Circular Economy Potential of Widescale Implementation of Sodium Carbonate Dosing for Zinc-rich Mine Water in Wales

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Abstract

Abandoned metals mines play a significant role in the contamination of water ways in Wales. Previous work has shown that dosing with sodium carbonate is an effective, low cost, low input treatment for circum-neutral mine drainage with elevated levels of Zn and Pb. The primary aims of this study were to (1) trial sodium carbonate dosing using a range of mine waters across Wales with differing chemistry to assess its applicability and (2) provide an estimate of the quantity of Zn that could be recovered and the potential contribution to the circular economy.

Keywords: Carbonate dosing, Zinc, Circular Economy

Introduction

The effect of mine drainage plays a major role on the quality of water bodies across the globe, impacting thousands of kilometres of rivers worldwide (Johnson and Hallberg, 2005). In England over 1500 km of rivers are polluted from mine discharge (Johnston *et al*., 2008) and 700 km of rivers in Wales are failing water quality standards due to high levels of dissolved metals such as zinc, lead and cadmium due to inputs from former metal mining areas (Robson and Neal, 1997; Rees *et al*., 1998; Neal *et al*., 2000; Environment Agency, 2002; Coal Authority, 2020). Zn has been reported to be the most common contaminant from metal mine discharges in England and Wales (Jarvis, Gandy and Gray, 2012). Elevated levels of ecotoxic Zn in water bodies can have highly detrimental effects on ecosystems, causing a reduction in abundance and diversity of biota and damaging ecosystem functions such as productivity and nutrient cycling (Younger and Wolkersdorfer, 2004). Due to its environmental persistence, solubility, mobility, toxicity and bioaccumulation potential, Zn is ranked as one of the most hazardous and common, metal pollutants (Ali, Khan and Ilahi, 2019). For waterways to meet water quality standards, it is vital that research into the remediation of metal mine water pollution continues; to protect aquatic organisms and deliver economic and environmental benefits to local communities.

The treatment of Zn rich mine drainage is well established (Johnson and Hallberg, 2005; Skousen, 2014; Skousen *et al*., 2017); using techniques such as chemical dosing with NaOH, CaO/Ca(OH)2, Na2S (Machemer and Wildeman, 1992; Olds *et al*., 2013; Mackie and Walsh, 2015; Carranza *et al*., 2016; Jacob, Save and Menard, 2018; Kaur *et al*., 2018; Kennedy and Arias-Paić, 2020; Williams *et al*., 2020; Vecino *et al*., 2021), adsorption (Ríos, Williams and Roberts, 2008; Pinto, Al-Abed and Reisman, 2011; Warrender *et al*., 2011; Sartz and Bäckström, 2013; Mashangwa, Tekere and Sibanda, 2017; Zendelska *et al*., 2019; Calugaru *et al*., 2020; Richard, Neculita and Zagury, 2021), coprecipitation (Sibrell *et al*., 2007; Mayes, Potter and Jarvis, 2009; Miller, Wildeman and Figueroa, 2013; Sapsford *et al*., 2015), electrocoagulation (Nariyan, Sillanpää and Wolkersdorfer, 2017; Singh and Mishra, 2017), ion exchange (Wingenfelder *et al*., 2005; Dlamini *et al*., 2019), sulphate reducing bacteria (Zagury, Kulnieks and Neculita, 2006; Gandy and Jarvis, 2012; Sobolewski *et al*., 2022) and passive constructed wetlands (Song *et al*., 2001; Dean *et al*., 2022). However, there are several drawbacks and trade-offs associated with these different treatment methods, including low removal efficiencies, high operational costs and initial capital investment, large land area requirements and risks associated with using hazardous chemicals. Another consideration is that mine water chemistry is very variable and it can be difficult to apply the same treatment method to a range of mine sites. The benefits however of using a single mine water treatment system include lower costs associated with procuring chemicals, less extensive knowledge needed of different mine water treatment systems and the need for one type of sludge management procedure.

Dosing with sodium carbonate has been shown to be an effective reagent for the precipitation of metals from a range of waste effluents (Gandy and Jarvis, 2012; Sartz and Bäckström, 2013; Xanthopoulos *et al.*, 2017) exhibiting some significant benefits. A study conducted by Chen *et al.* examined several chrmicals including lime, sodium carbonate and sodium sulphide were examined for Zn removal from synthetic solutions (Chen *et al.*, 2018). Sodium carbonate was found to offer the highest Zn removal rate (99.96%) whilst operating at pH 9, compared to pH 11.7 and 10.6 for lime and sodium sulphide. Previous work conducted by the authors and industrial partners has shown that Na2CO3 is an effective reagent for the precipitation of Zn from a Zn rich circum-neutral mine water (Abbey Consols), achieving 94% zinc removal in laboratory trials and 58%-91% Zn removal in a field study (Williams *et al.*, 2020; Dean, Alkhazraji and Sapsford, 2021). The primary aims of this study were to (1) trial sodium carbonate dosing using a range of mine waters across Wales with differing chemistry to assess its applicability and (2) provide an estimate of the quantity of Zn that could be recovered and the potential contribution to the circular economy.

Methods

Study sites and mine water chemistry

Mine drainage data was obtained from Natural Resources Wales (NRW) archives and study sites were chosen based on pH, alkalinity and metal contamination levels ensuring that a range of different mine water chemistries were included from across Wales. A summary of the mine water chemistry for the chosen sites is shown in Table 1.

On site mine water chemistry data collection

On-site data including temperature, electrical conductivity (EC), pH, dissolved oxygen (DO) were measured using was collected using a field calibrated Hanna meter and alkalinity was measured on site using Hach Digital Titrator, method number 8203.

Na_2CO_3 Dosing

The dosing experiments were conducted on-site since mine water is unstable due to reactions with air and/or degassing (Barnes and Romberger, 1968; Geroni, Sapsford and Florence, 2011). On-site jar tests using a range of Na_2CO_3 dosages (ca. 0.1:1 – 28:1

Table 1 *Mine drainage chemistry from chosen study sites**

Site	pH	Alkalinity mgL^{-1} as $CaCO_3$	Zinc mgL^{-1}	Iron mgL^{-1}	Estimated flow Ls^{-1}
Minera- Deep Day Level	7.4	29.4	0.94	0.23	50
Pengwern (Llangynog)	7.4	35	1.98	N/A	15
Cwmystwyth- Pugh's	6.6	14	20.6	0.40	9.6
Cwmystwyth- Gill's	6.5	2.5 (<5)	4.2	0.03	3.2
Frongoch Adit	7.0	13	12.9	0.03	17
Frongoch attenuation pond	5.1	2.5 (<5)	76.6	0.03	6
Cwm Rheidol- No.6	3.7	2.5 (<5)	12.1	3.4	8.3
Cwm Rheidol- No.9	2.8	2.5 (<5)	78	84	0.6
Level Fawr	7.3	2.5 (<5)	1.012	0.03	21
Nant y Mwyn- Lower Boat	5.8	76	4.2	N/A	51
Nant y Mwyn- Pannau Adit	7.2	76	11	N/A	3
Abbey Consols	6.6	24	16	N/A	3

CO_3:Zn molar ratios) were conducted to assess the effectiveness of Na2CO3 dosing for the removal Zn and other metal contaminants (As, Pb, Cd).The treated and untreated samples (20 mL) were filtered using 0.2µm syringe filters and preserved using 0.1 mL 10% nitric acid and metal concentrations were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Results and Discussion

Na_2CO_3 dosing was trialled on several selected sites across Wales for the removal of Zn and other metal contaminants. Out of the 12 sites studied, 11 achieved >95% Zn removal. However, Na_2CO_3 dose required to achieve these levels varied significantly between sites, the final pH after dosing varied between 7.28 and 10.46.

The data obtained from the field campaign was used to estimate Zn removal and potential Zn recovery per year for each site.

Table 2 shows that if Na_2CO_3 dosing was employed at the 11 sites where Zn removal was >95%, over 100,000 kg Zn could be prevented from entering Welsh water bodies each year. A cost estimate for the required quantity of Na2CO3 could be calculated based on the required dosages that were obtained from the field trials. Reagent costs for the treatment outlined in Table 2 can be estimated at £700k/year.

The current price of Zn metal is £3672/tonne. Thus, if Zn could be recovered from the sludge (e.g. by acid dissolution and electrowinning) then the recovery of the Zn might be sufficient to partly offset the reagent costs. An advantage of treating multiple sites with the same treatment is that the amount of sludge generated would be more attractive for potential Zn recyclers. As a circular economy proposition, not only would carbonate dosing zinc treat the metal mine water pollution, contributing substantial value in ecological restoration, but if recovered would cycle this Zn (which would have otherwise been lost) back to the economy, provide a modest revenue stream to offset the reagent costs and avoid landfill and associated costs.

In conclusion this study has shown that Na_2CO_3 can be used to treat a range of different Zn-bearing mine waters in Wales. In addition, widespread implementation of Na_2CO_3 dosing has the potential to prevent over 100,000 kg of Zn from entering Welsh rivers per year and potentially opens interesting opportunities for zinc recovery.

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Table 2 *Potential Zn recovery and reagent per year for selected sites*

Site	Estimated mass of Zn removed per year Kg per year	Estimated cost of Na_2CO_3 required per year £ per year
Minera- Deep Day Level	637	41456
Pengwern (Llangynog)	2053	26512
Cwm Ystwyth- Pugh's	9639	39930
Cwm Ystwyth- Gill's	868	13086
Frongoch Adit	9607	41977
Frongoch attenuation pond	38146	141060
Cwm Rheidol- No.6	13462	19097
Cwm Rheidol- No.9	989	4514
Level Fawr	1005	20645
Nant y Mwyn- Lower Boat	23787	882508
Nant y Mwyn- Pannau Adit	539	2262
Abbey Consols	1026	4803
Total	101758	709402

*Price Na_2CO_3 ca. £200/tn (July 2022)

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References

Ali, H., Khan, E. and Ilahi, I. (2019) 'Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation', Journal of Chemistry, 2019(Cd). doi:10.1155/2019/6730305.

Barnes, H.L. and Romberger, S.B. (1968) 'Chemical Aspects of Acid Mine Drainage', Journal (Water Pollution Control Federation), 40(3), pp. 371–384. Available at: http://www.jstor.org/stable/25036044.

Calugaru, I.L. *et al.* (2020) 'Removal and Recovery of Ni and Zn from Contaminated Neutral Drainage by Thermally Activated Dolomite and Hydrothermally Activated Wood Ash', Water, Air, and Soil Pollution, 231(5). doi:10.1007/s11270-020-04600-3.

Carranza, F. *et al.* (2016) 'Recovery of Zn from acid mine water and electric arc furnace dust in an integrated process', Journal of Environmental Management, 165, pp. 175–183. doi:10.1016/j.jenvman.2015.09.025.

Chen, Q. *et al.* (2018) 'Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates', Journal of Water Process Engineering, 26(October), pp. 289–300. doi:10.1016/j.jwpe.2018.11.003.

Coal Authority (2020) Metal Mine Failing Waterbodies Assessment - Overview Report (OP16-154/F13/0)

Dean, D.M. *et al.* (2022) 'Passive Treatment of Circumneutral Mine Drainage from the St . Louis Mine Tunnel , Rico CO : Part 2 — Vertical Biotreatment Train Pilot Study', Mine Water and the Environment [Preprint]. doi:10.1007/s10230-022-00857-8.

Dean, J., Alkhazraji, B. and Sapsford, D.J. (2021) 'Alternative Reagents for the Treatment of Pb-Zn Mine Drainage in Wales', in IMWA 2021 – "Mine Water Management for Future Generations", pp. 109–114.

Dlamini, C.L. *et al.* (2019) 'Acid mine drainage pollution remediation using hybrid chelating ion-exchange/HZrO2 nanocomposite adsorbents', SN Applied Sciences, 1(12), pp. 1–14. doi:10.1007/s42452-019-1580-3.

Environment Agency (2002) Metal Mine Strategy for Wales, Environment Agency Wales.

Gandy, C.J. and Jarvis, A.P. (2012) 'The Influence of Engineering Scale and Environmental Conditions on the Performance of Compost Bioreactors for the Remediation of Zinc in Mine Water Discharges', Mine Water and the Environment, 31(2), pp. 82–91. doi:10.1007/s10230-012-0177-5.

Geroni, J.N., Sapsford, D.J. and Florence, K. (2011) 'Degassing CO2 from mine water: implications for treatment of circumneutral drainage', Mine Eater-Managing the Challenges, (1), pp. 319–324.

Jacob, J.C., Save, M. and Menard, Y. (2018) 'Treatment of Mine Drainage with Significant Topographical Constraints: Case Study of the Bodennec Site (France)', Mine Water and the Environment, 37(4), pp. 839–848. doi:10.1007/s10230-018-0522-4.

Jarvis, A.P., Gandy, C.J. and Gray, N.D. (2012) Mitigation of pollution from abandoned metal mines. Part 1: Review of passive treatment technologies for metal mine drainage remediation.

Johnson, D.B. and Hallberg, K.B. (2005) 'Acid mine drainage remediation options: A review', Science of the Total Environment, 338(1-2 SPEC. ISS.), pp. 3–14. doi:10.1016/j.scitotenv.2004.09.002.

Johnston, D. *et al.* (2008) Abandoned Mines and the Water Environment, Environment Agency.

Kaur, G. *et al.* (2018) 'Alternative neutralisation materials for acid mine drainage treatment', Journal of Water Process Engineering, 22(February), pp. 46–58. doi:10.1016/j.jwpe.2018.01.004.

Kennedy, A.M. and Arias-Paić, M. (2020) 'Application of powdered steel slag for more sustainable removal of metals from impaired waters', Journal of Water Process Engineering, 38(August). doi:10.1016/j.jwpe.2020.101599.

Machemer, S.D. and Wildeman, T.R. (1992) 'Adsorption compared with sulfide precipitation as metal removal processes from acid mine drainage in a constructed wetland', Journal of Contaminant Hydrology, 9(1–2), pp. 115–131. doi:10.1016/0169-7722(92)90054-I.

Mackie, A.L. and Walsh, M.E. (2015) 'Investigation into the use of cement kiln dust in high density sludge (HDS) treatment of acid mine water', Water Research, 85, pp. 443–450. doi:10.1016/j.watres.2015.08.056.

Mashangwa, T.D., Tekere, M. and Sibanda, T. (2017) 'Determination of the Efficacy of Eggshell as a Low-Cost Adsorbent for the Treatment of Metal Laden Effluents', International Journal of Environmental Research, 11(2), pp. 175–188. doi:10.1007/s41742-017-0017-3.

Mayes, W.M., Potter, H.A.B. and Jarvis, A.P. (2009) 'Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide', Journal of Hazardous Materials, 162(1), pp. 512–520. doi:10.1016/j.jhazmat.2008.05.078.

Miller, A., Wildeman, T. and Figueroa, L. (2013) 'Zinc and nickel removal in limestone based treatment of acid mine drainage: The relative role of adsorption and co-precipitation', Applied Geochemistry, 37, pp. 57–63. doi:10.1016/j.apgeochem.2013.07.001.

Nariyan, E., Sillanpää, M. and Wolkersdorfer, C. (2017) 'Electrocoagulation treatment of mine water from the deepest working European metal mine – Performance , isotherm and kinetic studies', Separation and Purification Technology, 177, pp. 363–373. doi:10.1016/j.seppur.2016.12.042.

Neal, C. *et al.* (2000) 'The water quality of the River Wear , north-east England', Science of the Total Environment, 251/252, pp. 153–172.

Olds, W.E. *et al.* (2013) 'Nickel and Zinc Removal from Acid Mine Drainage: Roles of Sludge Surface Area and Neutralising Agents', Journal of Mining, 2013, pp. 1–5. doi:10.1155/2013/698031.

Pinto, P.X., Al-Abed, S.R. and Reisman, D.J. (2011) 'Biosorption of heavy metals from mining influenced water onto chitin products', Chemical Engineering Journal, 166(3), pp. 1002–1009. doi:10.1016/j.cej.2010.11.091.

Rees, J.G. *et al.* (1998) 'Sediment-borne Contaminants in Rivers Discharging into the Humber Estuary , UK', Marine Pollution Bulletin, 37(3), pp. 316–329.

Richard, D., Neculita, C.M. and Zagury, G.J. (2021) 'Removal of nickel from neutral mine drainage using peat-calcite, compost, and wood ash in column reactors', Environmental Science and Pollution Research, 28(12), pp. 14854–14866. doi:10.1007/s11356-020-11623-0.

Ríos, C.A., Williams, C.D. and Roberts, C.L. (2008) 'Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites', Journal of Hazardous Materials, 156(1–3), pp. 23–35. doi:10.1016/j.jhazmat.2007.11.123.

Robson, A.J. and Neal, C. (1997) 'A summary of regional water quality for Eastern UK rivers', Science of the Total Environment, 9697(96), pp. 15–37.

Sapsford, D. *et al.* (2015) 'Conversion of coal mine drainage ochre to water treatment reagent : Production , characterisation and application for P and Zn removal', Journal of Environmental Management, 160, pp. 7–15. doi:10.1016/j.jenvman.2015.06.004.

Sartz, L. and Bäckström, M. (2013) 'Treatment of Acidic and Neutral Metal-Laden Mine Waters with Bone Meal Filters', Mine Water and the Environment, 32(4), pp. 293–301. doi:10.1007/s10230-013-0248-2.

Sibrell, P.L. *et al.* (2007) 'An innovative carbonate coprecipitation process for the removal of zinc and manganese from mining impacted waters', Environmental Engineering Science, 24(7), pp. 881–895. doi:10.1089/ees.2006.0126.

Singh, H. and Mishra, B.K. (2017) 'Assessment of kinetics behavior of electrocoagulation process for the removal of suspended solids and metals from synthetic water', Environmental Engineering Research, 22(2), pp. 141–148. doi:10.4491/eer.2016.029.

Skousen, J. (2014) Overview of Acid Mine Drainage Treatment with Chemicals. Edited by J.A. Jacobs, J.H. Lehr, and S.M. Testa.

Skousen, J. *et al.* (2017) 'Review of Passive Systems for Acid Mine Drainage Treatment', Mine Water and the Environment, 36(1), pp. 133–153. doi:10.1007/s10230-016-0417-1.

Sobolewski, A.B. *et al.* (2022) 'Passive Treatment of Circumneutral Mine Drainage from the St. Louis Mine Tunnel, Rico CO: Part 3—Horizontal Wetlands Treatment Train Pilot Study', Mine Water and the Environment [Preprint], (0123456789). doi:10.1007/s10230-022-00856-9.

Song, Y. *et al.* (2001) 'Lead and Zinc Removal by Laboratory-Scale Constructed Wetlands', Water Environment Research, 73(1), pp. 37–44. doi:https://doi.org/10.2175/106143001X138660.

Vecino, X. *et al.* (2021) 'Valorisation options for Zn and Cu recovery from metal influenced acid mine waters through selective precipitation and ion-exchange processes: promotion of on-site/off-site management options', Journal of Environmental Management, 283. doi:10.1016/j.jenvman.2021.112004.

Warrender, R. *et al*. (2011) 'Field Trials of Low-cost Reactive Media for the Passive Treatment of Circum-neutral Metal Mine Drainage in Mid-Wales, UK', Mine Water and the Environment, 30(2), pp. 82–89. doi:10.1007/s10230-011-0150-8.

Williams, T. *et al*. (2020) 'Treatability Trials to Remove Zinc from Abbey Consols Mine Water , Wales , UK', in Pope, J. *et al*. (eds) 14th IMWA Congress. Christchurch, pp. 225–230.

Wingenfelder, U. *et al*. (2005) 'Removal of heavy metals from mine waters by natural zeolites', Environmental Science and Technology, 39(12), pp. 4606–4613. doi:10.1021/es048482s.

Xanthopoulos, P. *et al*. (2017) 'Zinc recovery from purified electric arc furnace dust leach liquors by chemical precipitation', Journal of Environmental Chemical Engineering, 5(4), pp. 3550–3559. doi:10.1016/j.jece.2017.07.023.

Younger, P.L. and Wolkersdorfer, C. (2004) 'Mining Impacts on the Fresh Water Environment: Technical and Managerial Guidelines for Catchment-Focused Remediation. In: Younger PL, Wolkersdorfer C (eds).', Mine Water and the Environment, Suppl. Iss, pp. 2–80.

Zagury, G.J., Kulnieks, V.I. and Neculita, C.M. (2006) 'Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment', Chemosphere, 64(6), pp. 944–954. doi:10.1016/j.chemosphere.2006.01.001.

Zendelska, A. *et al*. (2019) 'Removal of Zinc Ions from Acid Aqueous Solutions and Acid Mine Drainage Using Zeolite-Bearing Tuff', Mine Water and the Environment, 38(1), pp. 187–196. doi:10.1007/s10230-018-0560-y.