

IN SITU NEUTRALIZATION OF ACIDIC PIT LAKES: PROCESSES IN THE SEDIMENT AND LIMITING FACTORS

*Matthias Koschorreck, Katrin Wendt-Potthoff, Elke Bozau, Peter Herzsprung,
Walter Geller and Martin Schultze*

*UFZ - Helmholtz Centre for Environmental Research, Department Lake Research, Brückstr.3a, D-39114
Magdeburg, Germany*

Abstract

A strategy to neutralize acidic pit lakes was tested in a field mesocosm of 4500 m³ volume in the Acidic Pit Mine Lake 111 in Germany. After addition of the substrates Carbokalk and straw a neutral sediment layer formed, in which microbial sulphate and iron reduction as well as sulphide precipitation occurred. The neutralisation rate was limited by the precipitation of iron sulphides rather than by microbial reactions. Oxidation of H₂S by ferric iron in the anoxic sediment lowered the net sulphate reduction rate. During the experiment precipitation of ferric minerals formed an acidic sediment layer at the sediment surface. In that layer sulphides did not precipitate, but H₂S diffused into the overlying water where it was oxidised.

Introduction

The stimulation of the alkalinity producing microbial processes, sulphate reduction and iron reduction is a promising strategy for the neutralisation of acidic mining lakes. An advantage of the principle is the concurrent removal of sulphate (Brugam et al., 1995; Wendt-Potthoff and Neu, 1998; Brugam and Stahl 2000). Basing on detailed laboratory investigations (Frömmichen et al., 2003; Frömmichen et al., 2004) the Helmholtz Centre for Environmental Research – UFZ together with the consulting engineers Horn and UF-GmbH Fehrbellin carried out a field experiment at Mining Lake 111 in the Lusatian lignite mining region of Germany. By covering the sediment with Carbokalk and straw the 3 key processes sulphate reduction, iron reduction and the precipitation of the reaction products were stimulated in the sediment (Fig. 1, eq. 1).

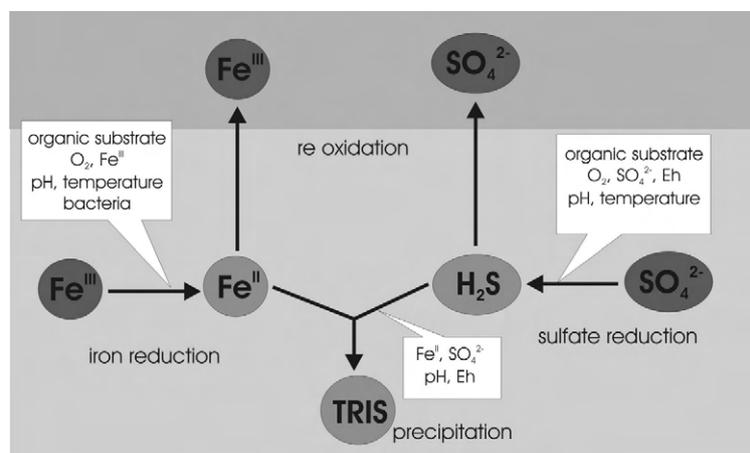


Figure 1. Key processes of passive pit lake treatment and regulating factors.



Because of oxic conditions these reactions do not proceed in the water column. In the anoxic sediment a reactive zone is established where the elevated pH allows the precipitation and sustainable deposition of iron-sulphides. The net neutralisation (NR) can be calculated as the sum of the formation of total reduced inorganic sulphur (TRIS) and non-sulphidic reduced iron (NS-Fe(II)_R) according to eq. 2 (Frömmichen et al., 2004):

$$\text{NR} = \frac{V}{t \times A} \sum_{i=1}^n \left([\text{TRIS}]_i + [\text{NS-Fe(II)}_R]_i \right) \Delta_i T_{R_i} \quad (\text{eq. 2})$$

where NR is the neutralization rate ($\text{eq m}^{-2} \text{yr}^{-1}$), [TRIS] is the accumulation of total reduced inorganic sulphur (eq kg^{-1}), [NS-Fe(II)_R] is the accumulation of non-sulphidic reactive ferrous iron (eq kg^{-1}), Δ is the density of fresh sediment layer (kg m^{-3}), T_R is the dry residue of fresh sediment layer (kg kg^{-1}), V is the volume of fresh sediment layer (m^3), A is the area (m^2), t is the time of accumulation (yr), i is the sediment layer, and n is the number of sediment layers.

The overall performance of the process depends on the efficient interaction of the different processes which are regulated by different factors (Fig. 1). For the appraisal and optimisation of the method it is crucial to know (i) which is the limiting step and (ii) which regulatory parameters can be used for optimisation.

Enclosure Experiment

The Mining Lake 111 is a long term research site of UFZ and has intensively been studied with respect to geochemistry, microbiology and limnophysics (Meier et al., 2004; Karakas et al., 2003). The lake is stratified during the warm season and the morphometry with a mean depth of 4.5 m make it suitable for a field experiment (Table 1). An experiment in a big enclosure (30 m diameter, $A = 700 \text{ m}^2$, $V = 4500 \text{ m}^3$; Luther et al., 2003) was started in 2001. On May 31st 2.8 t of Carbokalk were dispersed on the water surface. The Carbokalk was worked into the sediment by a rake in order to increase the thickness of the reactive sediment layer. Between June 6th and June 20th 400 straw bales were placed at the sediment surface (Fig. 2). Weights of iron scrap were used to sink the straw. On June 26th another 1.4 t of Carbokalk were added. The total substrate application was 6 kg m^{-2} Carbokalk ($10.7 \text{ mol TOC m}^{-2}$) and 8.5 kg m^{-2} straw ($436 \text{ mol TOC m}^{-2}$). Carbokalk is the solid precipitate of non-sugars after lime clarification of the extracted sugar beet juice. It contained about 50% (w/w) lime and 3 % organic carbon.

Table 1. Characterisation of Mining Lake 111.

Acidity = $[\text{H}^+]_{\text{aq}} + 3[\text{Fe}^{3+}]_{\text{aq}} + 3[\text{Al}^{3+}]_{\text{aq}} + [\text{HSO}_4^-]_{\text{aq}}$		17.6 meq/L			
max. depth	10 m	Na^+	10 mg/L	SO_4^{2-}	1200 mg/L
surface area	10.5 ha	Fe	150 mg/L	Cl^-	12 mg/L
volume	$505\,000 \text{ m}^3$	Al	35 mg/L	PO_4^{2-} (SRP)	0.011 mg/L
pH	2.6	Mn	8 mg/L	total P	0.014 mg/L
conductivity (25°C)	$2500 \mu\text{S/cm}$	$\text{NH}_4^+ \text{-N}$	3 mg/L	Si	17.5 mg/L
Ca^{2+}	230 mg/L	$\text{NO}_3^- \text{-N}$	0.32 mg/L	TIC	< 1 mg/L
Mg^{2+}	30 mg/L	$\text{NO}_2^- \text{-N}$	< 0.001 mg/L	DOC	< 1 mg/L
K^+	3 mg/L	Total N	3.5 mg/L	TOC	< 1 mg/L



Figure 2. Application of Carbokalk (left) and straw (right) to the enclosure in Mining Lake 111.

The water quality as well as the neutralising processes and the microbiology in the sediment have been monitored in the enclosure as well as in the untreated lake for more than 5 years. Since the rate of TRIS formation seemed to decrease another 2.1 t of Carbokalk were added to the enclosure in July 2004.

Results and Discussion

The addition of the substrates resulted in an instantaneous chemical neutralisation of the sediment surface (Fig. 3). During the experiment the neutral sediment layer became thicker but at the same time a re-acidification of the sediment surface was observed. This was probably caused by the precipitation and sedimentation of Fe^{III} minerals. The Fe/S ratio of 5 implies that schwertmannite was formed. The acidic sediment layer grew with a constant rate of 5.4 mm y^{-1} (Koschorreck et al., 2007).

TRIS accumulated in the upper 4 cm of the sediment. The TRIS content of the sediment was very heterogeneous. From the temporal increase of TRIS in the sediment a net sulphate reduction of $0.8 \text{ mol m}^{-2} \text{ y}^{-1}$ was calculated (Fig. 4a). This rate is in the typical range of sulphate reduction rates in normal lakes (Holmer and Storkholm, 2001). Addition of more Carbokalk in 2004 had no significant effect on TRIS accumulation. The gross rate of sulphate reduction was about five fold higher than the net rate and stayed high during the whole experiment (Fig. 5). This shows that the neutralisation rate was not limited by the activity of the sulphate reducing bacteria. There were also no signs of substrate depletion. The discrepancy between gross and net rate shows that there was a H_2S removing process other than TRIS precipitation. Under the anoxic conditions in the sediment H_2S was probably oxidized by ferric iron (Peiffer, 1994; Koschorreck et al., 2007).

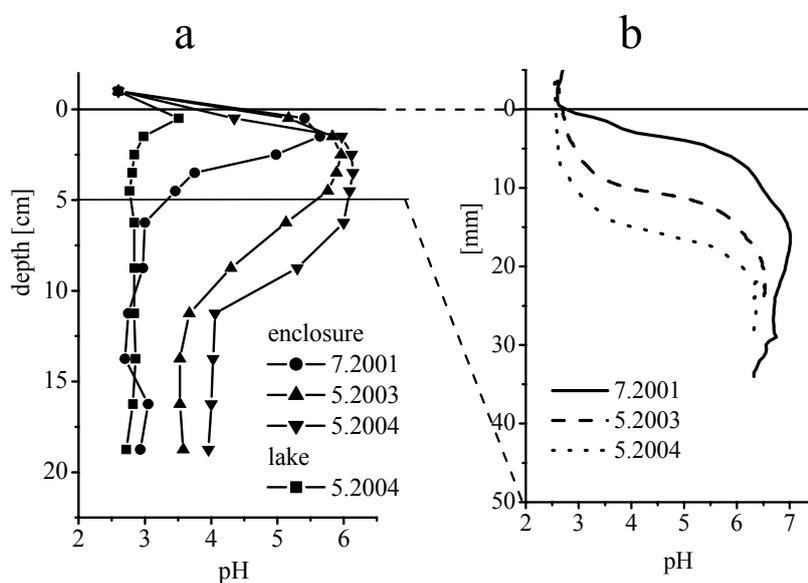


Figure 3. pH in the sediment measured with a conventional electrode in sediment cores (a) and with a microelectrode using an in situ profiler at the lake bottom (b) (after Koschorreck et al., 2007).

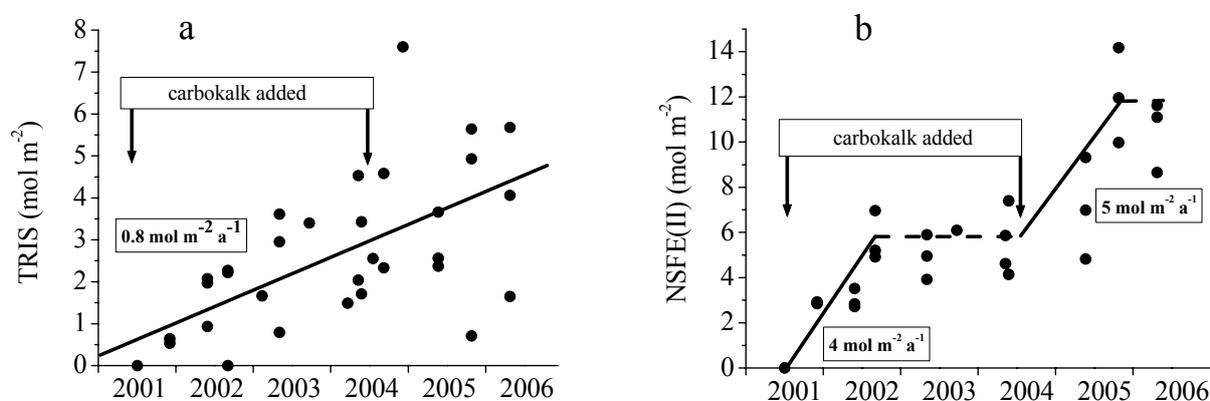


Figure 4. Development of TRIS (a) and NS-Fe(II)_R (b) in the sediment of the enclosure.

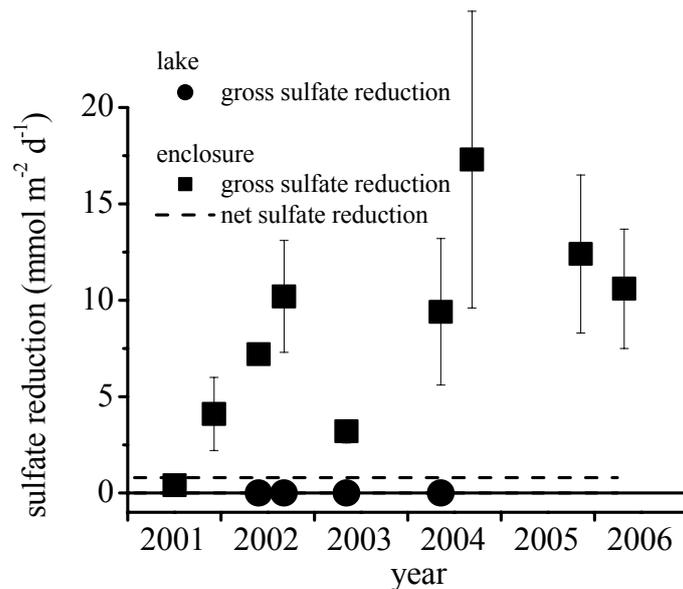


Figure 5. Sulphate reduction rates in the sediment. Gross sulphate reduction was measured by a ³⁵S-tracer technique (Meier et al., 2000). Net sulphate reduction was calculated from TRIS accumulation (Fig. 4a).

We observed high concentrations of dissolved ferrous iron in the porewater (up to 20 mmol L⁻¹; Koschorreck et al., 2007). Thus, the net neutralisation was not limited by the iron reduction rate. High concentrations of NS-Fe(II)_R accumulated in the sediment (Fig. 4b). Different to TRIS, the formation NS-Fe(II)_R was affected by the addition of Carbokalk. During the first year after Carbokalk addition NS-Fe(II)_R increased both after the initial and the second application. This can be explained by the reaction of iron with lime which probably led to the formation of siderite.

Because of the low pH at the sediment surface, there was a zone where FeS could not precipitate (Fig. 6). Thus, a part of the H₂S diffused into the overlying water, where it was re-oxidised.

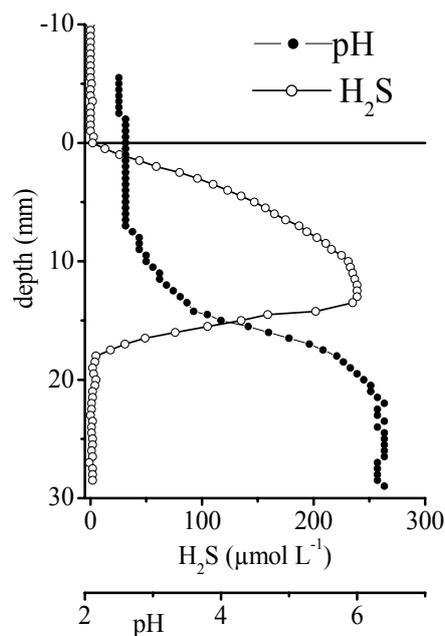


Figure 6. Microprofiles of pH and H₂S measured with an in situ profiler at the bottom of the enclosure in May 2004.

Conclusions

The sustainable precipitation of TRIS is the limiting step of passive mine lake treatment. To increase the neutralisation rate, there are two options:

1. The access of oxidants to the active sediment layer has to be minimized. The bottom water should be anoxic.
2. Sulphate reduction should be restricted to sediment layers with neutral pH in order to prevent loss and re-oxidation of H₂S.

Acknowledgements

Thanks to Corinna Völkner and Martin Wieprecht for excellent help in the field and in the laboratory. The help of the divers Michael Beyer, Michael Herzog, Klaus Ockenfeld and Burkhard Kuehn during *in-situ* measurements is acknowledged. Thanks to Jutta Meier for help during the field work and discussions. This study was financially supported by the Deutsche Bundesstiftung Umwelt DBU, project AZ 19296.

References

- Brugam R.B., Gastineau J., Ratcliff E. (1995). The neutralization of acidic coal mine lakes by addition of natural organic matter: a mesocosm test. *Hydrobiologia* 316, 153-159.
- Brugam R.B., Stahl J.B. (2000). The potential of organic matter additions for neutralizing surface mine lakes. *Transactions of the Illinois State Academy of Science* 93, 127-144.
- Frömmichen R., Kellner S., Friese K. (2003). Sediment conditioning with Organic and/or Inorganic Carbon Sources as a First step in alkalinity generation of acid Mine Pit Lake Water (pH 2-3). *Env. Sci. Technol.* 37, 1414-1421.
- Frömmichen R., Wendt-Potthoff K., Friese K., Fischer R. (2004). Microcosm studies for neutralization of Hypolimnetic Acid Pit Lake Water (pH 2.6). *Env. Sci. Technol.* 38, 1877-1887.
- Holmer M., Storkholm P. (2001). Sulphate reduction and sulphur cycling in lake sediments: a review. *Freshw. Biol.* 46, 431-451.
- Karakas G., Brookland I., Boehrer B. (2003). Physical characteristics of Acidic Mining Lake 111. *Aquat. Sci.* 65, 297-307.
- Koschorreck M., Bozau E., Frömmichen R., Geller W., Herzsprung P., Wendt-Potthoff K. (2007). Processes at the sediment water interface after addition of organic matter and lime to an acid mine pit lake mesocosm. *Env. Sci. Technol.* 41, 1608-1614.
- Luther G., Horn M., Koschorreck M., Müller M., Preuß V., Söding Z. (2003). Neutralisation schwefelsaurer Seen in der Lausitz: Vom Enclosure zum in situ-Bio-Reaktor. *Vom Wasser* 101, 123-136.
- Meier J., Babenzien H.D., Wendt-Potthoff K. (2004). Microbial cycling of iron and sulfur in sediments of acidic and pH-neutral mining lakes in Lusatia (Brandenburg, Germany). *Biogeochemistry* 67, 135-156.
- Meier J., Voigt A., Babenzien H.D. (2000). A comparison of ³⁵S-SO₄²⁻ radiotracer techniques to determine sulphate reduction rates in laminated sediments. *J. Microbiol. Meth.* 41, 9-18.
- Peiffer S. (1994). Reaction of H₂S with ferric oxides. In: *Environmental Chemistry of Lakes and Reservoirs*; Baker L.A. (Ed), American Chemical Society, 371-390.
- Wendt-Potthoff K., Neu T.R. (1998). Processes for potential in situ remediation of acidic lakes. In: *Acidic Mining Lakes*; Geller W., Klapper H., Salomons W. (Eds.), Springer, Berlin, 269-284.