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Pilot Scale RAPS-System in Gernrode/Harz Mountains

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Abstract. This paper presents experimental studies and first results of a pilot scale RAPS-treatment system to reduce the high iron content of an iron rich mine water. In 1985, economic reasons caused the closure of the fluorspar mine “Hohe Warte” near Gernrode in the German Harz Mountains. Though remediation works were conducted in the preceding years, mine water is currently flowing out freely of the dewatering adit and is impacting the environment and the receiving brook. The mine water is characterised by low pH-values, high conductivities and contains considerable amounts of iron, manganese, and arsenic. Annually, the mine discharges 0.7 Mio m³ of mine water with 7.8 tons of iron, 3.8 kg of manganese, 13 kg of arsenic, and 2,5 kg of uranium. Therefore, the discharging mine water has a great potential to affect the quality of the receiving streams and resulted in a decrease of biological diversity. Based on hydrogeological and hydrochemical investigations, a passive treatment system would be able to treat the mine water. In February 2003 a pilot system was installed near the dewatering adit consisting of a settlement pond, a RAPS system (reducing and alkalinity producing system) and a constructed wetland. It could be shown that this passive system was able to treat an aliquot of the mine water down to ecologically acceptable standards.

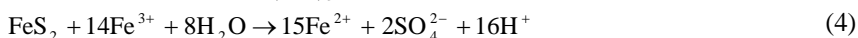
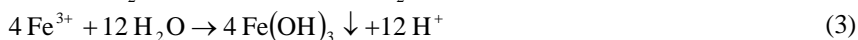
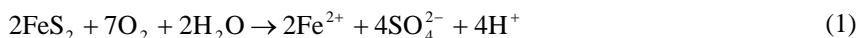
Introduction

Discharges of contaminated mine water from abandoned mine sites associated with ground and surface water pollution are a major environmental problem in many parts of the world. Aggravating factors in association with abandoned un-

derground mines commonly are large open, mined volumes with laterally extensive interconnections being usually flooded (Younger 2000a, Eger and Wagner 2000), access is restricted, and reliable mine maps are often unavailable (Skousen et al. 2000).

Acid mine drainage (AMD) results from the exposure of sulphides and iron bearing minerals to erosion and weather. Percolation of water through these materials results in a discharge water with low pH and high metal concentrations. Although AMD is naturally occurring, mining activities may greatly accelerate its production since mining exposes new iron and sulphide surfaces (e.g. underground mine walls, open pit walls, and overburden and mine waste piles) to oxygen. As such, AMD is one of the primary environmental threats at mining sites (Skousen et al. 2000; Ziemkiewicz et al. 2003).

The following chemical reactions represent the chemistry of pyrite weathering upon exposure to air and water (Stumm and Morgan 1996):



The first reaction in the weathering of pyrite includes the oxidation of pyrite by oxygen. Sulphur is oxidized to sulphate and soluble ferrous iron and acidity are released (equation 1).

The second reaction involves the conversion of ferrous iron to ferric iron by consuming acidity (equation 2). Certain bacteria increase the rate of oxidation from ferrous to ferric iron. This reaction rate is pH dependent, with the reaction proceeding slowly under acidic conditions (pH <5) with no bacteria present (Evangelou 1995; Hedin et al. 1994), at pH values > 8, the abiotic process is fast. This reaction is known to be the rate limiting step in the abiotic pyrite oxidation (Sigg and Stumm 1994).

The third reaction is the hydrolysis of iron (equation 3). The formation of ferric hydroxide precipitate (solid) is pH dependent. Solids form if the pH is above 3.5, but below pH 3.5, little or no solids will precipitate. Many metals are capable of undergoing hydrolysis (e.g. aluminium, manganese) and trace metals such as arsenic, cadmium, copper, lead, and zinc will coprecipitate with iron to some degree (Ford 2003).

The fourth reaction is the oxidation of additional pyrite (or other metals) by ferric iron (equation 4). The ferric iron is generated in reaction steps 1 and 2. This is the cyclic and self-propagating part of the overall reaction and takes place rapidly and continues until either ferric iron or pyrite (and other metals) is depleted. Note that in this reaction, iron is the oxidizing agent, not oxygen.

In view of the potential long time-scales over which water pollution from abandoned mines may persist (Younger 1997; Wood et al. 1999; Ermita Consortium 2004), there has been an increasing interest in the development of methods for mine water treatment which can operate over decades or even centuries with little maintenance and low investment and operational costs (e.g. Eger and Wagner

2002; Ford 2003; Wolkersdorfer and Younger 2002; Younger 2000b). Passive treatment systems are a relatively young technology that involves using sulphate-reducing bacteria or limestone or both to neutralize acidity and precipitate metals.

Advantages are low operating costs and low capital cost, usually no requirement to consume electrical power, and use of non-hazardous materials. Passive systems can often be directly integrated with surrounding ecosystems, and well-constructed passive systems can work for long time periods unattended (Younger et al. 2002).

Disadvantages may be that it is a relatively new technology; hence, experiences are still scarce, precise control of treatment effluent quality is not practicable, relatively high construction costs, and large areas of land are required.

Site description

Situated in the Mid Harz Fault Zone at the northern boundary of the German Harz Mountains, the underground mine “Hohe Warte” is located 1.5 km south-west of the city Gernrode. From 1974 to 1985 the “VEB Harzer Fluß- und Schwerspat Betriebe, Werk Rottleberode” mined there for fluorspar (Fig. 1). Extensive exploration works were conducted in the preceding years and the fluorspar deposit was made accessible through a 1.4 km long dewatering adit (1st level at 300 m above sea level, also referred to as “Hagental adit”).

Host rocks of the mineralization are shales with inclusions of calcite and silica, and greywackes of the Blankenburger zone at Devonian and Carboniferous age. During the Variscian phase the Ramberg granite intruded (Upper Carboniferous



Fig. 1. The working Fluorspar Mine “Hohe Warte” in 1983 (Kappe and Scheffer 1990).

age: 290 Mio \pm 10 Mio years; Mohr 1993) into the sediments of the Blankenburg zone, producing cherts by metamorphosis. Trace minerals are sulphide minerals like pyrite, galena, sphalerite, and chalcopyrite; fluorite, haematite, and silica, crystallised in the fractures and fissures of the cherts and granites (Stolle 1984).

During the production phase from 1978 to 1982, three underground levels (2nd and 2½ level at 350 m above sea level, and a 3rd level at 400 m above sea level) above the dewatering adit were mined, by which 200,000 tons of fluorite were extracted. Since 1981 production works above the 3rd level were conducted (Stolle 1984; Bodemann 1987).

On September 31st 1985, economic reasons caused the mine to stop production and in January 1987 the mine was finally closed, after remediation works were conducted in the underground mine (Bodemann 1987). After the cessation of mining, the underground mine “Hohe Warte”, especially the 1st level, should have been used as a water reservoir. Based on hydrogeological investigations conducted in April 1984, a poor water quality was predicted and no use of the mine water took place (Stolle 1984). Due to safety-engineering reasons, in 1987 the mine entrance was closed with a brick dam. In the mid 1990’s, after local people observed mine water seeping through the dam, a small hole has been broken into the wall to prevent the dam from failure (Fig.s 2 and 3).

Up to the beginning of 2004 nearly all the mine water was discharged through this hole (Fig. 4) into a 15 m long open channel and from there through a 30 m long pipeline to a natural cascade with a height of about 6 m. Since then construction works are going on but were not finished by the time this report has been written.

After the mine water passes the cascade, the water flows through a lagoon with an area of about 110 m², acting as a settlement basin. Thereafter, the mine water drains into the Hagentalbach, a brook with excellent surface water quality up to this confluent and flows into a north-eastern direction to Gernrode and Bad Suderode.

Since 2000 the TU Bergakademie Freiberg has been monitoring the mine water



Fig. 2. The mine entrance in 2000.



Fig. 3. The mine in 2001 (red colour in front of the dam: ochre precipitates; Tamme 2002).

and the brook. Table 1 summarises a comparison of parameters and metal ion concentrations of the mine water at the dewatering adit (MP1, Fig. 4). The mine water is characterised by low pH-values, high conductivities and contains considerable amounts of soluble salts and sulphates, iron, manganese, and arsenic. Annually, the mine discharges 0.7 Mio m³ of mine water with 7.8 tons of iron, 3.8 kg of manganese, 13 kg of arsenic, and 2,5 kg of uranium.

System Design

General Aspects

Over the last two decades, a variety of passive treatment systems has been developed and deployed for treating polluted mine waters. The primary passive treatment technologies are divided into three main types (Younger et al. 2002):

- Inorganic media passive systems (e.g. anoxic limestone drains, oxic limestone drains, closed systems Zn removal reactors, and siderite-calcite reactors for Cd and As removal)
- Wetland-type passive systems (aerobic wetlands [reed beds], compost wet-



Fig. 4. Discharge point at the dewatering adit (MP1).

lands, reducing and alkalinity producing systems [RAPS; originally termed SAPS by their originators (Kepler and McCleary 1994) recently renamed by Watzlaf et al. 2000]).

- Subsurface flow bacterial sulphate reduction systems (in-situ permeable reactive barriers to treat contaminated mine water discharges)

Selection, design, and effectiveness of the passive system used are based on water chemistry, flow rate, local topography, and site characteristics (Hedin et al. 1994; Skousen et al. 2000; Younger 2000b).

Based on the on-site conditions and the water chemistry of the fluorspar mine “Hohe Warte”, a passive pilot treatment system (Fig. 6) has been installed at the mine site in February 2003. The pilot system was designed to remove sufficient quantities of iron and manganese from the mine water. It consists of three containers with a length of 1.12 m, width of 0.96 m, and height of 0.95 m. Monitoring points (MP 11 – MP 13) are the inlets of the containers 1 – 3, and the outlet of container 3 (MP 14; Simon 2003).

Because the use of aerobic wetlands (container 3) is limited to the treatment of net alkaline drainage where $\text{pH} > 6.5$ and the total alkalinity $>$ total acidity (Eger and Wagner 2003; Younger et al. 2002; Hedin et al. 1994), the system is used after the alkalinity of the drainage water has been increased in container 2, the successive alkalinity producing system (RAPS). Before flowing into the RAPS-system of the pilot system, a settlement pond (container 1) is arranged to allow iron oxide precipitation.

In the following chapters, the design and construction of the three containers are explained.

Settlement Pond

An aliquot of the mine water flow is drained from the adit entrance (MP1) to the first container by a flexible tube. This container is used as a settlement pond, a preceding aeration cascade increasing the dissolved oxygen concentration and allowing the formation of iron oxide precipitates (Fig.s 5 and 7). The water inflow is $0.5 \text{ L} \cdot \text{min}^{-1}$ and is controlled by a “technical channel”. Due to the container’s size, the residence time is about 14 hours.

Table 1. Summary of hydrogeochemical parameters of the Gernrode mine water.

| | 5.10.99 | 30.5.00 | 22.10.02 | 21.11.02 | 19.12.02 | 30.1.03 | 24.2.03 | 25.3.03 | 24.4.03 | 19.5.03 | discharge per year |
|---|---------|---------|----------|----------|----------|---------|---------|---------|---------|---------|--|
| Flow (L·s ⁻¹) | 15.0 | 10.0 | — | 29.2 | 26.1 | — | 25.5 | 26.5 | 27.7 | — | 720,823 m ³ a ⁻¹ |
| T (°C) | — | — | 11.8 | 11 | 10.5 | 10.5 | 10.9 | 11.1 | 11 | 11.3 | — |
| pH | — | — | 5.42 | 6.13 | 6 | 5.67 | 5.57 | 5.99 | 5.65 | 5.95 | — |
| Lf (μS·cm ⁻¹) | — | — | 5772 | 5741 | 5499 | 5693 | 5689 | 5637 | 5590 | 5578 | — |
| Eh (mV) | — | — | 338 | 336 | 305 | 400 | 391 | 385 | 380 | 369 | — |
| O ₂ (mg·L ⁻¹) | — | — | — | 9.91 | 9.81 | 9.11 | 10.45 | 10.96 | 10.42 | 9.84 | — |
| TDS (ppm) | — | — | 4616 | 4590 | 4373 | 4456 | 4451 | 4405 | 4365 | 4354 | — |
| Fe _{total} (mg·L ⁻¹) | 9.74 | 8.10 | 10.98 | 9.7 | 12.21 | 10.67 | 11.5 | 9.35 | 16.17 | 10.48 | 7,850 kg a ⁻¹ |
| Fe ²⁺ (mg·L ⁻¹) | — | — | 9.21 | 8.23 | 9.13 | 8.97 | 10.45 | 6.71 | 9.76 | 8.55 | 6,398 kg a ⁻¹ |
| Na ⁺ (mg·L ⁻¹) | 203 | — | 253 | 250 | 245 | 248 | 252 | 249 | 243 | 235 | 174,439 kg a ⁻¹ |
| Ca ²⁺ (mg·L ⁻¹) | 548 | — | 801 | 691 | 675 | 690 | 690 | 665 | 653 | 641 | 484,874 kg a ⁻¹ |
| Cl ⁻ (mg·L ⁻¹) | 1390 | — | 1887 | 1769 | 1782 | 1774 | 1805 | 1711 | 1694 | 1621 | 1,236 t a ⁻¹ |
| SO ₄ ²⁻ (mg·L ⁻¹) | 76.9 | — | 74.7 | 56 | 73.1 | 113 | 112 | 89.6 | 86.1 | 77 | 60,741 kg a ⁻¹ |
| F ⁻ (mg·L ⁻¹) | — | — | 4.24 | 4.16 | 4.14 | 5.88 | 5.92 | 6.09 | 6.64 | 5.71 | 3,855 kg a ⁻¹ |
| Si (mg·L ⁻¹) | — | — | 39.5 | — | 60.1 | 43.1 | 44.9 | 40.9 | 44.2 | 40.1 | 32,210 kg a ⁻¹ |

RAPS-System

After the initial settlement pond in the pre-treatment stage, the surface flow is converted to a subsurface flow in container 2 (Fig. 5) with substrate consisting of a 30 cm bottom layer of limestone gravel overlain by a mixture of limestone and horse manure, and an upper layer of horse manure. Total quantities of limestone are 780 kg with a CaCO_3 -content of 97–98 %, and the horse manure has a volume of 0.5 m^3 . The limestone dissolves in the acidic mine water, and because CO_2 cannot escape, conversion of bicarbonate occurs, thus adding alkalinity. The horse manure creates a reducing environment, hence converting ferrous iron to ferric iron and preventing the formation of ferric hydroxide precipitates. The RAPS-System aims to increase the pH value and to create a net alkaline mine water. Because such systems may never fall dry, sufficient water must always flow through the system.

Aerobic wetland

Since March 2003, the aerobic wetland (container 3) operates in the pilot system. The aerobic wetland (Fig. 6) is designed to provide a sufficient residence time to allow metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe and Mn hydroxides. These dominant treatment processes make them applicable only to net alkaline mine water.



Fig. 5. View of the RAPS-System.



Fig. 6. View of the Aerobic wetland with *Juncus* and *Typha*.

The bottom of the constructed wetland is covered by a 10–30 cm layer consisting of soil and is planted with *Typha* and *Juncus*. The flow of mine water through the constructed wetland was fairly constant and the flow length was in the range of 3–4 m as a result of wooden guides installed, but the main residence time evaluated by tracer tests was only 9 min due to the small area (1 m²) involved.

Results and Discussion

In a first stage, about 10 L of mine water per minute were discharged through the pilot system. Tracer tests using Na-fluorescein and the chemical analyses of the treated water proved that the residence time was too low. Therefore the flow was continuously decreased to about 0.5 L·min⁻¹.

After optimisation of the flow rate, the pilot system was able to lower the Fe_{tot} content from about 20 mg·L⁻¹ to 5 mg·L⁻¹ and the pH could be raised from about 5.5 to 7. Acid capacity (Alkalinity) was increased from about 0.2 mmol·L⁻¹ to 0.7 mmol·L⁻¹ while the base capacity (Acidity) was reduced from 1.1 mmol·L⁻¹ to 0.6 mmol·L⁻¹. Nitrate concentrations in the discharged water after the RAPS decreased from about 4 mg·L⁻¹ in March 2003 to 0.3 mg·L⁻¹ in October 2003.

Unfortunately, the system was destroyed by vandalism in mid June 2003 and worked again until winter 2003; in spring 2004 the system had been destroyed again. Nevertheless, our field studies and the laboratory experiments proved that the system configuration chosen can treat the mine water on a long term basis.

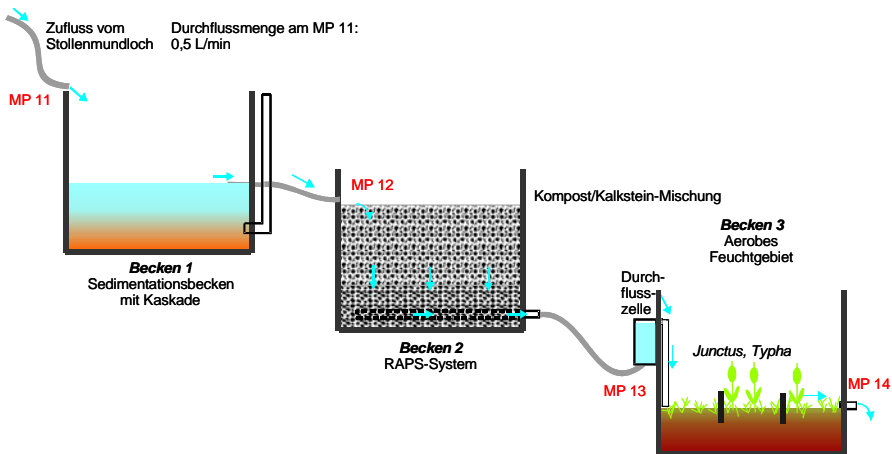


Fig. 7. Schematically View of the Pilot Scale system with its three treatment processes (Simon 2003).

Conclusion

It could be shown, that a RAPS system, based on intensive hydrogeological investigations and laboratory studies with the mine water that has to be treated, can be used at the abandoned Gernrode mine. Within the relatively small pilot plant, total iron could be reduced by about 50 %, the alkalinity increased, and the acidity decreased significantly, such resulting in a slightly net alkaline mine water.

We assume that even a comparatively small treatment plant would be able to increase the water quality of the receiving brook, the Hagentalbach, significantly. Based on the experiments we calculated the necessary area for such a treatment system and made a first sketch of the system (Fig. 8). Currently the responsible authorities and consultants are trying to find the best solution for the Gernrode mine site.

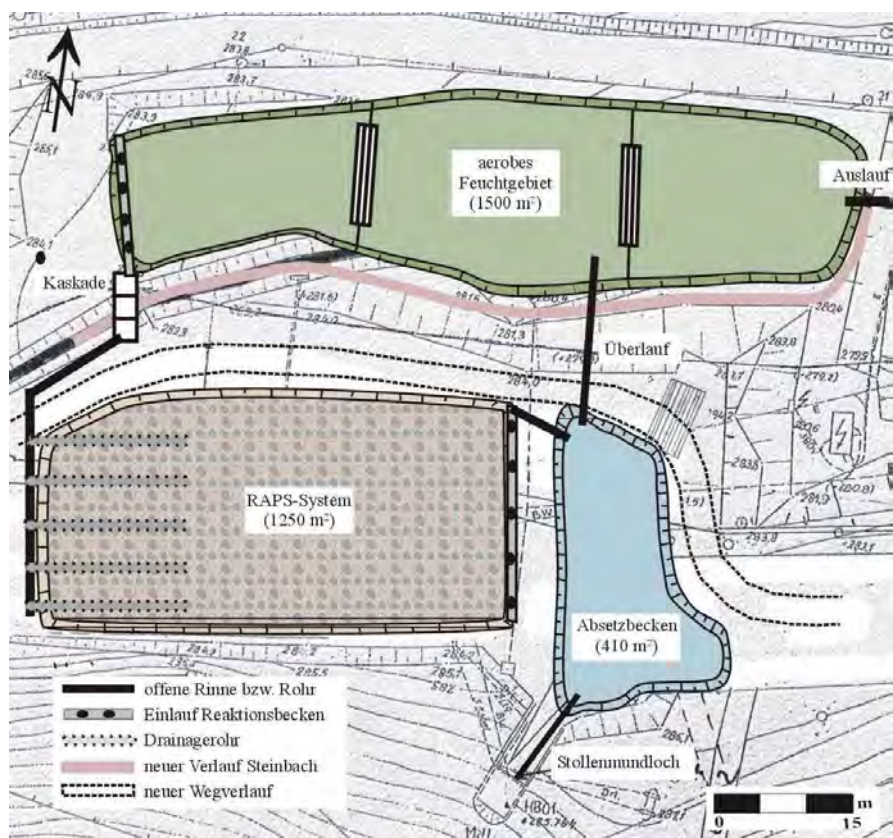


Fig. 8. Recommended passive treatment scheme at the abandoned Gernrode mine.

Acknowledgements

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