Alternative Reagents for the Treatment of Pb-Zn Mine Drainage in Wales

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Abstract

This paper presents the results of a laboratory-scale dosing experiment to test the efficacy of four low-cost / alternative reagents to removed dissolved Zn, Cd, and Pb from contaminated mine water. Hydrogen phosphate (Na_2HPO_4) achieved >95% Pb removal, but lower Zn and Cd removal. Sodium metasilicate (Na_2SiO_3) and sodium bicarbonate ($NaHCO_3$) did not achieve suitable metal removal. A 99-244 mg/L dose of sodium carbonate (Na_2CO_3) removed high levels of Zn (99% ±0.2), Cd (95% ±3), and Pb (88% ±3). Sodium carbonate dosing of Zn-Cd-Pb-contaminated mine water could form the basis of a new, low cost, and low input treatment process.

Keywords: Zinc, Lead, Mine Water, Alternative Reagents

Introduction

Over 1300 abandoned non-ferrous metal mines are known to exist in Wales. These sites contribute towards approximately 100 km of river reaches in Wales failing to meet Environmental Quality Standards (EQS) for Zn, Cd, and Pb (Jarvis *et al*. 2007). Contaminated mine water must be treated to avoid wide-spread pollution of surface water bodies, however treating water from these sites is both challenging and costly (Jarvis *et al*. 2012). Passive treatment of circumneutral Zn-contaminated mine water often requires systems with a large footprint (e.g. Nairn *et al*. 2010), which can be inappropriate for remote upland mine sites. Alternatively, adsorption-based treatment systems may achieve high metal-removal efficiencies, but they can be high-cost and may quickly become saturated with respect to contaminants (e.g. Warrender *et al*. 2010). Active treatment systems can be costly to operate (URS 2014) and typically use reagents such as lime (CaO) and sodium hydroxide (NaOH). These strong bases present operational challenges in relation to control of dosing, reagent dispensing and health and safety, especially when lone operators are maintaining systems in remote locations. Previous work conducted by this research group has identified that a carbonate-based system may be appropriate to treat circumneutral Pb-Zn mine drainage in Wales (Williams *et al*. 2020). This paper seeks to build on this existing work by investigating the effect of dosing two real mine waters with Na_2CO_3, a relatively safe-to-handle and low-cost reagent, alongside three more low cost and/or relatively safe alternative mine water treatment reagents. It is envisaged that this work will be expanded in the future and will lead to the development and implementation of a 'semi-passive' mine water treatment system whereby circumneutral metal mine drainage in Wales will be treated in a low cost, low input system.

Methods

Mine water was collected from two abandoned Pb-Zn mines in mid Wales. The first mine site, Abbey Consols, is located 1 km east of the village Pontrhydfendigaid in Ceredigion. Water draining Abbey Consols mine water is circumneutral and contains elevated levels of Zn (>15 mg/L), Cd (>40 µg/L) and Pb (>130 µg/L). Mine water (3 L/s) drains into the River Teifi, a Special Area of Conservation, which contributes towards the river failing to meet its Water Framework Directive (WFD) target for Zn for 29 km (NRW, 2016). Water was also sampled from Nant y Mwyn Pb mine, Rhandirmwyn, Carmarthenshire. Nant y Mwyn water is also circumneutral and it is similarly contaminated with Zn, Pb, and Cd. This mine is an important source of Zn to the River Tywi, which fails to meet its WFD target for Zn for approximately 65 km downstream (NRW, 2014). Treating mine water discharges from these sites has the potential to prevent a combined total of 14 tonnes of Zn, Cd, and Pb from entering local surface water courses.

Mine water was treated using four low cost/alternative reagents: sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), sodium hydrogen phosphate (Na_2HPO_4), and sodium metasilicate (Na_2SiO_3). These reagents are summarised in Table 1.

A 10 g/L stock solution was made-up for each reagent. Between 0 and 2.5 mL stock was mixed with 100 mL of mine water in magnetically stirred borosilicate glass beakers. Experiments were run for between 1 and 120 minutes to test the effect of variable reaction time on metal removal. Following the predefined reaction time, samples were filtered through 0.45 µm filter membranes, acidified using 0.1 mL of 10% (v/v) HNO_3, and analysed by ICP-MS. Sample pH was recorded before and after each treatment using a Mettler Toledo Seven Multi S40 m along with an InLab Expert Pro ISM pH probe. All experiments and pH measurements were completed in triplicate.

***Table 1** A summary of water treatment reagents used in this study.*

Reagent	Common application(s)
Na_2CO_3	pH adjustment and softener in water treatment
$NaHCO_3$	Acid neutralisation
Na_2HPO_4	Water treatment to prevent plumbosolvency
Na_2SiO_3	Coagulant in water treatment

Results and Discussion

A summary of the unamended mine waters is provided in Table 2. This data is presented alongside a target value for each metal, defined here as 3-times the approximate Environmental Quality Standard for the respective metal. This is the desired concentration of each metal following treatment. Over 99% removal is required to meet the target value for Zn and Cd, and >97% removal is required to meet the target value for Pb. Evidently, for any of these dosing strategies to be considered for future research, they must be shown to achieve very high (>97%) metal removal rates.

All four of the reagents tested have the potential to raise the pH of mine water. The effect of dose on water pH is presented in Figure 1.

Following 120-minute reaction time, the pH of Abbey Consols and Nant y Mwyn water containing 244 mg/L Na_2CO_3 was almost identical (pH 8.75 and pH 8.76, respectively). Indeed, the pH of the two mine waters responded to being dosed with Na_2CO_3 in a very similar fashion, as indicated by a strong positive correlation between dose and pH (r = 0.93). Under the same conditions, $NaHCO_3$ increased the pH of these waters to between 7.59 and 7.81. Na_2HPO_4 increased the Abbey Consols water from pH 5.50 to 6.44 and the Nant y Mwyn water from pH 6.60 to 6.95. Interestingly, Na_2SiO_3 was found to be quite insoluble in Nant y Mwyn water, hence the dose was adjusted to a maximum of 24.4 mg/L which resulted in a final pH of 8.78, whereas a 244 mg/L dose of Na_2SiO_3 in Abbey Consols water resulted in a lower final pH of 8.11.

***Table 2** Summary of unamended mine water. Target values refer to an appropriate effluent concentration for a mine water treatment system, as suggested by URS (2014).*

	pH	Zn (mg/L)	Zn target (mg/L)	Cd (µg/L)	Cd target (µg/L)	Pb (µg/L)	Pb target (µg/L)
Nant Y Mwyn	6.6	13.0	0.036	50.7	0.3	138.7	6
Abbey Consols	5.5	15.9		41.7		132.7	

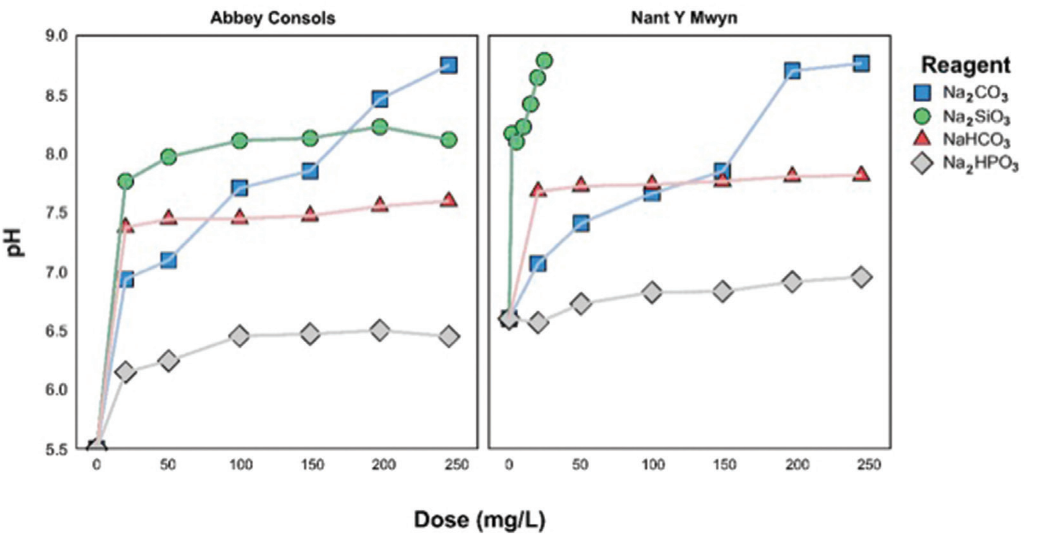

Figure 1 *pH of two mine water samples with a variable dose of the four reagents.*

A Comparison of Reagent Efficacy in the Removal of Dissolved Metals

The removal of dissolved metals from Abbey Consols and Nant y Mwyn mine water following 120 minutes reaction time is presented in Figure 2. Sodium carbonate was highly effective at removing Zn (maximum 99.3% removal), Cd (maximum 98.0% removal), and Pb (maximum 92.2% removal) from solution. Between 0 and 99 mg/L dosage, metal removal from both waters increased sharply (Figure 2). The maximum removal of dissolved metals from mine water by Na_2CO_3 did not necessarily correspond to the maximum reagent dose (244 mg/L), but always occurred at >99 mg/L. Above 99 mg/L dosage, metal removal plateaued at 99% ±0.2 (Zn), 95% ±3 (Cd), and 88% ±3(Pb). These removal rates result in a final Zn, Cd, and Pb concentration within one order of magnitude of the target values presented in Table 2. Sodium carbonate dosing appears to be a viable method to treat mildly acidic to circumneutral Pb-Zn mine drainage.

Sodium hydrogen phosphate (Na_2HPO_4) was more effective at removing Pb from Nant y Mwyn water (maximum 95.4% removal) than sodium carbonate, although this was not true for Abbey Consols water where Na_2CO_3 outperformed Na_2HPO_4: maximum removal by Na_2HPO_4 and Na_2CO_3 was 48% and 92%, respectively. The maximum Zn and Cd removal by Na_2HPO_4 was 50.5% and 50.1%, respectively This demonstrates that although it performed well for Pb removal from the Nant y Mwyn water, Na_2HPO_4 is not suitable for the treatment of Zn and Cd in these waters and would, without removal of residual phosphate, potential cause further pollution.

Neither $NaHCO_3$ or Na_2SiO_3 performed particularly well in this set of experiments for any of the elements studied. The maximum removal of dissolved Zn by $NaHCO_3$ (32%) was much lower than by Na_2SiO_3 (69%), and both were outperformed by Na_2CO_3 (maximum 99.3% removal). Similar results are observed for Pb and Cd, although maximum removal for these elements was lower than for Zn. Based on the comparatively low metal removal rates by these reagents, $NaHCO_3$ or Na_2SiO_3 should not be considered further for Pb-Zn removal from these mine waters.

A geochemical equilibrium model was run in PHREEQC, using the wateq4f thermodynamic database, to predict the saturation state of relevant Zn-based minerals in mine water containing 99 mg/L of the various reagents. All reagents caused the mine water pH to increase (Figure 1). Despite this pH increase, $Zn(OH)_2$ was never predicted to be oversaturated. Zinc carbonate, silicate, and phosphate minerals were all predicted to be oversaturated in

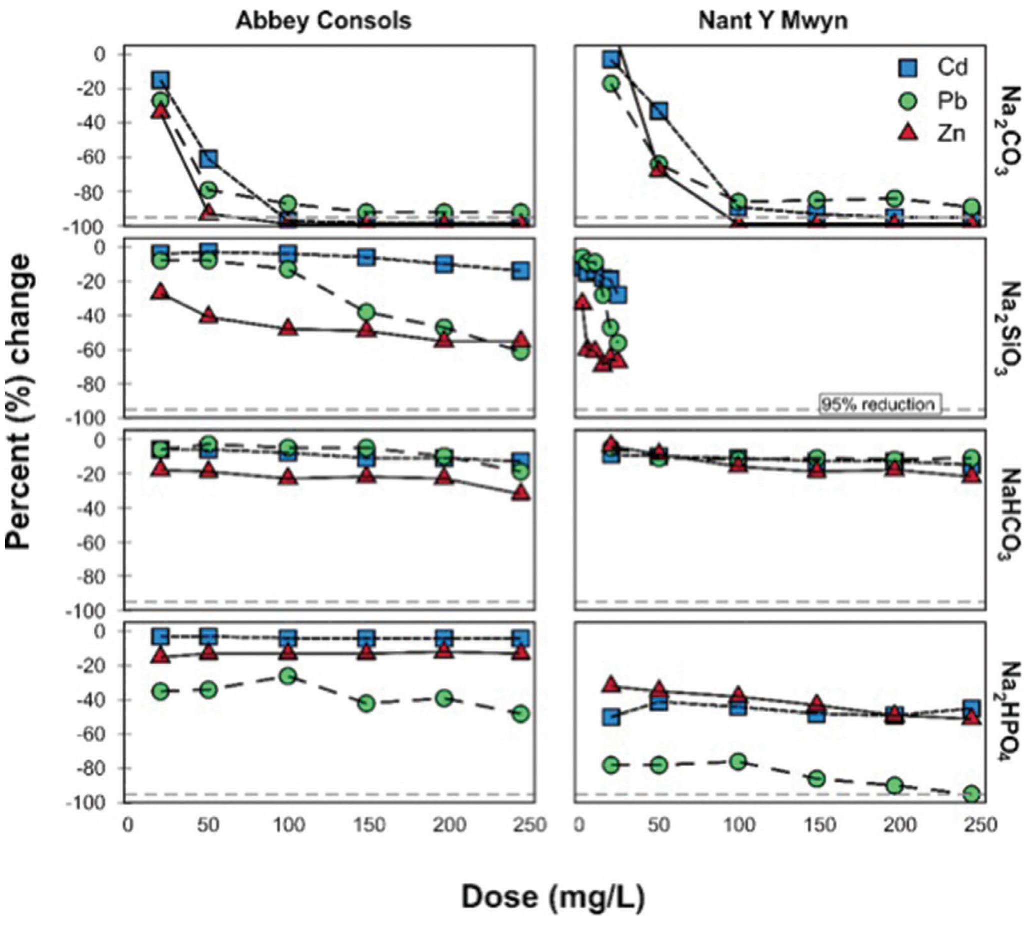

Figure 2 Percent change in dissolved (<0.45 μm) metal concentration following dosing with Na_2CO_3 (top row), Na_2SiO_3 (second row), $NaHCO_3$ (third row), and Na2HPO4 (bottom row). Grey, dashed horizontal line represents 95% reduction in metal concentration.

response to dosing with their respective salts under the abovementioned conditions. Based on the high efficacy of the Na_2CO_3 treatment for Zn removal, multiple Zn carbonate-based minerals were considered in this modelling exercise. Smithsonite, $ZnCO_3$, is predicted to be oversaturated and may therefore form in these waters and remove Zn from solution. Other Zn hydroxycarbonate minerals, namely hydrozincite ($Zn_5[OH]_6[CO_3]_2$), are known to form in place of pure Zn carbonates under similar conditions (Zachara *et al.* 1989). As such, the thermodynamic database was amended with the solubility constant for hydrozincite (6.41) taken from Apps and Wilkin (2015). Hydrozincite was also found to be oversaturated in the Na_2CO_3-dosed water. Based on the Pourbaix diagram constructed for a Zn-H_2O-CO_2 system presented by Meda *et al.* (2014) and the experimental work by Zachara *et al.* (1989), it would be expected that hydrozincite will form from these CO_3-amended waters. This is an important point because it has implications for designing a field-scale water treatment system. Hydrozincite typically forms small (10's of μm) flake-like crystals which can be slow to settle. It will be important to properly characterise the Zn-based precipitate to design a suitable Na_2CO_3 dosing system.

The effect of reaction time

Sodium carbonate was found to be the most effective reagent for Zn, Cd, and Pb removal from solution. Metal removal by Na_2CO_3 was not greatly affected by the range of reaction

Table 3 *Metal removal from two mine water samples dosed with 99 mg/L and 244 mg/L Na_2CO_3 after 1 minute and 120-minute reaction time.*

Site	Dose (mg/L)	Reaction Time (min)	Zn	Cd	Pb
			Percent removal (%)		
Abbey Consols	99	1	98.0	95.7	82.6
Abbey Consols	99	120	99.2	97.2	87.5
Nant Y Mwyn	99	1	98.4	87.3	81.7
Nant Y Mwyn	99	120	98.6	89.4	85.9
Abbey Consols	244	1	98.7	97.4	89.2
Abbey Consols	244	120	99.2	98.0	92.0
Nant Y Mwyn	244	1	98.7	94.5	84.9
Nant Y Mwyn	244	120	99.2	95.0	89.3

times employed in this work (Table 3). For example, Zn removal from Abbey Consols water was 1.2% higher after 120 minutes following a 99 mg/L Na_2CO_3 dose than after 1 minute reaction time. Similar results can be observed for Zn, Cd, and Pb following a 99 mg/L and 244 mg/L dose in both Abbey Consols and Nant y Mwyn water.

A longer reaction time (120 minutes) resulted in there being 0.19 mg/L (Abbey Consols) and 0.03 mg/L (Nant y Mwyn) less Zn in the final solution than after 1 minute reaction time. Similar results are observed for Cd and Pb. Although the majority of Zn (>98%), and other metals, was removed from solution after just 1 minute, the comparatively small decrease in concentration between 1 and 120 minutes is important when considering the target value of 0.036 mg/L for Zn presented in Table 2. Following 1 minute reaction time, Abbey Consols water contained 0.32 mg/L Zn, approximately 10-times more than the target value. After 120 minutes, however, the Abbey Consols water contained 0.12 mg/L Zn, only 3.8-times greater than the target value. The same general trend holds true for Cd and Pb.

The typically high metal removal rates irrespective of time are of interest because it may be possible to design a water treatment system which is able to handle water with variable residence time. For example, it may be desirable to treat water using a 120 minute reaction time under 'normal' operating conditions, but then at times of higher flow treat a much greater volume of water using the same sized treatment plant by allowing for a shorter reaction time. This could offer a pragmatic solution to treating high volumes of contaminated mine water during infrequent times of heavy rainfall without the cost or space requirements of building a larger treatment facility, both of which are important considerations when treating water from abandoned mines in remote upland areas.

Conclusions

This work tested the efficacy of four commonly used water treatment reagents in removing dissolved Zn, Cd, and Pb from two mine water samples. Na_2HPO_4 achieved high Pb removal (>95%) in one of these waters but failed to remove sufficient Zn and Cd. Na_2SiO_3 and $NaHCO_3$ both performed poorly in comparison with Na_2HPO_4 for Pb, and Na_2CO_3 for Zn, Cd, and Pb. Na_2CO_3 clearly outperformed all other reagents tested. A 99 mg/L dose of Na_2CO_3 resulted in a final water pH of 7.66-7.70 and achieved over 99% (Zn), 95% (Cd), and 88% (Pb) metal removal. The bulk of dissolved metals were removed from solution after just 1 minute reaction time, although increasing the reaction time pushed the final metal concentration down towards the target value following treatment. Assuming that the cost of Na_2CO_3 is approximately £200/tonne (UPS 2014) and a 99 mg/L dose is used, 1 m3 of mine water could be treated for <£0.02. Sodium carbonate dosing offers an effective and low cost means of treating Zn-Cd-Pb-contaminated circumneutral mine water in Wales.

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