing system which would further reduce costs.

ACKNOWLEDGEMENTS

The authors wish to thank Natural Resources Wales for the financial support and supporting data for this study.

REFERENCES

- Achterberg, E. P., Herzl, V., Braungardt, C. B., & Millward, G. E. (2003). Metal behaviour in an estuary polluted by acid mine drainage: the role of particulate matter. *Environmental Pollution*, 121(2), 283-292.
- Barrett, T. J., MacLean, W. H. and Tennant, S. C. 2001. 'Volcanic sequence and alteration at the Parys Mountain volcanic-hosted massive sulphide deposit, Wales, United Kingdom: applications of immobile element litho-geochemistry', *Economic Geology*, 96, 1279-1305
- Braungardt, C. B., Achterberg, E. P., Elbaz-Poulichet, F., & Morley, N. H. (2003). Metal geochemistry in a mine-polluted estuarine system in Spain. *Applied Geochemistry*, 18(11), 1757-1771.
- Muraviev, D., Nogueroles, J., & Valiente, M. (1997). Seawater as auxiliary reagent in dual-temperature ion-exchange processing of acidic mine waters. *Environmental science & technology*, 31(2), 379-383.
- Sapsford, D., Barnes, A., Dey, M., Williams, K., Jarvis, A., & Younger, P. (2007). Low footprint passive mine water treatment: field demonstration and application. *Mine Water and the Environment*, 26(4), 243-250.