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Ecological water treatment processes for underground uranium mine water: Progress after three years of operating a constructed wetland

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Abstract. Sustainable treatment approaches are sought for U mine waste water utilizing constructed wetlands. In 1998 a pilot system was constructed to remove U, ²²⁶Ra, As, Fe and Mn from the effluents of the flooded workings of the Pöhla-Tellerhäuser mine of Wismut in Germany. Gravel beds and their biofilms in the system concentrate ²²⁶Ra. As is co-precipitated/adsorbed onto iron-oxyhydroxide particles collecting in treatment cells. U occurs as uranyl carbonate at pH 7.3-8.0 and is not removed. An ecological system oxidizes iron, provides particulates for adsorption and organic matter to support bio-mineralization in anaerobic sediments.

Introduction

Metal and radionuclide-contaminated waters from underground mine workings, waste rock piles and tailings deposits represent long-term environmental and financial liabilities. Low cost, environmentally sustainable approaches to waste water treatment are sought by utilizing wetlands, sometimes constructed specifically for this purpose. Wetlands as treatment systems are very effective in addressing organic water pollution (Hammer 1989; Moshiri 1993; Kadlec and Knight 1996). Similar passive treatment techniques have begun to show value to the mining industry with a number of successful applications over the past two decades. However, in many systems, metal adsorption onto organic/ inorganic material used in the construction of the wetland will ultimately cease, and so will the capacity of the wetland to generate sufficient new organic material (Fyson et al. 1995). These approaches have certainly assisted in advancing knowledge and awareness of the potential of natural systems, and contribute to the resolution of these industrial challenges. However, they fall short of providing a sustainable ecological solution

to water treatment, as such systems are likely to have a limited functional life span.

A long-term, sustainable wetland is composed of three integrated but critical parts; an oxidation pond, a biological section, and a settling pond. Metals must be reduced in an oxidation pond, before the waste stream is allowed to enter the biological section, to prevent them from coating the organics that would then cease to function as adsorption sites and serve as microbial carbon source. In the biological section, productivity must be high to produce organic matter at a rate equal to or higher than adsorption sites are needed to adsorb metals. Finally, settling ponds must provide anaerobic conditions in the sediments in which the metals can be bio-mineralized by reducing microbial consortia.

When a pilot wetland test system was constructed in 1998 to treat passively underground water from the Pöhla-Tellerhäuser mine it was believed that U, ²²⁶Ra, Fe, As and Mn would be removed primarily by the actions of plants (Gerth and Kießig, 2001). Three years of monitoring data from each section of the system are assessed. It is suggested that in fact plants play a minor role in contaminant removal.

Pilot test system description

In Fig.1 a schematic overview is presented of the pilot system components that were constructed from a former storm water retention pond. The overall system has a volume of 415m³ covering a surface area of 474 m² and is divided into 5 cells, constituting the passive pilot system. Two small additional cells are used to test reactive materials after the passive treatment, which are not discussed here. After it has passed over a 21 m long cascade, the mine effluent arrives through a pipe at the bottom of the first cell, a sludge collection cell (2.5x5.8x2.1 m). From the sludge cell the water travels along a trough to the entrance of a larger settling cell (21.4x5.8x2.1 m). The water overflows into a gravel bed installed in cell 3 (16.7x5.8x2.18 m) where it leaves through 5 drainpipes at the bottom and flows upward into a second gravel bed into cell 4 (17.3x5.8x2.8 m). This third cell consists of 0.8 m of gravel, a thin layer of sewage sludge and straw to supply nutrients for plant and microbial growth, covered by an additional layer of 0.4 m of gravel. This 3rd cell serves as a source of nutrients to the fourth cell, where a 1.9 m deep gravel and sand bed is planted with reeds, rushes and cattails., representing the first "wetland" component of the pilot system. The water overflows into the final treatment cell, #5 (23.6x5.8x2.8 m) where swamp iris, rushes, reeds and cattails grow in a substrate consisting from top to bottom of a 0.4 m layer of gravel, a 1.16 m layer of soil, followed by a 0.25 m layer of compost.

Flow through the system was 3.5 m³.h⁻¹ from January 1999 to August 2000. A reduced flow of 1 m³.h⁻¹ passed through the system between September and December 2000. From January 2001 to the beginning of March 2001 the system was operated at 2.0 m³.h⁻¹ when the flow was again reduced to 1.0 m³.h⁻¹ until Novem-

ber 2001. From November until the end of monitoring period reported here, December 19th 2001, the system was operating at $2.0 \text{ m}^3 \cdot \text{h}^{-1}$.

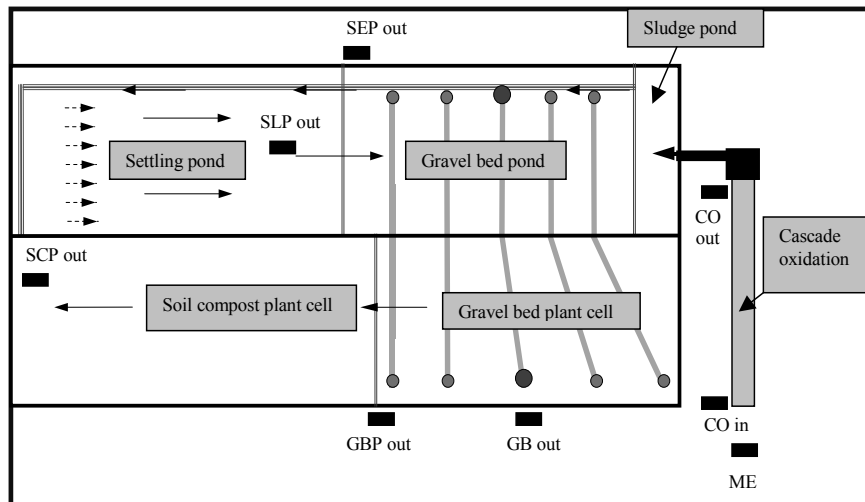


Fig. 1. Overview of the pilot system components and sampling locations.

Water sampling and analysis

Water quality was measured weekly at 9 sampling stations located throughout the pilot system, but only 8 are relevant to the discussion of the system performance. The sampling stations are: 1) mine effluent (ME) sampled before it enters the oxidation cascade 2) (CO in) and as it is leaving the cascade 3) (CO out) to enter the sludge pond. The overflow from the sludge pond after the water has traveled through a trough is sampling point 4) (SLP out), where the flow enters the settling cell. The water is sampled at the overflow to the first gravel cell 5) (SEP out) entering the first gravel bed in cell 3 from the top. After flowing through the gravel bed and before it enters the next gravel bed 6) (GB out) is located, followed by station 7) (GBP out), as the water is leaving the first cell with wetland plants. The final outflow 8) (SCP out) is collected after the water flows over surface of the soil, compost cell through the plants.

Water samples were filtered on site through a $0.45 \mu\text{m}$ filter, acidified for the determination of As, Fe, Mn and U and are shipped to the laboratory of Wismut for chemical analysis by ICP-OES for As, Fe and Mn. U is determined by the KPA method (Kinetic-Phosphorescence). The values of ^{226}Ra are determined on unfiltered samples by Alpha spectrometry. pH, Eh, electrical conductivity and dissolved oxygen concentration are measured in the field with a combination probe on a WTW Multi Line meter.

Results and discussion

The pH values of the mine effluent ranged from 6.8 to 7.6, with an average value of 7.3. The pH leaving the sludge cell (SLP) ranged from 7.6 to 8.4 with an average pH of 8.0. Overall, the average pH of the system was 7.6. The bicarbonate concentrations in the effluent averaged 416 mg.L^{-1} .

Uranium: Concentrations of U in the pilot system, covering three years of weekly sampling have been summarized in Table 1. Both total and filtered concentrations are shown.

Table 1. Average uranium concentration in water at Pöhla system, 1999-2001

	ME	CO in	CO out	SLP out	SEP out	GB out	GBP out	SCP out
			Total	U	mg.L^{-1}			
N	141	142	92	92	150	149	140	144
Avg	0.09	0.08	0.07	0.07	0.09	0.09	0.09	0.08
Stdev	0.02	0.03	0.01	0.05	0.03	0.02	0.02	0.02
			Filtered	U	mg.L^{-1}			
N	149	19	19	134	148	138	143	141
Avg	0.09	0.06	0.06	0.09	0.08	0.09	0.08	0.08
Stdev	0.03	0.01	0.01	0.02	0.02	0.02	0.02	0.03

In freshwater, U is present in its oxidized form as UO_2 , uranyl, or uranyl hydroxide as a cation. In the presence of carbonate, it forms uranyl carbonate $\text{UO}_2(\text{CO}_3)_3^{4-}$. With the high bicarbonate concentration, U is most likely in the uranyl carbonate form, which is a stable anion (Langmuir 1978). As an anion, U is less attracted to the negatively charged cell walls of plants, algae and microbes (Myers et al. 1973; Neihof and Loeb 1972). This may explain why uranium concentrations are unaffected throughout the system.

If pH were lowered, more U would be removed by the biomass in the system. In several studies of U uptake by algae, the optimum pH for U removal was between 3 and 7, with most having pH optima around 5 (Liu and Wu 1993; Pribil and Marvan 1976; Yang and Volesky 1999; Franklin et al. 2000). In another example, pond algae accumulated U favourably in waters with higher calcium carbonate ratios, which had lower pH values, than waters with higher calcium carbonate ratios (Duff et al. 1997).

Iron and Arsenic: The concentrations in total and filtered Fe and As are given in Fig. 2a and 2b. Both iron and arsenic concentrations decrease significantly in the system. Most of the iron and arsenic concentrations are reduced as the water oxidizes passing over the cascade (CO out). A further reduction in total As concentration is evident after the water leaves the sludge pond (SLP out) but the filtered As remains at the same concentration of $444 \text{ } \mu\text{g.L}^{-1}$. After the settling pond (SEP out) both total and filtered As concentrations are essentially the same, suggesting little removal through the planted cells and on the biofilms on the gravel. The average concentration of As leaving the system is $390 \text{ } \mu\text{g.L}^{-1}$.

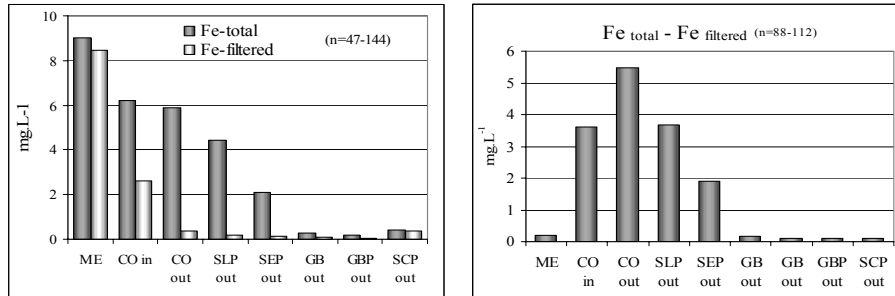


Fig. 2a. Average [Fe] and Fe particulates in water at Pöhla system, 1999-2001

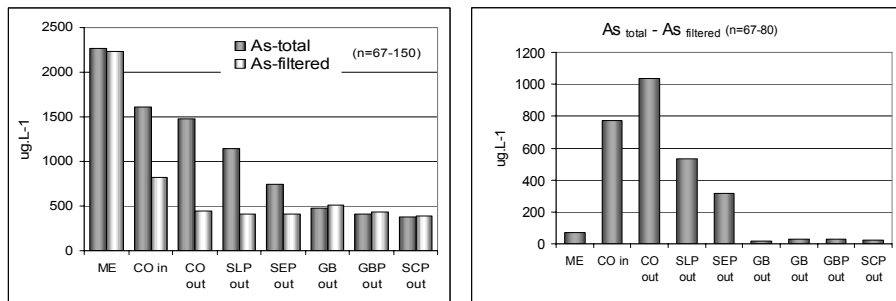


Fig. 2b. Average [As] and As particulates in water at Pöhla system, 1999-2001

The total Fe concentration leaving the cascade (CO out) has the same pattern as As, being reduced as the water passes through the sludge pond and the settling pond. The smaller particles of iron in the filtered water further decrease in concentration coming out of the cascade at 0.37 mg.L^{-1} (CO out) reducing to 0.04 mg.L^{-1} in the first planted cell (GBP out) only to increase again to an average concentration of 0.37 mg.L^{-1} at the outflow (SCP out).

Iron is found in the mine effluent as reduced Fe^{+2} . In the cascade and settling sections, most of the Fe^{+2} is oxidized to Fe^{+3} , with a concomitant hydrolysis forming $\text{Fe}_3(\text{OH})_2$, and settling out of the water column. Subtracting the filtered concentrations from total concentrations, gives the amount of particulate Fe and As (Fig. 2a and Fig. 2b). The distribution of the particulates is identical for both Fe and As suggesting clearly that they are associated in the removal process. Particulates of Fe are present in sizes as low as 1 nm (Buffle et al. 1992). In fact, iron oxyhydroxide is considered a colloid (Stumm and Morgan, 1995 Pizarro et al. 1995) Arsenic readily adsorbs to iron hydroxide colloids and particulates, removing it as well. As adsorption capacity of iron hydroxides is an extensive field of study and is not discussed in detail here (Paige et al 1996; Pierce and Moore 1982). Equally active is the field of microbial interactions with the iron-hydroxide particulates and the liberation of adsorbed As (Niggemeyer et al. 2001; Glasauer et al 2001; Oremland et al. 2002).

The pilot system was operated under different flow regimes ranging from $1 \text{ m}^3 \cdot \text{h}^{-1}$, to $2 \text{ m}^3 \cdot \text{h}^{-1}$ and $3.5 \text{ m}^3 \cdot \text{h}^{-1}$. Multiplying the flow by the concentration gives contaminant load, the unit that is needed to assess removal in relation to the retention time of the water in the system, or the rate of particulate formation. In Fig. 2c the % of the daily Fe load that did get removed is plotted for the different flow rates in relation to the load entering the cascade from the mine. The flow regime does not largely influence removal as the water passes over the cascade, but the retention time reflects removal in the sludge pond and the settling pond (SLP out and SEP out) when total iron load is considered. The filtered iron load removal suggests that the cascade affects particulate formation. Burlap mats have been installed in the settling pond to test if Fe and As removal can be improved by increasing surface area. From the first gravel bed to the outflow, essentially 100 % iron is removed (Fig.2c).

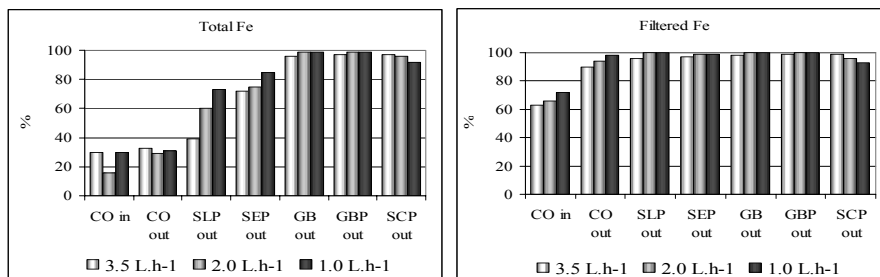


Fig. 2c. Fe removal from mine effluent at Pöhla system, 1999-2001

The same evaluation for As total load and filtered load indicates the stepwise increase of total As removal increasing only in the sludge pond (SLP out). The high flow rate with 40 % removal and 70 % at low flow rate. For the filtered load, the smaller particles, flow rate has a minimal effect on the removal (Fig.2d). As may be present as As III and remains in the water (Driehaus et al, 1999).

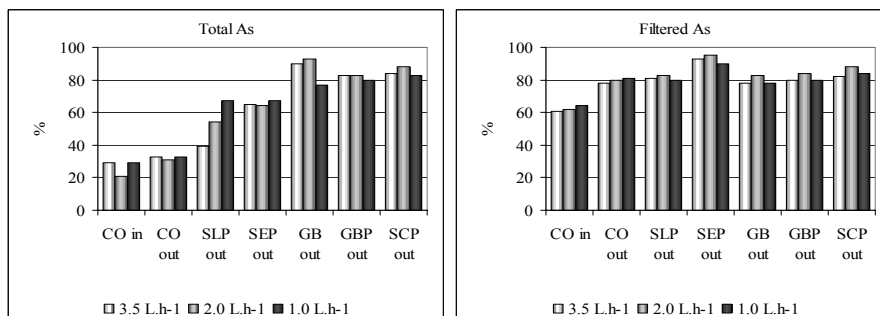


Fig. 2d. As removal from mine effluent at Pöhla system, 1999-2001

²²⁶Radium: Concentrations of ²²⁶Ra in $\text{mBq} \cdot \text{L}^{-1}$ are shown in Fig.3a. ²²⁶Ra concentrations decreased from $4500 \text{ mBq} \cdot \text{L}^{-1}$ to about $1325 \text{ mBq} \cdot \text{L}^{-1}$, a 70.6 % decrease,

over the entire system. Each successive sampling contained lower concentrations of radium. Unlike iron and arsenic, a fraction of the radium was removed in each section of the system. Between the mine effluent (ME) and the settling pond (SEP out) the reduction in ^{226}Ra concentration is 31 % followed by a 58 % reduction in the gravel and plant cells (SEP out). This suggests that the removal process is related to a factor or media, which are present throughout the system, but more prevalent in the gravel bed. The largest reduction between two components of the system occurs between the settling pond and the gravel bed.

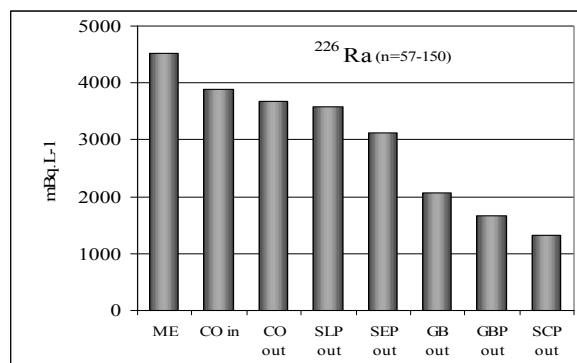


Fig. 3. Average [^{226}Ra] in water at Pöhla system, 1999-2001

Geochemical processes that influence radium removal include co-precipitation and adsorption to particulates. Iron hydroxide sludge analyzed from the sludge cell contained 73 Bq.g^{-1} of ^{226}Ra . When gravel from the first gravel bed was removed for analysis of ^{226}Ra and washed free of sludge and biofilms, it contained 140 Bq.g^{-1} of gravel, compared to its original concentration of 5 Bq.g^{-1} . The biofilm and sludge washed off the gravel contained 5.9 Bq.g^{-1} . Beneš (1982) compared the adsorption of ^{226}Ra to ferric hydroxide, kaolinite, quartz sand and silica over a broad range of conditions. He concluded that adsorption increases in the order of Kaolinite > ferric hydroxide > quartz sand > silica at pH 6 and ferric hydroxide is the highest adsorbent at pH 8. Pradel (1976) concluded that co-precipitation with ferric hydroxide can account for a rapid decrease in the concentration of dissolved radium in river water receiving untreated iron rich mine drainage water. This explains the large reductions of ^{226}Ra concentration between the settling pond and the gravel beds and the high concentrations in the hydroxide sludge.

In water, radium exists primarily as a divalent ion (Ra^{2+}) and has chemical properties that are similar to barium, calcium and strontium. Radium favours coordination with oxygen donors and does not usually form complex ionic species (Kabata-Pendias and Pendias 1984). Radium itself cannot form precipitates, as its mass concentrations are low, measured in Bq where 1 Bq is equivalent to $2.7 \cdot 10^{-9}$ mg. However it can co-precipitate with suitable solids. Sebesta et al. (1980) found that radium can co-precipitate with barium sulphate. Barium concentrations in the mine effluent are around 1.4 mg.l^{-1} but sulphate concentrations were reported as less than 5 mg.l^{-1} . As both sulphate and barium are low in this water, barium sulphate precipitation is an unlikely removal process for ^{226}Ra .

The chemical properties of ^{226}Ra suggest that it might be taken up by living cells via the same mechanism as other alkaline earth elements (Mg, Sr, Ba), but the evidence on such relations is contradictory. Williams (1982) analysed 19 species of aquatic and semi-aquatic macrophytes and found that the radium distribution was not significantly correlated with that of Ca, Mg, Na, Cu, Zn, Fe or S but was positively correlated with that of Mn. In 18 samples of five organs (lamina, petiole, fruit, peduncle, rhizome), from a single species, *Nymphaea gigantea*, radium distribution was not correlated with that of Ca, Mg, Na, Zn, U or S but was positively correlated with that of Cu, Fe and Mn and negatively correlated with that of K and P.

Radium can also be incorporated into calcium carbonate as it is being laid down by some marine and freshwater algae, such as the stonewort (Smith and Kalin, 1989). Given the documented adsorption of ^{226}Ra to gravel, it is postulated that diatoms incorporate ^{226}Ra into siliceous structures. As diatoms are present in the system as biofilms throughout the gravel beds it is reasonable to suggest that the latter may play a role in the removal throughout the system.

Manganese: Average concentrations of Mn in different sections of the pilot system are shown in Fig. 3. Initial concentrations entering the system averaged a little over 0.6 mg.L^{-1} . This dropped slightly to about 0.5 mg.L^{-1} as the water passed through the cascade, and settling cells. The initial loss of Mn is probably due to co-precipitation with iron hydroxide in the sludge cell. The major reduction of the concentration of Mn occurs for both the total and the filtered as the water pass through the gravel bed. Mn oxidizes slower than Fe and this facilitated by microbes, which is well documented (Ehrlich 1990). Mn nodules, streaks or varnish as the black precipitates are referred to, where abundant on the gravel bed surfaces.

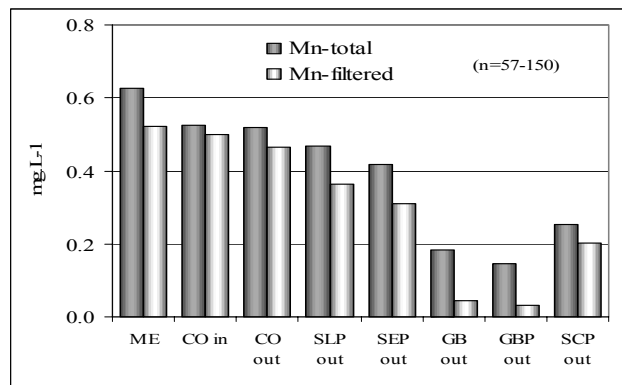


Fig. 4. Average [Mn] in water at Pöhla system, 1999-2001

Conclusions

After three years of operations the pilot system constructed to treat the mine water from the water-flooded Pöhla-Tellerhäuser mine of Wismut in Germany has produced some very interesting results. The data show that the system does remove iron, arsenic, manganese and ^{226}Ra and that the removal processes are based on geochemical characteristics of the contaminants. For Mn and ^{226}Ra some biologically facilitated removal is suggested through biofilm formation. Uranium, at the pH value and in the presence of high bicarbonate concentrations in this mine water, is not removed. The monitoring data generated from the Pöhla pilot system facilitate greatly the understanding of the natural removal processes at work and have laid the foundation for scale-up following the principles of ecological engineering.

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