

Neutralizing extremely acidic mining lakes by chemical and microbial treatment – Mesocosm Studies

Oliver Totsche¹, Andrew Fyson^{1,2} and Christian E.W. Steinberg¹

¹ Leibniz Institute of Freshwater Ecology and Inland Fisheries
Post Box 850119, D-12561 Berlin, Germany

² Brandenburg Technical University of Cottbus, Chair of Water Conservation,
Seestrasse-45, D-15526 Bad Saarow, Germany

Abstract

This study is investigating the buffering of extremely acidic mining lakes in the Lusatian open cast lignite mining area and treatment options for these lakes through mesocosm experiments.

First results concerning the different buffering systems in the lakes will be shown and discussed. In acidic lakes with similar pH and from the same mining area, the strength of the buffering system can be very different. The most important buffers are aluminum and iron(III) ions.

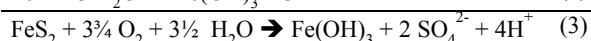
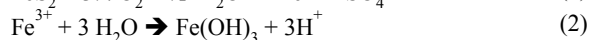
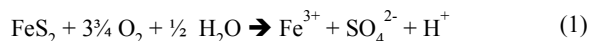
Two types of alternative acidity removal treatments are possible, namely chemical neutralization or microbiological alkalinity production. With chemical treatment, alkaline material in the form of soda is applied. The microbiological treatment acts as the reverse of the acidification processes i.e. the reduction of Fe(III) and sulfate. These processes are carried out by bacteria in anoxic conditions such as found in sediments. To enhance these microbial processes, the bacteria need an increased supply of organic carbon as substrate. This requires addition of organic materials such as agricultural wastes (saprobitation) or organics produced within the water column of the lake through enhanced primary production achieved through fertilization (eutrophication).

Both of these remediation strategies have disadvantages. Chemical treatment is not self-sustaining, biological sulfate reduction processes are hindered by the low pH values and primary production is limited by an extremely low nutrient supply. Therefore a combined chemical/biological treatment options are being investigated.

First results show an enhancement in primary production as well as in iron reduction when combined with chemical neutralization.

Introduction

In Lusatia (north-eastern Germany), there are several hundred flooded open cast lignite pits forming a new lake district (Nixdorf et al. 1997). During mine operation, the groundwater level is lowered (by pumping) and a vast quantity of overburden as well as waste material exposed. The exposure of these materials to oxygen results in the chemical and microbiological oxidation of iron sulfide (pyrite and marcasite) and consequent acidification (1). Following mine closure, the water level rises again and fills the mined holes. Hence, the oxidized iron is hydrolyzed and is a secondary source of acidification (2). Overall, for each mole of iron sulfide, 4 moles of H⁺-ions (= acid) are produced (3).



As a result of this, process the lakes are characterized by very low pH and a high iron and sulfate content. (Fyson et al 1998a)

Although most lakes have a pH in the range 2.1-3.5, they differ greatly in terms of the acidity. This is because of varying strength of buffering systems of the lakes (Geller et al. 2000)

There is much political pressure to remove the acidity from the lakes and develop the region for recreational purposes. The preferred treatment option is the diversion of neutral river water into the infilling lakes. However, there is insufficient water and many lakes require alternative treatment. Two types of alternative acidity removal treatments are possible, namely chemical neutralization or microbiological alkalinity production.

With chemical treatment, alkaline material is applied in the form of lime (CaCO_3) or soda ash (Na_2CO_3).

The microbiological treatment essentially acts as the reverse of the acidification processes i.e. the reduction of Fe(III) and sulfate. These processes are carried out by bacteria in anoxic conditions such as found in sediments. Sulfate reduction requires a sustained high concentration of available substrates which are usually organic molecules. This can be assured through addition of organic materials as agricultural waste (controlled saprobization). (Fyson et al 1998b)

In the long run, a solution is required which does not need new additions of organic material to treat the permanently inflowing acidic runoff and groundwater.

The substrate could be built within the lake by an increase in primary production.

The biomass, built through primary production, can be used as substrate for the iron and sulfate reducing bacteria as the introduced organic waste material. Thereby carbon dioxide and minerals are released which can be used again to form new biomass through photosynthetic processes. Nutrients can be recycled and used again in a circuit powered by sunlight (Figure 1).

Existing remediation strategies have serious disadvantages.

Chemical treatment is not self-sustaining. It can only treat the “standing” water. Treatment of additional inflowing acidic groundwater, percolating water and run-off requires further chemical additions.

The biological sulfate and iron reduction processes are slowed down by the extremely low pH values as occur in these mining lakes (Odem & Singleton 1993, Wendt-Potthoff & Koschorreck 2002).

In addition, primary production is limited through removal of inorganic carbon and phosphate from the water. Due to low pH, no carbonate-buffer is able to form and inorganic carbon leaves the water as gaseous CO_2 into the atmosphere. Because of the high iron concentration, phosphate is removed very effectively by coprecipitation with iron hydroxide (Krumbeck et al. 1998).

Therefore, primary producers in the mining lakes must operate with low inorganic carbon and phosphorus concentrations. The built up of new Biomass by primary production through fertilization (controlled eutrophication) alone or nutrient recycling may be ineffective. (However, see Fyson et al. 2002 this volume)

With a combined treatment strategy, the advantages of both the chemical and the biological treatments can be harnessed. The water should first be chemically neutralized and thereafter the nutrient status increased by controlled saprobization or eutrophication. The neutral conditions should provide better living conditions for the primary producers and also for the iron and sulfate reduction processes. Following eutrophication, the enhanced carbon inputs should fuel the biological alkalinity generating processes and hinder further acidification from inflowing groundwater, percolating water and surface run-off.

Materials and Methods

Lake water samples were taken from the surface. Enclosure water samples from a depth of 6 m, 0.5 m above the Sediment. Acidity titrations and pH were carried out with a Titrino 702 titrator (Metrohm) with 0.1 N NaOH. Iron and aluminum concentrations were determined on filtered (0.45 μm pore size) water samples by atomic absorption spectrophotometry. Iron (II) was determined photometrically using the phenanthroline method. TIC was determined with a C-analyzer (TOC 5000, Shimadzu).

pH and Chlorophyll fluorescence were measured *in situ* at 0.5 m depth intervals from the water surface to the sediment with multi parameter probes (either YSI 8260 or Hydro-Lab H20 and Haardt chlorophyll fluorescence probe). The values shown are the profile means.

Primary production was measured with a ^{14}C method modified according to Mischke et al. (1997)

pH, Acidity and Buffering

In this first phase of the project, the buffering capacity of extremely acidic mining lake waters was studied. The understanding of the buffering system is important for the better implementation of neutralization mechanisms as well as for the inhibition of acidification.

A comparison of the buffering of surface waters from three extremely acidic mining lakes has been carried out. Titration curves for these three lakes (RL107, RL111, RL117) from the same small mining area within the Plessa mining region of Lusatia (state of Brandenburg) were generated and are shown in Figure 2. The pH values of these waters are similar (2.6-3.0) but differ considerably in terms of the titratable acidity and the buffering systems (Table 1). Plateaus in the curves at pH around 3 and 4.5 are present in all three waters (the pH 4.5 plateau is not clear in Figure 2 due to the scales employed).

Lake	pH	Acidity 4.3 [mmol/l]	Acidity 8.2 [mmol/l]
RL107	2.42	26	36
RL111	2.59	10	15
RL117	3.08	0.2	0.25

Table 1:
pH-values and corresponding acidity for pH 4.3 and 8.2 for the lakes RL107, RL111 und RL117

To explain the course of the titration curves and the buffering systems involved, various quantities of neutralizing material were added to water from RL111. The iron, aluminum and carbonate buffering in the various treatments were subsequently studied. After 10 days, the pH values and TIC (total inorganic carbon) as well as dissolved iron and aluminum concentrations were measured. From these values, the buffering capacity β of the three buffer systems were calculated as in (4) and are shown in Figure 3.

$$\beta = \frac{\Delta C_B}{\Delta pH} = - \frac{\Delta C_A}{\Delta pH} \quad (4)$$

C_A = concentration of acid (dissolved iron, dissolved aluminum)

C_B = concentration of base (HCO_3^- as TIC)

Figure 3 shows that the titration curve plateaus up to pH around 3 in Figure 2 are due to iron buffering. The area under the curve represents the total buffering capacity of the studied waters. The area between pH 3.5 to 5.5 represents the

aluminum buffering capacity which because of its wider range is still about half that of the iron buffering despite the small peaks. The aluminum buffer is represented by the second plateau in the titration curves. After 10 days, no carbonate buffering was found. It may be that in the long-term, a carbonate buffering would develop in the circum-neutral pH zone through the incorporation of carbon dioxide from the air into the aqueous phase.

Enclosure Experiment

We chose the moderate acidic mining lake RL117 (pH = 3.0; acidity ($KB_{8.2}$) = 2.5 mmol/l) for our enclosure experiment.

This lake has an area of 95.9 ha and a maximum depth of 14 m and developed following lignite mining activity in the period 1956 to 1966.

The enclosures comprise 1 m diameter tubes of PVC sheeting with a surface float and embedded in the sediment with a metal cylinder at a depth of 6.5 m (Figure 4).

For a long-term neutralization, two biological processes are necessary: primary production and microbial iron and sulfate reduction (Figure 1). With this experiment we wanted to determine whether these processes can be substantially enhanced by pre-neutralization of the water body.

Therefore, half of the Enclosures were neutralized to approximately pH 7 by addition of soda ash (Na_2CO_3) after the first sampling. The other half remained acidic. Subsequently, phosphate (0.5 mg/l) or potatoes (3 kg/enclosure) were added. The enclosure treatments to examine the controlled saprobization and controlled eutrophication are summarized in Table 1.

(C)	control (no additions)
(S)	addition of soda ash
(P)	addition of phosphate (0.5 mg/l)
(SP)	addition of soda ash and phosphate
(O)	addition of organics in form of potatoes
(SO)	addition of soda ash and organics in form of potatoes

Table 1. RL117 enclosure treatments.

Chlorophyll fluorescence was used as a measure of algal biomass. Figure 5 shows that neutralization alone (S) did not result in an increased chlorophyll concentration in comparison to the control (C).

On the other hand, addition of phosphate to the acidic water resulted in a moderate increase in chlorophyll fluorescence.

A combination of neutralization and fertilization with phosphate (SP) led to an enormous short-term increase in algal biomass, dominated by the green alga *Scenedesmus sp.* which was not found in this lake before.

One week after this extreme value of more than 350 μg chlorophyll per liter, the population crashed and chlorophyll concentrations decreased to values higher but of the same order of magnitude as the acidic, phosphate fertilized enclosure.

In parallel to chlorophyll fluorescence, primary production was measured every two weeks. One week before these extremely high chlorophyll values, the particulate primary production in the neutralized and fertilized enclosure (SP) was with more than 1400 $\mu\text{g C l}^{-1} \text{h}^{-1}$ about 150 times higher than the control (C). One week after this high chlorophyll peak, the primary production rate had declined to less than 60 $\mu\text{g C l}^{-1} \text{h}^{-1}$ but still much more than in the control (C) and in the neutralized, unfertilized enclosure (S) and an extremely high value in comparison to the lake where values were generally less than 1 $\mu\text{g C l}^{-1} \text{h}^{-1}$.

Anyway the biomass produced is much higher with the combined strategy than just with fertilization. Therefore, the availability and recycling of the nutrients present is much better if the water is pre-neutralized. Therefore, the supply of organic carbon for the iron and sulfate reducing bacteria is much better.

To examine the effect of controlled saprobization, total iron and iron(II) concentrations were measured in the control (C) the acidic (O) and neutralized enclosure (SO) with the addition of organic material (Figure 6).

At the start of the experiment, all iron is in the form of iron(III), the difference between total iron and iron (II).

In the unamended control (C), no iron(II) was detected over the whole observed period.

In the acidic organic enclosure (O), a short increase in iron (II) concentration up to almost 2 mg/l was found, indicative of the establishment of reducing conditions, presumably in the vicinity of the sediment and the decomposing potatoes.

After neutralization, the total iron concentration dropped almost to zero. in the potato-amended enclosure (SO) because of iron hydroxide precipitation. Subsequently, the iron concentration rose steadily up to 2.5 mg/l. This increase was almost exclusively due to iron(II) formation.

In the observation period after addition of organic material, we noted a brief increase in iron(II) in the acidic enclosure and a more sustained increase in the neutral enclosure. However, there are not yet enough data to verify this trend.

Summary

In summary, one can say that in the extremely acidic mining lakes of Lusatia, dissolved iron and aluminium in addition to pH, are an important component of water acidity.

First results of an enclosure experiment show an enormous enhancement in primary production as well as a rising trend in iron reduction when combined with chemical neutralization.

This supports the hope of developing an combined (chemical and biological) neutralization technique to treat extremely acidic mining lakes.

Acknowledgement

We are grateful to all people helping us with setting up, sampling and analyzing.

We also thank for the funding by the scholarship program of the German Federal Environmental Foundation and the German Federal Ministry of Education and Research

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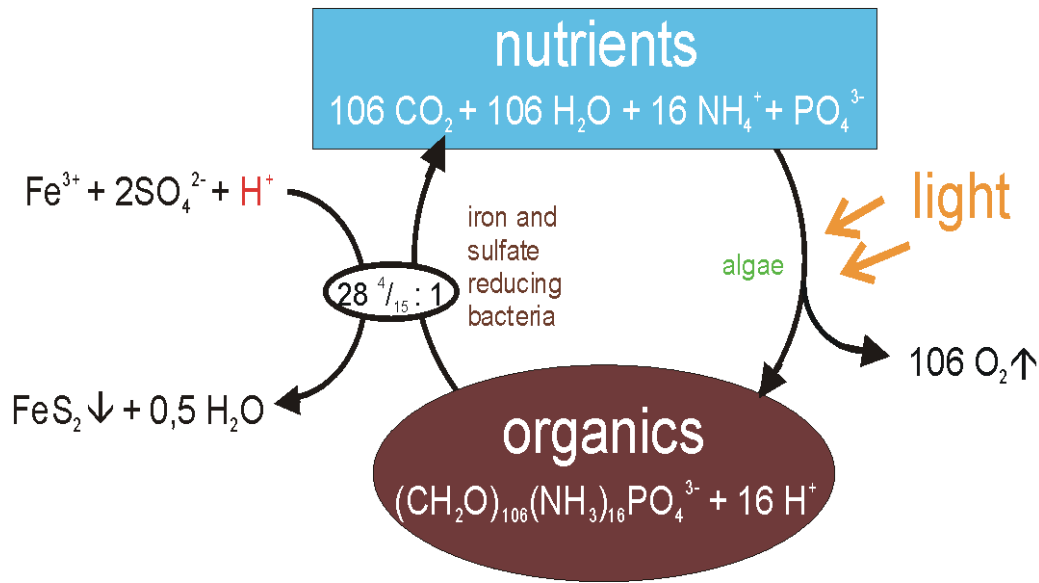


Figure 1: Illustration of the biological Neutralization of acidic mine water with nutrient recycling. The phrase 28⁴/₁₅ : 1 indicates, that one mole of the biomass with the given equation is able to reduce 28 ⁴/₁₅ Mol iron(III) und sulfate and neutralize as much acid.

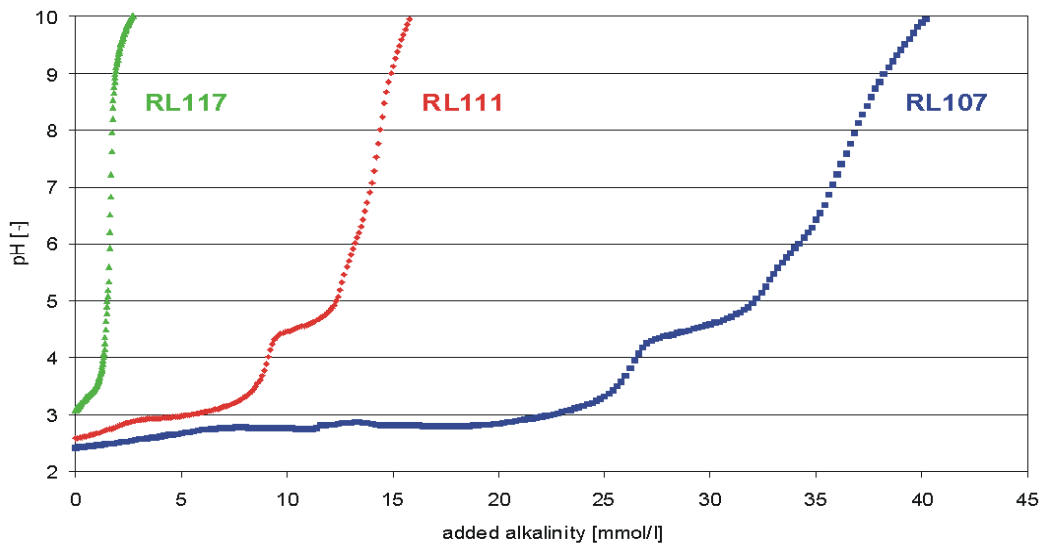


Figure 2: Titration curves of mixolimnion water from the mining lakes RL107, RL111 und RL117.

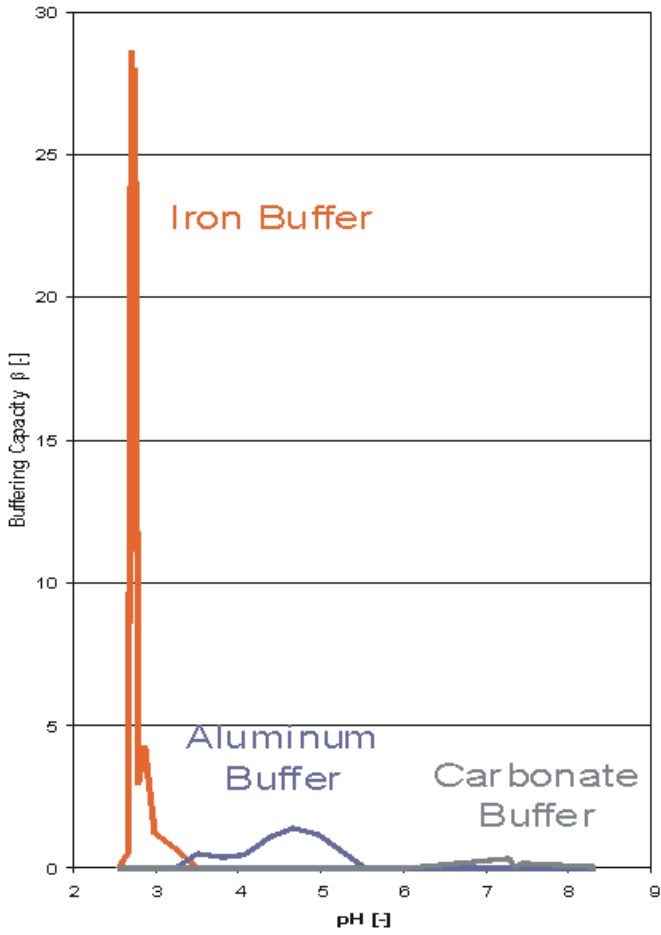


Figure 3:
Buffering capacities of the iron(III), aluminium and carbonate buffer in RL111

Figure 4:
RL 117 enclosures



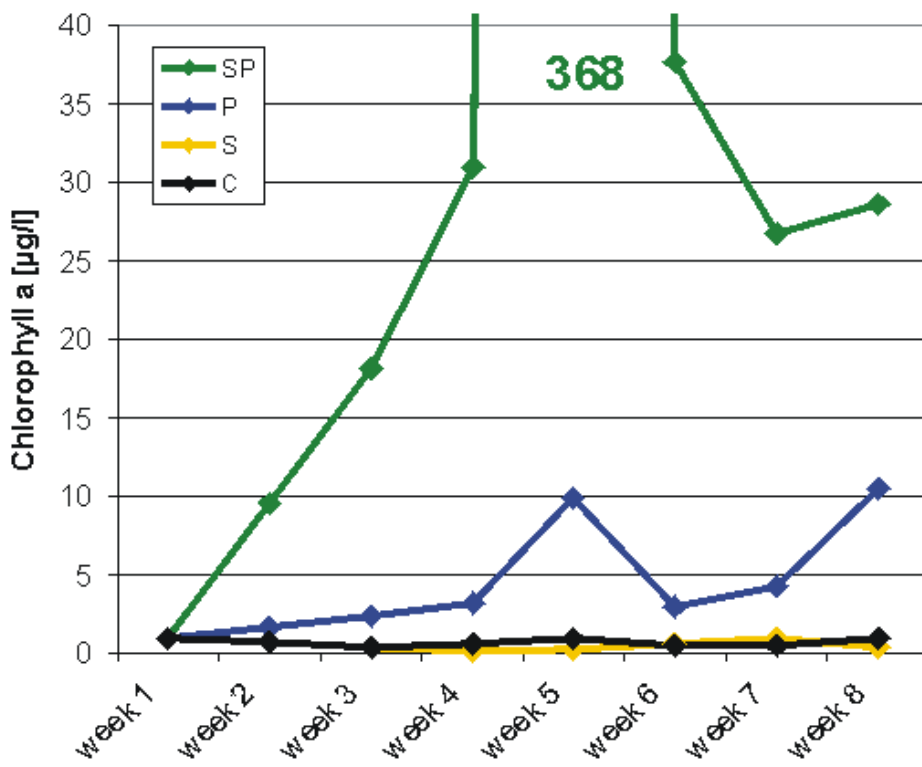


Figure 5: Chlorophyll-a concentration analyzed by chlorophyll fluorescence for the treatments (C) control, (P) phosphate, (SP) soda ash & phosphate and (S) soda ash

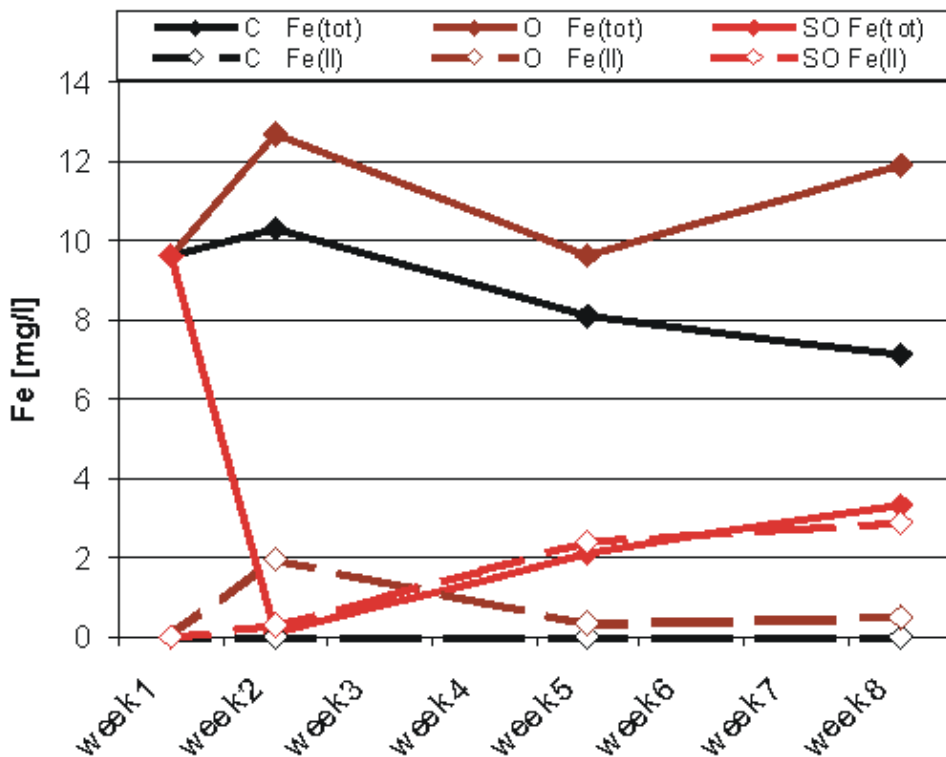


Figure 6: Iron(II) and total Iron concentration for the treatments (C) Control, (O) organics and (SO) soda ash & organics