Evaluating Manganese in Mine Water in UK Coal Authority Mine Water Schemes

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Abstract

Manganese is a naturally occurring, abundant element in the environment, and is a common contaminant of coal and metal mine drainage.

Environmental Quality Standards (EQS) proposed in 2014 under Water Framework Directive as applied in the UK established that manganese discharge limits should be based on Predicted No-Effect Concentrations (PNECs), with an EQS of 123µg/L bioavailable in freshwater for manganese.

The Coal Authority is undertaking research into the treatment of manganese in our existing mine water treatment schemes (MWTSs) including assessment of manganese dynamics and removal efficiency in our MWTSs, and complementary R&D trials investigating alternative treatment technologies.

Keywords: Coal Mine Waters, Treatment, Manganese, Innovation

Introduction

Manganese (Mn) is a naturally occurring and abundant element in the environment, and can originate from the natural weathering of geological material, such as Mn oxides (i.e. pyrolusite, vernadite), carbonates (i.e. rhodochrosite), silicates, and sulphides. However, Mn can also originate from point sources arising from its use in heavy industries such as steel manufacture and coal mining, with Mn a common contaminant of both coal and metal mine derived mine water drainage.

Passive removal of acidity, iron, aluminium and many trace elements from acid mine drainage has been extensively discussed in recent years, but less attention has been focused on Mn. Although the ecotoxicological consequences of elevated Mn are less severe than the other metals, Mn loading in mine discharges can cause deleterious effects to natural watercourse and bodies. Several technologies for Mn removal are available (e.g. Hallberg&Johnson, Vail&Riley, Sikora *et al*), but limited information is available on their long-term success or implementation.

New Environmental Quality Standards (EQS) were proposed in 2014 under the Water Framework Directive as applied in the UK recommending that Mn discharge limits should be based on Predicted No-Effect Concentrations (PNECs). Using available long-term ecotoxicity data for Mn, an EQS of 123µg/L bioavailable Mn in freshwater was established. In 2016, the Scottish Environment Protection Agency (SEPA), for example, identified approximately 14 water bodies in coalfield areas that fail to meet these proposed EQS limits. The 2014 EQS limits are therefore likely to impact future mine water treatment design for Mn removal, increasing land area required. In order to mitigate the potential risk, the Coal Authority is undertaking research into the treatment of Mn in both coal and metal mine waters across the UK, via a series of R&D reviews, monitoring and trials. This work has included assessment of Mn dynamics and removal efficiency in over thirty existing passive mine water treatment systems (MWTS), with complementary R&D trials investigating low footprint and alternative treatment technologies.

This paper presents initial findings of the efficiency of our passive schemes with respect to Mn removal, which consist of a combination of one or more of settlement lagoons and wetlands, along with an introduction to the coal mine water R&D currently being completed at the Coal Authority. This paper is not a full review of our data to date, nor an exhaustive account of all R&D treatment technologies that are available or may be applicable for Mn removal from mine waters, but an interim report of findings on ongoing works that the Coal Authority are undertaking on Mn in Coal mine waters in the UK.

Methodology

As part of the Coal Authority's R&D programme, a series of investigations have been completed on our coal mine waters at our existing MWTSs, to both understand the Mn dynamics in our existing schemes (Mn removal) and to identify new technologies/methodologies that may be suitable to remove Mn from our coal mine waters. These new technologies would be used either as a standalone system for Mn removal, or as a 'bolt-on' support to our existing treatment, as a 'polisher'.

The works being undertaken as part of our Mn-focused R&D research consist of the following key areas, which are being undertaken in two parallel, contemporary activity streams and are both still ongoing.

Activity stream 1: Assessment of Mn dynamics in our current MWTSs:

1. Identify mine water discharges containing Mn (>0.5mg/L) at Coal Authority MWTSs (the candidate sites), and review their sampling regime, geochemistry and current Mn removal dynamics.
2. Design and undertake a focussed sampling campaign on each of these candidate sites to focus on Mn removal dynamics within each component of the scheme (settlement ponds, reed beds)
3. To analyse the findings and to assess key factors that promote Mn removal within our MWTSs

Activity stream 2: Assessment of key new technologies that could be used as standalone treatment systems or as a bolt on to our exiting schemes:

1. Compile a short list of MWTSs and other sites that could be used as candidates for Mn removal trials, focusing on assessing a range of different mine water chemistries (i.e. low and high Mn, net alkaline, net acidic, variable Fe and other metals)
2. Undertake a literature review of existing and available technologies for Mn removal.
3. Assess the feasibility and design of pilot (field based) trials on the shortlisted mine waters from a selection of the identified candidate sites, followed by one or more field scale trials.
4. Based on the pilot results, identify key locations where Mn treatment systems could be placed at the end of scheme as a Mn 'polisher'.

Results

Manganese removal within our Passive MWTSs:

Typically, our passive treatment scheme configuration adopted in the UK for coal mine water (and ironstone mine water) remediation comprises of aeration cascades, settlement lagoons and reed beds. Reed beds are generally planted with common reed (*Phragmites australis*) and bull rush (*Typha Latifolia*) with marginal vegetation consisting of sedges and rushes and grasses. Initial analysis of our data showed that although it is not part of our consented permits, many of our schemes successfully remove Mn. What was unclear was both where and how this Mn is removed within the schemes, as our permit monitoring, apart from iron, does not routinely examine the metal removal efficiency of each scheme component (ponds, reed beds, etc).

Thirty-one sites were chosen (based on an influent Mn concentration of >0.5mg/L) as suitable sites on which to perform an in depth sampling campaign, in order to identify the location and fate of Mn in our treatment systems. The study sites are listed in Table 1, the majority are of a circum-neutral pH, ferruginous pumped coal mine water from Carboniferous Coal Measures strata with variable chemistry. Manganese concentrations in raw waters across these sites range from 0.88mg/L to 4mg/L, with an average across all sites of 2mg/L.

These works were carried out between February 2019 and March 2021 and consisted of a bespoke sampling regime at each site, focusing on Mn removal in the reed beds. Water samples were taken alongside

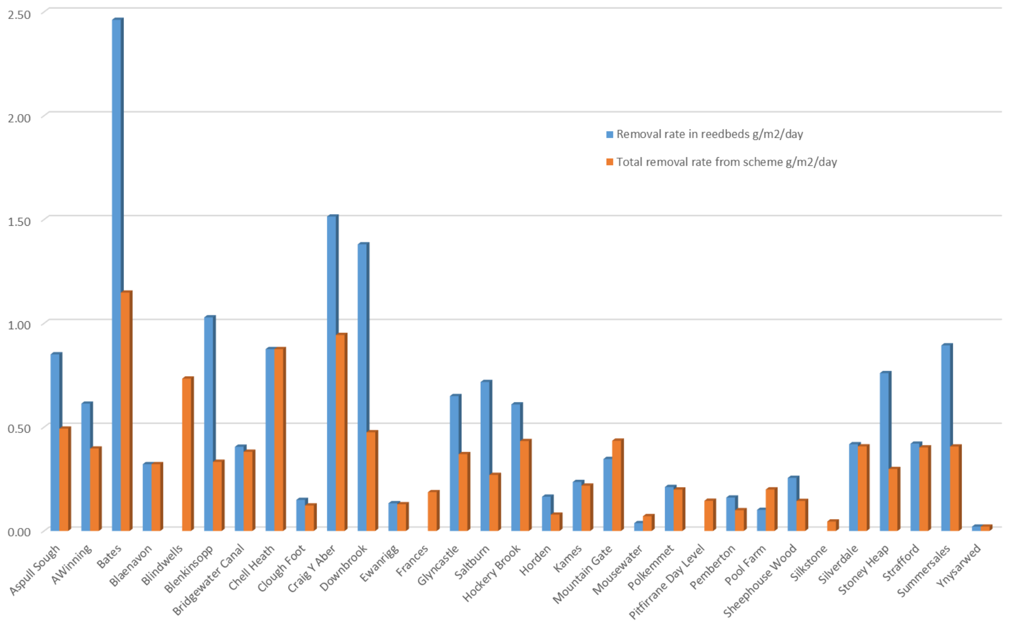

Figure 1 *Summary of manganese removal as g/m²/day from a selection of Coal Authority Mine Water Treatment Schemes, for the period February 2019 to March 2021.*

the routine consented monitoring by our operational contractor, with flow rates through the schemes taken either from pump abstraction rates or via weir plate reading at discharge.

The key results from our schemes indicate that the majority of the Mn in the MWTSs is almost exclusively removed and held within the reed beds, as shown in Figure 1. This confirms not only that our schemes are successful in removing Mn, but can remove up to 89%, with an average removal across all of our schemes of 50%. Assembled chemistry data (manganese, iron, alkalinity, acidity, salinity, pH and dissolved organic carbon), along with assessment of flow data is ongoing, however initial assessment of the data does not show any immediate relationship between the Mn removal rates and flow, iron concentration, chemical dosing and reed bed areas.

Biotically mediated (plant, microbial, mycorrhizial etc.) removal of Mn is likely to be one of the key mechanisms that will be influencing the efficiency of Mn removal in our reed beds. This, along with assessment of how seasonal trends, flow rates and operational and maintenance events can impact treatment efficacy are currently being investigated.

Assessment of key new technologies:

Over the last few years numerous field scale trials have been undertaken by the Coal Authority using a range of novel substrates, including natural fibres (hemp and coir), fish bone apatite, and biological filter media (Bioballs®; Warden Biomedia), along with mineral substrates such as Basic Oxygen Steel Slag, limestone and granite. R&D trials have been in general undertaken at IBC scale (International Bulk Container, 1,000L volume), and always at the site on the 'fresh' raw mine water rather than laboratory scale. This is critical to ensure representative results, as both the microbiology and geochemistry of water will change when transported away from the source site, such as to a laboratory.

Results from an ongoing trial of coconut coir at a coal mine water treatment scheme in the North West of England is presented as an example of the potential of alternative treatment technologies for manganese removal. A trial was installed at Summersales

Table 1 Summary of flow, area and Mn data from a selection of Coal Authority Mine Water Treatment schemes February 2019 - March 2021

Site	Total treatment area (*reed bed area in parentheses*)	Flow average	Number Lagoons	Number reed beds	Mn conc. Raw	Mn removal	Removal rate reed beds	Total removal rate scheme
	m^2	L/s			mg/L	%	$g/m^2/day$	
Aspull Sough	6893 *(3230)*	27.9	3	3	2.67	53	0.85	0.49
AWinning	11434 *(6977)*	76.2	2	1	0.88	78	0.61	0.40
Bates	19522 *(8382)*	205.9	4	3	3.2	39	2.46	1.15
Blaenavon	4803 *(4803)*	12	0	3	1.68	89	0.32	0.32
Blindwells	16960 *(16960)*	153.3	0	3	2.27	41	0.73	0.73
Blenkinsopp	9312 *(2909)*	25.1	2	2	1.64	87	1.03	0.33
Bridgewater Canal	22500 *(15000)*	54.6	3	6	2.31	79	0.41	0.38
Chell Heath	2900 *(2900)*	20	0	8	3.23	46	0.88	0.88
Clough Foot[*1]	4938 *(1738)*	25.1	2	1	2.07	14	0.15	0.12
Craig Y Aber	5750 *(3318)*	31.1	2	2	2.66	76	1.51	0.94
Downbrook	3783 *(1267)*	19.1	2	1	1.38	79	1.38	0.48
Ewanrigg	6400 *(4800)*	7	2	1	1.62	84	0.13	0.13
Frances[*1]	26710 *(-)*	125.7	3	0	4	12	N/A	0.19
Glyncastle	5532 *(2761)*	17.3	2	3	1.57	87	0.65	0.37
Saltburn[*2]	15000 *(4500)*	21.6	4	1	2.7	80	0.72	0.27
Hockery Brook	7530 *(4500)*	25	2	1	2.04	74	0.61	0.43
Horden	16715 *(10400)*	46.2	2	2	1.83	18	0.17	0.08
Kames	4000 *(3634)*	6.4	1	4	1.98	80	0.24	0.22
Mountain Gate	2385 *(2385)*	17.4	0	2	1.11	62	0.35	0.43
Mousewater[*3]	11200 *(8900)*	48.7	1	2	1.74	11	0.04	0.07
Polkemmet[*3]	6025 *(4325)*	66.3	2	1	2.41	9	0.21	0.20
Pitfirrane Day Level	17868 *(17861)*	27	0	2	1.904	59	0.15	0.15
Pemberton	6629 *(3069)*	13	2	3	1.02	58	0.16	0.10
Pool Farm[*2]	5538 *(4839)*	71.2	1	1	2.29	8	0.10	0.20
Sheephouse Wood	4160 *(1400)*	10.1	2	1	2.03	34	0.26	0.14
Silkstone	815 *(611)*	8.6	1	1	2.16	2	[*4]	0.05
Silverdale	5471 *(4331)*	37.4	2	1	1.8	38	0.42	0.41
Stoney Heap	3160 *(960)*	10.3	2	1	1.7	62	0.76	0.30
Strafford	7025 *(6130)*	57.4	1	3	0.91	63	0.42	0.4
Summersales	5368 *(2168)*	17.8	2	1	1.75	81	0.89	0.41
Ynysarwed[*5]	9894 *(9894)*	11.5	0	2	1.51	14	0.02	0.02

*1 Sodium hydroxide is dosed at this site to support iron removal
*2 Metal mine treatment system treating mine water draining from an Ironstone mine
*3 Hydrogen peroxide is dosed at this site to support iron removal
*4 Sampling directly upstream of the reed bed was not possible due to scheme design
*5 Has active chemical precipitation of iron using lime slurry upstream of reed bed treatment

Figure 2 *Coir R&D trial at Summersales Mine water treatment scheme, during installation and in operation (images: Selina Bamforth).*

MWTS (Greater Manchester) in November 2021, in a 1m^3 glass reinforced plastic tank. The Summersales MWTS consists of two pairs of aeration cascades and settlement ponds, in series, and a reed bed. Water for the R&D trial is captured from the effluent point of settlement pond 2, and conveyed to the trial via a siphon.

The trial consist of a 2m long, 1m wide, 0.5m tall tank, in which the water flows laterally through coir media. A header tank controls the flow rate into the tank at a set 0.13L/s. This gives a total residence time within the reactor of between 35 and 50 minutes, depending on porosity of the coir, assumed to be between 50% and 35% from a simple jar test, with reduction in porosity of the media expected over time due to compression of the coir and clogging of pore spaces with metal precipitates (Figure 2).

Results indicate that the coir was successful in removing both iron and manganese from the mine water, in what is most certainly a microbially mediated and maintained removal process (see Figure 3). Manganese removal commenced in the coir reactor at around 6 weeks of operation, which is in line with the time taken for a microbiological community to establish in bioreactor systems (pers. obs.). There appears to be a steady decline in the removal efficiency of the coir reactor from mid May, suggesting that the coir has a minimum 6 month effective life. Samples of the coir material were taken at 0 weeks and after 11 weeks of operation of the trial, and analysed by the Camborne School of Mines. They have been successful in selectively isolating Mn oxidising microorganisms from the coir material from the week 11 samples; but found no evidence of Mn oxidising microorganisms identified in the time 0 samples. Further support for microbial process is that biomass extracted from the time 11 samples was found to be much greater than from the time 0 (pers. comm.). DNA sequencing to identify the specific microorganisms present on the coir is currently ongoing.

Mn concentrations in the reed bed are also presented in Figure 3, which treats the full flow of 18L/s and has an area of 2,168m^2, to provide a numerical comparison between the trial and the reed bed performance. A simple scale up calculation, based on failure/breakthrough of the coir reactor after 6 to 7 months, suggest that the area of a coir bed with over a 5 year lifetime before requiring changing, would be in the region of 1,250m^2, which is a substantially smaller area than the current reed bed. Furthermore, there would be no reed bed preparation, planting, cutting, and it is anticipated that there will be minimal maintenance required during operation. So both operationally and financially, this system could be a viable and superior alternative to a full-scale reed bed. Assuming a 5-year life; this system could be used at a much smaller footprint for shorter-term reactive deployment. The '6 week 'start up time' could also potentially be reduced by seeding the reactor with coir from established reactors at the same site.

Conclusions

It is clear that there is still a lot of data analysis, interpretation, and assessment to do as we process our results. This paper provides an update on our research aims and efforts, rather than an exhaustive account of Mn dynamics in MWTSs. Further works continues on operating treatment sites and with R&D on emerging technologies.

At the time of writing this paper, further investigation of non-calcareous substrates for Mn removal is required, with a focus on the surface structure of the substrate and the associated role of the microbiological/biotic communities, rather than the chemical composition of the substrate is required. Coconut coir fibres have demonstrated high Mn removal rates over short time periods without any additional alkalinity and/or pH adjustment and warrant further investigation at much larger scale (both size and duration). This work will be done in tandem with assessment and interpretation of data on the current functioning of our reed beds. This combination of works, with support from the numerous researchers and academics working in the same and similar areas, will provide us with a robust foundation of understanding on how to both manage Mn in our current treatment schemes, and how to better design new schemes to remove and retain Mn.

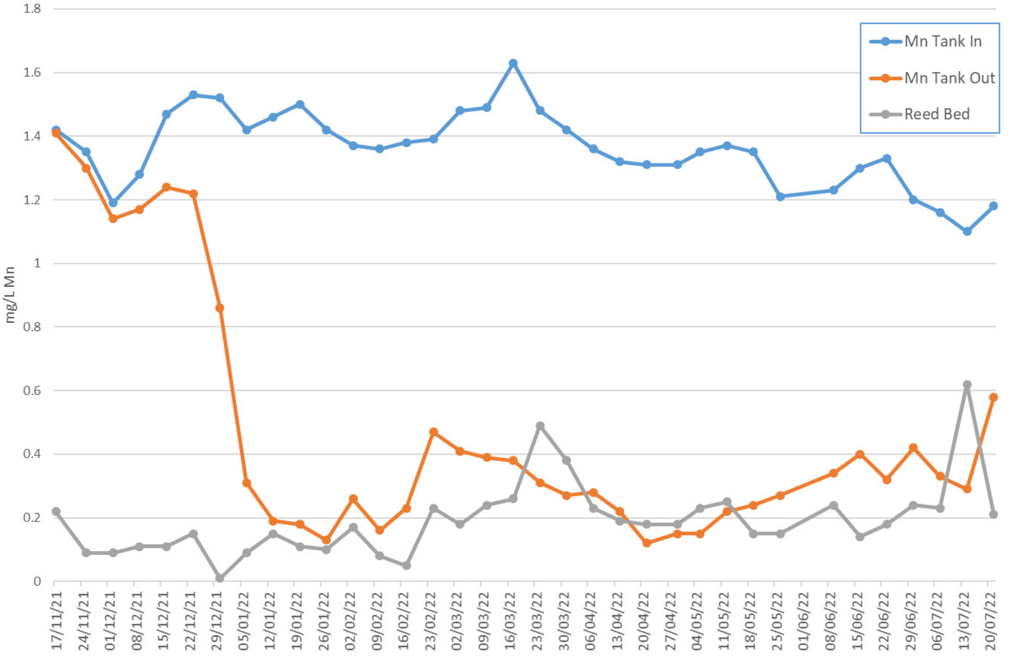

Figure 3 Manganese time series at Summersales R&D trial. 'Mn Tank in' is mine water that has been partially treated by two settlement lagoons in series, 'Mn Tank out' is the effluent from the coir tank, and 'Reed Bed' is the final discharge from the MWTS.

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