USING CARBON DIOXIDE TO REMEDIATE ACIDIC MINING LAKES

Yvonne Unger
Department of Geology, TU Bergakademie Freiberg, Gustav-Zeuner-Straße 12, 09596 Freiberg, Germany

Abstract

The aim of the study is to investigate whether alkaline by-products such as iron (oxy)-hydroxides together with carbon dioxide can be used to improve the water quality (especially acidic buffer capacity) in acidic mining lakes. Resulting from the treatment of the mining lake, the water quality in the groundwater outflow will be improved and additional carbon dioxide emissions can be reduced. Sludge from acid drainage treatment plants consists of iron and calcium compounds that can be used to sequestrate carbon dioxide in the form of carbonates (e.g. siderite and calcite).

Introduction

In Lusatia (Germany) many brown coal pits were operating in the 1950s until 1980s. Most of these open pits were closed in the 1960s and in the 1990s; as a consequence the groundwater level rose and filled the existing holes. The complete and fast flooding of open pits by river waters occur rarely in Lusatia, while most holes were flooded due to rising groundwater. The weathering of sulphides (e.g. pyrite) in the Lusatia pit lakes plays an important role for the water quality in the surrounding area. Similarly to other mining areas, the water problems in the Lusatia mining area are related to low alkalinity, low pH values, high concentrations of iron and sulphate. This problem affects the lake water in the pit and also the groundwater at the outflow of the lakes. Thus, even regions formerly not affected by the active mining can be endangered. To prevent acidification, many lakes in Lusatia were filled partly with industrial products such as fly ash from brown coal combustion or low-density sludge from acid drainage treatment plants. An example of such a lake is Spreetal-Nordost in the Saxony Part of Lusatia (Fig. 1).

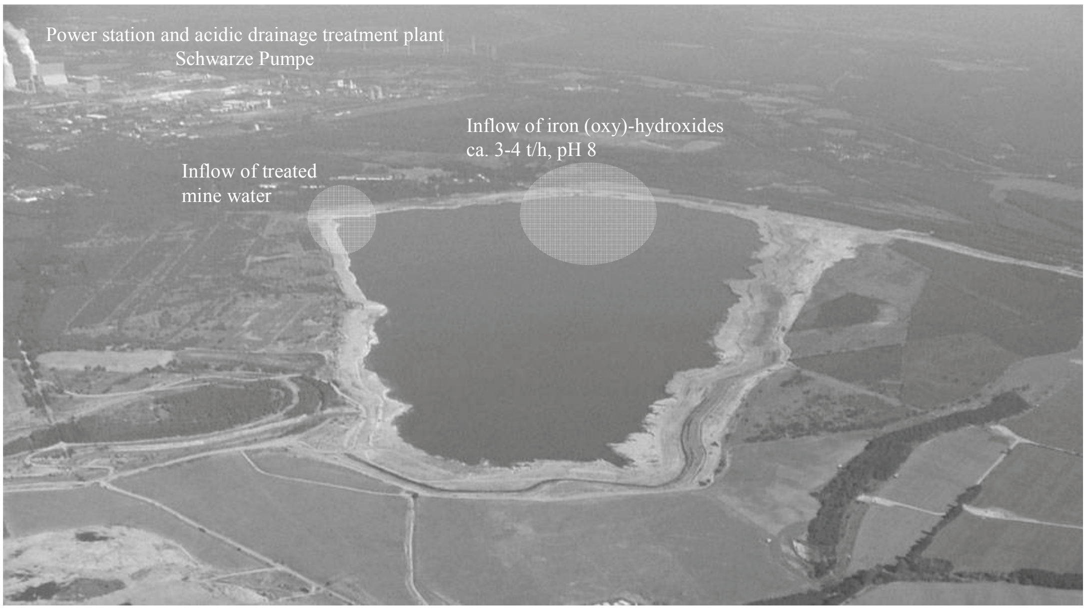

Figure 1. Aerial view of the Spreetal-Nordost mining lake (September 23rd 2005 at 1000 m height eta-AG, orientation to East). The acid mine treatment plant Schwarze Pumpe is located in the upper left corner.

Normally acid drainage treatment sludge contains amorphous iron hydroxides, gypsum, un-reacted lime and calcite (Zinck, 2006). The Fe and Ca cations, together with carbon dioxide, can be used to build up a carbonate buffer to improve the water quality in the lake. Initially, carbon dioxide will be dissolved in the pore water of the sediments depending on the pH value:

(Equation 1) $CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$

Under pH values above 8, CO_3^{2-} ions will react with metallic cations to form siderite and other carbonates, so that the acidic buffer capacity will raise:

(Equation 2) $CO_3^{2-} + Me^{2+} \leftrightarrow MeCO_3$

An additional positive effect of this treatment scheme is to store CO_2 as siderite and calcite (mineral trapping), reducing emissions of the greenhouse gas. Neutral to slightly alkaline pH values are necessary to form carbonates. Thus carbonates probably are not formed in the lake itself but in the sediments. In this study we show with thermodynamic simulations that sludge from acid drainage treatment plants together with carbon dioxide can be used to precipitate siderite and to raise the buffering capacity in acidic pit lakes. Postma (1982) described the formation of carbonates as a natural process. Injections of carbon dioxide can support and accelerate this process.

Study Area

Spreetal-Nordost is the first lake of a chain of mining lakes in Lusatia. The brown coal pit Spreetal was opened in 1983 and closed in 1991. Since 1998 the pit is continuously filled with rising groundwater and more or less continuously with low density sludge from the acid drainage treatment plant Schwarze Pumpe. The treatment plant Schwarze Pumpe is used to treat acid drainage from nearby mining areas by addition of hydrated lime. After treatment the produced low density sludge is pumped into the lake at the bottom. Additionally the neutralized solutions are used to flood the lake discontinuously. The pH value in Spreetal-Nordost ranges between 3.5 and 6.5. This is caused by the discontinuous inflow of treated mine water and slow rates of groundwater inflow into the lake (0.05 to 0.06 m^3/s; LMBV, 2003). The inflow of the alkaline treated mine water immediately increases the pH value in the lake, but this is only a temporary process. The alkalinity in the treatment sludge is not high enough to buffer the acidic groundwater from dumps. The Spreetal-Nordost lake water shows alkalinity values < 0.01 mmol/L, high sulphate concentrations (about 1150 mg/L) but low concentrations of iron (about 0.3 mg/L Fe^{2+} and about 1.1 mg/L Fe^{3+}). The formation of a carbonate buffer in Spreetal-Nordost could have a positive effect to the other lakes of the chain. Spreetal-Nordost will have a volume of 97 million m^3 if steady state conditions are reached in 2008. The groundwater discharges into the lake from south/southwest and southeast (LMBV, 2003). Two million cubic meters of iron hydroxide sludge discharges into the lake yearly. Currently, 15 million cubic meter sludge are deposited at the bottom of Spreetal-Nordost. The low density sludge from the treatment plant Schwarze Pumpe contains only 1 to 3 % solids and consists of amorphous iron (oxy)-hydroxides, calcite and small amounts of quartz.

Methods

Thermodynamic calculations are performed with the code PHREEQC 2.12.05 (Parkhurst and Appelo, 1999). PHREEQC is a computer program for simulating chemical reactions and transport processes in natural or polluted water. The program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. PHREEQC computes aqueous activity coefficients using ion association and Debye-Huckel expressions that are adequate at low ionic strength (Parkhurst and Appelo, 1999). For all calculations with PHREEQC the database of the aqueous model WATEQ4F (Ball and Nordstrom, 1991), distributed with the code, was used.

Table1. Analysis of lake water used as input to PHREEQC.

pH	4.05	SO_4 [mg/L]	1172	Fe(II) [mg/L]	0.33
pe	5.1	NH_4 [mg/L]	294.0	TIC [mg/L]	1.2
O_2 [mg/L]	20.0	Cl [mg/L]	23.7	Zn [mg/L]	0.39
Ca [mg/L]	345.5	Si [mg/L]	11.6	NO_3 [mg/L]	0.26
Mg [mg/L]	70.8	Mn [mg/L]	2.2	Ni [mg/L]	0.23
Na [mg/L]	18.1	Al [mg/L]	2.0	PO_4 [mg/L]	0.054
K [mg/L]	8.5	Fe(III) [mg/L]	1.2	Cu [mg/L]	0.018

Results and Discussion

The calculations have been carried out using the solution composition of lake Spreetal-Nordost (Table 1). The treatment scheme was simulated stepwise as equilibrium processes. The solution is in equilibrium with amorphous iron hydroxide, gypsum and atmospheric carbon dioxide (0.036 %) but supersaturated with dissolved oxygen. In the first step ferric iron is reduced by addition of Fe^0. Thermodynamic data for Fe^0 are taken from Hummel et al. (2002). The addition of the reducing agent Fe^0 increases the concentration of ferrous iron in the solution (Fig. 3) whereas the saturation index for pyrite stays at the same level. The formation of pyrite in mining lakes is not controlled only by supersaturation in the solution. Blodau (2006) observed that the formation of total reduced inorganic sulphur (TRIS) is smaller than reduction rates of iron and sulphate. He mentioned that sulphate and iron have to be reduced nearby or at the same time to form pyrite. In this study ferrous iron would be available at the same place as carbonate ions to form siderite.

The addition of at least 0.1 mmol Fe^0 /kg water is necessary to reach supersaturation for siderite. Thus 5.6 mg Fe^0 has to be added to precipitate siderite. In Figure 2a it can be seen that the concentration of total inorganic carbon rises with increasing partial pressure of CO_2. The distribution of species changes with increasing partial pressure caused by the decreasing pH value in the solution. For a partial pressure of about 3 bar the main aquatic carbon species is undissociated H_2CO_3. The HCO_3^- concentration in the solution stays nearly at the same level for partial pressure greater than 0.01 bar and the concentration of carbonate ions decreases due to the pH lowering beneath values of 8. The greatest saturation index for siderite is also reached for carbon dioxide partial pressures between 0.003 and 0.01 bar (Fig. 2b). This pressure corresponds to CO_2 concentrations of 0.06 to 0.2% at a water depth of 40 m. It is problematic that pyrite also reaches a high saturation index. At CO_2 partial pressures greater than 0.03 bar the saturation index for pyrite shows a broad decreasing to negative values. Thus the carbon dioxide fraction of the gas phase has to be at least 3% at atmospheric pressure and 0.6% at a depth of 40 m, respectively. Although the highest saturation index for siderite is reached between 0.003 and 0.01 bar, the concentration of precipitated siderite is nearly constant at 40 mmol/L also for higher CO_2 partial pressures (Fig. 2c).

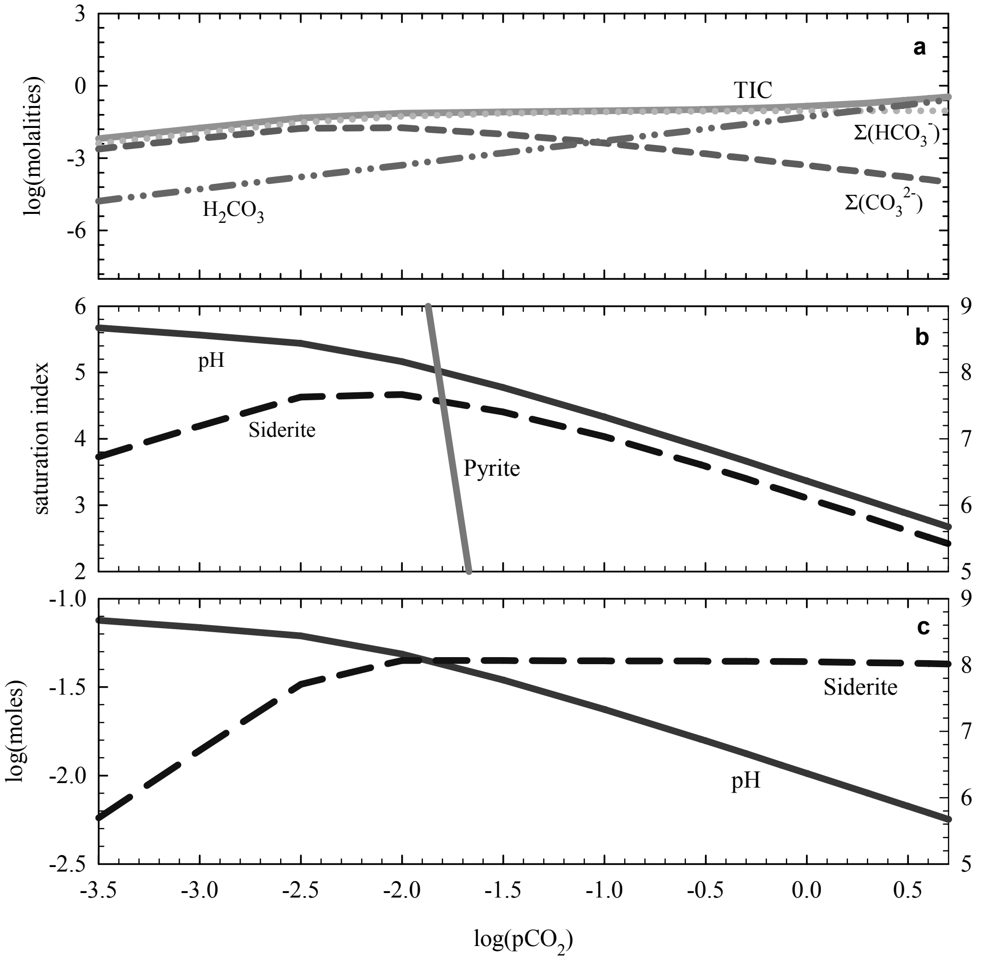

Figure 2. Species distribution for the reaction of lake water with CO_2 at 10 °C after addition of 2.5 mmol Fe^0; simulated at equilibrium.

The aim of these theoretical simulations is to increase acidic buffer capacity (alkalinity) in acidic mining lakes. Stumm and Morgan (1996) define alkalinity in the following way:

(Equation 3) $\text{alkalinity} = [HCO_3^-] + [CO_3^{2-}] + [OH^-] - [H^+]$.

Resulting from equation 3 the alkalinity in mining lake Spreetal-Nordost is -0.01 mmol/L. Reduction of deposited sludge and addition of carbon dioxide can increase the alkalinity in the lake to about 4 mmol/L (Fig. 3). The pH reaches values of 5 to 6 after complete precipitation of siderite to a saturation index of 0. Normally carbonate precipitation is a relative fast reaction, but whether the complete precipitation of siderite occurs this has to be considered in experimental tests. Jimenez-Lopez and Romanek (2004) investigated saturation indices ranging from near equilibrium to 3.53. For saturation index of 1 the pH value is 0.5 units higher and the alkalinity triples (Fig. 5).

The more reducing agent is used the higher is the pH value caused by the consumption of protons during reduction. Because of the higher pH values more carbon dioxide can be dissolved in the solution. In Figure 4 can be seen that the addition of Fe^0 influences the alkalinity in the resulting solution after carbon dioxide addition. Especially at lower partial pressures of carbon dioxide the alkalinity can be increased by higher addition of the reducing agent.

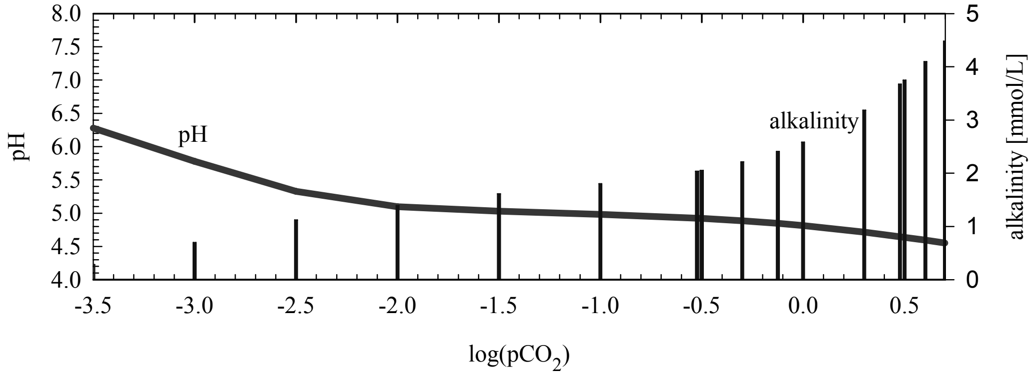

Figure 3. Reaction lake water with CO_2 at 10 °C after addition of 2.5 mmol Fe^0; simulated at equilibrium pH after precipitation of siderite.

Conclusions

Theoretical calculations show that ferric iron (oxy)–hydroxides derived from plants after treatment of acid mine drainages can be used to trap carbon dioxide in ferrous iron carbonates and improve the water quality (alkalinity) in acidic pit lakes. The ferric iron containing sludge deposited in several mining lakes in Germany has to be reduced (e.g. with Fe^0). The best results with regard to alkalinity, pH and the volume of precipitated siderite were simulated at moderate partial pressure of carbon dioxide. Also pyrite precipitation can be nearly precluded. Further investigations of raising alkalinity in acidic mining lakes using carbon dioxide and iron (oxy)-hydroxide sludge, and including laboratory experiments, should be undertaken.

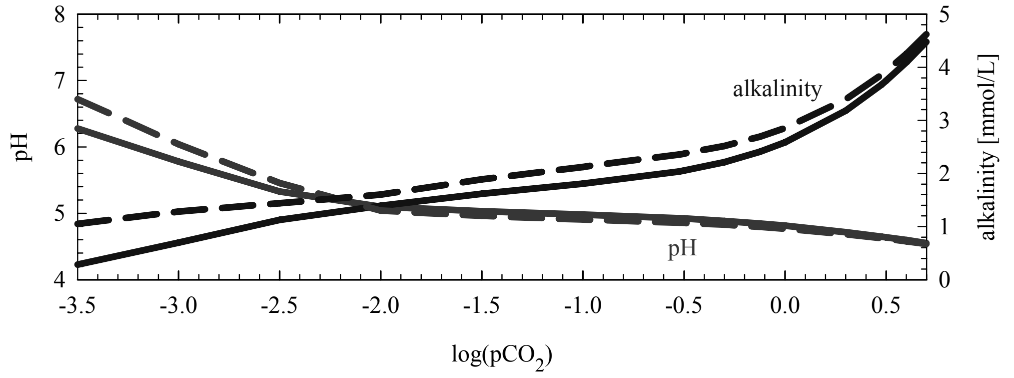

Figure 4. Comparison of alkalinity, pH and siderite precipitation after reaction of lake water, iron (oxy)-hydroxides and CO_2; solid lines: addition of 2.5 mmol Fe^0, dashed lines: addition of 10 mmol Fe^0.

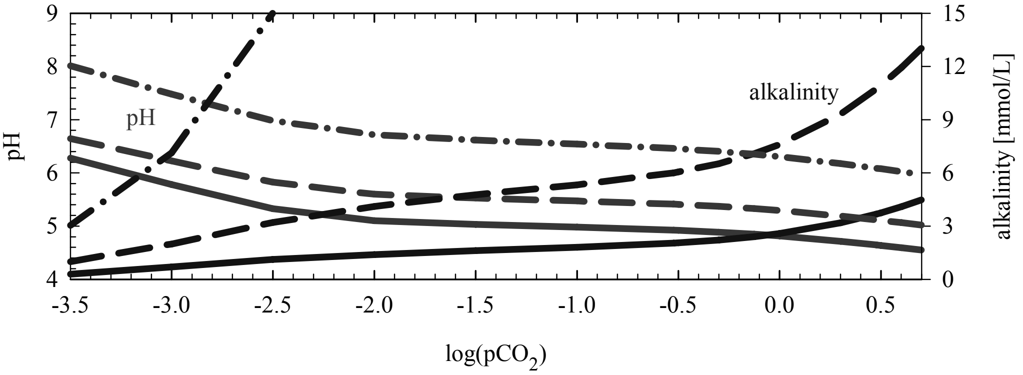

Figure 5. Comparison of alkalinity and pH after precipitation of siderite at different saturation indices; solid lines: $SI_{siderite}$= 0, dashed lines: $SI_{siderite}$= 1; addition of 2.5 mmol Fe^0.

Acknowledgements

The author wishes to thank the Saxon Ministry of Environment and Agriculture for funding the research project and the Lausitz and Central-German Mining Administration Company for supporting this project.

References

Ball J.W., Nordstrom D.K. (1991). User's Manual for WATEQ4F. US Geological Survey, Open File Report 91-183, p. 188.

Blodau C. (2006). A review of acidity generation and consumption in acidic coal mine lakes and their watersheds. Science of the Total Environment 369 (1-3), 307-332.

Hummel W., Berner U., Curti E., Pearson F.J., Thoenen T. (2002). Nagra/PSI: Chemical Thermodynamic Data Base 01/01. Parkland: Universal, p. 565.

Jimenez-Lopez C., Romanek C.S. (2004). Precipitation kinetics and carbon isotope partitioning of inorganic siderite at 25°C and 1 atm. Geochimica et Cosmochimica Acta 68 (3), 557-571.

LMBV (2003). Aktualisierung des Gutachtens zur Entwicklung der Wasserbeschaffenheit in den Tagebauseen der Erweiterten Restlochkette (Spreetal-NO, Spreetal-Bluno, Skado, Koschen, Sedlitz). Brandenburgisch Technische Universtät Cottbus, unpublished work.

Parkhurst D.L., Appelo C.A.J. (1999). User's guide to PHREEQC (Version 2): a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey, Water Resources Investigations Report 99-4259, p. 312.

Postma D. (1982). Pyrite and Siderite Formation in Brackish and Fresh-Water Swamp Sediments. American Journal of Science 282 (8), 1151-1183.

Stumm W., Morgan J.J. (1996). Aquatic Chemistry. New York, John Wiley & Sons, p. 1022.

Zinck J. (2006). Disposal, reprocessing and reuse options for acidic drainage treatment sludge. 7th ICARD 2006, St. Louis, 2604-2617.