

Site Specific Optimisation Assessment

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Abstract

A large amount of mine sites globally are recognised to generate discharges in the circum-neutral range, and in recent times regulatory and social pressures have resulted in an increased focus on improving discharge quality for these sites. Because treatment of circum-neutral drainage depends on site specific conditions, and is very sensitive to water quality targets, an assessment methodology based around a treatability curve approach has been developed. This allows generation of a cost-treatability curve that can be based on site specific factors or “levers” that drive water treatment efficiency and cost.

Keywords: Circum-neutral, Water Treatment, Cost-treatability Curve, Zinc.

Introduction

There has been considerable research into mine water treatment, and numerous well developed technologies are commercially available. The majority of research and available technologies are predominantly targeted to acidic mine drainage (AMD) environments. Circum-neutral mine water tends to have low acidity and a circum-neutral pH, with low concentrations of iron. Metal species, such as zinc, are often still found at higher concentrations. Circum-neutral mine waters can be produced if there is little or no pyrite available to oxidise and produce acid, or there is carbonate host rock or gangue producing an acid buffering effect (Warrander and Pearce 2007). Treatment of low Fe circum-neutral mine waters is more challenging because of the lack of Fe and therefore reduced production of Fe(III) that can be used as a sorbent for other metal cations (Gooyong *et al.* 2018). In general the key “levers” for the removal of metal cations are;

- pH
- Oxidation for example Fe(II) to Fe(III)
- Sorption onto suitable media such as iron (hydr)oxide surfaces.
- Reduction potential to sulfides.

In this study we have reviewed the effect of these “levers” as applied to circumneutral drainage based on a literature study

complimented by a program of laboratory testing to demonstrate how varying key “levers” will impact on water treatment outcomes. In brief beaker trials were carried out on low iron circum-neutral mine water from Nant-y-Mwyn lead mine, UK (Chemical properties for Nant-y-Mwyn mine drainage used in test work are shown in the Appendix) to explore the effect of:

- pH using a range of pH amendment products (lime, sodium hydroxide and sodium carbonate)
- sorption (using media such as iron oxide powder)
- Aeration (using air sparging)

In general an increase in pH causes metal removal from the soluble phase due to precipitation (hydrolysis) and increase in cation adsorption. The process of adsorption can happen from nearly 0% to 100% in a range of 1 or 2 pH units known as the ‘adsorption edge’ (Smith *et al.* 1999). Different types of adsorbent have been studied, whilst very few have been brought to commercial viability. For high Fe mine waters the “choice” of sorbent is simple, precipitation of Fe(III) oxides from the minewater itself creates a catalyst for further oxidation of Fe(II) and promotes sorption onto the Fe oxides with no requirement to add additional sorbents (Younger 2000). This

makes high Fe waters theoretically amenable to passive treatment options.

For low Fe mine waters (common for circumneutral drainage) however to achieve sorption as metal removal pathway, an external product is likely to be required as there is no natural sorbent that can be formed from within the minewater (unless the water is heavily reduced in which case it may carry elevated dissolved iron). Standard practice is to buy in produced sorbents such as activated carbon or aqueous ferric oxide, these are effective but can be expensive and in the case of aqueous ferric oxide makes the removal from water more complex (Chaudrhy *et al.* 2016). INAP (2009) recognises this factor and as such recommends that the generic passive treatment category for treatment of water with elevated circumneutral metals such as Zn are systems that aim to reduce dissolved metal species to soluble sulfides. Examples being anaerobic systems such as vertical flow ponds (VFPs) that utilise organic matter as a substrate (which acts as both a sorbent and a reducing agent). This is likely due to limestone treatment-based systems not generating high enough pH conditions to enable hydrolysis of such metals (i.e. minimum solubility for Zn occurs at $\text{pH} > 8$) and because of the lack of dissolved iron in the mine water to effect sorption. Examples of passive treatment for metals such as zinc using VFP have been noted (Force Crag UK) as possible reference sites.

Aeration has been long recognised as a key feature in mine water treatment due to the effect of oxidation state on metal mobility, and also the effect of dissolved gases such as CO_2 on the carbonate system and ultimately solution pH. Underground mine drainage waters are often depleted in oxygen and may be reducing, and also may be supersaturated with carbon dioxide due to a reaction with limestone or oxidation of organic carbon (Geroni *et al.* 2012). Given many circum-neutral mine waters are sourced from carbonate rich host rock or gangue (Warrender and Pierce 2007), circum-neutral mine waters may be affected by increased dissolved carbon dioxide. Previous studies on the introduction of aeration steps into mine drainage treatment systems have shown a profound affect on water chemistry with an increase in dissolved oxygen (DO)

and driving off dissolved carbon dioxide, increasing pH and the oxidation potential of Fe(II), allowing increased precipitation (Kirby *et al.*, 2009).

The Cost of Traditional High Density Sludge (HDS) Treatment

As would be anticipated based on an understanding of the key “levers” of water treatment described above the most common form of active mine drainage treatment is oxidation and chemical precipitation (metal hydrolysis). In this technology alkali reagents are added to mine water to increase the pH and promote metal precipitation (hydrolysis). HDS was developed as a more efficient form of oxidation and chemical precipitation to reduce the volume of sludge produced, from a maximum of 5% solids (w/w) in conventional systems to between 15% and 35% solids (w/w) for HDS (Bullen 2006). Chemical precipitation plants are used because they are effective at contaminant removal, allow precise process control which gives the ability to adapt to variable influent and effluent standards and are inherently scalable which means they can take up smaller land area than alternatives including passive treatments, particularly for higher treatment volumes (Trumm 2010).

Estimates of typical HDS costs can vary through a range (Table 1). Given these indicative unit costs are for general chemical precipitation treatment, and CAPEX for HDS is generally higher than for conventional systems, the maximum CAPEX value calculated here is likely to be closest to the actual cost of an HDS system. Further to this, when compared with the actual cost of Wheal Jane, UK phase 1 plant (treating $1240\text{m}^3/\text{hr}$) of around US\$4.7 million (Coulton *et al.* 2003) and estimated cost of an HDS treatment plant at Force Crag, UK (treating $22\text{m}^3/\text{hr}$) of US\$2.3 million (Bailey *et al.* 2016) this may be an underestimate. OPEX for HDS systems are usually lower than for conventional systems due to the reduced sludge production, leading to lower storage and disposal costs (Bullen 2006).

URS (2014) gives a breakdown of annual OPEX for water treatment facilities, reagent costs are the largest constituent of OPEX at 31.8%. For active treatments such as HDS the largest amount of reagent used is lime to

Table 1 Minimum and maximum CAPEX and OPEX estimates for a chemical precipitation plant treating 72m³/hr mine drainage.

		Minimum		Maximum
Indicative CAPEX per m ³ /day treated	\$	300.00	\$	1,250.00
Indicative OPEX per m ³ /day treated	\$	0.20	\$	1.50
CAPEX estimate	\$	518,400.00	\$	2,160,000.00
OPEX estimate per day	\$	345.60	\$	2,592.00
Annual OPEX estimate	\$	123,033.60	\$	922,752.00

increase the pH high enough for precipitation. These costs were used for a cost-treatability curve (Figure 1) based on preliminary titrations of samples of mine drainage from the study site.

Metal Hydroxide Precipitation vs Cation Adsorption

Water treatment by pH amendment is generally through addition of a chemical to increase mine water pH to promote precipitation of metal species. Metals are most commonly precipitated as hydroxides, the pH of hydrolysis for each metal cation is different. However it should be noted that during the process of raising pH and precipitation of iron and aluminium, that many other metals are removed from solution by sorption onto newly formed secondary iron minerals and not by precipitation. The relative proportion of metals removed by precipitation and sorption is not typically

recorded as part of water treatment system design (sludge composition is not typically a design parameter) and is an inherently site specific function, as such the relative importance of sorption in systems like HDS is a relative unknown factor.

For metals of concern (Zn, Pb and Cd) in low Fe circum-neutral mine drainage, precipitation is most likely to occur between pH 9 and 11. This leads to some chemical precipitation treatment to amend mine water pH to at least 9.5–10 (Bullen 2006; Aubé 1999). Even from circum-neutral pH this can require a large amount of alkali reagent, this is due to pH being a logarithmic function and supersaturation of mine water with CO₂, found in some cases to be at levels 100 times greater than at atmospheric conditions (Jarvis 2006). Before treated water can be discharged the pH generally needs to be reduced to pH 8–9 in line with discharge requirements.

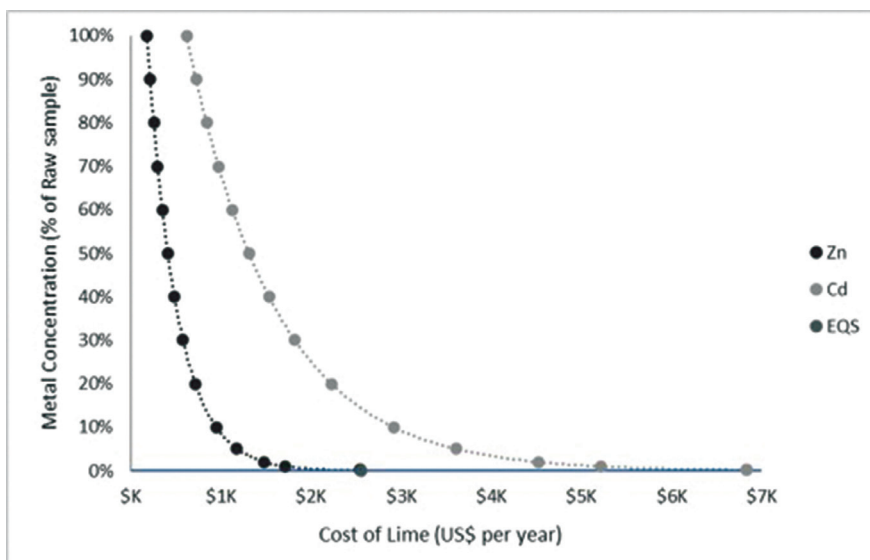


Figure 1 Cost Treatability curve showing lime costs against metal concentration for Zn and Cd.

As part of beaker trials (Figure 2) it has been demonstrated that the addition of Ferric Oxide (FeOx) at a rate of 5 g/L (over a 1 hour period) while raising the pH of water from Nant-y-Mwyn can change the primary treatment driver from precipitation as hydroxides to adsorption onto FeOx. Thus, metal removal occurs at much lower pH than by precipitation alone. Zinc concentration reduction (Figure 2) very clearly occurs at a much lower pH following the addition of FeOx.

Reducing the Cost and Increasing the Sustainability of Active Treatment

Although active treatment such as HDS can be considered “efficient” on the basis of typical cost effectiveness the consideration of sustainability and “green credentials” is becoming increasingly more important with an industry focus on environment and social governance (ESG) and decarbonisation. As such “passive” treatment systems have attracted much interest and investment/research as they are considered to be more aligned with sustainability/ESG/ decarbonisation metrics. However, for many sites active treatment is likely to be continued to be required for a number of practical reasons and as such if true life cycle sustainability is to be assessed then a more holistic view is required to be taken. As such we consider an alternative

approach termed Sustainable Active Treatment (SAT) that applies a more holistic and whole life cycle methodology to consideration of active treatment technology. This approach deals with the main drivers of cost for active treatment such as reagent use and sludge transport and disposal, as well as consideration of the nature of the sludge, and factors such as energy usage produced by applying sustainable solutions. In the first instance the largest component of OPEX cost is reagents, particularly chemicals to increase pH (Table 2). As such an obvious consideration is to look at the potential for reduction of reagent use which would be both more sustainable and would reduce OPEX costs. To demonstrate this, we performed beaker trial degassing experiments by sparging air through a sample of the mine water from the study site and recording pH at tie intervals (Figure 3). It is noted that the pH increased from 6.53 to >7.6 within \approx 10 minutes without the use of any reagents (due to degassing of CO₂).

Another major OPEX cost is sludge transportation and disposal. As described herein sludge is produced if precipitation by pH increase is being used as the main means of metal removal, however our experiments show that sorption is an alternative means to remove metals that does not produce sludge. Addition of suitable sorption media for example allows

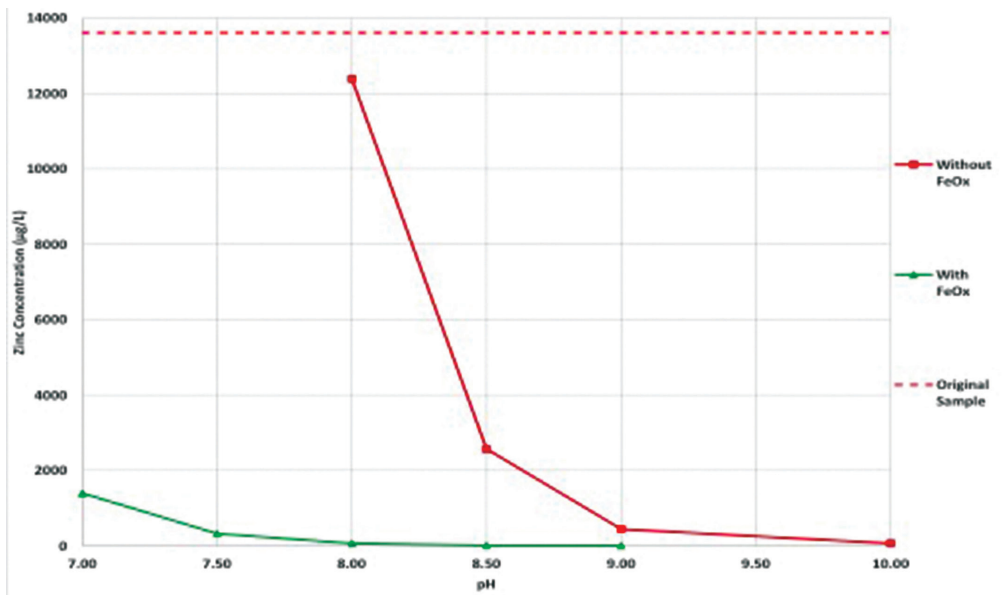


Figure 2 Zn concentration (dissolved) as a function of pH, with and without FeOx addition.

the metal cations to adsorb to media surfaces in a manner that does not generate sludge and is geochemically reversible. As reported by URS (2014), 40% of CAPEX costs are for sludge management infrastructure, clarification, sludge thickening and effluent polishing suggesting that avoiding sludge may allow important gains for life cycle sustainability and cost reduction. This approach also opens the possibility for recovery of metals that have been “reversibly” adsorbed if ‘stripping’ of the sorbed metals is carried out. Selective stripping of metals may be possible to produce relatively “pure” products (or concentrates) which may increase the economic value of this process. In addition, the use of industry by products as sorption media can be explored to further enhance sustainability gains. Iron ochre from coal mine drainage treatment facilities for example has been studied by Mayes *et al.* (2009) and Sapsford *et al.* (2015) as a potential sustainable FeOx media. Further because energy is one of the other major OPEX costs and has major influence on carbon footprint then using systems that have reduced energy demand opens up the possibility of using sustainable renewable sources of energy, such as photovoltaic cells and wind turbines. These would assist with both decarbonisation and OPEX reduction.

Conclusions

Based on our work we consider that consideration of a holistic approach to water treatment when considering active system provides many opportunities to reduce cost and improve sustainability metrics. For circumneutral sites adoption of a cost curve based assessment and the SAT approach will facilitate increased focus on both cost reduction and an increase in sustainability (this may be particularly so for legacy sites). This holistic approach further opens the possibility to look at water treatment as a ‘Whole Catchment Approach’ whereby consideration of treatment of multiple discharges are considered together rather than focusing on achieving very high removal rates from single point source discharges.

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References

Aubé BC (1999) Innovative modifications to high density sludge process. Proceedings for Sudbury '99, Mining and the Environment II. September 13-17, 1999. Sudbury, Canada.

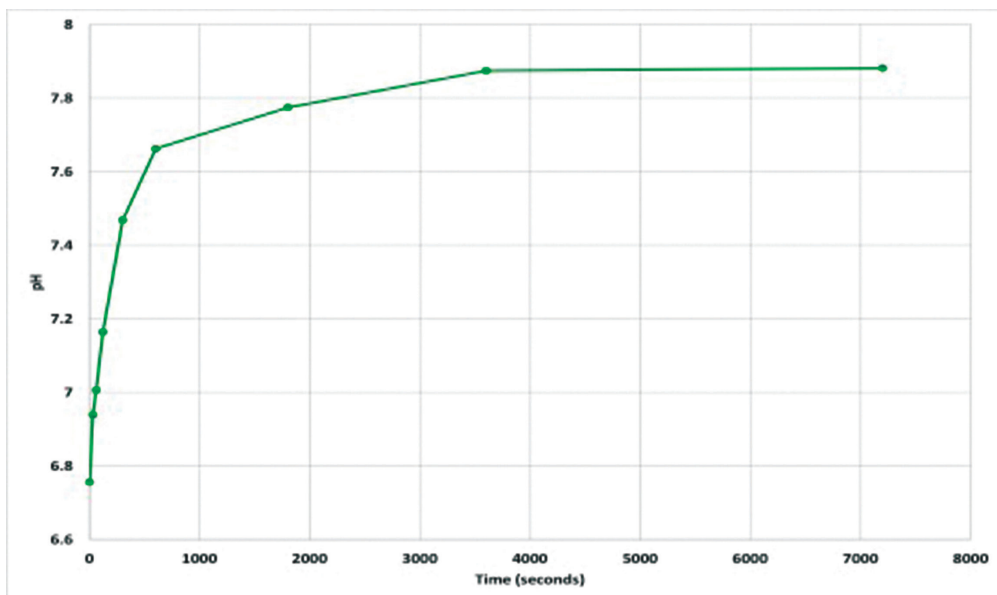


Figure 3 Results of degassing experiment, change in pH with time.

- Bailey MT, Gandy CJ, Jarvis AP (2016) Reducing life-cycle costs of passive mine water treatment by recovery of metals from treatment wastes. Proceedings IMWA 2016, Freiburg, Germany.
- Bekényiová A, Štyriaková I, Danková Z (2015) Sorption of Copper and Zinc by Goethite and Hematite. Archives for Technical Sciences 2015, 12(1), 59-66, doi:10.7251/afts.2015.0712.059B.
- Bullen CJ (2006) An investigation into the mechanics controlling the formation of high density sludge. Thesis submitted to the University of Wales for the Doctor of Philosophy. School of Engineering University of Wales, Cardiff, United Kingdom.
- Chaudhry SA, Khan TA, Ali I (2016) Adsorptive removal of Pb(II) and Zn(II) from water onto manganese oxide-coated sand: Isotherm, thermodynamic and kinetic studies. Egyptian Journal of Basic and Applied Sciences 3 (2016) 287-300.
- Coulton R, Bullen C, Dolan J, Hallett C, Wright J, Marsden C (2003) Wheal Jane mine water active treatment plant – design, construction and operation. Land Contamination & Reclamation, 11 (2), 2003, doi:10.2462/09670513.821.
- Florence K (2014) Mechanisms of the removal of metals from acid and neutral mine water under varying redox systems. Thesis submitted for the Degree of Doctor of Philosophy, School of Engineering, Cardiff University, United Kingdom.
- Geroni JN, Sapsford DJ, Florence K (2011) Degassing CO₂ from mine water: implications for treatment of circumneutral drainage. Proceeding IMWA 2011, Aachen, Germany.
- Geroni JN, Cravotta III CA, Sapsford DJ (2012) Evolution of the chemistry of Fe bearing waters during CO₂ degassing. Applied Geochemistry 27 (2012) 2335-2347.
- Gooyong L, Cui M, Yoon Y, Khim J, Jang M (2018) Passive treatment of arsenic and heavy metals contaminated circumneutral mine drainage using granular polyurethane impregnated by coal mine drainage sludge. Journal of Cleaner Production 186 (2018) 282-292.
- Jarvis AP (2006) The role of dissolved carbon dioxide in governing deep coal mine water quality and determining treatment process selection. Proceedings of the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis, MO, USA.
- Kirby CS, Dennis A, Kahler A (2009) Aeration to degas CO₂ increase pH, and increase iron oxidation rates for efficient treatment of net alkaline mine drainage. Applied Geochemistry 24 (2009) 1175-1184.
- Mayes WM, Potter HAB, Jarvis AP (2008) Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. Journal of Hazardous Materials 162 (2209) 512-520.
- Sapsford D, Santonastaso M, Thorn P, Kershaw S (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 (2015) 7-15.
- Smith KS (1999) Metal sorption on mineral surfaces: An overview with examples relating to mineral deposits. In: Reviews in Economic Geology, Volumes 6A and 6B, The Environmental Geochemistry of Mineral Deposits, Chapter 7. Published by the Society of Economic Geologists, Inc. (SEG) 1999.
- Trivedi P, Axe L, Dyer J (2001) Adsorption of metal ions onto goethite: single-adsorbate and competitive systems. Colloids and Surfaces, A: Physicochemical and Engineering Aspects 191 (2001) 107-121.
- Trumm D (2010) Selection of active and passive treatment systems for AMD – flow charts for New Zealand conditions. New Zealand Journal of Geology and Geophysics, 53:2-3, 195-210, doi: 10.1080/00288306.2010.500715.
- URS (2014) Metal Mine Water Treatment Review. Prepared for: The Coal Authority, United Kingdom.
- Younger PL (2000) The adoption and adaptation of passive treatment technologies for mine waters in the United Kingdom. Mine Water and the Environment (2000) 19: 84-97.
- Warrander R, Pearce NJG (2007) Remediation of circum-neutral, low-iron waters by permeable reactive media. IMWA Symposium 2007: Water in Mining Environments, 27-31 May, 2007, Cagliari, Italy.

Appendix

Chemical properties of Nant-y-Mwyn raw water sample.

	pH	Ca	K	Mg	Na	As	Ba	Cd	Co	Cu	Mn	Mo	Ni	Pb	Sb	Se	Sr	Ti	Tl	Zn
Unit		ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Conc.	6.756	23.47	0.941	8.223	7.84	0.549	14.98	40.31	24.69	26.09	13.52	0.119	41.76	137.4	0.258	0.258	51.34	10.74	0.11	13610