Chemical and microbial sulphuric acid production from aerated mine lake sediment that was treated by different additions of NaOH (speech)

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We examined sediment from an open pit lake that was intensively used for coal mining during the first decade of 20th. century. Today, the site (Lake 111, Lusatia, Germany) is flooded and water has extreme chemistry: low pH values (2-3), high concentrations of sulphate (up to 2000 mg/l) and elevated concentrations of Fe, Zn and Mn. As a result, anoxic sediment accumulated elevated concentrations of these elements, especially high levels of reduced sulphur compounds.

Generally, microbial processes that take place in anoxic sediments lead to a reduction of dissolved sulphate, i.e. sulphuric acid, to the immobile sulfidic form or elemental sulphur is formed. At the same time, pH of the sediment usually slightly increases, compared to the water. When remaining under anoxic conditions (i.e. under water), the reduced compounds are relatively stable. However, when such sediments are aèrated, they become easily sources of acidity and pollution. The aeration happens e.g. during a temporary draught period, by changes in hydrological situation or by terrain works on the origin. As a result, spontaneous chemical and/or microbial oxidation of reduced sulphur compounds leads in sulphuric acid production that is followed by a rapid pH decrease. Subsequently, other previously immobile elements are re-mobilised, e.g. toxic metals or other inorganic pollution. The stoichiometric reaction of the most reduced sulphurous compound, i.e. dihydrogen sulphide is given in Equation 1, the oxidation of pyrite as the most common sulfidic mineral is shown in Equation 2.

$$H_2S + 2O_2 \dashrightarrow SO_4^{2-} + 2H^+ \qquad (1)$$

$$FeS_2 + 15/4O_2 + 7/2H_2O \dashrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad (2)$$

Oxidative processes can have both microbial and spontaneous chemical character. However, the pH-optimum for chemical and microbial processes differs: chemical oxidation occurs more intensively when pH of the substrate is high (pH 8-10), whereas for microbial oxidation proceeds with maximum reaction rates at low pH (pH 1-7). However, even when chemical and microbial oxidation rates are considered at their appropriate pH-optima, the microbial oxidation could be still 100 000 times faster than chemical one. Microbial sulphur oxidation is mainly mediated by neutrophilic and acidophilic thiobacilli. Acidity is also produced by Fe(II) oxidation, e.g. by the activity of Thiobacillus ferrooxidans.

Our experimental work was set up to find NaOH-supplement for a representative aerated mine lake sediment that leads to minimum sulphuric acid production to the environment. This production of the acid could be only reached when resulting pH of the sediment leads to the slowest intensity of both chemical and microbial oxidative processes. At the same time, we intended to calculate the levels of sulphuric acid produced by chemical and microbial processes, to compare them, and to express these velocities in dependence of pH values of the sediment.

Representative sediment was sampled from the deepest part of the lake 111 (Lusatia) using Birge-Ekman sampler. For the purposes of the experiment, only the black part of the sediment was taken. Finally, we collected 10 litres of fresh sediment with its interstitial water that was transferred to the laboratory in polyethylene bottle under anoxic conditions. Afterwards, it was stored at 5°C in the dark. Sampled sediment showed the following characteristic: pH 5,83±0.02, ox/red potential -25±3 mV, conductivity 2.24±0.03 mS/cm^2, acidity 0.025±0.001 mol/l, total sulphur content of AVS 81.1±4.5 mol/kg, CRS 85.2±9 mol/kg and S0 9.1±0.2 mol/kg (dry mass), and concentrations of dissolved sulphate, Fe^{2+} and Fe^{3+} in pore water of 1935±5, 836±1 and 32.1±0.1 mg/l, respectively.

Before the experiment, original pore water was removed by centrifugation (3750 rpm, 30 minutes) and sediment was mixed with distilled water at a resulting solid/liquid ratio of 1:7.5 (kg dry mass: litre).

13 experimental flasks were filled with sediment suspension, and NaOH at final concentrations from 0.002 to 0.16 mol/l was added. At the same time, a treatment without any NaOH-supplement was prepared. All experimental variants were agitated on a horizontal shaker (95 rpm) at 27°C in the dark for 375 hours. During the experiment pH, oxidative-reduction potential, conductivity and oxygen concentration were measured directly in the sediment slurries. Afterwards, sub-samples of sediment suspensions were taken and titrated by 1N NaOH under Ar-atmosphere. At the same time, a part of slurries was centrifuged (3750 rpm, 30 minutes), and samples for dissolved sulphate, calcium, manganese, zinc and iron were

taken. Sampled sediment suspensions from each treatment were also cultivated to calculate numbers of acidophilic, neutrophilic and iron oxidising thiobacilli by MPN method. For selected representative samples, oxygen consumption by a fluorometric method was measured. All measurements were done after 1, 15, 40, 64, 92, 116, 136, 169, 184, 208, 232, 260, 304, 328 and 376 hours of the experiment.

Parallel, the same experiment was performed with irradiated sediment (25kGray). Here, all previously living microbes were killed. This gave us a chance to express the rate of chemical oxidation.

From these two independent experiments, sulphuric acid production by chemical and microbial processes was calculated in time course of the experiment. In data processing, the sulphate desorption/adsorption behaviour and sulphate precipitation to the form of poorly soluble gypsum were taken into account.

Geochemische und mikrobiologische Vorgänge in Sedimenten und an der Sediment-Wasser-Grenzschicht in Restseen von Bergbaufolgelandschaften

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