Assessment of Manganese Removal in Passive Systems Based on Operational Data and Experience of Treating Net-alkaline Coal Mine Waters in the UK

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Abstract

Passive treatment of net-alkaline coal mine waters in the UK is well established, with over seventy schemes currently operated by the Coal Authority. Some of these mine waters contain appreciable amounts of manganese, which is coming under increasing scrutiny from environmental regulators following the introduction of a bioavailable environmental quality standard in 2015. To date, the Coal Authority's mine water treatment schemes have been designed remove iron. However, there is now a possibility that some future schemes may also need to treat manganese. This paper reviews operational data from sixteen sites across the UK to improve understanding in designing future passive systems to remove manganese.

Keywords: net-alkaline, manganese, passive treatment, operational data

Introduction

Information for the passive removal of manganese from mine waters is much more limited when compared to the existing knowledge base on the passive removal of iron, and its application to the design of mine water treatment schemes in the UK is still in its infancy. This is despite passive manganese removal being discussed by Hedin *et al.* (1994) and in the Piramid Guidelines (2003). In order to improve understanding in designing future conventional passive systems for manganese treatment, or to facilitate the retro-fitting of existing schemes to reliably achieve a target concentration, a review of sixteen operational mine water treatment schemes (MWTS) located across the UK (ten in England, three in Scotland and three in Wales) has been conducted. These sites have been chosen as they provide a range of raw manganese concentrations (0.7 – 3.4 mg/L) and have sufficient operational flow and reed bed chemistry data available for review.

All sixteen sites included in this review treat net-alkaline mine waters and have iron concentrations that range between ≈3 and ≈130 mg/L. This review focuses exclusively on sites where chemical dosing is not used, in order to provide information on fully passive treatment for manganese. Table 1 provides a summary of the schemes included in this review, in addition to an overview of the typical flow rates, mean raw total iron and manganese concentrations and the total area of reed beds present at each site.

Data sourcing and limitations

This paper solely focuses on reporting operational observations recorded at selected sites, with the aim to improve future scheme design for manganese removal. Further investigations are required to better understand the control mechanisms of manganese removal and any relationships that may exist with other parameters. Operational data, going back to 2015 for some sites, and ending in December 2022 have been used in this review. Any data collected during reed bed refurbishments or maintenance activities when reed beds were either offline, or treatment performance was impacted, are excluded from the dataset. Previous work undertaken by the Coal Authority has shown that manganese removal predominantly takes place in reed beds rather than settlement ponds (Bamforth and Satterley, 2022). This paper therefore focuses on manganese removal in reed beds. Where multiple reed beds are present at site, they are considered together as a whole, rather than

Table 1 Summary of mine water treatment scheme locations included in this review with raw total iron and manganese concentrations (mg/L), flow rate (to the nearest 5 L/s) and reed bed area (to the nearest 100 m²)

Mine Water Treatment Scheme	Location	Start of Dataset	Mean Raw Concentration		Flow Rate	Reed Bed Area
			Iron	Manganese		
A Winning+	England, Derbyshire	2018	10.5	0.67	50	7000
				0.75	75	
				0.9	95	
Aspull Sough	England, Lancashire	2015	37.6	2.76	20	3200
Bates	England, Northumberland	2015	15.0	3.20	210	8400
Blenkinsopp (RB2)	England, Northumberland	2015	77.2	1.64	25	2200
Blindwells	Scotland, East Lothian	2015	4.63	2.24	280	17000
Chell Heath	England, Stoke-on-Trent	2016	20.3	3.28	10	2900
Craig-yr-Aber	Wales, Bridgend	2018	18.4	2.77	20	3300
Downbrook	England, Lancashire	2018	8.52	1.62	15	1300
Glyncastle	Wales, Neath Port Talbot	2016	18.9	1.58	15	3200
Hockery Brook	England, Lancashire	2017	14.8	2.09	20	2600
Mountain Gate	Wales, Carmarthenshire	2015	4.13	1.18	10	2400
Mousewater	Scotland, S. Lanarkshire	2016	16.0	1.73	45	8900
Pitfirrane	Scotland, Fife	2016	2.39	1.95	225	17900
Saltburn*	England, Cleveland	2016	128	2.64	30	4500
Stony Heap	England, County Durham	2016	15.0	1.91	20	1500
Summersales	England, Lancashire	2019	29.0	2.76	20	3200

+ Seasonal pumping takes place at A Winning, resulting in seasonal variation in chemistry. * Ironstone mine

individually, to maximise the available data. For treatment schemes that are comprised solely of reed beds, the raw mine water manganese concentrations have been used in this review for the influent concentration, in conjunction with the consented discharge point as the final effluent. For schemes where settlement ponds are present however, data from partially treated water between the final ponds and primary reed beds have been used where available.

Datasets based on routine operational sampling and monitoring have their limitations. Intermediate sample points often solely focus on iron, as this is the metal for which permit conditions are set, and is therefore the main focus for operational sampling budgets. Where no manganese data are available from settlement pond outlets, the raw manganese concentrations have therefore been used as a proxy. A more intensive sampling programme was established between 2019 and 2021 (Bamforth and Satterley, 2022), therefore some settlement pond outlet data are available for most sites during this specific timeframe. These data have therefore been used to ascertain what, if any, manganese removal occurs in the ponds, to enable a correction to be applied to the raw mine water concentrations in the remaining data set if applicable. This adjustment has been applied in order to model manganese concentrations entering the reed bed across the entire available data range. Such an approach introduces some conservatism to the dataset, reducing the risk of calculated removal rates being over estimated.

Manganese Removal

All the schemes listed in Table 1 were designed to remove iron, with any manganese removal considered an added benefit. Despite the range of mine water flow rates (≈10 – ≈300 L/s) examined in this review, the data from the schemes assessed to date suggest that iron concentrations entering the reed beds need to be low before manganese removal occurs. Blenkinsopp MWTS, which comprises two settlement ponds operating in parallel, followed by two reed beds operating in series, provides a good example. Figure 1 shows that the majority of the manganese removal at Blenkinsopp takes place in the second reed bed, where inlet total iron concentrations are lower (mean concentration ≈10 mg/L), compared to those entering the first reed bed (mean concentration ≈20 mg/L) see (fig. 2). Data from other sites suggest that iron

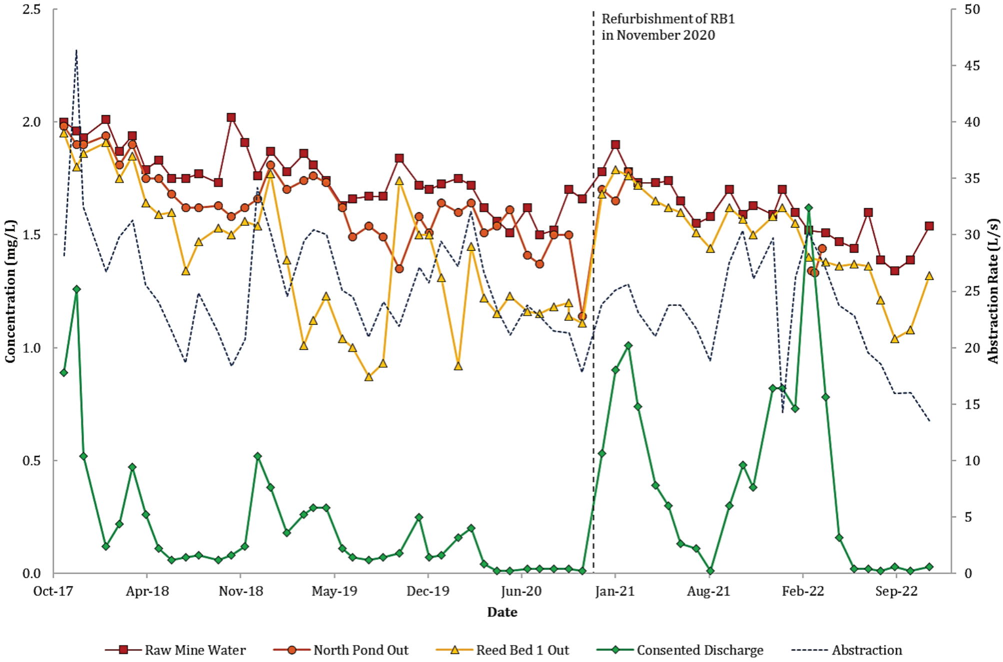

***Figure 1** Manganese removal at Blenkinsopp mine water treatment scheme vs. abstraction rates*

concentrations ideally need to be lower than those measured at Blenkinsopp however. At schemes where iron concentrations are sufficiently high to warrant settlement ponds, iron concentrations entering the reed beds are generally lower (≈5 mg/L) than those reported at Blenkinsopp (see tab. 2). This corroborates a review undertaken by Batty *et al.* (2008), who found that iron concentrations at Whittle MWTS needed to be reduced to ≈5 mg/L before manganese removal commenced. Raw manganese concentrations at Whittle today are ≈0.4 mg/L (vs. ≈1.5 mg/L during 2004 - 2005), therefore this site has not been included in this review.

For the purpose of any treatment design intending to include manganese removal, it is therefore recommended that iron concentrations are reduced to ≈5 mg/L, either by settlement ponds or primary reed beds, depending on raw iron concentrations. Additional secondary reed beds can then be incorporated into the design, where manganese removal is more certain to occur.

In November 2020, Reed Bed 1 at Blenkinsopp was refurbished, albeit unsuccessfully as the replacement reeds failed to establish (hence why this reed bed has been excluded from this review). This resulted in manganese removal being restricted to Reed Bed 2 (see fig.1), with very limited removal taking place in Reed Bed 1. Following the refurbishment, the removal of manganese at this site became more varied, with a strong seasonal pattern developing. This seasonal pattern in manganese removal is repeated at other MWTS across the UK (see fig. 3).

Figure 3 shows that manganese removal rates are generally at their highest during the months when ambient temperatures in the reed beds are at their warmest (May – October), compared to the cooler months (November – April) when temperatures fall. It is postulated that microbial activity is a primary control mechanism of manganese removal (Batty *et al.*, 2008), which increases when temperatures in the reed beds rise as the summer progresses, with latent heat sustaining activity into the autumn; in the colder winter / spring months, the autocatalytic effect of manganese oxide for manganese oxidation is most likely the predominant control mechanism for manganese removal. This seasonal trend appears to differ nationally however, with the start of the manganese removal season

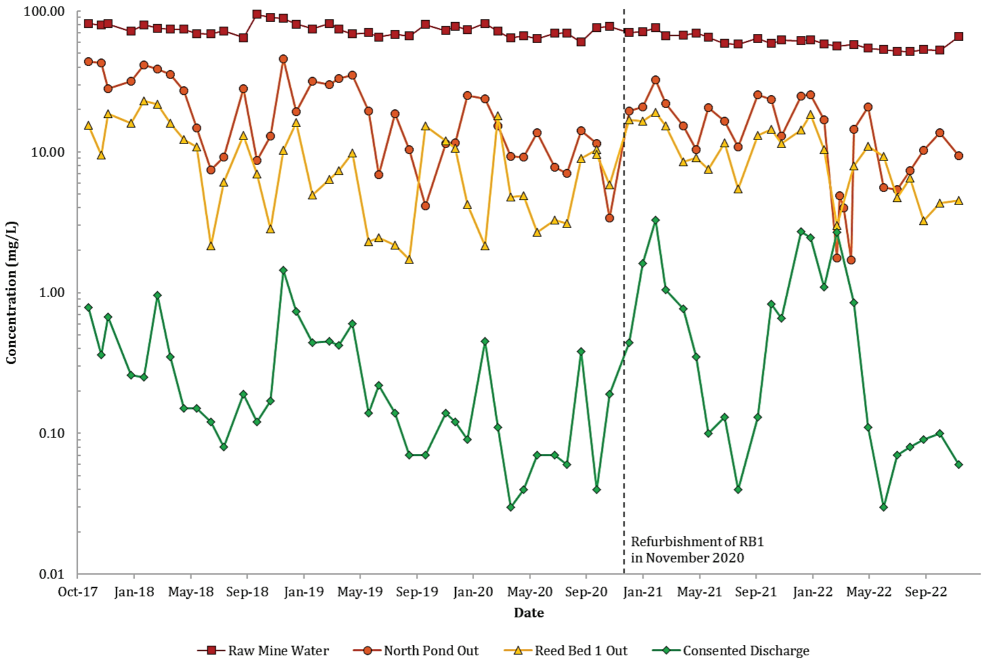

Figure 2 *Iron removal at Blenkinsopp mine water treatment scheme*

Table 2 *Summary of mean iron concentrations entering reed beds at treatment schemes where primary iron removal takes place in settlement ponds (all data quoted in mg/L)*

Treatment Scheme	Treatment Unit	Mean Iron Concentration	Treatment Scheme	Treatment Unit	Mean Iron Concentration
A Winning	Pond 1	5.08	Downbrook	Pond 1	3.4
	Pond 2	4.97		Pond 2	3.39
Aspull Sough	Pond 3	4.97	Glyncastle	Pond 1	7.68
				Pond 2	4.97
Bates	Pond 3	6.51	Hockery Brook	Pond 3	3.79
	Pond 4	5.95	Mousewater	Pond 1&2	9.53
Blenkinsopp	North Pond	22.2	Saltburn	Pond 4	2.06
	Reed Bed 1	10.4	Stony Heap	Pond 1	5.56
Craig-yr-Aber	Pond 1	5.64		Pond 2	5.78
	Pond 2	5.17	Summersales	Pond 2	4.31

generally commencing later further north, where spring arrives slightly later in the UK. This could have an implication for manganese removal at schemes in Scotland or at sites with a higher elevation, where the manganese removal season may be relatively shorter compared to sites located either further south, or at a lower elevation.

Manganese Removal Rates

Reed bed areal removal rates (g/m^2/day) for manganese have been calculated for each scheme included in this review (see tab. 3). Data collected during initial reed bed establishment, or periods when reed beds were offline for maintenance work have been excluded in this review in order to provide realistic removal rates that are achievable during normal operating conditions. A review of the operational data included in this review suggests that areal removal rates between 0.2 – 3.4 g/m^2/day are possible. This compares to a range of 0.17 – 1.07 g/m^2/day quoted by Hedin *et al.* (1994) and a nominal

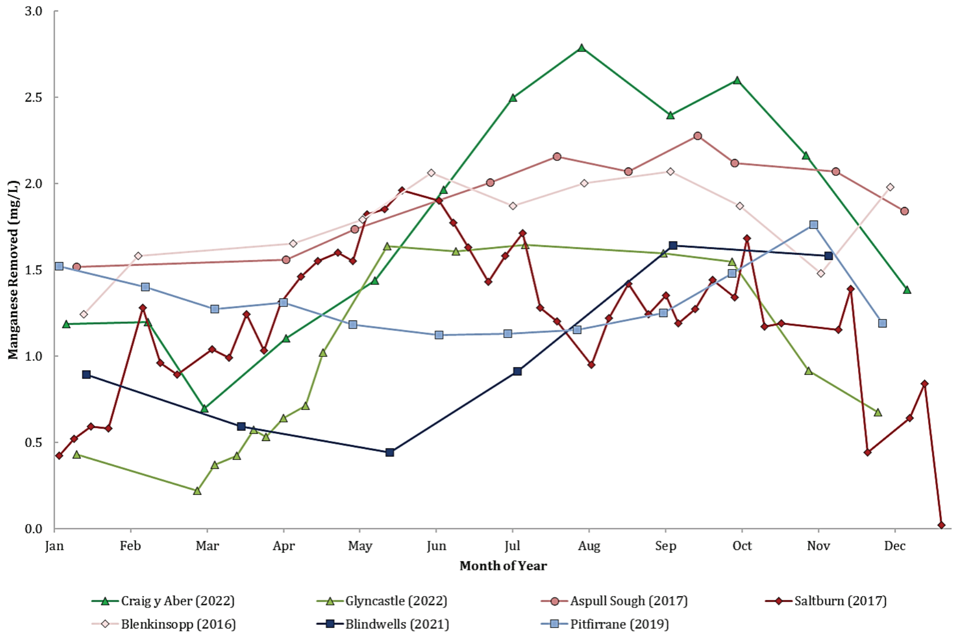

Figure 3 *Seasonal manganese removal patterns at seven sites across the UK from the south (Craig-yr-Aber) moving northwards (Pitfirrane). The years data are taken from are shown in brackets*

removal rate of 0.5 g/m²/day quoted in the Piramid Guidelines (2003). Table 3 indicates that most sites included in this review (11 out of the 16) have areal removal rates that fall between 0.6 and 1.5 g/m²/day. If the sites with the highest (Bates) and lowest (Mousewater) removal rates are discounted, the mean areal removal rates for manganese in the UK is estimated at 0.75 g/m²/day. This value is based on an annualised mean in order to offset the seasonal variation seen in manganese removal.

Reasons behind the high removal rate at Bates are currently unknown, although it may in part be driven by the higher raw manganese concentrations compared to the other schemes considered here. It is worth noting however, that the five sites in North America reviewed by Hedin *et al.* (1994) had raw manganese concentrations >9 mg/L, which is twice the amount typically seen in the UK. The relatively poor performance of the reed bed at Mousewater is down to the poor recovery of the reeds after maintenance works.

Table 3 *Summary of mean areal removal rates (g/m2/day) for manganese at each site included in this review in additional to the amount of manganese removed in the reed beds (mg/L)*

Site	Mean Areal Removal Rate	Manganese Removed			Site	Mean Areal Removal Rate	Manganese Removed		
		Min	Mean	Max			Min	Mean	Max
A Winning (50L/s)	0.38	0.02	0.58	1.01	Downbrook	0.68	0.01	0.69	1.62
A Winning (85L/s)	0.62	0.31	0.61	0.88	Glyncastle	0.39	0.03	1.12	1.89
A Winning (100L/s)	0.65	0.49	0.57	0.74	Hockery Brook	0.80	0.03	1.23	1.96
Aspull Sough	0.74	0.10	1.63	2.63	Mountain Gate	0.35	0.26	0.96	1.29
Bates	3.39	0.90	2.10	3.89	Mousewater	0.22	0.04	0.50	1.36
Blenkinsopp RB2	1.17	0.54	1.27	1.91	Pitfirrane	1.30	0.70	1.20	1.86
Blindwells	1.49	0.34	1.02	1.90	Saltburn	0.78	0.02	1.51	2.51
Chell Heath	0.49	0.40	2.06	3.48	Stony Heap	0.38	0.22	1.32	1.80
Craig yr Aber	0.86	0.57	1.84	3.04	Summersales	0.84	0.47	1.23	1.59

Reed Bed Maintenance

Figure 1 clearly demonstrates the potential negative impact of maintenance activities on the performance of reed beds to remove manganese, as effluent concentrations at Blenkinsopp prior to the works taking place were ≤0.5 mg/L, whereas afterwards, at times they increased to >1 mg/L, particularly in the colder months. Similarly, Figure 4 shows that after Reed Bed 1 at Mousewater was replanted in 2017, manganese removal also decreased, primarily due to the poor regrowth of *Phragmites sp.* reeds despite the newly planted *Typha sp.* reeds re-establishing well.

Calculated areal removal rates at both sites decreased from a mean value of 0.21 $g/m^2/day$ to 0.10 $g/m^2/day$ in Reed Bed 1 at Blenkinsopp (noting that manganese removal in Reed Bed 1 at Blenkinsopp is low due to the elevated iron concentrations), and decreased from 0.68 $g/m^2/day$ to 0.22 $g/m^2/day$ at Mousewater. Figure 4 also illustrates that it took six months before the reed bed at Mousewater began to remove manganese after the scheme was commissioned. This suggests manganese removal will only commence once the reed beds have established.

Conclusions

Although the number of schemes looked at in this review is relatively small, two key design principals have been identified that build on the Hedin *et al.* (1994) work, which can be taken forward for further investigation. Firstly, iron concentrations must be low (ideally ≤5 mg/L) before manganese removal will take place in reed beds and secondly, an areal removal rate of 0.75 $g/m^2/day$ is proposed for designing reed beds for future schemes where manganese concentrations exceed 0.7 mg/L. Furthermore, this review has also highlighted two key considerations that apply to manganese removal that contrast to iron removal. Firstly, manganese removal tends to be seasonal with greater concentrations typically removed in the warmer months and secondly, manganese removal will likely only commence once reed beds have established. Finally, this work has highlighted that reed beds can also be

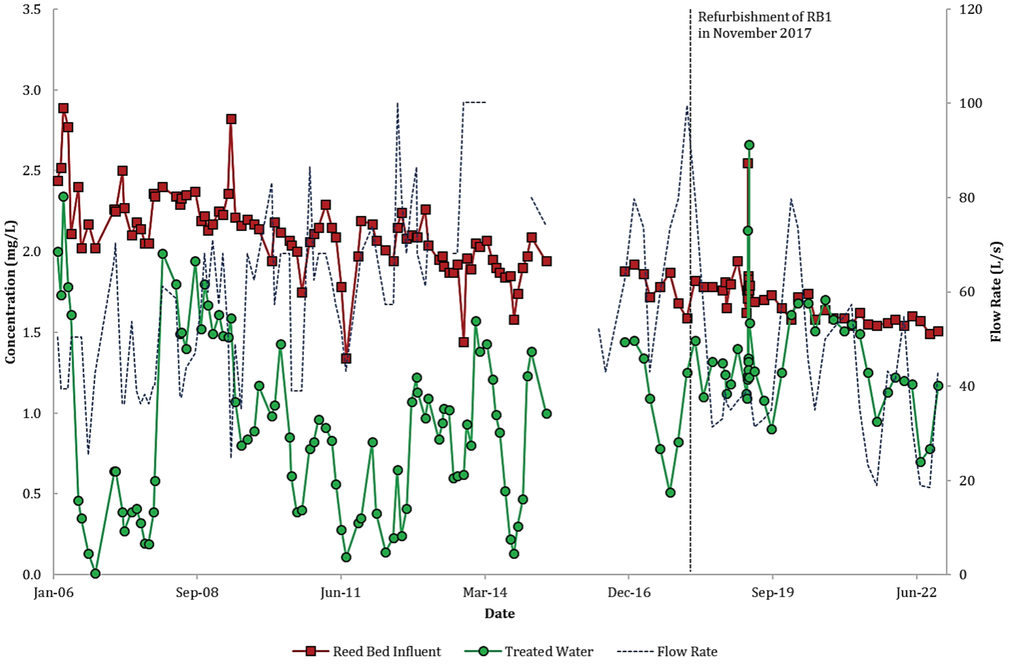

Figure 4 *Manganese removal in the reed beds at Mousewater mine water treatment scheme vs. flow rate (no data are available between June 2015 and May 2016)*

negatively impacted by refurbishment works for several years if the freshly replanted reeds fail to establish correctly.

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