Effect of ironstone mine spoil reclamation on drainage water chemistry

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Abstract: Reclamation of acidic mine spoil involves establishment of a vegetation cover, increasing the amenity value of the land and reducing the time of spoil stabilisation. Methods used in spoil reclamation (spoil reworking and the addition of nutrients and lime) have been demonstrated to increase the generation of acid mine drainage in the short-term. To counteract a deterioration in drainage water quality, constructed wetland systems (CWS) are widely used to increase the pH and reduce concentrations of metals. The impacts of reclamation on drainage water chemistry from an ironstone spoil heap in Central Scotland were monitored for three years. Reclamation resulted in significant increases in concentrations of iron, aluminium and manganese in site drainage. Drainage water chemistry improved after passage through a passive treatment system, consisting of a settling pond and CWS, but was still worse than prior to reclamation. Treatment system performance varied considerably during the monitoring period. Cumulative monthly temperature and antecedent rainfall were correlated with settling pond and CWS performance. The performance of CWS for treating drainage from acidic spoil is difficult to predict as site hydrology, climate and chemistry must be considered.

1 INTRODUCTION

Acidic mine spoil can leave an environmental legacy of sparsely vegetated land and highly acidic drainage, with elevated concentrations of Fe and other metals mobilised by the acidity, such as Mn and Al. Acid mine drainage has a detrimental impact on receiving watercourses, rendering water resources unfit for agricultural, industrial or potable water supply and reducing aquatic biodiversity. Reclamation of mining spoil by woodland establishment stabilises the material and reduces land and water contamination over a number of years (Sopper, 1993). Reworking of the spoil and amendment with nutrients, organic material and limestone are often necessary to create suitable conditions for tree growth. These treatments have been shown to intensify acid production from spoil containing iron pyrite (Costigan *et al.,* 1981).

Iron pyrites in ironstone and coal spoil are oxidised to form sulphuric acid when exposed to air and water, the exact chemical pathway depending on the spoil pH (Pulford, 1988). At pH above 4, acid production proceeds slowly and is controlled by the rate of oxygen diffusion into the spoil (Equation 1). When spoil pH falls below 4, an alternative oxidation pathway is followed, catalysed by the bacterium *Thiobacillus ferrooxidans* (Equation 2).

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4 \qquad \text{(Equation 1)}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{(Equation2)}$$

Spoil disturbance exposes new reaction surfaces for pathway 1 and at the same time nutrient addition may nourish iron-oxidising bacteria which catalyse oxidation pathway 2 (Equation 2). Enhanced nutrient leaching may also occur from sewage sludge applications to acidic spoil (Cravotta, 1998). The reclamation of ironstone spoil may therefore cause a short-term deterioration in drainage quality until spoil stabilisation occurs. Measures are required to treat increased concentrations of nutrients, metals and acidity in drainage from reclaimed spoil.

Constructed wetland systems (CWS), comprising surface and subsurface flow systems of aquatic macrophytes planted in an organic substrate, are increasingly used to treat acid mine drainage. The low capital and maintenance costs of CWS are especially advantageous for treating diffuse pollution from mining spoil where liability is frequently impossible to enforce and cleanup is not undertaken by the polluter (Younger *et al.*, 1997). Metals are removed by a combination of physical, chemical and biological processes in CWS. Precipitation occurs as the result of reduced flow velocities in CWS, and also at aerobic sites around macrophyte roots. Adsorption occurs onto the wetland substrate. The design and functioning of CWS for acid mine drainage treatment are well-documented elsewhere (e.g. Hedin & Nairn, 1993; Wieder, 1993; Faulkner, 1994). Despite the increasing operational experience with CWS, considerable variability in performance has been reported (Wieder, 1989) and information on long-term effectiveness is sparse. In this paper we report the results of a three year evaluation of drainage water chemistry from a reclaimed ironstone mine spoil heap in Central Scotland and treatment in a CWS, and discuss their implications for mine spoil reclamation.

2 METHODS

Benhar ironstone spoil heap (locally known as Benhar “bing”) covers 5 ha and is located at 230 m elevation, 45 km east of Glasgow in Central Scotland, UK (Figure 1). Although mining ceased in the early 20th century, the bing has remained mostly unvegetated due to the highly acidic and infertile spoil (pH 2.7, available P 2.3 mg/kg, total N 0.11 g/kg). Acidic metal-rich drainage from the bing (pH 2.7, 47.7 mg/l total Fe, 49.2 mg/l total Al) entered the headwaters of the River Almond, resulting in water quality degradation from Class 1 (unpolluted) to Class 3-4 (poor quality-grossly polluted) in the Scottish River Classification Scheme (River Almond Catchment Partnership Group, 1997).

Reclamation began in 1996 with regrading of the bing to a landform suitable for tree planting and visually more pleasing. In March 1997 the top 0.3 m of spoil was treated with peat at 30 t/ha, dried pelleted sewage sludge (BIOGRAN) at 35 t/ha, coarse limestone chips at 60 t/ha and ground limestone at 30 t/ha. After conventional forestry ploughing the site was planted with common alder (*Alnus glutinosa*) and downy birch (*Betula pubescens*) in May 1997. Drainage from the bing was diverted through a settling pond (15 x 25 x 1.4 m) and 0.4 ha surface flow CWS. The wetland is excavated in peat and has a substrate of 0.5 m of mushroom compost on 0.1 m of crushed limestone. It is split into 16 cells by straw bale dikes and has a design water depth of 0.3 m. Cattails (*Typha latifolia*) were chosen as the wetland vegetation due to their tolerance of acid mine drainage (Samuel *et al.*, 1988) and rapid growth and planted in August 1997.

Throughflow and surface water samples have been collected at the site at monthly intervals from June 1997 to June 1999 and September 1999, respectively. Throughflow is collected in 18 *in-situ* drain pipe samplers, inserted into the spoil at about 0.3 m depth in experimental plots. Surface water is sampled in the drainage ditches surrounding the bing and at the wetland inlet and outlet (sampling sites 1-5 in Figure 1). Sample point 1 is located in moorland upstream of the bing and acts as a control. In November 1998 drainage from the moorland was diverted away from the bing in order to reduce the hydraulic loading on the treatment system and thereby to reduce the variability in treatment performance. Spot measurements of discharge were made at sample points 2 and 3 to calculate overall concentrations entering the treatment system. Rainfall is monitored with a tipping bucket raingauge connected to a datalogger, and located at the CWS outlet. All water samples are collected in polyethylene bottles and analysed in replicate on return to the laboratory. Unfiltered sample is analysed for pH and acidity and Fe, Al and Mn by flame atomic absorption spectrophotometry (FAAS) (total Fe, Mn and Al). The remaining sample volume is passed through a 0.45 μm membrane filter and analysed for: dissolved (diss) Fe, Mn and Al by FAAS; and SO_4^{2-} by ion chromatography.

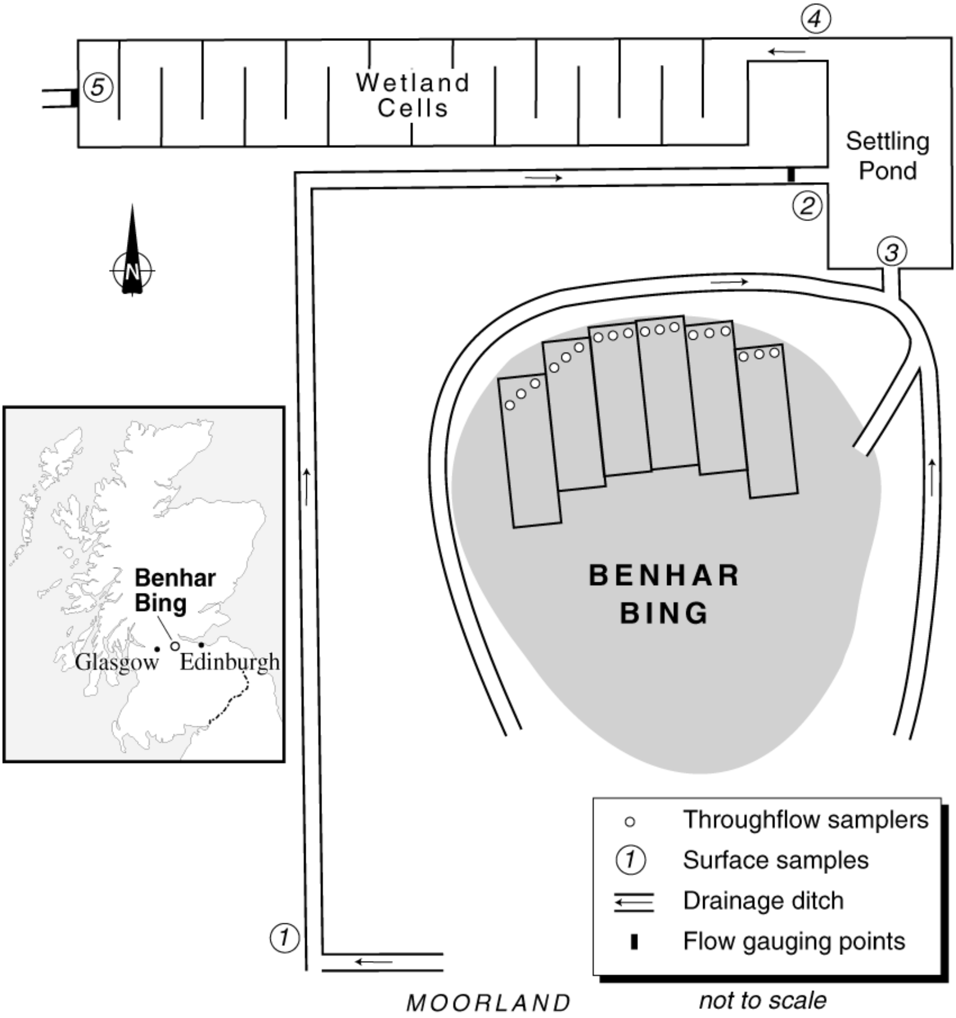
3 RESULTS AND DISCUSSION

Effect of spoil reclamation on drainage water chemistry

Table 1 shows that the chemistry of the moorland control site has not changed and throughflow chemistry has on average improved after spoil reclamation. In throughflow the pH has increased and acidity, dissolved Fe, Al and Mn have declined, although metal concentrations still exceed the moorland control site. SO_4^{2-} concentrations have increased after reclamation, perhaps due to intensified pyrite oxidation in the spoil. The range of values measured for each parameter in throughflow is wide, indicating that the treatment effect is spatially very variable. Closer examination of individual throughflow samplers shows that out of 18 sites in total, two sites show abnormal behaviour with distinctly lower pH and higher metal concentrations.

Figure 1 Location of Benhar bing and water sampling sites

Comparison of throughflow and bing drainage after reclamation in Table 1 shows that the treatment effects in throughflow are not apparent in drainage from



the entire spoil heap. From the water volumes collected in the throughflow samplers, throughflow from amended spoil is estimated to account for < 1% of total bing drainage. The purpose of the treatment system at Benhar bing is to prevent any deterioration in drainage chemistry from the site as the result of spoil reclamation. To test whether this objective has been achieved, drainage chemistry from the bing prior to reclamation was compared with the wetland site (sample site 5) using the non-parametric Mann-Whitney test. At the 95 % significance level pH, acidity, and SO_4^{2-} were unchanged, but dissolved Al, Fe and Mn were significantly higher in drainage from the bing after reclamation.

Table 1 Water chemistry before and after reclamation. Median values with ranges in brackets. All units mg/l, apart from acidity in mg/l $CaCO_3$

		pH	Acidity	SO_4^{2-}	Diss Fe	Diss Al	Diss Mn
Moorland	Before[1]	6.3 (5.6-6.7)	0	164 (65-507)	0.1 (0-9.1)	0 (0-0.6)	0 (0-0.1)
Moorland [3]	After[2]	6.8 (6.2-8.0)	0	69.8 (10.3-382)	0.5 (0.2-5.3)	0.2 (0-0.8)	0.2 (0-1.4)
Through-flow	Before[1,4]	2.6 (2.3-2.9)	351 (112-960)	830 (161-2106)	30.3 (7.6-45.9)	16.8 (3.3-52.7)	11.9 (2.9-29.1)
Through-flow	After[5]	3.9 (2.3-6.8)	64.0 (1-2888)	1647 (534-7162)	0.3 (0-1870)	4.3 (0-324)	7.4 (0-334)
Drainage below bing	Before[1]	2.7 (2.6-2.9)	533 (221-650)	1716 (713-2810)	47.7 (28.9-54.3)	49.2 (12.7-57.4)	18.8 (5.6-25.4)
Drainage below bing [6]	After[2]	2.7 (2.1-3.2)	562 (74.5-799)	2412 (365-3917)	222 (6.5-305)	70.8 (14.2-93.7)	56.7 (5.5-101)
Wetland outlet [7]	After[2]	2.8 (2.6-3.4)	345 (28.2-580)	1745 (364-2603)	105 (8.3-279)	42.7 (2.4-809)	49.9 (3.7-72.4)

[1]7 dates, July-Sept 1995 (Burrows, 1996). [2]31 dates, June 1997- Sept 1999.
[3]Sample site 1. [4]6 throughflow samplers. [5]27 dates, July 1997 – Aug 1999.
[6]Sample site 2. [7]Sample site 5.

Treatment system performance

The efficiency of the settling pond and wetland in removing acidity and metals from the bing drainage was assessed by calculating percentage treatment efficiencies (Equation 3) on a monthly basis for June 1997-September 1999. Positive values indicate retention and negative efficiencies are indicative of losses. Treatment efficiencies and chemistry of CWS inflow at Benhar bing are compared with other sites in Table 2.

$$Treatment\ \ efficiency\ (\%) = \frac{Inflow\ conc - Outflow\ conc}{Inflow\ conc} \times 100 \qquad \text{(Equation 3)}$$

Treatment efficiencies are lower than the efficiencies for acidity, Fe, Al and Mn reported by Wieder (1989) and Younger *et al.* (1997), but drainage from Benhar bing is more contaminated than the drainage typically treated by the wetlands surveyed. Compared with Lick Run, a wetland of similar design and treating drainage of comparable chemistry, the CWS at Benhar is less efficient in removing Fe, Al and SO_4^{2-}, but has a similar performance for Mn. Treatment efficiency for Mn may be impaired at Benhar and Lick Run due to preferential adsorption of high concentrations of Fe onto organic sites in the substrate (Machemer & Wildeman, 1992).

Table 2 Comparison of treatment efficiencies and CWS inflow chemistry at Benhar with other sites

	Median treatment efficiency (percent)				Inflow chemistry (mg l^{-1}, acidity in mg l^{-1} $CaCO_3$)			
	Benhar[1]	US Survey[2]	Quaking Houses[3]	Lick Run[4]	Benhar[5]	US Survey[2]	Quaking Houses[3]	Lick Run[4]
Acidity	30	67	58	---	616	257	175	1174
Total Fe	29	81	60	82	217	61	18	139
Total Al	17	48	65	40	60	21	15	58
Total Mn	5	34	---	6	55	38	---	3.9
Sulphate	8	8	---	23	2265	1194	---	1246

[1] *Diss metals.*
[2] *Survey of 142 CWS treating coal mine drainage in eastern USA (Wieder, 1989).*
[3] *County Durhan, UK (Younger et al., 1997).*
[4] *Ohio, USA (Mitsch and Wise, 1998). Total metals acid-digested.*
[5] *Median concentrations at site 4.*

Efficiencies were also calculated on a monthly basis before and after the moorland drainage diversion in November 1998 to determine whether there was any improvement in performance of the CWS. Table 3 shows that the median efficiency of the total treatment system declined after the drainage diversion for all parameters, apart from for SO_4^{2-}. However the decline in treatment efficiency occurred in the settling pond, perhaps due the lack of dilution of concentrations at site 3 from moorland drainage. Treatment efficiencies improved for all parameters in the CWS after the moorland drainage diversion, probably as the result of the reduced hydraulic loading and increase in retention time in the CWS.

Table 3 Efficiencies (%) of total treatment system, settling pond and wetland before and after moorland drainage diversion. Median values with ranges in brackets

		Acidity	SO_4^{2-}	Diss Fe	Diss Al	Diss Mn
Total treatment system	Before	41 (14-91)	20 (-6-41)	50 (0-79)	34 (1-65)	24 (7-47)
	After	36 (-10-97)	21 (4-90)	39 (14-97)	29 (1-97)	23 (2-96)
Settling pond	Before	12 (0-41)	14 (-34-50)	37 (-169-77)	22 (1-55)	25 (7-45)
	After	6 (-41-10)	4(-13-26)	19 (6-24)	10 (-47-23)	10 (-57-69)
CWS	Before	17 (-46-68)	5 (-85-44)	23 (-215-75)	14 (-34-62)	-1 (-67-43)
	After	32 (8-96)	16 (0-90)	32 (3-97)	20 (1-97)	10 (-2-95)

The ranges of treatment efficiencies in Table 2 show that performance of the treatment system at Benhar bing is highly variable, so predicting the future performance of the system is problematic.

Results from the first year of monitoring suggested that treatment efficiency is lower in winter, probably due to plant dieback and cooler temperatures reducing the rate of microbiological activity in the CWS (Heal & Salt, 1999). The relationships between treatment efficiency and 30 days antecedent rainfall and cumulative temperature were investigated for the settling pond and CWS separately and show contradictory effects for all parameters. Figures 2 and 3 show typical results for Fe and Mn.

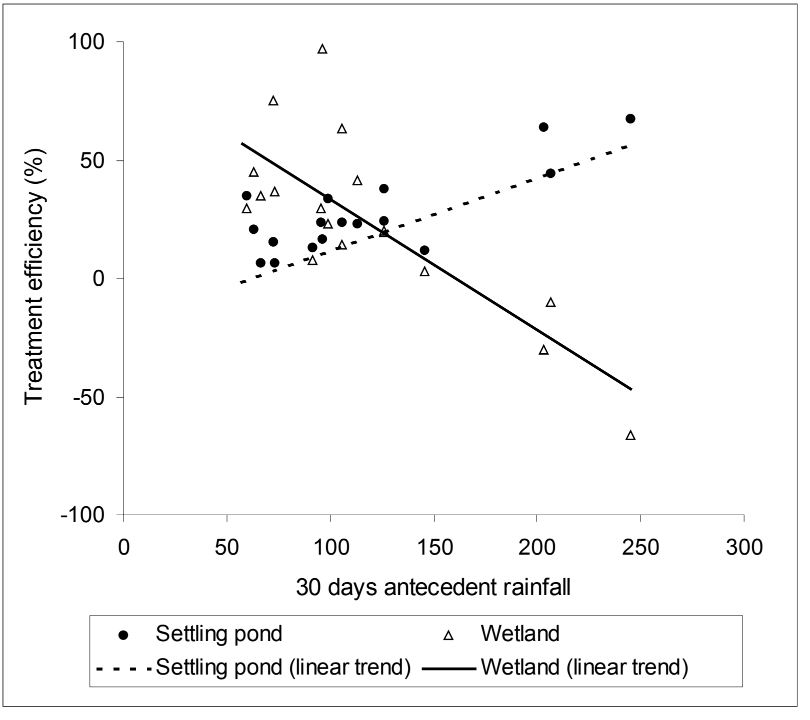


Figure 2 Relationship between treatment efficiencies for diss Fe and antecedent rainfall

The treatment efficiency of the settling pond increases with antecedent rainfall, perhaps due to dilution of input concentrations, and decreases as cumulative temperature increases, possibly as the result of concentration of pollutants by evaporation. In contrast the treatment efficiency of the CWS increases as antecedent rainfall decreases, due to longer retention times, and increases with cumulative temperature, as the result of increases in the rate of microbial activity. It is therefore possible to predict treatment efficiency of the settling pond and CWS from site climate information. Another method for predicting future drainage water quality from the site (at the CWS outlet - site 5) is from water chemistry at the major inflow to the system (site 2). Chemical concentrations at site 2 are significantly correlated with concentrations at site 5 for acidity, sulphate and dissolved Fe, Al and Mn (Figure 4).

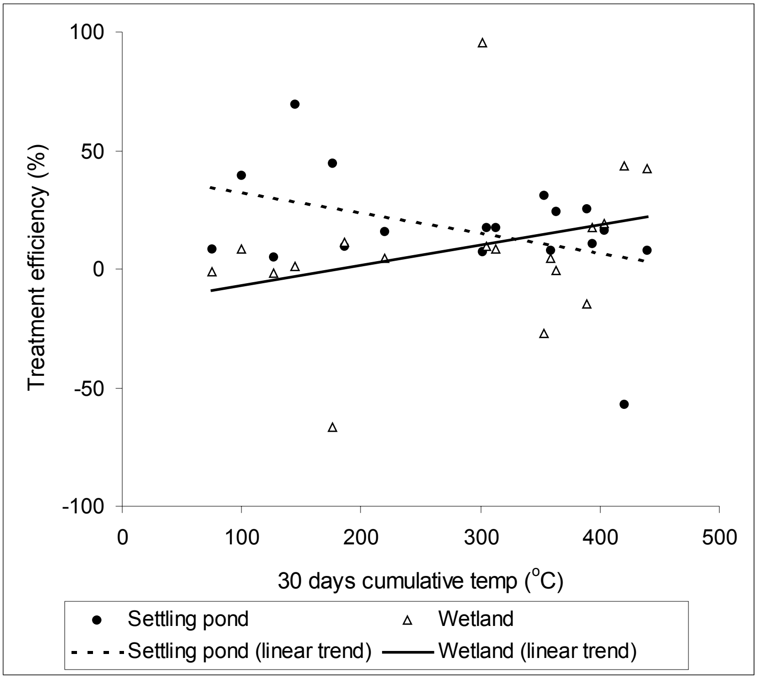


Figure 3 Relationship between treatment efficiencies for diss Mn and temperature

4 CONCLUSIONS

Reclamation of highly acidic, metal-rich ironstone spoil with dried pelleted sewage sludge, peat and limestone has resulted in a decrease in drainage water quality from the site for up to three years after reclamation commenced. The passive treatment system of a settling pond and CWS is improving drainage water quality but is insufficient to treat drainage to the quality preceding spoil reclamation. The CWS performance is sub-optimal as a result of the low inflow pH, but corresponds to wetlands of similar design treating highly acidic mine drainage. Changes to the site hydrology which have reduced the hydraulic loading onto the CWS have resulted in improved treatment efficiencies. The efficiency of the treatment system is highly variable and the settling pond and CWS components respond differently to changes in temperature and rainfall. The most robust method of predicting the performance of the treatment system appears to be from inflow concentrations. CWS have been demonstrated to improve drainage water quality from acid mine spoil, but they are not able to maintain drainage water quality from highly acidic mine spoil in the years immediately following reclamation.

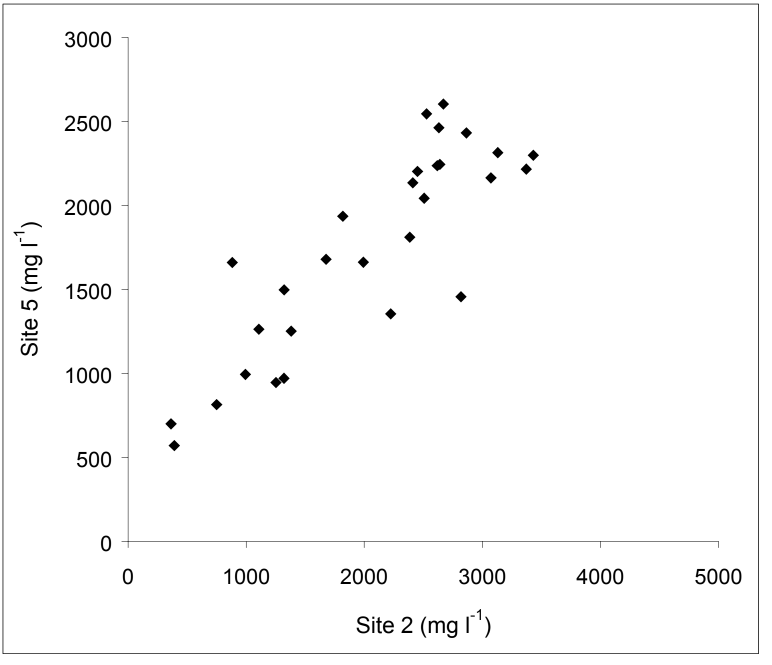


Figure 4 Relationship between SO_4^{2-} concentrations at sites 2 and 5

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Wpływ rekultywacji odpadów z kopalń syderytu na skład chemiczny odprowadzanych wód

Kate Heal & Carol Salt

Streszczenie: W wyniku rekultywacji kwaśnych odpadów kopalnianych powstaje na nich szata roślinna oraz następuje polepszenie jakości gruntu oraz skraca się czas stabilizacji odpadów. Metody stosowane w rekultywacji (przetwarzanie odpadów oraz dodawanie składników odżywczych i wapna) przyspieszają kwaśny drenaż. Aby przeciwdziałać pogorszeniu jakości odprowadzanej wody, na szeroką skalę stosuje się system osadników z filtrami roślinnymi (CWS), który wpływa na podniesienie pH i redukuje stężenie metali. Wpływ rekultywacji na skład chemiczny wody odprowadzanej ze składowiska odpadów kopalnianych syderytu w centralnej Szkocji był monitorowany przez okres trzech lat. Wskutek rekultywacji znacznie wzrosło stężenia żelaza, glinu oraz manganu w wodach w miejscu drenażu. Chemizm wód odprowadzanych uległ poprawie po przejściu przez system biernego oczyszczania składający się ze stawu osadnikowego i filtru roślinnego. Skuteczność działanie systemu oczyszczania była zmienna w okresie przeprowadzonego monitoringu.

Skuteczność systemu CWS przy stosowaniu w przypadku kwaśnych składowisk jest trudna do przewidzenia, gdyż należy wziąć pod uwagę lokalne warunki hydrologiczne, klimatyczne i geochemiczne obszaru badań.