

ASSESSMENT OF A TREATMENT SCHEME FOR ACIDIC MINING LAKES USING CO₂ AND CALCIUM OXIDES TO PRECIPITATE CARBONATES¹

Florian Werner², Bastian Graupner³, Broder Merkel⁴, Christian Wolkersdorfer⁵

Abstract. Carbon dioxide and calcium oxides may be used to neutralize acidic lakes. In lignite producing areas combustion power plants producing CO₂ are often close to pit lakes. If fly ashes from these power plants could be used as calcium oxide source, carbonate precipitation in lakes could also be used as a mineral trap to dispose of CO₂. In a preliminary step the feasibility of this treatment scheme is investigated and includes a model based assessment of expected effects on the surface water, the reactivity of the chemical components, and the technical prerequisites. A pit lake in the Lausitz (Lusatia) post mining area in Germany was chosen as a test site, where fly ash has been deposited for more than 25 years. The feasibility of re-suspending these deposits to neutralize the lake was demonstrated in the years 2000 and 2003, and additional CO₂ is proposed to increase the buffering capacity of the lake water, to precipitate, and store carbonates in the lake sediments.

Additional Key Words: Mineral trapping, lake treatment

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² Florian Werner is leading a research group on post mining landscapes at the Dresden Groundwater Research Centre (DGFZ e.V.), Meraner Str. 10, 01217 Dresden, Germany. ³Bastian Graupner is PhD-Student at the Dresden Groundwater Research Centre. ⁴Broder Merkel is Full Professor for Hydrogeology and Environmental Geology at the University Bergakademie Freiberg, 09599 Freiberg, Germany. ⁵Christian Wolkersdorfer is Research Fellow at the University Bergakademie Freiberg

Introduction

A large number of Pit Lakes exists in the German Lausitz Mining District, where flooding with surface water and continued flushing is the main strategy to obtain an acceptable water quality. Nevertheless the discharge from some lakes, or the lakes themselves, needs to be treated before pit lake water can be discharged into rivers. Attempts to neutralize the large seasonally stratified (dimictic) lakes in this area has been with the addition of lime, ashes from combustion power plants or soda, which has provided mixed results.

The planning of a pit lake treatment needs to consider lake-internal and lake-external processes. The external processes are controlled by the interrelation with the groundwater flow system and the behavior of the slopes. As a result of lake-external processes a mass flux of dissolved constituents that is imported into the lake exists (Werner, Bilek, Luckner, 2001). The key parameter of this mass flux is acidity, defined as the acid generating potential treatment (Uhlmann, Büttcher, Schulze, 2004) and the intensity of this acidity flux controls the expected sustainability of a lake treatment.

Lake internal processes in the acidic Lausitz Pit Lakes are of hydrodynamic, chemical and biological nature. Biological processes in these lakes are dominated by microorganisms that are involved in the Fe and S cycle (Wendt-Potthoff and Koschorreck, 2004), whereas primary production is limited by the availability of P and C (Beulker and Nixdorf, 2004). The dominant chemical reactions in these acidic lakes are the oxidation of Fe and the precipitation of Fe containing solid phases (Peine 1998). Hydrodynamic mixing controls the transport of dissolved constituents within the lakes. The exchange of O₂ and CO₂ with the atmosphere across the surface boundary of the lakes is mainly controlled by the properties of the water surface (Vlahos et al. 1995) and the transport to and from surface near layers.

Pit Lake volumes in the Lausitz area range from 10 to 300 x·10⁶ m³. Acidic lakes are often treated with lime by applying the lime directly onto the lake's surface (Evans and Dillon, 1995). In the Lausitz area, lime has recently been successfully applied to a lake by spraying a lime slurry with a nozzle used for agricultural irrigation onto the surface. The device was fitted on floating pipes and moved during operation, while the slurry was provided by a station located at the shore line (Scholz, 2005). The main problem in treating large bodies of water with lime (with a base consumption of several moles per m³) is to assure a sufficiently high flux of lime on the one hand and to avoid over saturation and massive sedimentation on the other hand.

Proposed Treatment Scheme

The general concept is to combine CO₂ mineral trapping and the treatment of acidic mine waters by increasing alkalinity. In the Lausitz mining district intensive mining during the last century has produced large deposits of fly ash, C slurry, and Fe(OH)₃ sludge containing overdosed lime (from the treatment of acid mine drainage) in the abandoned and flooded mine pits. One of these former pits is the acidic Burghammer pit which contains large amounts of these substances deposited on its bottom (LMBV, 2003). In our opinion a treatment of lake Burghammer sediments and water with CO₂ appears thermodynamically feasible using carbonation. Kinetic aspects, the real world phase assemblage, and technical aspects of the dosage, mixing, precipitation, and settling of the carbonate solid will be investigated in the

project CDEAL (Geotechnologien 2005) during the next 3 years. An acidic water with a typical concentration of Ca (3 to 10 mmol/L) will cause a calcite saturation during a base titration if CO₂ is allowed to reach equilibrium concentrations. Calcite precipitation will reduce the Ca concentration as long as saturation is maintained and Dissolved Inorganic Carbon (DIC) concentration increases as pH rises and Ca concentrations decrease (Nordstrom and Munoz 1986, Bethke 1996). These considerations show that there is a potential for acidic lakes to uptake of CO₂ to the H₂O if the treatment is combined with a neutralization of the H₂O. Consequently the natural pH-buffer HCO₃⁻ is introduced to the H₂O and improves both the chemical condition and the biological potential.

The amount of calcite that can be precipitated if only pH is raised is of course low and dependant of the initial Ca concentrations of the H₂O. Unlimited amounts of calcite can be produced if unlimited quantities of Ca and carbonate are delivered to the solution, precipitated calcite can be stored in the sediment, supported by the fact that lake sediments are natural calcite sinks in the geosphere. The storage mechanism consequently is not based on technical elements but rather on the geochemical conditions and calcite precipitation should not be used in lakes that have a longtime tendency of becoming acidic through geological setting. However, should the acidic conditions return to a lake used for calcite storage, this will not result in instantaneous CO₂ release. Dissolution of calcite will buffer imported acidity and improve the water quality but is not desirable in terms of C storage. A slow release of CO₂ is expected because the surface area (boundary sediment/lake) is small compared to the total mass of the sediment.

Furthermore, Fe precipitation, occurring during neutralization, is expected to act as a capping mechanism, which will limit exchange. Further Fe precipitation can produce sediment layers that support a progressive exclusion of the carbonates from participating in lake internal processes as the sediment consolidates. Active sediment capping is applied as a remediation technique to exclude contaminants in lake sediments from lake water (EPA 1993).

Hence calcite precipitation is best applied in acidic lakes that will be circum neutral after the initial water treatment. Lake Burghammer is part of a planned storage system, which will receive high fluxes of surface waters (LMBV 2003). A water treatment station at its inflow point can be used to maintain neutral conditions if necessary.

However the supply of cations (Ca, Mg) is a limiting factor for the utilization of the storage strategy. A positive effect concerning the overall CO₂ budget can be achieved using cations from the fly ashes of combustion power plants.

Lake Burghammer

Lake Burghammer (Fig. 1 and 2) occupies an old mine pit, is located 5 km east of the city of Hoyerswerda in Saxony and is part of the river Spree catchment. The mining lakes, Dreiweibern, Lohsa II and Burghammer, are planned to be operated as a single storage pond system. The outflow out of this system will discharge from Lake Burghammer into the Kleine Spree River which is a tributary to the River Spree.

The lake is currently 72% full and its final water volume will be $36 \cdot 10^6 \text{ m}^3$. From 1974 to 1997 fly ash from the Schwarze Pumpe combustion power plant has been dumped in the abandoned surface mine, before the lake was flooded. During the years 2002 to 2003 a re-suspension of the dumped ashes was tested and demonstrated (Fig. 3), using an excavator on a floating platform equipped with a suction tube and a rinsing device (Fig. 4). It was shown that this re-suspension activity was successful in neutralizing the acidic lake water, but that no buffer

capacity could be built up in the water by this action (LMBV 2003). Consequently it was decided to postpone a further operation of the suction excavator until Lake Burghammer begins to discharge water into public streams (Kleine Spree River) and to keep an instrument of controlling the effluent pH.

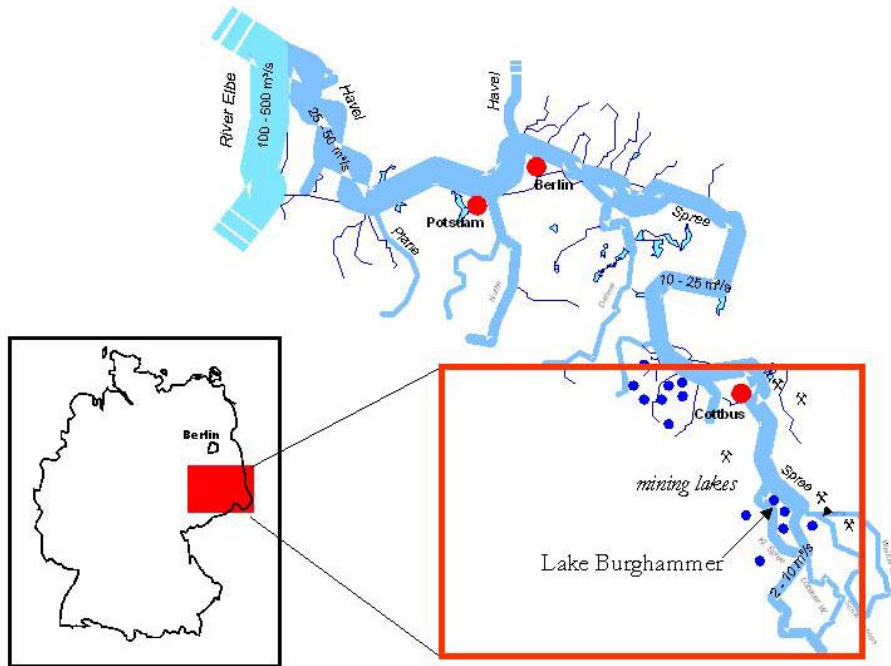


Figure 1. Map of Germany (left) showing the location of the Lausitz post mining area in the River Spree catchment and Lake Burghammer

Based on the presented cornerstones of the treatment scheme the authors propose the hypothesis, that the effects of the re-suspension of the alkaline sediments on the acidity of the lake water can be enhanced by the application of CO_2 and that CO_2 can be stored as carbonate on the lake bottom. To prove this hypothesis the presented study is conducted. The presentation is focused on the methods rather on results, as this study is still ongoing. The study will consider the effects of the treatment on a technical and a hydrological scale. These scales are addressed as internal and external processes.



Figure 2. Aerial view of lake Burghammer (courtesy of eta AG engineering Cottbus).



Figure 3. Re-suspension of fly ashes from the lake bottom without the use of CO₂ (courtesy of eta AG engineering Cottbus).



Figure 4. Excavator used in the re-suspension tests (courtesy of eta AG engineering Cottbus).

Lake Internal Processes

The following solution composition was analyzed in the epilimnion of Lake Burghammer in 2004: pH 3.1, Na 3 mmol/L, Mg 2.5 mmol/L, K 0.5 mmol/L, Ca 9 mmol/L, C 0.2 mmol/L, S(6) 14 mmol/L, Fe 0.2 mmol/L, Cl 2.0 mmol/L. A stepwise simulation of the equilibrium processes that might occur was performed using PHREEQC2.7 (Parkhurst an Appelo, 1999). In the first step CaO and CO₂ was dissolved into the water and calcite was allowed to precipitate. Then CO₂ was introduced by assigning a partial pressure of 2 bar, assuming a treatment depth of 10 m and the use of the CO₂ gas. In the second step this water was equilibrated with atmospheric CO₂ partial pressures to approximate the release of CO₂ from the treated water into the atmosphere (Tab. 1).

Table 1. Results of PHREEQC modelling with CO₂ partial pressure of 2 bar.

Step	CaO input	pCO ₂	CO ₂	Calcite	Ca	C	pH
			in/out	precip.	in solution	in solution	in solution
	mmol/L	bar	mmol/L	mmol/L	mmol/L	mmol/L	–
0	0	0.006	–	–	9	0.2	3.1
1	1000	2	1078	988	21	90	5.8
2	0	0.0004	-78	12	9.5	0.4	7.8

This rough calculation shows that calcite may precipitate in the same magnitude as CaO is dissolved in the water. The main influence of the partial pressure of CO₂ is the control of pH. Low pH favours CaO dissolution, but hinders calcite precipitation and CO₂ dissolution. A second calculation was performed with a pCO₂ of 0.1 bar (Tab. 2). Best results seem to be possible if CO₂ supply is controlled depending on the dissolution of CaO and the pH. The higher the pH in step 1 (the lower the partial pressures of CO₂ will be) the less CO₂ degasses unused into the atmosphere after the water equilibrates with atmospheric gases. In these calculation examples the unused fraction of CO₂ ranges from 0.6 to 7 %. Gypsum saturation was not exceeded in these examples.

Table 2. Results of PHREEQC modelling with CO₂ partial pressure at 0.1 bar.

Step	CaO input	pCO ₂	CO ₂	Calcite	Ca	C	pH
			in/out	precip.	in solution	in solution	in solution
	mmol/L	bar	mmol/L	mmol/L	mmol/L	mmol/L	–
0	0	0.006	–	–	9	0.2	3.1
1	1000	0.1	1006	997	12.5	10	6.5
2	0	0.0004	-6	3	9.5	0.4	7.8

The control of the mass fluxes during the reaction is a key task to provide thermodynamic preconditions for the turnover of CO₂ into calcite. The rates for this reaction were studied by Plummer et al. (1978) and Kunz and Stumm (1984). They are reported as first order law with respect to the activity product $a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}$, the rate constant is given in mmol CaCO₃ cm⁻² s⁻¹. An estimate of the expected rates cannot yet be given, as the surface area that will be available for nucleation is unknown. From the first sampling of the sediments, a Ca concentration released in the first step (adsorptive bound) of a sequential extraction (Zeien, 1995) of 1 to 2wt% was found.

Experimental setup to investigate the reaction processes

Samples from the fly ash deposits of Lake Burghammer are investigated by using batch and bench experiments. Batches with stirred water/ash suspensions and a gas head space to control CO₂ partial pressures were set up (Fig. 5). It will be investigated if the solid phases that precipitate are the defined phases for which the thermodynamic data are available. The distribution of Ca in the solid and liquid phase will be analyzed. In addition C will be analyzed in the gas phase. Another aim of the experiments is to determine the reaction rates and the limiting reactions of the process. The batch experiment is designed in a way to minimize physical controlled transfer rates. The batch will be stirred to maximize the contact between the solid, liquid and gaseous phases. The influence of the Ca-source will be investigated by using sampled fly ash from the lake bottom and fresh fly ash from a combustion power plant.

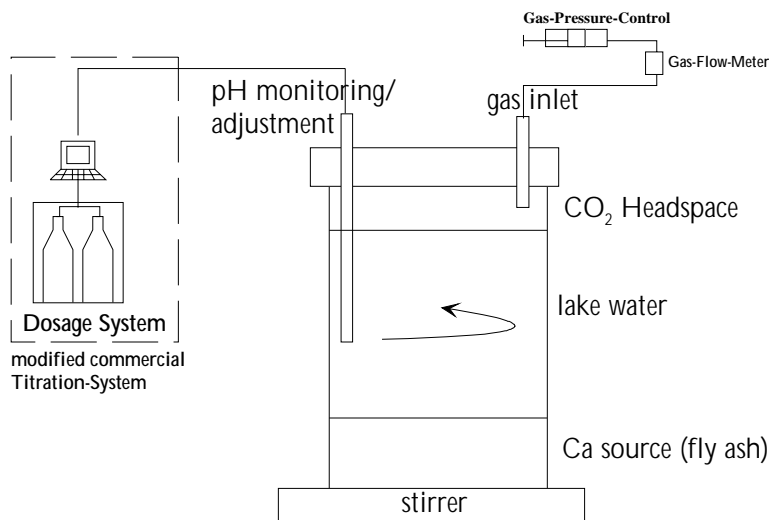


Figure 5: Sketch of the batch experiment setup

After a successful completion of the batch experiments the system will be scaled up to bench scale (Fig. 6) where the fly ash dissolution and the carbonate precipitation process are investigated with physical dimensions that are closer to reality, that is contact surfaces and contact times are maximized to exclude their influence. The field scale excavator on a floating platform equipped with a suction tube and a rinsing device is the scale that has to be bridged with the bench experiments. A key question investigated is whether the removal of CO₂ and the supply of fly ash can achieve the same rate. If this can not be achieved in the bench experiments, a modification to the existing excavator technology must be considered. The layout for the

bench experiments is shown in Fig. 6. Apart from the strategy of transporting the reactants and using a technical reactor, the injection of CO₂ into the ash is also considered.

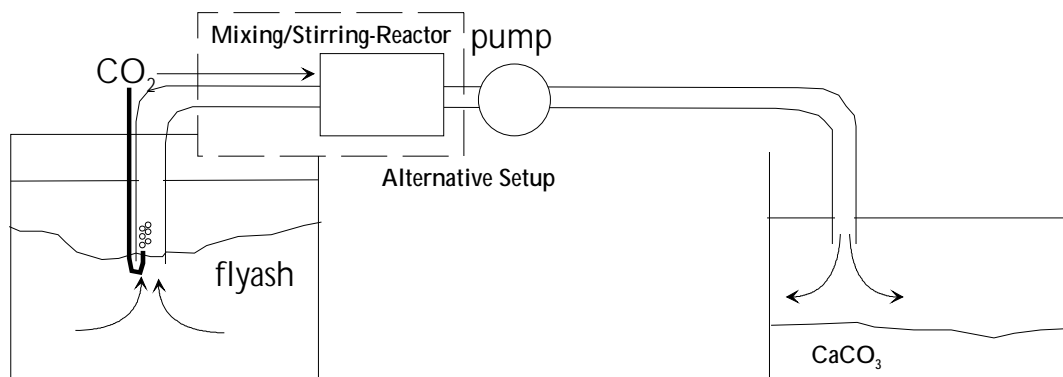


Figure 6: Sketch of the bench experiment setup

Lake External Processes

The external processes to the lake that affect the sustainability of C storage within the water and the sediment are the ones that import acidity into the lake. The three sources of acidity are (i) the ground water influx, (ii) the leaching of the bank materials and (iii) the surface water inflow from upstream mining lakes and a small river. These fluxes have been investigated and predicted for the future hydrologic system by the owner of the lake (LMBV 2005). A regional ground water flow model and a reactive balancing approach were used for these predictions. The acid-base budget of the lake is, according to these findings, dominated by the operation of the surface water inflow from the upstream lakes. A treatment plant that neutralizes this inflow, with a maximum flow rate of 10 m³/s, is planned to be built. This treatment plant will be able to maintain neutral conditions in Lake Burghammer. The existing modeling results concerning the future regional water and mass budget will be checked with recent data of the flooding process (surface water input, water quality). The mass budget calculations will be updated based on the existing flow model results (LMBV, Winkler). A prediction will be made how the proposed CO₂ storage technology will work in Lake Burghammer as a whole and what effect this will pose on the lake water. The possibility of a re-dissolution of the precipitated calcite, which is closely connected to the future pH in the lake has to be considered. The predictive modeling will be performed with a model called MODGLUE (Müller 2004). Functionalities of existing and proven models were modified and extended to build a new model termed MODGLUE (MODEL for Prediction of Groundwater and Erosion influenced Lake Water Quality Using Existing Models). This interdisciplinary model integrates all major processes as well as their temporal and spacial interactions. The model was developed for acidified mining lakes. It incorporates a lake model (CEQUALW2, Cole and Buchak (1995)) that was modified to simulate acidic as well as neutral systems. Inorganic processes are simulated with PHREEQC. The model was programmed using object oriented programming schemes in the language PYTHON. To simulate the lake treatment/calcite storage a model of Lake Burghammer has to be set up and changes in the code have to be made.

Conclusions

The proposed technology is not feasible for treating the CO₂ mass flux that is produced in lignite combustion power plants, as a whole. The amount of fly ash that is simultaneously produced with CO₂ is significantly less than would be required for a stoichiometric ratio of one to one. Nevertheless, this seems to be a strategy to bring benefits to both the CO₂ emitter and the water quality of acidic lakes, which strongly affects the public. Land use of post mining areas is connected to a good water quality of the surface and ground water. Accepting these limitations, the prospects of scientific and technical success are viewed to be high. The storage mechanism for CO₂ can be addressed as a low risk strategy. No instantaneous release is to be expected. An acidification of the deposit that might lead to dissolution of the deposit can be controlled by the technical means that will be installed to neutralize the influx from upstream lakes.

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