



An assessment of the efficacy of sodium carbonate for semi-passive treatment of circumneutral zinc-bearing mine waters

J. Kennedy^{*}, J. Dean, I. Okeme, D. Sapsford^{*}

School of Engineering, Cardiff University, Queens Buildings, The Parade, Cardiff CF243AA, United Kingdom of Great Britain and Northern Ireland

ARTICLE INFO

Keywords:

Metal treatment
Mine
Zinc
Pollution
HDS
Water
Precipitation

ABSTRACT

This study reports on the novel application of sodium carbonate dosing specifically for the semi-passive precipitation of Zn from circum-neutral mine water and demonstrates the use of Na₂CO₃ as a readily available, safe to handle reagent which can precipitate Zn at pH within environmental quality standards. >95 % Zn removal was achieved for each mine drainage investigated, requiring differing dosages of Na₂CO₃ with residual Zn concentrations <1 mgL⁻¹. Geochemical modelling and precipitate characterisation using XRD, SEM-EDS, TGA and full chemical digest suggests that the precipitate predominantly comprised of hydrozincite. Laboratory trials demonstrated that (i) adding the precipitant dropwise could reduce the sludge volume by *circa* 50 %, and (ii) That following a laboratory protocol for simulating type II High Density Sludge (HDS) process resulted in substantial decreases in sludge volumes compared to single pass sludge, with 5.3 mL per litre mine water treated compared to 55.3 mL per litre for conventional single pass treatment after 25 cycles. Such reductions in sludge volume are a very advantageous outcome for practical applications. Particle size distribution and zeta potential determinations on the resultant HDS sludge suggest that increased heterogenous precipitation and decrease in zeta potential are important in the formation of HDS when using sodium carbonate to treat zinc-bearing waters. This work demonstrates that sodium carbonate is an efficacious reagent for semi-passive treatment of zinc-bearing mine waters and as such could find widescale application to this pressing global problem.

1. Introduction

Mining influenced waters are a major global contributor to poor freshwater quality. Current and legacy mines result in many thousands of kilometres of impacted rivers world-wide [1]. Estimates of the total number of abandoned mines globally are not available, however it is likely to be in the millions [2]. In England and Wales alone >2100 km of rivers fail to achieve European Union Water Framework Directive standards (WFD), 2000/60/EU. Even when excluding coal mine drainage (a major pollution source in England and Wales), 226 water bodies are impacted by pollution from non-coal mines with a further 226 probably impacted [3,4]. The damaging effects of acid mine drainage (AMD) on receiving water bodies is widely acknowledged but circum-neutral mine water, also known as neutral mine drainage (CNMD) can also cause widespread water quality failures. This latter type of drainage can occur where pyrite is absent, or of subordinate abundance to metal sulphides that do not produce protons upon oxidation (*e.g.* sphalerite or galena) [5] and is prevalent in many parts of the world, including the UK. CNMD can also arise when AMD is subsequently neutralized by the

host lithology (or after initial mine water treatment *e.g.* with limestone). In the UK, the majority (>80 %) of confirmed abandoned metal mine discharges are circumneutral [6] and although AMD is typically more environmentally hazardous, CNMD poses significant harm to receiving water bodies and surrounding areas due to the mobilisation and transport of ecotoxic metals/metalloids (*e.g.* Zn, Cd, Pb, Cu, Ni, As) which remain soluble at circumneutral pH [7–9].

The common occurrence of Zn as a constituent of CNMD is often due to the presence of sphalerite (ZnS) and related minerals in ore and gangue. Sphalerite undergoes either acid or oxidative dissolution (Eqs. (1)–(2)), the dissolved Zn can then be transported into surrounding water bodies causing water quality failures and Zn contamination levels above environmental quality standards (10.9 µgL⁻¹ dissolved, bioavailable Zn Water Framework Directive standard [10]).



^{*} Corresponding authors.

E-mail addresses: kennedyj10@cardiff.ac.uk (J. Kennedy), sapsforddj@cardiff.ac.uk (D. Sapsford).

Zn is an important micronutrient for both animals [11] and plants [12]. However, at elevated concentrations Zn can have severe adverse effects to aquatic life, reducing the abundance and diversity of biota and having a damaging effect on ecosystem functions such as productivity and nutrient cycling [13]. Due to its environmental persistence, mobility, toxicity and bioaccumulation in aquatic organisms, Zn is classed as one of the most hazardous metal/metalloid pollutants along with Cr, Ni, Cu, Cd, Pb, Hg and As [14]. Zn is the most prevalent metal contaminant in metal mine discharge in England and Wales, where a low end estimate of *circa* 170 t of Zn has been reported to discharge into water bodies each year [3].

Mine water treatment technologies have been developed to combat the problem of mine water pollution. Treatment methods are often categorized as either passive or active. Passive treatment refers to a technology where there is no supply of power or reagents whereas active treatment involves powered operations and the continual addition of chemical reagents [15]. Passive technologies developed specifically for the removal of Zn from CNMD include using flow-through bioreactors and low-cost reactive or sorbent media [16–22]. The disadvantages of these approaches generally relate to the typically lower area or volumetric removal rates in passive systems compared to active treatment systems, which translates to requirements for relatively large surface area or volume for treating a given flow and concentration which may not be feasible at a given site. Active treatment processes specifically for Zn removal from CNMD include carbonate coprecipitation [23] and ZnS precipitation [24]. These technologies however require higher levels of operational complexity than passive methods. Semi-passive methods of mine water treatment [25–30] seek to blend active/passive methods to combine or balance the benefits and disbenefits of both options. The work described herein is considered in the context of semi-passive treatment where envisaged treatment method might utilise unmanned dosing stations, (possibly controlled remotely and powered by renewable energy such as solar); periodic reagent deliveries and operational/maintenance visits.

The current work presents an examination of the efficacy of sodium carbonate (Na_2CO_3) dosing as a semi-passive approach to treating Zn bearing CNMD. Na_2CO_3 has been shown to be an effective, relatively cheap reagent for the precipitation of metals from waste effluents [31,32] offering high Zn removal efficiencies [33] by raising the pH to precipitate Zn within environmentally permissible levels [34] (*circa* 7.8–8.5) but has not been applied specifically to Zn-bearing mine waters. One of the key advantages of using Na_2CO_3 as a base for mine water treatment (particularly in lone person operations in remote locations where the implications of accidents could be worse) is its lower chemical hazard compared to other caustic chemicals. The hazard statement for Na_2CO_3 is H319: causes serious eye irritation [35]. The hazards associated with using other alkali reagents such as NaOH [36], CaO [37] and $\text{Ca}(\text{OH})_2$ [38] include H314: skin corrosion, H318: serious eye damage and H335: respiratory irritation. Therefore, the use of Na_2CO_3 poses a substantially lower risk to the operator than other alkali reagents which is one of the key considerations for remote mine water treatment systems. Other than our own works [39,40] we can find no literature on the application of Na_2CO_3 dosing specifically for zinc-bearing circumneutral mine drainage, despite the well-known decrease in solubility of zinc carbonates such as smithsonite and hydrozincite at moderately alkaline pH.

Alkali dosing/precipitation is often the first step in active treatment and additional unit operation(s) are typically required for subsequent solid/liquid separation. Coagulants and/or flocculants are often used to improve separation in gravity-based liquid/solid separation, which can add operational costs (reagent and time). The residual precipitated sludge can also be voluminous with low density, have low solids content (*circa* 1 % w/v) [41] and have a high resistance to filtration, making them difficult to dewater. Therefore, increasing solids settling velocity and volume is advantageous, cutting cost implications for sludge storage, dewatering and disposal. The High Density Sludge (HDS) process is

a well-established method to reduce the density of sludge generated through an increase in solids content per unit volume. The basic principle involves recirculating the sludge to contact raw mine water and/or alkali which leads to sludge “densification”, increased settling velocity, sludge volume and dewaterability [42,43]. Zn has been shown to readily form HDS in the presence of Fe using NaOH as the alkali [44,45] however there are no studies on the formation of HDS from a Zn-rich effluent where Fe nor flocculant is present and using Na_2CO_3 as the alkaline reagent.

The primary aims of this study were two-fold. The first was to assess the effectiveness of Na_2CO_3 dosing on zinc removal and determine residual zinc concentrations after dosing for a range of real circumneutral Zn bearing mine waters and to physicochemically characterize the precipitates. The second (pertinent to the development of a semi-passive approach to mine water treatment using Na_2CO_3) was to investigate the influence of dosing strategy and sludge recirculation on particle size distribution and settling properties using synthetic and real circumneutral Zn-bearing mine water.

2. Materials and methods

2.1. Study sites

Zn-rich mine waters from a range of locations around Wales (UK) were selected based on locations of known Zn-bearing mine water discharges [46]. A range of mine water chemistries were selected, (see Table 1). The majority were CNMD but these were supplemented by mine water from two acidic sites to assess the wider applicability of Na_2CO_3 dosing. The primary study site selected for further study into the process chemistry and engineering was a circumneutral Zn-bearing mine water, sourced from Abbey Consols; an abandoned Zn and Pb mine located in Ceredigion, Wales, UK which was operated between 1848 and 1909. Drainage from the site is a target for remediation [47] because the mine water is the primary contributory source of Zn to the river Teifi contributing to exceedances of WFD WQS. 100 L of mine water was collected from the discharge adit. The mine water was tested for changes in chemistry upon storage which confirmed minimal changes in the mine water chemistry over two weeks (Table S1), the time period in which the water was used for further experiments.

2.2. Batch experiments

2.2.1. Field tests

On-site jar tests using a range of Na_2CO_3 dosages (*circa* 1–6500 mgL^{-1}) were conducted to assess the effectiveness of Na_2CO_3 dosing for the removal Zn and other metals. The experiments were conducted on site as mine water can be unstable due to Fe oxidation/ CO_2 degassing [48,49]. The doses were based on multiples of the Zn molar concentration in each mine water, where the Zn concentration values were obtained from historical data from the NRW archives. Stock Na_2CO_3 dosing solutions were prepared at 1, 10 and 50 gL^{-1} . 100 mL of unfiltered mine water was decanted into HDPE sample bottles. Samples were then dosed with <5 mL of 1, 10, or 50 gL^{-1} Na_2CO_3 stock solution. In addition to carbonate-dosed solutions, one control (unamended raw mine water), one pH control (mine water dosed with NaOH to pH 8.5–9.5), and one deionized water blank was included. Reaction vessels were loosely covered, and periodically gently swirled, for two hours. pH was immediately measured for the raw (unamended) samples and measured after 2 h for the dosed samples. The treated and untreated samples (20 mL) were filtered using 0.2 μm syringe filters and preserved using 0.1 mL 10 % nitric acid and metal concentrations were measured using Inductively Coupled Plasma Mass Spectrometry ICP-MS (Thermo X-Series 2). Ion chromatography was performed on untreated filtered samples (0.2 μm syringe filters) using a Metrohm 761 compact ICD.

Table 1

Mine water chemistry and conditions for >95 % Zn removal efficiency for circumneutral mine waters including two acidic drainages.

Site	Initial dissolved Zn ^b mgL ⁻¹	Initial pH	Alkalinity ^c as CaCO ₃ mgL ⁻¹	Dissolved Fe mgL ⁻¹	Dissolved Ca mgL ⁻¹	Flow ^d Ls ⁻¹	Temp °C	Na ₂ CO ₃ dose mgL ⁻¹	Molar ratio Zn: Na ₂ CO ₃	Residual dissolved Zn ^b mgL ⁻¹	Final pH	Final alkalinity as CaCO ₃ mgL ⁻¹
Frongoch adit	17.92	7.26	25	<0.2	16.9	17	19.7	224	7.7	0.145	9.39	89
Nant y Mwyn	14.79	5.74	76	1.19	36.1	51	18.2	874	37	0.876	9.95	828
Cwmystwyth Pughs	31.84	6.40	0	0.51	26.4	10	12.7	189	3.7	0.084	8.82	188
Cwmystwyth Gills	8.689	5.92	0	<0.1	4.20	3	11.9	367	26	0.066	10.43	NA
Pengwern	4.429	6.29	36	<0.1	13.6	15	10.3	32	4.5	0.084	7.84	63
Pannau Adit	5.695	7.21	70	<0.1	31.0	3	12.1	34	3.5	0.313	9.01	95
Abbey Consols ^a	16.77	6.58	24	<0.1	NA	3	17.3	82	3.5	0.023	9.00	NA
Frongoch Att. Pond	201.6	3.88	0	0.60	18.7	6	27.9	749	2.3	0.086	8.85	32
Cwm Rheidol 9	53.90	2.99	0	148	89.3	1	27.3	6001	78	0.624	10.47	NA

^a Abbey Consols dosing experiments performed in laboratory.

^b 20 mL sample, filtered at 0.2 µm into 0.1 ml 10 % HNO₃.

^c Alkalinity was measured on site using Hach Digital Titrator, method number 8203.

^d Contains Natural Resources Wales information © Natural Resources Wales and database right. All rights reserved.

2.2.2. Laboratory tests

Synthetic mine water (SMW) Zn solutions were made using zinc sulphate heptahydrate (ZnSO₄·7H₂O) from Sigma Aldrich, ≥99.0 % in deionized water (18.2 MΩ-cm) and Na₂CO₃ dosing solution was prepared using Na₂CO₃ VWR, ≥99.0 % in deionized water. All tests were performed in triplicate to obtain mean values.

Laboratory jar tests using different Na₂CO₃ doses were conducted on synthetic and Abbey Consols mine water. For each dosing experiment performed in the laboratory, 900 mL of synthetic mine water or Abbey Consols mine water was added to a 1000 mL borosilicate glass beaker, stirred using an overhead stirrer and pH recorded using a Mettler Toledo Seven Multi Expert Pro 15 M pH meter (calibrated before each experiment). 100 mL of Na₂CO₃ dosing solution was added and stirred at 200 rpm for 2 min, then allowed to settle for 30 min. Na₂CO₃ dosages were based on molar ratios of Zn:Na₂CO₃ from 1:0.5 to 1:5 (12–117 mgL⁻¹). Final pH was recorded and 20 mL samples of treated synthetic or real mine water were slowly withdrawn at a depth of 2 cm using a syringe and filtered at 0.2 µm into 0.1 ml 10 % HNO₃ for dissolved Zn analysis. For total Zn analysis, samples were pipetted directly into 0.1 ml 10 % HNO₃. Metal concentrations were determined using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (Perkin Elmer, Avio 220 Max).

The effect of the rate of addition of Na₂CO₃ dosing solution was investigated using jar tests. 900 mL of SMW (200 mgL⁻¹ Zn) was added to a 1000 mL borosilicate glass beaker and the beaker was stirred at 200 rpm using an over stirrer. 100 mL of Na₂CO₃ (1000 mgL⁻¹) was added either by instantaneous or dropwise addition (dropping funnel set to add 2 mL min⁻¹ of Na₂CO₃ solution). Both regimes were stirred for 50 min followed by 30 min settling before recording pH and taking samples of treated synthetic mine water for ICP-OES analysis as described above for laboratory dosing experiments.

A simulation of a “Type II” HDS process [50] was conducted at laboratory scale on a batch basis where “Type II” refers to a HDS process where the cycled sludge is mixed with the fresh mine water prior to alkali addition. The procedure was modified from the method proposed by Bosman for Type I HDS [51] 900 mL SMW (200 mgL⁻¹ Zn) was added to a 1 L borosilicate glass beaker and 100 mL Na₂CO₃ solution was added (1000 mgL⁻¹). The vessel was stirred at 200 rpm for 2 min using an overhead stirrer and the contents transferred to a 2 L measuring cylinder. The suspension was allowed to settle, and the time taken for sludge to settle/sludge volume was recorded. The supernatant was carefully decanted off and added to a fresh solution of SMW (200 ppm Zn) and stirred for 10 min before the next dose of Na₂CO₃ solution was added.

This method was repeated 25 times with subsamples of sludge (*circa* 2 mL) and supernatant taken at regular intervals. The pH was recorded before and after each dose of Na₂CO₃ was added. The procedure was performed in triplicate to obtain a mean sludge volume with standard deviation. Sludge samples were only taken from the first run to eliminate the possibility that sampling was causing the reduction in sludge volume.

2.3. Physicochemical and mineralogical characterisation of precipitates

The particle size distribution of precipitates was measured using a Beckman Coulter LS-13-320-XR Particle Sizer and zeta potential measurements were performed using a Malvern Zetasizer Nano series Nano-2. Particle size measurements and zeta potential were measured directly on precipitate from laboratory dosing experiments, suspended in the treated mine water or SMW. To prepare samples for XRD (X-ray diffraction spectroscopy), TGA (thermogravimetric analysis) and Scanning Electron Microscopy (SEM) precipitate samples were dried at 40 °C for 24 h, allowed to cool in a desiccator and finely ground with a pestle and mortar prior to analysis. Mineralogical characterisation was performed using XRD (Seimens diffractometer D5000) using the following operating parameters; wavelength 1.54 Å, voltage 40 kV, current 30 mA, scan range 10–80, step length 0.05°, 0.5° min⁻¹, radiation source Cu Kα. TGA was conducted on a Perkin Elmer Pyris instrument. Samples of between 0.20 and 0.25 mg were heated from 40 °C to 900 °C (5 °C min⁻¹) under flowing air (20 mL min⁻¹). Elemental composition of the precipitate was determined *via* microwave acid digestion followed by ICP-OES analysis on the digested sample. A sample of precipitate (0.1 g, dried at 40 °C for 24 h) was weighed into a 40 mL digestion vessel and HNO₃ (3 mL, 68–70 %, Fisher analytical reagent grade for analysis) and HCl (3 mL, 37 %, Fisher analytical grade) was added and digested in an Ethos Easy microwave at 180 °C for 45 min. The contents of the vessel were transferred to a volumetric flask and made up to 50 mL using deionized water and analysed using ICP-OES.

Micro and bulk mineralogical analysis was performed using a Tescan Maia3 Field Emission Gun Scanning Electron Microscope (FEG-SEM) for Abbey Consols and synthetic samples and a Zeiss Sigma Field Emission Scanning Electron Microscope (FE-SEM) with Energy Dispersive (X-ray) Spectroscopy (EDS) for all other samples. The field trial precipitates were analysed at a voltage of 30 keV, whereas the synthetic and Abbey Consols samples were analysed at 15 keV due to charging effect. For samples analysed on the Tescan Maia3 FEG-SEM, an Energy Dispersive X-ray detector (X-EDS, Oxford Instruments X max 80NT SDD) was used

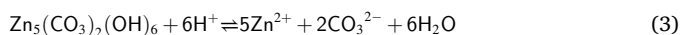
for elemental analysis and mapping with Aztec software. The elemental composition was determined using an EDAX™ Octane Plus high-resolution EDS system and data analysis undertaken using the associated EDAX (AMETEK Inc.) TEAM™ software for the Zeiss FE-SEM.

3. Results and discussion

3.1. Field campaign Zn-rich mine waters

Recorded pH for the mine waters varied between pH 2.99 and pH 7.34, alkalinity ranged from 0 to 235 mgL⁻¹ and Fe concentrations varied from 0.1 to 148 mgL⁻¹. The Na₂CO₃ dose required to achieve >95 % Zn removal is presented in Table 1 with additional dosing data in Table S2. Na₂CO₃ is an effective reagent for the precipitation of Zn; all drainages achieved >95 % Zn removal with varied Na₂CO₃ dosage. It is important to note that not all discharges would require this level of removal as it is the residual Zn which will impact the receiving water body. For example, it was reported that at least 70 % Zn removal would be required at the Abbey Consols site [40] for the river Teifi to meet WFD standards. For all sites the residual Zn concentration was below 1 mgL⁻¹, which would be likely to meet WFD standards of 10.9 µgL⁻¹, upon combining with the receiving water body, providing that the mine discharge flow to be <1 % of the river flow. When utilising alkaline reagents, the pH of the final treated water should (in many regulatory jurisdictions) be ≤pH 9 and may require acid addition to meet this pH reduction. Semi-passive treatment approaches seek to minimise reagent addition. Importantly, data in Table 1 shows that for the majority of sites, Na₂CO₃ dosing can precipitate >95 % Zn within the typical pH limits environmental standard (≤ pH 9), thus negating the need for additional reagent addition for pH reduction. For the three mine waters above the acceptable pH limit, further process optimisation would be required to obtain the optimum dose where Zn removed but there is not an overshoot of the pH. This is a limitation of the study where the final dose was excessive to ensure total Zn removal. Although Zn was the highest concentration contaminant in the mine drainages, other contaminants were present at lower concentrations. The removal efficiency for other metals was measured and is shown in Table 2. Reasonable removal rates (Table 2) were achieved for Cd, Pb, Mn, Ni and Cu however poor removal rates were observed for As. This is unsurprising as oxyanionic forms of As are soluble at alkaline pH [52].

Known Zn carbonate precipitates include smithsonite, hydrozincite and zinc hydroxide, which can further dehydrate to zincite [53]. Geochemical modelling was performed using PHREEQC software [54] (version 3.7.3.15968, MINTEQA.v4 database) to identify minerals predicted to be oversaturated (and this able to precipitate under defined conditions). The database was updated to include hydrozincite using logK value 9.1 and the equilibrium shown in Eq. (3) [55].



For all mine waters modelled, hydrozincite was found to be consistently oversaturated, along with smithsonite, zincite and zinc hydroxide.

Table 2

Initial metal concentration and removal efficiency using Na₂CO₃ dosing at dose required for >95 % Zn removal.

Site	As (dissolved)		Cd (dissolved)		Cu (dissolved)		Mn (dissolved)		Ni (dissolved)		Pb (dissolved)	
	µgL ⁻¹	%	µgL ⁻¹	%	µgL ⁻¹	%	µgL ⁻¹	%	µgL ⁻¹	%	µgL ⁻¹	%
Frongoch Adit	0.11	0	29.5	99	6.50	76	21.1	91	19.0	69	532	88
Nant y Mwyn	ND	NA	32.9	>99	10.3	95	ND	NA	41.1	99	ND	NA
Cwmystwyth Pugh's	2.19	58	33.7	98	7.96	94	475	81	36.3	83	339	96
Cwmystwyth Gill's	0.19	74	23.1	>99	9.41	86	6.31	92	8.43	94	600.	97
Pengwern	1.09	70	25.6	80	ND	NA	27.4	19	4.09	11	15.2	85
Pannau	ND	NA	10.5	99	ND	NA	ND	NA	4.48	78	ND	NA
Frongoch attenuation pond	1.63	10	300	99	56.5	99	3415	96	176	100	5973	99
Cwm Rheidol- No.9	0.57	82	132	>99	90.9	99	4320	>99	1944	>99	25.2	>99

ND – under detection limit NA – not applicable.

For drainages with elevated levels of Fe, ferrihydrite, hematite and goethite were also found to be oversaturated. Fig. 1 displays data for the residual Zn against final pH for the tested mine waters. The hydrozincite solubility curve was (derived using PHREEQC) and compared with the residual Zn concentrations. For all sites residual Zn concentrations after precipitation are close to, or below those expected from hydrozincite solubility. Residual concentrations lower than hydrozincite solubility could be attributable to solubility differences from the logK value used in the modelling [56] or the presence of precipitating Fe minerals which are known to exert influence on zinc solubility in the circumneutral pH range through sorption and coprecipitation [57]. This is notable in mine water where there are elevated levels of Fe such as Cwm Rheidol 9 (148 mgL⁻¹ Fe). XRD analysis identified 2-line ferrihydrite in Cwm Rheidol 9 precipitate along with hydrozincite (Fig. S4). Zn co-precipitation with ferrihydrite has been reported to occur at pH ≥5 [58] which is consistent with the pH at which Zn starts to precipitate for Cwm Rheidol 9.

Although the presence of Fe in the mine waters can lower the pH at which Zn precipitation occurs, it also increases acidity and consequently the dose of Na₂CO₃ required to adjust the pH and precipitate the Zn. The dose required at Cwm Rheidol 9 to remove the Zn was 6001 mgL⁻¹ which equates to a molar ratio (Zn:Na₂CO₃) of 1:78; significantly higher than the stoichiometric dose or the dose required for other drainages which generally ratios of circa 1:3.5 (Table 1). The higher Na₂CO₃ dose required is attributable to the high mineral and metal acidity for this mine water.

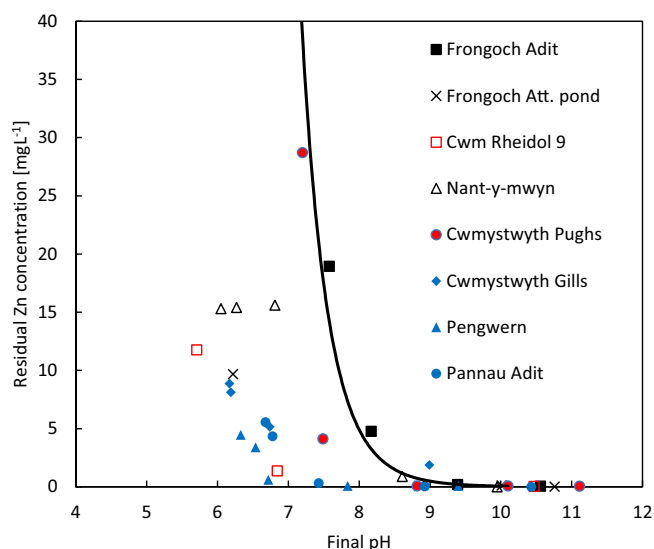


Fig. 1. Residual Zn concentration at the final pH after Na₂CO₃ dosing. Line represents hydrozincite solubility curve (logK 9.1 [55]). Red symbols signify elevated Fe levels and blue symbols indicate mine water <15 °C at time of on site dosing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

XRD analyses demonstrated that most of the precipitates were X-ray amorphous however, the XRD pattern for Frongoch Attenuation Pond (Fig. S3) showed peaks corresponding to hydrozincite with additional peaks indicative of goethite and rhodochrosite. TGA of Abbey Consols precipitate (Fig. 4b) shows a mass loss of 19 % occurring at 170–270 °C which suggests that the major mineral present is hydrozincite [53,59]. However, the theoretical mass loss should be 25 %, indicating that only 76 % of the precipitate is hydrozincite. Real mine waters often contain clays and other minerals [60] which do not decompose below 700 °C possibly accounting for reduced mass loss. In addition, PHREEQCi modelling identified zincite (ZnO) as an oversaturated phase which would also not decompose further. SEM-EDS was conducted on Abbey Consols, Frongoch Attenuation Pond and Nant y Mwyn (Fig. S2 and Table S4). The overall wt% of Zn was between 38.82 and 47.66 %, with low levels of other metals and C and O as other main elements. Mapping shows Zn evenly dispersed throughout the precipitates. SEM-EDS analysis and total digest of Abbey Consols precipitate gives a Zn wt% of 44.7 and 48.9 %, respectively. This is consistent with the TGA finding that 76 % of the precipitate is hydrozincite and the remaining material is clay.

Sludge produced in treatment systems can require costly disposal to landfill depending on the metals/metalloids it contains and the local landfill waste acceptability criteria [61]. It is, therefore, highly beneficial if the sludge can be reused/recycled or if the metal value can be recovered. The high proportion of Zn present in the precipitates may be promising for Zn recovery. The effectiveness of Na₂CO₃ dosing for all mine waters investigated is promising for its widespread application which would result in the generation of a substantial amount of Zn rich sludge with high potential value. Based on Zn removal rates and Zn load in the mine discharges, it can be estimated that *circa* 87,000 kg would be removed per year. As the same Na₂CO₃ treatment scheme would be applied at multiple sites, which would use the same reagents and produce similar sludges, it is therefore likely that only one post treatment sludge processing/Zn recovery facility would be required; easing the logistics of sludge management. The Zn is present in form that is amenable to Zn recovery processes (characterisation indicates mainly hydrozincite) [62,63] indicating the potential of the precipitate as a valuable Zn resource which may contribute to offsetting remediation costs.

The field campaign of dosing experiments has demonstrated that Na₂CO₃ is an effective Zn precipitation reagent which can be used successfully on a range of mine water chemistries. During the jar tests it was visually noted that the precipitates were fine and slow to settle, improving settling behavior is thus an important aspect to optimise mine water treatability.

3.2. Impact of reagent dosing on precipitate properties

Mine water from the Abbey Consols was used to study how precipitate properties were affected by varying the Na₂CO₃ dosing strategy. For practical purposes, a synthetic equivalent was used for some laboratory experiments due to volume of precipitate/mine water required. The synthetic analogue responded to Na₂CO₃ dosing in the same manner as real Abbey Consols mine water (Fig. S1a and S1b, Table S3) and was therefore deemed a reasonable proxy for the real mine water.

3.2.1. Dosing regimes (immediate vs dropwise reagent addition)

The rate at which the precipitant is added is known to have to the ability to influence precipitation mechanisms [64]. This is achieved by controlling the level of supersaturation of the system which influences nucleation, growth and aggregation rates [65]. Typically, a high level of supersaturation, leads to a faster rate of homogeneous nucleation resulting in many small particles, which can then aggregate. Lower levels of supersaturation typically encourage heterogeneous nucleation on existing particles, facilitating particle growth. Jar tests were conducted using instantaneous and dropwise addition of Na₂CO₃ (82 mgL⁻¹) into synthetic mine water.

No difference in settling velocity was observed, however particle size and sludge volume were reduced by almost 50 % when Na₂CO₃ solution was added dropwise (Table 3). This is counter to the trend expected from crystallization theory where high supersaturation levels (from instantaneous addition) typically result in a higher degree of homogenous nucleation. However, particle size analysis of the particles from the two regimes show a higher distribution of particle sizes (6–100 μm with a standard deviation of 16.3 μm) from instantaneous addition of Na₂CO₃ solution, compared to 2–60 μm with a standard deviation of 8.3 μm. This may reveal the importance of aggregation and/or pH effects on the final particle size distribution produced [66]. Zhou et al. reported a higher rate of heterogeneous precipitation and less homogeneous nucleation with dropwise addition [64] which supports the present findings. Dropwise addition of Na₂CO₃ yielded particles with similar zeta potential; -21 mV compared to -28 mV for the instantaneously dosed precipitate, indicating similar stability in solution. Zeta potentials above 30 mV are generally regarded as stable suspensions [67] thus in the measured range of zeta potential the settling rate is likely to be slow.

3.2.2. High density sludge (HDS)

The densification of sludge using the HDS process is a well-known method of reducing sludge volume, increasing settling velocity and sludge dewaterability characteristics of sludges formed from metal hydroxide precipitation reactions [42–44] however there is no journal literature on the formation HDS using Na₂CO₃ as the precipitant. The HDS processes involve cycling previously produced sludges into fresh precipitation reactions. A bench scale Type II HDS method was trialled where the sludge was mixed with fresh mine water before introducing the Na₂CO₃ dose, note that no coagulant or flocculant was added.

Fig. 2 shows that the Zn/Na₂CO₃ system readily forms HDS the sludge volume does not increase linearly with repeated cycles. Densification appears to begin after cycle 4 where the measured sludge volume starts to deviate from the projected total accumulated sludge volume (no HDS). After cycle 10, the sludge volume increase ceases (definition of HDS formation) yielding a recycle ratio of 10:1. Recycle ratios are typically between 10:1 and 30:1 meaning 10–30 kg of solids are recycled for each kg of solids formed in the process [68]. After 25 cycles the sludge volume has decreased from the projected accumulated total by a factor of 10. The projected volume of sludge per litre of mine water treated for the HDS was found to be *circa* 5.3 mL/L *versus* *circa* 55.5 mL/L for 25 cycles of conventional single pass sludge. A similar bench scale HDS trial was conducted by Mackie et al. [69] using a Zn rich AMD, Ca(OH)₂ and polymer flocculant. HDS was achieved after 20 cycles with 33 mL/L of sludge formed per litre of mine water treated and the final dry solids content was 2.39 %. Although a direct comparison cannot be made, Na₂CO₃ dosing achieved a higher dry solids content (4.11 %) with a lower sludge volume per litre of mine water treated without the use of flocculant. The settling velocity was found to increase with HDS cycles, settling velocity increasing to 2.48 mhr⁻¹ at cycle 25 from 1.18 mhr⁻¹ at cycle 1.

The mechanism of HDS formation is not fully understood however

Table 3

Zn removal efficiency of Na₂CO₃ using 82 mgL⁻¹ (molar ratio 1:3.5), zeta potential and sludge volume and particle size using different dosing regimes.

Dosing regime	Instantaneous ^a	Dropwise ^a
Zn removal (dissolved)	>99.9 % (0.02)	>99.9 % (0.02)
Zn removal % (total)	96.5 % (1.22)	99.8 % (0.42)
Final pH	9.09 (0.01)	9.29 (0.13)
Zeta Potential [mV]	-28 (4.97)	-21 (4.91)
Sludge volume ^b [mL]	56 (7.07)	35 (2.36)
Mean Particle size (range) [μm]	42 (6–100)	18 (2–60)
Settling Velocity [mhr ⁻¹]	1.2 (0.10)	1.2 (0.05)

^a Values given as mean with standard deviation in brackets (with the exception of particles size which gives the range instead of standard deviation).

^b Sludge volume measured after 30 min settling time.

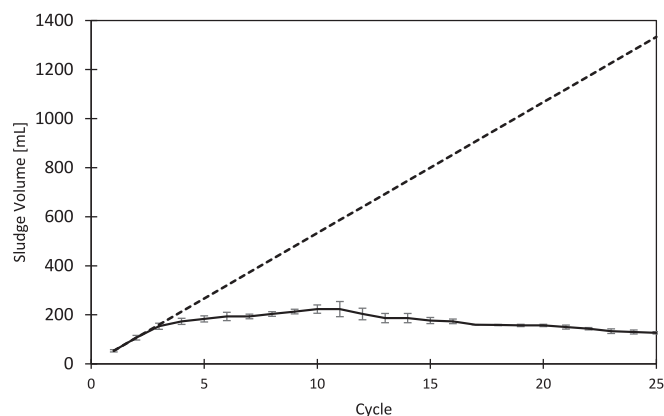


Fig. 2. Sludge volume after each reaction cycle using type II HDS lab method with error bars (standard deviation). Dotted line is extrapolation of single pass sludge representing projected total sludge volume in the absence of any sludge densification.

theories centre around slower precipitation due to lower pH of slurry, recycled sludge acting as seeds for heterogeneous nucleation, ageing/dewatering effects and compression effects due to increased ionic concentrations [51,70,71]. To assess whether compression effects were occurring, the zeta potential of the sludge was measured at regular cycles throughout the HDS process (Table 4). A decrease in the absolute value of the zeta potential was observed as the reaction cycles progress. After 1 cycle the zeta potential of the suspension was -28 mV, decreasing to 5.6 mV after 25 cycles. This supports the theory that the increase in ionic concentration from cations in the slurry (e.g. Zn^{2+} , Na^{2+}), decreases the zeta potential which then increases the compression of the double layer and allows the precipitates to pack more closely. It is important to note that the pH of the treated sludge samples analysed was constant (9.28–9.78) and therefore zeta potential measured can be considered to be the absolute zeta potential of the particles with no effect from change in pH.

FE-SEM was conducted on the single pass sludge (Fig. 3a) and the HDS sludge after 25 cycles (Fig. 3b) to further characterize the precipitate and identify any morphological differences between the sludges. Both SEM images show typical hydrozincite morphology; 2-dimensional platelets flattened on (100) [55,72] which are cemented together as larger particles. However, the size of the platelets on the single pass sludge is smaller than the size of platelets on the HDS SEM image. Several platelet length measurements were taken, averaging 0.13 μm for single pass and 0.57 μm for the HDS, indicating more long-range order in the HDS precipitate. This was supported by XRD analysis (Fig. 4a); the XRD pattern of single pass sludge shows highly amorphous material whereas the XRD of the HDS has defined peaks corresponding to hydrozincite (Fig. S5). This, coupled with an increase in particle size (from 36 to 53 μm) indicates that more heterogenous precipitation is occurring, with the recycled sludge acting a seed particles. TGA conducted on single pass and HDS shows a total mass loss of circa 25 %, corresponding to the theoretical mass of seen with hydrozincite. For both the single pass and HDS sludge the major mass loss occurs between

170 and 270 °C corresponding to the loss of chemically bound H_2O and CO_2 in hydrozincite (circa 25 %) however the single pass sludge also sees a 3 % mass loss at 150–160 °C attributed to the loss of surface bound water. The presence of this mass loss seen only in the TGA for the single pass sludge supports the theory that there is less surface bound water in HDS allowing densification of the particles. This is supported by the high dry solids content in the HDS compared with the single pass sludge (4.11 % compared to 0.36 %).

3.3. Implications for semi-passive treatment of zinc-bearing CNMD

The authors anticipate that Na_2CO_3 could find application in semi-passive treatment of zinc-bearing mine waters achieved with no on-site operators, an automatic dosing system and passive separation process e.g. gravity separation. The only operational input would be replenishing of dosing reagents and sludge management and some general maintenance. The data presented in this paper demonstrates the efficacy of Na_2CO_3 as a reagent for dosing of Zn-bearing mine waters. Na_2CO_3 could be used to reduce dissolved concentrations of zinc (and other metals) and enabling waterbodies to achieve environmental quality standards (EQS) whilst staying within environmentally acceptable effluent pH, eliminating the need for an additional pH correction process (reducing reagent and operational costs). It should be noted that some of the sites investigated where the resulting pH was above 9 would need further process optimization with regards to dosage or it may be that Na_2CO_3 dosing is not feasible for this particular mine water. The authors acknowledge that the addition on Na_2CO_3 could increase the salinity in the receiving body however the increased salinity of the effluent would likely be diluted substantially by the receiving water body and currently, there is no EQS for salinity in the UK. Nevertheless, in other locations where salinity can pose a significant problem and there are strictly water quality standards for salinity, an investigation into the effect of the added salinity on the receiving body would need to be completed as part of the trial process. Dosing of Na_2CO_3 can be achieved in a straightforward way using Na_2CO_3 solution which can be made up on site or tankered in. In remote locations it may be more feasible for the dosing solution to be made up on site. For temperate climates it is recommended that 5 % w/v solution is used [73]. This is to prevent Na_2CO_3 crystallizing in the dosing tank when temperatures. It may also be possible to use treated mine water to make up the dosing solution, reducing transport costs. Simple systems involving semi-passive dosing of Na_2CO_3 in briquette form have already been used in the USA for AMD control [74]. Further work would be required to investigate whether dosing solid Na_2CO_3 is as effective for Zn (and other metal) removal. When compared to other alkali reagents such as NaOH, $Ca(OH)_2$ and CaO, Na_2CO_3 has less severe safety hazard rating meaning it is lower risk reagent for lone operators. Na_2CO_3 is readily available as it is commonly used in potable water treatment facilities and for pH correction [73]. The combination of these factors means that Na_2CO_3 dosing can lend itself effectively and practically for the treatment of Zn bearing mine waters.

However, whilst the Na_2CO_3 can readily remove dissolved Zn (and other target contaminant metals), the resultant precipitate sludge has a high water content (>99 %) and volume which may require extended dewatering times. In addition, the particles within the sludge were found

Table 4

Volume, settling velocity and zeta potential of sludge from dosing synthetic mine water with Na_2CO_3 after different numbers of HDS cycles (initial Zn concentration 200 mgL^{-1}).

HDS cycle	Final zinc [mgL^{-1}]	Zinc removal [%]	Final pH	Volume per L mine water treated [mLL^{-1}]	Zeta potential [mV]	Mean particle size (range) [μm]	Settling velocity [mhr^{-1}]	Dry solids content [%]
1	0.174	>99.9	9.28	55.5	-28.4	36 (5–98)	1.18	0.36
5	0.189	>99.9	9.65	37.7	-25.8		1.30	0.55
10	0.333	>99.9	9.62	22.2	-16.2		1.36	1.00
20			9.78	8.3	4.4		1.37	3.06
25	0.078	>99.9	9.54	5.3	5.6	53 (1–200)	2.48	4.11

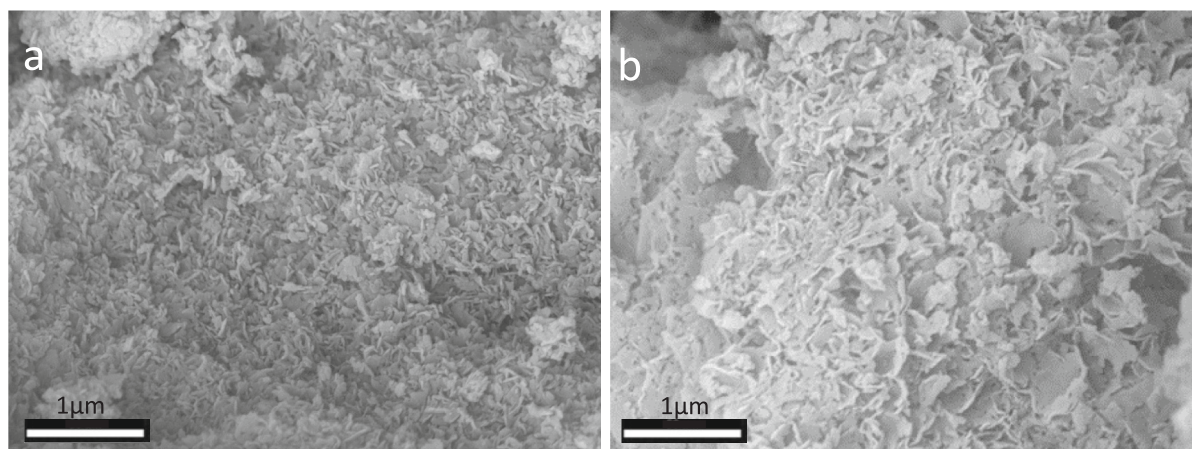


Fig. 3. SEM of a) single pass sludge and b) HDS sludge at 83000× magnification.

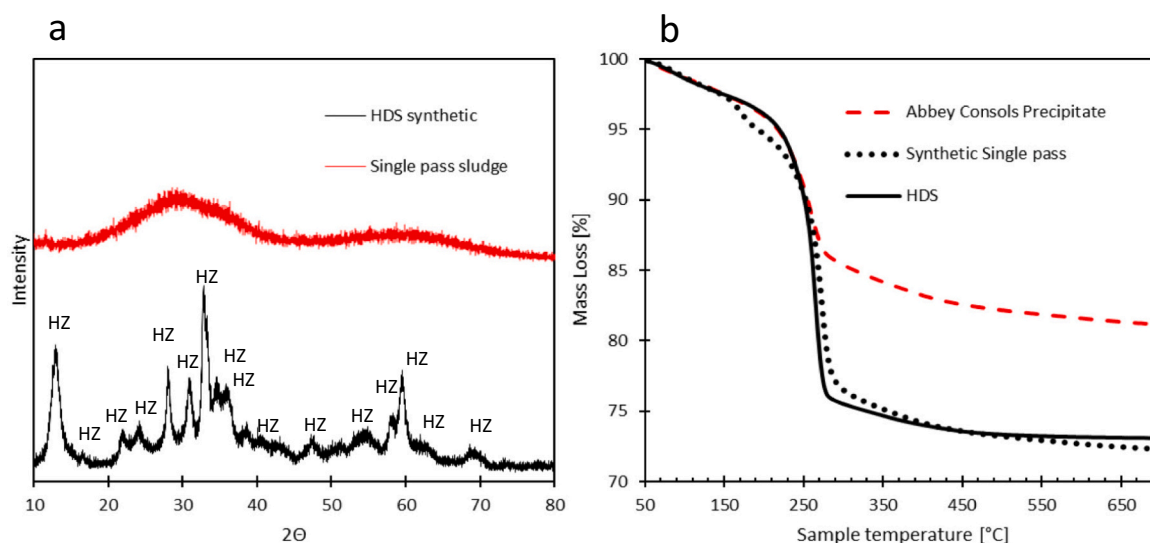


Fig. 4. a) XRD pattern of synthetic single pass sludge and HDS sludge (HZ denotes peak corresponding to hydrozincite (ref 00-019-1458) Fig. S5) b) TGA of Synthetic Single Pass sludge, HDS and Abbey Consols sludge.

to be relatively small (2–100 μm) and stable (zeta potential of -24 – 28 mV), likely to make solid liquid separation difficult. The work has established some strategies which should be explored further. Laboratory trials have shown that by adding the Na_2CO_3 precipitant dropwise, the sludge volume can be reduced (Section 3.2.1). For semi-passive dosing mine water treatment systems where sludge volumes are high, dropwise addition could offer a simple technique that can be employed passively e.g. multiple dosing points across precipitation tank/pond, with potential to reduce the cost and operational implications of high sludge volumes. Contacting the precipitated solids with the mine water during dosing may encourage HDS formation. Whilst this has not been tested passively, existing passive mine water technologies that encourage contact with precipitates include Vertical Flow Reactors [75,76]. Similarly, configurations from wastewater treatment such as sludge bed clarification may also be considered. Here, we have shown that HDS can readily be formed from the $\text{Zn}/\text{Na}_2\text{CO}_3$ system proposed without the use of flocculant or other reagents. The sludge had better settling characteristics, with higher dry solids content, showing potential for rapid settling velocities and better dewatering. Incorporation of a process to encourage HDS would result in large reductions in sludge volume.

Na_2CO_3 dosing has been shown to be effective on a range of mine

water chemistries and is therefore a promising option for widescale implementation. If considering just the mine drainages studied in this paper a total of 3387 million litres of mine water would be treated each year, removing *circa* 87,000 kg Zn (Table 5). The sludge produced has a high in Zn content (*circa* 45 % Zn dry solids) which suggests that the sludge could be used as a potential Zn resource which might partially offset operational costs and retain Zn in a circular economy and prevent pollution. The main contributor to the operational cost is the cost of reagents as the scheme is to be operated semi-passively. From these experiments it can be estimated that the reagent costs to treat mine water with sodium carbonate ranges from $\pounds 0.01$ – 0.18 per m^3 . Although a direct comparison is not possible, other study and reports have shown these values are comparable to other water treatment dosed schemes [77] but do not require additional OPEX costs such as energy or operating staff.

4. Conclusions

Na_2CO_3 dosing was successfully applied to a range of Zn-rich circum-neutral mine waters, achieving a final Zn concentration of <1 mgL^{-1} and a final pH <9 . Precipitates were characterized using elemental digest, XRD, SEM-EDS and TGA indicating that the precipitate was

Table 5

Estimated Zn removal, Zn value^a and reagent costs^b per year for Na₂CO₃ dosing of studied mine drainages.

	Estimated mass of Zn removed per year	Potential Zn value recovered	Cost sodium carbonate per year	Cost sodium carbonate per m ³ mine water treated
	kg yr ⁻¹	£ yr ⁻¹	£ yr ⁻¹	£ m ⁻³
Frongoch Adit	9607	24,950	23,987	0.05
Nant y Mwyn	23,787	61,776	504,291	0.18
Cwmystwyth Pugh's	9639	25,034	22,817	0.07
Cwmystwyth Gill's	868	2254	7478	0.07
Pengwern	2053	5332	15,150	0.02
Pannau	539	1399	1293	0.01
Abbey Consols	1026	2663	2038	0.02
Frongoch att. pond	38,146	99,065	80,606	0.13
Cwm Rheidol No. 9	989	2569	2579	0.14
Total	86,655	225,042	660,238	0.69

^a Based on value of pure Zn metal accessed at [LME.com](https://www.lme.com) October 2022.

^b Based on Na₂CO₃ cost of £350/t.

hydrozincite. This was corroborated by PHREEQCi modelling. The high Zn content in the precipitates and the fact that all sites would produce a precipitate with similar elemental composition is promising for the potential recovery of Zn metal. Sludge volume and settling characteristics were shown to be improved by varying process conditions. Dropwise addition of precipitate yielded lower sludge volumes with smaller particles; a promising simple approach to sludge reduction that easily be implemented semi-passively. HDS was shown to readily form using Na₂CO₃ dosing and cycling the Zn sludge without flocculant; reducing the sludge volume substantially and improving the settling velocity. Characterisation of the HDS sludge was conducted to improve understanding of the mechanism of HDS formation in this system. The findings of the characterisation provided evidence for increased heterogenous precipitation, increased compressibility of particle suspension and increased agglomeration due to decrease in zeta potential. The study demonstrates the efficacy and suitability of Na₂CO₃ dosing for semi-passive treatment of Zn, offering high removal rates for a range of mine water chemistries.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Devin Sapsford reports financial support was provided by Cardiff University. Devin Sapsford reports a relationship with Cardiff University that includes: employment.

Data availability

Data will be made available on request.

Acknowledgements

The authors would like to thank Peter Stanley, Tom Williams and Louise Siddorn (Natural Resources Wales) for permitted access to sample mine water and for advice in site selection. Thanks to Dr. Andrew Barnes and Dr. Mark Roberts (Geochemic Ltd) for ICP-MS and IC analysis. This work was funded by the Welsh European Funding Office Smart Expertise under the METAL-SolVER project (#82347).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2023.103764>.

[org/10.1016/j.jwpe.2023.103764](https://doi.org/10.1016/j.jwpe.2023.103764).

References

- [1] D.B. Johnson, K.B. Hallberg, Acid mine drainage remediation options: a review, *Sci. Total Environ.* 338 (1–2 SPEC. ISS) (2005) 3–14, <https://doi.org/10.1016/j.scitotenv.2004.09.002>.
- [2] C. Wolkersdorfer, Water management at abandoned flooded underground mines: fundamentals, tracer tests, modelling, water treatment, 2008, <https://doi.org/10.1007/978-3-540-77331-3> no. January 2008.
- [3] A.P. Jarvis, W.M. Mayes, Prioritisation of abandoned non-coal mine impacts on the environment: the national picture, 2015, <https://doi.org/10.13140/2.1.2024.1440>.
- [4] W.M. Mayes, D. Johnston, H.A.B. Potter, A.P. Jarvis, A national strategy for identification, prioritisation and management of pollution from abandoned non-coal mine sites in England and Wales. I. Methodology development and initial results, *Sci. Total Environ.* 407 (21) (2009) 5435–5447, <https://doi.org/10.1016/j.scitotenv.2009.06.019>.
- [5] M.B.J. Lindsay, M.C. Moncur, J.G. Bain, J.L. Jambor, C.J. Ptacek, D.W. Blowes, Geochemical and mineralogical aspects of sulfide mine tailings, *Appl. Geochem.* 57 (2015) 157–177, <https://doi.org/10.1016/j.apgeochem.2015.01.009>.
- [6] A.P. Jarvis, C.J. Gandy, N.D. Gray, Mitigation of pollution from abandoned metal mines. Part 1: review of passive treatment technologies for metal mine drainage remediation, 2012.
- [7] D.K. Nordstrom, Mine waters: acidic to circumneutral, *Elements* 7 (6) (2011) 393–398, <https://doi.org/10.2113/gselements.7.6.393>.
- [8] P.H. Mascheleyn, R.D. Delaune, W.H. Patrick Jr., Arsenic and selenium chemistry as affected by sediment redox potential and pH, *J. Environ. Qual.* 20 (3) (1991) 522–527, <https://doi.org/10.2134/jeq1991.00472425002000030004x>.
- [9] A.W. Mann, R.L. Deutscher, Solution geochemistry of lead and zinc in water containing carbonate, sulphate and chloride ions, *Chem. Geol.* 29 (1980) 293–311.
- [10] Water Framework Directive, The Water Framework Directive (Standards and Classification) Directions (England and Wales), no. 2, in: *Water Framework Directive vol. 40*, 2015, p. 66 [Online]. Available: https://www.legislation.gov.uk/ukxi/2015/1623/pdfs/ukxi02_20151623_en_auto.pdf.
- [11] R.B. Saper, R. Rash, Zinc: an essential micronutrient, *Am. Fam. Physician* 79 (9) (2009) 768–772.
- [12] A. Sharma, B. Patni, D. Shankhdhar, S.C. Shankhdhar, Zinc - an indispensable micronutrient, *Physiol. Mol. Biol. Plants* 19 (1) (2013) 11–20, <https://doi.org/10.1007/s12298-012-0139-1>.
- [13] P.L. Younger, C. Wolkersdorfer, Mining impacts on the fresh water environment: technical and managerial guidelines for catchment-focused remediation, in: P. L. Younger, C. Wolkersdorfer (Eds.), *Mine Water Environ. vol. Suppl. Iss.*, 2004, pp. 2–80.
- [14] H. Ali, E. Khan, I. Ilahi, Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation, *J. Chem.* 2019 (Cd) (2019), <https://doi.org/10.1155/2019/6730305>.
- [15] D. Trumm, Selection of active and passive treatment systems for AMD—flow charts for New Zealand conditions, *N. Z. J. Geol. Geophys.* 53 (2–3) (2010) 195–210, <https://doi.org/10.1080/00288306.2010.500715>.
- [16] A.B. Sobolewski, A.C. Riese, T.J. Moore, A.R. Brown, Passive treatment of circumneutral mine drainage from the St. Louis Mine Tunnel, Rico, CO: part 3—horizontal wetlands treatment train pilot study, *Mine Water Environ.* (2022), 0123456789, <https://doi.org/10.1007/s10230-022-00856-9>.
- [17] W.M. Mayes, H.A.B. Potter, A.P. Jarvis, Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide, *J. Hazard. Mater.* 162 (1) (2009) 512–520, <https://doi.org/10.1016/j.jhazmat.2008.05.078>.
- [18] R. Warrender, et al., Field trials of low-cost reactive media for the passive treatment of circum-neutral metal mine drainage in mid-Wales, UK, *Mine Water Environ.* 30 (2) (2011) 82–89, <https://doi.org/10.1007/s10230-011-0150-8>.
- [19] C.J. Gandy, A.P. Jarvis, 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 Environ.* 31 (2) (2012) 82–91, <https://doi.org/10.1007/s10230-012-0177-5>.
- [20] I.L. Calugaru, C.M. Neculita, T. Genty, G.J. Zagury, Removal and recovery of Ni and Zn from contaminated neutral drainage by thermally activated dolomite and hydrothermally activated wood ash, *Water Air Soil Pollut.* 231 (5) (2020), <https://doi.org/10.1007/s11270-020-04600-3>.
- [21] P.T. Abongwa, E.A. Atekwana, J.O. Puckette, Hydrogeochemical investigation of metal evolution in circum-neutral mine discharge, *Water Air Soil Pollut.* 231 (4) (2020), <https://doi.org/10.1007/s11270-020-04542-w>.
- [22] C.A. Nuttall, P.L. Younger, Zinc removal from hard, circum-neutral mine waters using a novel closed bed limestone reactor, *Water Res.* 34 (4) (2000) 1262–1268.
- [23] P.L. Sibrell, M.A. Chambers, A.L. Deaguero, T.R. Wildeman, D.J. Reisman, An innovative carbonate coprecipitation process for the removal of zinc and manganese from mining impacted waters, *Environ. Eng. Sci.* 24 (7) (2007) 881–895, <https://doi.org/10.1089/ees.2006.0126>.
- [24] R. Holanda, D.B. Johnson, Removal of zinc from circum-neutral pH mine-impacted waters using a novel 'Hybrid' low pH sulfidogenic bioreactor, *Front. Environ. Sci.* 8 (March) (2020) 1–10, <https://doi.org/10.3389/fenvs.2020.00022>.
- [25] G. Nielsen, et al., Semi-passive in-situ pilot scale bioreactor successfully removed sulfate and metals from mine impacted water under subarctic climatic conditions, *Water Res.* 140 (2018) 268–279, <https://doi.org/10.1016/j.watres.2018.04.035>.

- [26] C. Diaz-Vanegas, et al., Performance of semi-passive systems for the biological treatment of high-as acid mine drainage: results from a year of monitoring at the Carnoules mine (Southern France), *Mine Water Environ.* 41 (3) (2022) 679–694, <https://doi.org/10.1007/s10230-022-00885-4>.
- [27] M. Rezahebbashi, S.A. Baldwin, Core sulphate-reducing microorganisms in metal-removing semi-passive biochemical reactors and the co-occurrence of methanogens, *Microorganisms* 6 (1) (2018), <https://doi.org/10.3390/microorganisms6010016>.
- [28] K. Lounate, L. Coudert, T. Genty, G. Mercier, J.F. Blais, Performance of a semi-passive sulfate-reducing bioreactor for acid mine drainage treatment and prediction of environmental behavior of post-treatment residues, *Mine Water Environ.* 39 (4) (2020) 769–784, <https://doi.org/10.1007/s10230-020-00702-w>.
- [29] M. Kalin, Passive mine water treatment: the correct approach? *Ecol. Eng.* 22 (4–5) (2004) 299–304, <https://doi.org/10.1016/j.ecoleng.2004.06.008>.
- [30] J.C. Jacob, M. Save, Y. Menard, Treatment of mine drainage with significant topographical constraints: case study of the Bodenec Site (France), *Mine Water Environ.* 37 (4) (2018) 839–848, <https://doi.org/10.1007/s10230-018-0522-4>.
- [31] H. Junuzovic, S. Begic, A. Selimovic, A. Dozic, R. Cvrk, M. Ahmetovi, Efficiency of carbonate precipitation and removal of copper and nickel ions from their monocomponent and two-component aqueous solutions, *Int.J.Res.Appl.Sci. Biotechnol.* 06 (06) (2019) 11–15, <https://doi.org/10.31033/ijrass.6.6.3>.
- [32] W. Zhang, C.Y. Cheng, Y. Pranolo, Investigation of methods for removal and recovery of manganese in hydrometallurgical processes, *Hydrometallurgy* 101 (1–2) (2010) 58–63, <https://doi.org/10.1016/j.hydromet.2009.11.018>.
- [33] Q. Chen, Y. Yao, X. Li, J. Lu, J. Zhou, Z. Huang, Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates, *J. Water Process Eng.* 26 (October) (2018) 289–300, <https://doi.org/10.1016/j.jwpe.2018.11.003>.
- [34] P. Xanthopoulos, S. Agatzini-Leonardou, P. Oustadakis, P.E. Tsakiridis, Zinc recovery from purified electric arc furnace dust leach liquors by chemical precipitation, *J. Environ. Chem. Eng.* 5 (4) (2017) 3550–3559, <https://doi.org/10.1016/j.jece.2017.07.023>.
- [35] Sigma-Aldrich, “Sodium Carbonate,” Material Safety Data Sheet. <https://www.sigmaaldrich.com/GB/en/sds/sial/s7795>, 2021 accessed Oct. 31, 2022.
- [36] Sigma-Aldrich, “Sodium Hydroxide,” Material Safety Data Sheet. <https://www.sigmaaldrich.com/GB/en/sds/sigma/s2770>, 2021 accessed Oct. 31, 2022.
- [37] Sigma-Aldrich, “Calcium Oxide,” Material Safety Data Sheet, no. 2, <https://www.sigmaaldrich.com/GB/en/sds/sigald/248568>, 2021 [Online]. Available: https://www.legislation.gov.uk/uk/si/2015/1623/pdfs/ukstd_20151623_en_auto.pdf.
- [38] Sigma-Aldrich, “Calcium Hydroxide,” Material Safety Data Sheet. <https://www.sigmaaldrich.com/GB/en/sds/sial/c7887>, 2021 accessed Oct. 31, 2022.
- [39] J. Dean, B. Alkhazraji, D.J. Sapsford, Alternative reagents for the treatment of Pb-Zn mine drainage in Wales, in: *IMWA 2021 – “Mine Water Management for Future Generations, 2021*, pp. 109–114.
- [40] T. Williams, J. Dent, T. Eckhardt, M. Riding, D. Sapsford, *Treatability trials to remove zinc from Abbey Consols Mine Water, Wales, UK*, in: 14th IMWA Congress, 2020, pp. 225–230.
- [41] B.H. Sukati, P.C. de Jager, J.G. Annandale, The hazardous status of high density sludge from acid mine drainage neutralization, *Sustainability* 10 (4185) (2018), <https://doi.org/10.3390/su10114185>.
- [42] R. Coulton, C. Bullen, J. Dolan, C. Hallett, J. Wright, C. Marsden, *Wheal Jane mine water active treatment plant - design, construction and operation*, *Land Contam. Reclam.* 11 (2) (2003) 245–252, <https://doi.org/10.2462/09670513.821>.
- [43] D.J. Bosman, Improved densification of sludge from neutralized acid mine drainage, *J.S.Afr.Inst.Min.Metall.* 74 (9) (1974) 340–348.
- [44] P. Suvio, D. Sapsford, A.J. Griffiths, K. Williams, J.D. Davies, S. Maynard, High density sludge process applied to metal-containing effluent, *WIT Trans. Ecol. Environ.* 135 (2010) 289–299, <https://doi.org/10.2495/WP100251>.
- [45] R.H. Coulton, C.J. Bullen, C.R. Williams, K.P. Williams, The formation of high density sludge from mine waters with low iron concentrations, in: *Mine Water, 2004*, pp. 25–30 [Online]. Available: https://www.imwa.info/docs/imwa_2004/IMWA2004_04_Coulton.pdf.
- [46] *Natural Resources Wales, Metal Mine Strategy for Wales*, Environment Agency Wales, 2002.
- [47] The Coal Authority, *A review of priority metal mine sites in Wales - options appraisal for metal mine water remediation*, 2016.
- [48] J.N. Geroni, D.J. Sapsford, K. Florence, Degassing CO₂ from mine water: implications for treatment of circumneutral drainage, in: *Mine Water-Managing the Challenges 1*, 2011, pp. 319–324.
- [49] H.L. Barnes, S.B. Romberger, Chemical aspects of acid mine drainage, *J. Water Pollut. Control Fed.* 40 (3) (Aug. 1968) 371–384 [Online]. Available: <http://www.jstor.org/stable/25036044>.
- [50] G.B. Keefer, W.A. Sack, Sludge recycle and reuse in acid mine drainage treatment, *J. Water Pollut. Control Fed.* 55 (3) (1983) 278–284.
- [51] D.J. Bosman, Lime treatment of acid mine water and associated solids/liquid separation, *Water Sci. Technol.* 15 (2) (1983) 71–84.
- [52] G. Cornelis, C.A. Johnson, T. van Gerven, C. Vandecasteele, Leaching mechanisms of oxyanionic metalloids and metal species in alkaline solid wastes: a review, *Appl. Geochem.* 23 (5) (2008) 955–976, <https://doi.org/10.1016/j.apgeochem.2008.02.001>.
- [53] K.A. Baltpurvins, R.C. Burns, G.A. Lawrance, A.D. Stuart, N. Laboratories, P.O. Box, Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater, *Environ. Sci. Technol.* 30 (5) (1996) 1493–1499.
- [54] D.L. Parkhurst, C.A.J. Appelo, User’s Guide to PHREEQC (Version 2): A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, And Inverse Geochemical Calculations, 1999, <https://doi.org/10.3133/wri994259>.
- [55] D. Medas, G. de Giudici, F. Podda, C. Meneghini, Apparent energy of hydrated biominer surface and apparent solubility constant: an investigation of hydrozincite, *Geochim. Cosmochim. Acta* 140 (2014) 349–364, <https://doi.org/10.1016/j.gca.2014.05.019>.
- [56] P. Schindler, M. Reinert, H. Gamsjäger, Zur Thermodynamik der Metallcarbonate 3. Mitteilung [1]. Löslichkeitskonstanten und Freie Bildungsenthalpien von ZnCO₃ und Zn₅(OH)₆(CO₃)₂ bei 25°, *Helv. Chim. Acta* 52 (8) (1969) 2327–2332, <https://doi.org/10.1002/hlca.19690520814>.
- [57] D. Sapsford, M. Santonastaso, P. Thorn, S. Kershaw, Conversion of coal mine drainage ochre to water treatment reagent: production, characterisation and application for P and Zn removal, *J. Environ. Manag.* 160 (2015) 7–15, <https://doi.org/10.1016/j.jenvman.2015.06.004>.
- [58] S. Martin, et al., A high-resolution TEM-AEM, pH titration, and modeling study of Zn²⁺ coprecipitation with ferrihydrite, *Geochim. Cosmochim. Acta* 69 (6) (2005) 1543–1553, <https://doi.org/10.1016/j.gca.2004.08.032>.
- [59] M.C. Hales, R.L. Frost, Thermal analysis of smithsonite and hydrozincite, *J. Therm. Anal. Calorim.* 91 (3) (2008) 855–860, <https://doi.org/10.1007/s10973-007-8571-0>.
- [60] N. Kumari, C. Mohan, Basics of clay minerals and their characteristic properties, in: G.M. do Nascimento (Ed.), *Clay And Clay Minerals*, IntechOpen, Rijeka, 2021, <https://doi.org/10.5772/intechopen.97672>.
- [61] D.M. McDonald, J.A. Webb, J. Taylor, Chemical stability of acid rock drainage treatment sludge and implications for sludge management, *Environ. Sci. Technol.* 40 (6) (2006) 1984–1990, <https://doi.org/10.1021/es0515194>.
- [62] S. Kursunoglu, N. Kursunoglu, S. Hussaini, M. Kaya, Selection of an appropriate acid type for the recovery of zinc from a flotation tailing by the analytic hierarchy process, *J. Clean. Prod.* 283 (2021), 124659, <https://doi.org/10.1016/j.jclepro.2020.124659>.
- [63] F. Soltani, H. Darabi, R. Aram, M. Ghadiri, Leaching and solvent extraction purification of zinc from Mehdiabad complex oxide ore, *Sci. Rep.* 11 (1) (2021) 1–11, <https://doi.org/10.1038/s41598-021-81141-7>.
- [64] P. Zhou, J.C. Huang, A.W.F. Li, S. Wei, Heavy metal removal from wastewater in fluidized bed reactor, *Water Res.* 33 (8) (1999), [https://doi.org/10.1016/S0043-1354\(98\)00376-5](https://doi.org/10.1016/S0043-1354(98)00376-5).
- [65] O. Söhnle, J. Garside, *Precipitation, in: Basic Principles And Industrial Applications*, Butterworth-Heinemann, Oxford, England, 1992.
- [66] T.P. Mokone, R.P. van Hille, A.E. Lewis, Effect of solution chemistry on particle characteristics during metal sulfide precipitation, *J. Colloid Interface Sci.* 351 (1) (2010) 10–18, <https://doi.org/10.1016/j.jcis.2010.06.027>.
- [67] M.H. Hidayat Chai, N. Amir, N. Yahya, I.M. Saaid, Characterization and colloidal stability of surface modified zinc oxide nanoparticle, *J. Phys. Conf. Ser.* 1123 (1) (2018), <https://doi.org/10.1088/1742-6596/1123/1/012007>.
- [68] B.C. Aube, J.M. Zinck, Comparison of AMD treatment processes and their impact on sludge characteristics, in: *Proceedings for Sudbury '99, Mining And the Environment II*, 1999, pp. 261–270.
- [69] A.L. Mackie, M.E. Walsh, Bench-scale comparison of conventional and high rate clarification treatment processes for acid mine drainage, *Water Qual. Res. J. Can.* 50 (3) (2015) 279–286, <https://doi.org/10.2166/wqrj.2015.048>.
- [70] P.d. Kostenbader, G.F. Haines, High density sludge treats acid mine water, in: *Coal Age*, 1970.
- [71] W. Yong Gan, C. Selomulya, G. Tapsell, R. Amal, Densification of iron(III) sludge in neutralization, *Int. J. Miner. Process.* 76 (3) (2005) 149–162, <https://doi.org/10.1016/j.minpro.2004.12.008>.
- [72] R. Wahab, S.G. Ansari, Y.S. Kim, M.A. Dar, H.S. Shin, Synthesis and characterization of hydrozincite and its conversion into zinc oxide nanoparticles, *J. Alloys Compd.* 461 (1–2) (2008) 66–71, <https://doi.org/10.1016/j.jallcom.2007.07.029>.
- [73] M.J. Brandt, K.M. Johnson, A.J. Elphinston, D.D. Ratnayaka, Chapter 12 - chemical storage, dosing and control, in: M.J. Brandt, K.M. Johnson, A.J. Elphinston, D. D. Ratnayaka (Eds.), *Twort’s Water Supply (Seventh Edition)*, Seventh ed., Butterworth-Heinemann, Boston, 2017, pp. 513–552, <https://doi.org/10.1016/B978-0-08-100025-0.00012-0>.
- [74] J. Skousen, K. Politan, T. Hilton, A. Meek, Acid mine drainage treatment systems: chemicals and costs, *Green Lands* 20 (4) (1990) 31–37.
- [75] D.J. Sapsford, K.P. Williams, Sizing criteria for a low footprint passive mine water treatment system, *Water Res.* 43 (2) (2009) 423–432, <https://doi.org/10.1016/j.watres.2008.10.043>.
- [76] I. Blanco, et al., International trials of vertical flow reactors for coal mine water treatment, *Mine Water Environ.* 37 (1) (2018) 4–17, <https://doi.org/10.1007/s10230-017-0491-z>.
- [77] S. Bhojwani, K. Topolski, R. Mukherjee, D. Sengupta, M.M. El-Halwagi, Technology review and data analysis for cost assessment of water treatment systems, *Sci. Total Environ.* 651 (Feb. 2019) 2749–2761, <https://doi.org/10.1016/j.scitotenv.2018.09.363>.