

## Field trial of an ion exchange based metal removal technology in the treatment of mine waters

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### Abstract

A pilot scale field trial for a novel metal removal technology in the treatment of mine waters was performed using mine water from White Tip, part of the former Snailbeach lead mine in Shropshire, United Kingdom (UK). The water is circum-neutral pH and contains elevated zinc (Zn), cadmium (Cd) and lead (Pb). The novel treatment process is based on ion exchange (IE) using a bespoke mesh in a rotating disc reactor. Effects of process parameters such as regeneration of IE mesh, residence time (RT) and rotation speed (RS) of the discs were investigated.

Treatment performance of the system was consistent for the removal of Zn and Pb whereas for Cd it was more variable. The order of removal efficiencies was Pb (75.04%) > Zn (64.18%) > Cd (22.37%). Accordingly, 4.15 kg of Zn, 5.22 g of Pb and 5.55 g Cd were removed from 131.46 m<sup>3</sup> of mine water in 170 days. Removals of metals / metalloids such as iron (Fe), aluminium (Al), manganese (Mn), copper (Cu), barium (Ba), arsenic (As), nickel (Ni), boron (B), chromium (Cr) and small amounts of sodium (Na), potassium (K) and strontium (Sr) and non-metallic water quality parameters such as acidity, suspended solids (SS), alkalinity and small amounts of nitrate (NO<sub>3</sub>-N) and total anions were also observed. The system generated a small amount of ammoniacal nitrogen (NH<sub>3</sub>-N), sulfate (SO<sub>4</sub>-S) and hardness. An average rise of pH by ~0.5 unit in treated water was observed. Performance of the treatment system was not significantly affected by the regeneration of the mesh and RS of the discs. The treatment process was not affected by the temperature variations in the range of 0.7°C to 20°C. Maximum removals of metals were observed when RT ≥ 1.33 hours.

Key words: mine water, metals, regeneration, removal efficiency, ion exchange

### Introduction

Water is undoubtedly the single greatest pathway and receptor for mining-related contamination. Oxidative dissolution of rock or waste soil and rock heaps when exposed to water and oxygen results in the generation of contaminated mine water (Brown et al. 2002, Mayes et al. 2009). Mine drainages continue to be a significant environmental problem for decades after cessation of mining (Younger et al. 2002). Mine water can contain elevated concentrations of toxic contaminants such as Zn, Cd and Pb. Although some of the metals, e.g. Zn, in the mine water are essential trace elements for plants and mammals (Förstner & Wittman 1981), they can be toxic to aquatic ecosystems even at relatively low concentrations, which is reflected in the Water Framework Directive (2000/60/EC) and in the European Union (EU) environmental quality standards (EQS). For example, the maximum acceptable concentration of Zn for salmonid fish is 8-125 ppb in the hardness (as ppm CaCO<sub>3</sub>) dependent EQS. Thus, treatment of mine waters is an important aspect of managing the environmental impacts associated with mining (Sengupta 1993).

Literature shows a wide range of active and passive remedial options available for the treatment of mine waters contaminated with metals such as Zn, Cd and Pb. Selection of appropriate treatment methods not only depends on mine water chemistry but also on economic factors. Active and passive treatment systems are established for acidic mine waters enriched with Zn, Cd and Pb where these metals are prevalent as Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>. However, in circum-neutral mine waters, which occur in many metal mine discharges in the UK (Jarvis et al. 2007), Zn is present predominantly as carbonate (CO<sub>3</sub><sup>2-</sup>) complex ([ZnCO<sub>3</sub>]<sup>3-</sup>), which will not readily react to form non-carbonate solids. In such cases, aerobic passive

treatment systems have not always been successful. Conventional alkali dosing active treatment systems could be used but are often not cost effective.

Ion Exchange (IE) is a well-established water treatment process. Dissolved salts and metals can be extracted from wastewater by passing through beds of IE resins. Traditional IE uses resins in the form of small (0.5-1mm) diameter beads to achieve a high surface area. These beads can be very susceptible to fouling by particulate matter (e.g. soil or Fe precipitates), which need to be removed prior to treatment. Therefore, this study investigated an innovative technology in the treatment of mine waters heavily contaminated with Zn, Cd and Pb. This technology removes metals using IE fibrous mesh supported on rotating discs in a novel patented reactor.

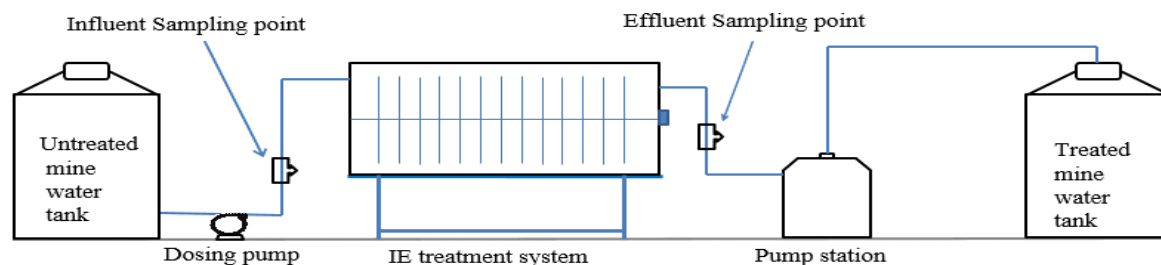
The mesh contains a mixture of cationic, anionic and chelating IE sites supported by a cross-linked polymer matrix. Cation exchange (CE) sites on the mesh are predominantly weak carboxylic (-COOH) acid groups, and chelating oxime (-NOH) groups. The precise CE capacity of the -COOH groups depends on the pH of the influent water. Below pH 6 the majority of the -COOH groups are un-ionised and do not pick up cations very well. However, the chelating -NOH groups are unaffected and are very selective for complexing with heavy metal cations. The mesh also contains amine (-NH<sub>2</sub>) groups, which protonate below pH 6 and act as anion exchangers removing sulfate and CO<sub>3</sub><sup>2-</sup> groups.

This technology has been trialled in the UK at pilot scale to investigate its effectiveness in the treatment of mine waters. The mine water used in this trial was drainage water infiltrating through the White Tip site, part of the former Snailbeach lead mine at Minsterley, Shropshire, UK. The mine water has a circum-neutral pH containing a mixture of metal cations (mainly Zn- ~ 50 ppm, Cd- ~ 0.14 ppm and Pb- ~ 0.06 ppm). Removal of these metals was investigated in this trial. Ratios of Zn-total to Zn-dissolved (Zn-T/Zn-D=1.05), Cd-total to Cd-dissolved (Cd-T/Cd-D=1.09) and Pb-total to Pb-dissolved (Pb-T/Pb-D=4.75) suggest that Zn and Cd are mostly present in dissolved form whereas ~80% of Pb is present in an insoluble form. This trial aimed to assess reactor performance in the field, in particular considering the effect of regeneration of the mesh, RT, and the RS of the discs.

## Methods

### Treatment set up

Figure 1 shows a schematic diagram of pilot scale set up for the treatment of mine water. A 60 litre (L) reactor housed thirty discs covered with 11 kg of IE mesh. The discs were fixed onto a shaft connected to a motor (90 W), equipped with an inverter enabling the RS to be varied, via a timing belt. A dosing pump was connected to a 5 m<sup>3</sup> influent storage tank and to the inlet side of the reactor. The outlet of the reactor was connected to a collection pump station comprising a tank (300 L) and a submersible pump with a float switch. The inlet sampling tap was located between reactor influent and the dosing pump whereas the effluent sampling tap was located between reactor outlet and the collection pump station. Data loggers comprising pH and temperature probes were positioned inside the reactor at both inlet and outlet ends and readings were taken every two minutes.



**Figure 1** Schematic diagram showing mine water treatment set up

Mine water was tankered ~weekly from Minsterley and was stored in the influent storage tank. Mine water was pumped by the dosing pump into the reactor, where the rotating discs ensured effective mixing and contact with the novel IE mesh with a desired typical RT of approximately 2 hours. The flow rate was determined by measuring the volume exiting the reactor per unit time. The effect of RT on metal removal efficiency was investigated. Treated effluent was fed by gravity from the reactor outlet into the pump station which was pumped into an effluent storage tank for disposal.

This trial was commissioned on 5<sup>th</sup> November 2014 and terminated on 17<sup>th</sup> August 2015. During this trial, the treatment process was stopped twice due to logistical and access constraints: for two weeks from Day 44 and for fourteen weeks from Day 125. Therefore, this trial was run for a total of 170 days. Regeneration of the mesh was performed on Day 79. Accordingly, the system was run for a total of 79 and 91 days before and after the regeneration process respectively.

*Sampling, sample handling and analyses*

Un-acidified influent and effluent samples were collected five days per week for internal analysis at De Montfort University (DMU). Samples were stored and transported in cool dark conditions. Samples were allowed to settle and the supernatants of the samples were taken for analysis. Double distilled water was used in all analyses when dilution was required. AAnalyst™ 200 Flame Atomic Absorption Spectrophotometer (F-AAS) (Perkin Elmer Instruments, LLC) was used to analyse the water samples and was calibrated using AA standard solutions supplied by Fisher Scientific. Weekly influent and effluent samples were collected for independent analysis by an UK Accreditation Service (UKAS) accredited external commercial laboratory.

*Regeneration of the mesh*

The regeneration of the IE mesh was performed on Day 79 using hydrochloric acid (HCl) and sodium hydroxide (NaOH). Desorption of metals and other contaminants was performed in three batches. In each batch, the reactor was filled with 50 L of 5% HCl and left to react with the mesh for approximately 30 minutes. After acid wash, the mesh was normalized to pH 8.5 with NaOH solution, ensuring the pH never exceeded 12.5. A total of 205 moles of HCl and 19 moles of NaOH were used during the regeneration process.

**Results**

*Removal of water quality parameters*

A very important aspect of this treatment technology in terms of longevity is the regeneration of the IE mesh. Regenerated process was trialled on Day 79 (note annotation on Figure 2). Thus, the performance of the system is presented in three forms; overall, before and after the regeneration process. Table 1 presents a detailed breakdown of system performance before and after the regeneration process.

*Table 1 Summary of the pilot scale trial of mine water based on internal analyses.*

<b>Parameters</b>	<b>Overall</b>	<b>Before Regen- eration</b>	<b>After Regenera- tion</b>
Treatment duration (days)	170	79	91
Average flow rate (L/hr)	32.22	28.18	35.60
Volume of treated mine water (m <sup>3</sup> )	131.46	53.43	77.75
Average influent/effluent Zn concentration (ppm)	49.14/17.23	53.43/15.51	45.36/18.73
Average Zn removal efficiency (%)	64.18	70.40	58.78
Amount of Zn exposed/removed (kg)	6.46/4.15	2.85/2.01	3.53/2.07
Average influent/effluent Cd concentration (ppb)	188.8/146.2	248.5/192.3	137.1/106.2
Average Cd removal efficiency (%)	22.37	21.54	23.08
Amount of Cd exposed/removed (g)	24.82/5.55	13.28/2.86	10.66/2.46
Average influent/effluent Pb concentration (ppb)	53.00/14.00	42.30/8.70	62.00/18.50
Average Pb removal efficiency (%)	75.04	77.73	72.75
Amount of Pb exposed/removed (g)	6.95/5.22	2.26/1.76	4.82/3.51

The treatment system consistently removed Zn and Pb from the mine water. Removal of Cd was more variable. Figure 2 shows the internal results for influent and effluent concentrations of Zn, Cd and Pb

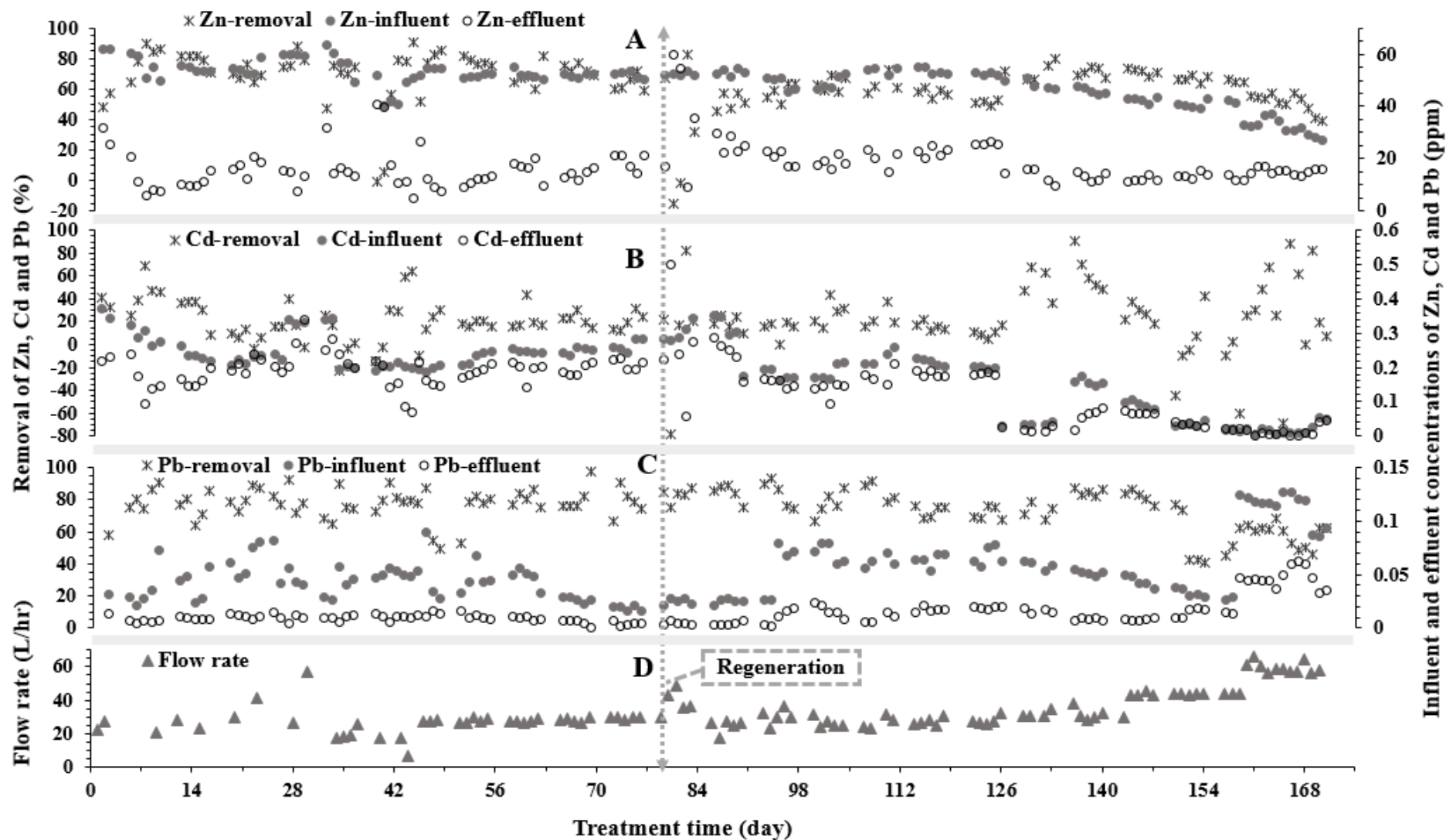
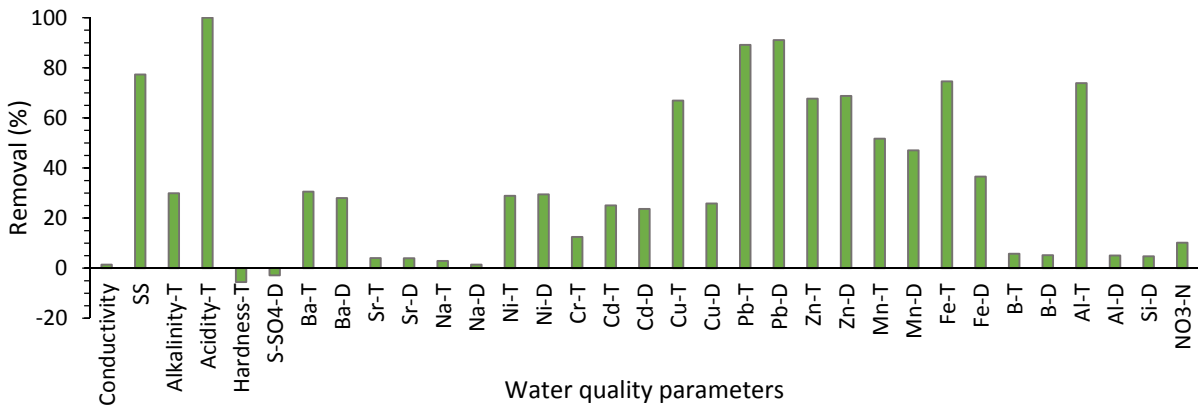


Figure 2 Influent and effluent concentrations and removal efficiencies of a) Zn, b) Cd and c) Pb with respect to the corresponding flow rates (d).

and their removal efficiencies with respect to the corresponding flow rates. Average removal efficiencies for Zn, Cd and Pb achieved during this trial were 64.18% (max-90.58%), 22.37% (max-90.16%) and 75.04% (max-97.28%) respectively. Accordingly, 4.15 kg of Zn, 5.55 g of Cd and 5.22 g of Pb were removed from 131.46 m<sup>3</sup> of mine water.

Figure 3 shows the external results for average removal efficiencies of water quality parameters. In addition to Zn, Cd and Pb, the treatment system also removed a wide range of metals; in particular Fe, Al, Cu, Mn, Ba and Ni. The system also removed non-metallic parameters such as acidity, SS, alkalinity, NO<sub>3</sub>-N and total anions but contributed to the NH<sub>3</sub>-N, SO<sub>4</sub>-S, hardness and total cations. Conductivity was also reduced by the system.

Leaching of NH<sub>3</sub>-N from the mesh occurred for the first four weeks but subsequently decreased, with most of the outlet concentrations for the remainder of the trial within the range of 0.2-0.3 ppm. This initial flush of ammonia could be mitigated by pre-washing of mesh at the manufacturing stage.



**Figure 3** Average removal efficiencies of water quality parameters analysed by UKAS accredited lab (D = dissolved, T = total).

Effluent pH increased by ~0.5 pH unit with respect to degassing of carbon dioxide (CO<sub>2</sub>). Continuous stirring of mine water without mesh performed in the lab showed a similar rise in pH. Degassing of dissolved CO<sub>2</sub> from the mine water is believed to have shifted the equilibrium from bicarbonate towards carbonic acid resulting in the consumption of hydrogen ions, thereby increasing pH.

**Effect of regeneration of mesh on removal of metals**

Regeneration of the mesh should be performed after breakthrough in the performance of the system. In this study, regeneration of the mesh was performed before reaching breakthrough of the system due to time constraints. Regeneration of the mesh was performed on Day 79 of the trial. Figure 2a shows that after the regeneration process, the removal efficiency of Zn gradually increased for a week and reached to the same extent (70%) as before the regeneration process. However, the average removal efficiency of Zn after the regeneration process dropped to 59% thereby bringing the overall treatment efficiency to 64%. This decrease is linked with the higher flow rates towards the end of the trial. Figure 2b and 2c show removal efficiencies for Cd and Pb were not affected by the regeneration process.

Mesh samples were taken from the first and the last discs in the reactor and digested in conc. HCl (37%) for two hours at 148°C to determine metal content; 98% of Zn, 81% of Cd and 91% of Pb (based on Pb-T) removed by the system before the regeneration process were desorbed off the mesh.

**Effect of residence time (RT) on removal of metals**

Flow rate determines both RT and mass transfer in the reactor. Lower flow rates decrease the pollutant load and increase the RT and vice versa. Lower flow rate are considered to increase removal efficiency by ensuring effective mass transfer between the solution and the rotating discs. This effect was investigated (from Day 126 to Day170) by increasing the flow rate from 30 L/hr to 45 L/hr and 60 L/hr respectively. Flow rates of 30 L/hr, 45 L/hr and 60 L/hr correspond to RTs of 2 hrs, 1.33 hrs and 1 hr respectively. Flow rate was increased from 30 L/hr to 45 L/hr on Day 143 and further increased to 60 L/hr on Day 159. The effect of flow rates on the removal of metals can be seen in Figure 2.

There was no significant drop in removal efficiency of Zn when the flow rate was increased by 1.5 fold (30 L/hr to 45 L/hr). Meanwhile, a 21% reduction in the removal efficiency of Zn was observed when the flow rate was doubled (30 L/hr to 60 L/hr). Removal efficiency of Pb dropped by 18% when the flow rate increased by 1.5 fold. However, further increase in flow rate did not result in a significant decrease in removal efficiency; removal of Pb decreased to 21% when the flow rate doubled. As most of the Pb was present in insoluble form, the minimal decrease in the removal efficiency of lead could be attributed to filtration by mesh. Meanwhile, the removal efficiency for Cd did not follow a particular trend. Overall, these results suggest that a minimum RT of 1.33 hrs should be used for the IE to liquor ratio and contamination levels reported in the present study. In full-scale treatment schemes, this will vary depending on the flow rate, reactor size, mine water quality and amount of IE mesh in the reactor.

#### *Effect of rotation speed (RS) of the discs on metal ions removal*

Disc RS was expected to potentially affect the removal efficiency by influencing the mixing and contact time. This was investigated by varying the RS of the discs. The field trial commenced with an initial disc RS of ten revolutions per minute (rpm), which was lowered to 2.5 rpm on Day 118. Lowering the rotation speed by a factor of four did not have significant effect on the removal of Zn, Cd and Pb.

#### **Removal mechanism**

Continuous removal of metals after exhaustion of IE capacity of the mesh suggests the existence of another removal mechanism, which is likely to be sorption and/or co-precipitation. To enable an estimation of metal removal arising from precipitation in comparison to IE, the solid residue was removed from the mesh samples taken at the end of the trial by gently squeezing and tapping. The mesh and the residues were each digested separately in conc. HCl (37%) for two hours at 148°C to determine metal content. Analysis of the residues suggested that at least 77% of Zn, 47% of Cd and 63% of Pb were removed by means of precipitation onto the surface of IE mesh. Amounts of Zn, Cd and Pb desorbed off the mesh were equivalent to the corresponding amounts removed after the regeneration process. X-Ray Diffraction (XRD) analysis of the solid residue on the mesh confirmed the presence of some variant of hydrozincite, a basic  $ZnCO_3$ , with general formula  $Zn_4(CO_3)(OH)_6 \cdot H_2O$ . Diffraction peaks were extremely broad, consistent with very small particle size in the powdered specimen. Both lines of evidence indicate that precipitation occurred on the surface of IE mesh and not at the base of the reactor.

It is suggested that the metal removal mechanism first begins with ion-exchange, which seeds the mesh to favour co-precipitation and sorption. Results of the control experiments performed in the laboratory using raw mesh (before chemical conversion into an IE mesh) and IE mesh support this hypothesis. Removal of Zn by IE mesh was 72% whereas that of raw mesh limited to 24%. This mechanism was aided by persistent rise in pH due to degassing of dissolved  $CO_2$ . Degassing of  $CO_2$  and precipitation of  $CO_3^{2-}$  resulted in a decrease in alkalinity. This is supported by an average decrease of 29.3% in alkalinity in the effluent.

Predominant Zn species in the mine water change as pH rises. Nuttall and Younger (2000) found that, on raising the pH from 6 to 8.5, zinc carbonate ( $ZnCO_3$ ) and zinc hydroxide ( $Zn(OH)_2$ ) species increase at the expense of free Zn ions and  $ZnSO_4$ . According to Hem (1972), stable  $ZnCO_3$  (smithsonite) can be formed over a narrow pH range of 7.5-8.0 in natural waters.

Clever et al. (1992) documented that solubility of  $ZnCO_3$  increases with partial pressure of  $CO_2$  and temperature and decreases rapidly as pH rises around circum-neutral. A study by Paulson et al. (1989) found that, with 2 mM/L total dissolved  $CO_2$  and at pH below 8.2, crystalline hydrozincite forms, whereas above pH 8.2 poorly crystalline hydrozincite forms and eventually at high pH zinc oxide ( $ZnO$ ) forms. This is further backed up by Alwan and Williams (1979), who explained the anomalous stability of hydrozincite in nature based on the calculated solubility product constant of hydrozincite in natural waters as  $\log K_{sp} = -14.9$ . Stumm and Morgan (1970) suggest that below pH 7.5  $ZnCO_3$  is the most insoluble species and as pH increases, as is the case in this study, a basic  $ZnCO_3$ , hydrozincite, becomes controlling. These previous studies are consistent with the XRD analysis of the white precipitate on the mesh.

According to Miller et al. (2011), cation removal by sorption to an amphoteric surface is dependent on pH and is best at the pH which correlates with the point zero charge. The extent of Zn removal depends

on a complex interplay between the nature of the aqueous medium and the speciation of the surface. As pH increases  $\text{CO}_3^{2-}$  sorbs onto the surface of the substrate to form  $\text{ZnCO}_3$ . As pH increases further, Zn sorption increases forming  $\text{Zn(OH)}_2$ . There is competition between aqueous and substrate phases for Zn complexation. As pH and alkalinity increase, the increased concentration of  $\text{CO}_3^{2-}$  in the aqueous phase outcompetes the substrate bound  $\text{CO}_3^{2-}$  stripping Zn from the surface of the substrate resulting in increased concentration of  $\text{ZnCO}_3$  in solution. When surface sites are in abundance, the pH dependent removal dominates and alkalinity effects are minimal. When surface sites are restricted then a more complex behaviour is exhibited dependent on pH, alkalinity and number of sites.

The IE mesh used in this trial is a complex material comprising both anion exchanging  $-\text{NH}_2^+$ , cation exchanging  $-\text{COOH}$  and complexometric  $-\text{NOH}$  sites. At pH of around circum-neutral the  $-\text{NH}_2^+$  sites are likely to be partially protonated,  $-\text{COOH}$  sites completely deprotonated and  $-\text{NOH}$  sites unchanged. Thus, the mesh provides excellent sites to support both IE and sorption of Zn cations and  $\text{CO}_3^{2-}$  / hydroxide etc. ions.

Miller et al. (2011) showed that the presence of alkalinity and dissolved Fe in the drainage water helps remove almost all dissolved Zn by precipitation or sorption onto precipitated Fe-oxy, hydroxyl species. However, on moving to continuous flow field trials where RT on the limestone drain was reduced to 1-3 hours (batch RT=4days) the removal efficiencies were significantly reduced almost to zero. Mayes et al. (2009) used high surface area hydrous ferric oxide (HFO) while removing Zn from 1.5-2.2 ppm to 0.9-1.5 ppm and found that the presence of alkalinity and dissolved Fe also helps in removing Zn by precipitation or sorption. Warrender et al. (2010) investigated the use of a range of materials in the circum-neutral removal of Zn at 23.5ppm, RT=15mins, flow rate=1 L/min in beds containing 1.5-12 kg of material. The presence of Fe in the wastewater formed Fe-oxy-hydroxide precipitates adversely affecting flow rates.

A significant advantage of the treatment system trialled is the openness of the IE mesh, which, together with its high surface area combined with agitation from the rotating discs, allows excellent flows whilst providing a variety of charged sites for IE / precipitation / sorption of metals.

### **Applicability of the technology**

The results presented in this paper show the tremendous potential of this technology for the treatment of mine waters. This technology would be suitable for most metalliferous mine waters. However, if the pH of the mine water is highly acidic ( $\text{pH}<2$ ) and alkalinity is low, then pre-treatment for pH and alkalinity is needed. Younger et al. 2002 used Oxidic Limestone Drains (OLDs) to increase pH and alkalinity in RT=2-3 hrs.

For mine waters with very high SS, pre-treatment involving settlement might be advisable. If the mine water contains low concentration of metal ions then it may be necessary to increase the RT; longer RTs improve IE and precipitation processes by enhancing contact between metal ions and the active sites on the IE mesh. If the mine water contains an excessively high concentration of Fe then pre-treatment might be necessary to prevent clogging of mesh with ochre. Pre-treatment may avoid competition of Fe with the uptake of the desired metal ions. However, as discussed above the presence of Fe is likely to enhance the precipitation / sorption of the Zn. If the mine water contains low concentrations of Fe then this will be removed together with other metal ions by an IE process and will eventually assist in the co-precipitation / sorption of the other metal ions onto the IE mesh.

### **Conclusion**

The IE mesh developed at DMU and incorporated in the innovative rotating contactor has been successfully applied in the removal of metal ions from mine water heavily contaminated with Zn, Cd and Pb. The order of removal efficiencies was  $\text{Pb (75.04\%)} > \text{Zn (64.18\%)} > \text{Cd (22.37\%)}$ . Accordingly, 4.15 kg of Zn, 5.55 g of Cd and 5.22 g of Pb were removed from 131.46 m<sup>3</sup> of mine water in 170 days. Amongst the other metals / metalloids removed by the system include Fe, Al, Mn, Cu, Ba, As, Ni, B, Cr and small amounts of Na, K and Sr. Amongst non-metallic water quality parameters include acidity, SS, alkalinity and small amounts of  $\text{NO}_3\text{-N}$  and total anions. Conductivity was also reduced by the system. However, the system generated small amounts of  $\text{NH}_3\text{-N}$ ,  $\text{SO}_4\text{-S}$  and hardness. An average rise of pH by ~0.5unit in treated water was also observed.

Performance of the treatment system was not significantly affected by the regeneration of mesh and RS of the discs. The treatment system was successfully regenerated in-situ, indicating minimal downtimes for full scale units. The treatment process was not affected by temperature variations within the range of 0.7°C to 20°C. This suggests that the treatment system can be used for the continuous flow treatment of mine water under high temperature fluctuation throughout the year. The maximized removals of metals were observed when  $RT \geq 1.33$  hrs. However, this will vary for full-scale treatment schemes depending on the liquor to mesh ratio and water quality.

The system removed the metals mainly by IE and co-precipitation / sorption on the surface of the mesh. The openness of the mesh means that when Zn is co-precipitated / sorbed onto the mesh, this does not result in blocking of the sites and there is no reduction in flow rates unlike particulate systems. This treatment system has been proved to be suitable for mine waters with high alkalinity and circum-neutral pH and would be suitable for the most metalliferous mine waters. However, pretreatment may be required for mine waters of low pH, alkalinity and very high suspended solids. Performance will not be hindered by the presence of Fe, rather it is likely to be enhanced.

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