A new technology of pit lake treatment using calcium oxide and carbon dioxide to increase alkalinity

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Abstract

Pit lakes are often subject to acidic groundwater inflow and therefore prone to short term re-acidification. Hence, the increase of alkaline buffer capacity is the main treatment aim to develop stable pH-conditions that allow biological processes to take place.

To increase alkalinity in pit lakes one needs to apply alkaline materials in combination with CO_2. A test of this treatment approach that uses CaO (phase 1) and $CaCO_3$ (phase 2) in combination with CO_2 is presented in this paper.

The treatment process was established in a closed reactor system, which produces high alkaline waters. The treatment process itself consists of a standard lime slaking technology, which is only necessary in the case of CaO application, and a carbon dioxide dissolution reactor. The alkaline suspension (CaO or $CaCO_3$) and the CO_2 enriched water enter an HCO_3^- producing reactor. Since CO_2 is an expensive product, a gas recovery reactor (GRR) was installed downstream of the HCO_3-reactor. The produced HCO_3^- was then applied to the pit lake using an injection system based on submerged buoyant jets.

Between both test phases the acidic groundwater inflow caused a decrease in pH and alkalinity due to re-acidification. That period was closely monitored to determine the alkalinity decline and therefore the treatment success. Also, the impact of the processed water, which was discharged into the lake, on the lake water quality is described.

The pit lake chosen for the tests is called Drehnaer See. It is a small sized pit lake with a total volume of 13 Mio. m^3. The acidity before the treatment was between 3.4 and 4.1 mol/m^3. Prior to the actual test the lake was neutralised using lime (CaO). During this initial treatment step pH-values of the lake water increased from around 3.0 to 7.0. After the neutralisation the determined alkalinity was 0.3 mol/m^3.

The treatment process was successfully tested. Values between 20 and 30 mol/m^3 in the discharge of the closed reactor system (HCO_3-reactor) were measured. It was demonstrated, that it is possible to produce an almost clear and particle free solution with an alkalinity of 30 mol/m^3. Alkalinities of 40 to 50 mol/m^3 are possible as well, but could not be achieved with the treatment plant at the test site due to limitations in the CO_2-supply.

After a treatment period of just 3 months alkalinities in the entire water body were determined to be around 0.7 mol/m^3 in phase 1 and 0.9 mol/m^3 in phase 2.

Key words: Mine water, treatment technology, pit lakes, carbon dioxide, CO_2, lime, CaO, calcite, $CaCO_3$, alkalinity

Introduction

Pit lakes in Germany are often characterized by low pH values and elevated concentrations of Fe, Al, Mn and NH_4-N as well as a lack of organic and inorganic carbon. Therefore, the main aim of pit lake treatment is the neutralisation of the water body and the associated mineral precipitation of Fe, Al and Mn. While neutralisation with lime is no technological challenge anymore, buffer capacities of most lakes will not exceed values between 0.3 mol/m³ and 0.4 mol/m³.

Due to acidic groundwater inflow pit lakes are often subject to short term (months) re-acidification. Hence, the increase of alkaline buffer capacity is needed after the initial neutralisation is achieved to help trigger biological processes. For the long term stabilisation of pH-values the alkalinity needs to be elevated to levels of around 1.0 mol/m³

In general several options to build up alkalinity are currently tested and available in pit lake treatment. The technologies can be divided into two approaches, based on the location where the main reactions take place. One approach is the use of the water body as the main reactor (open system). The second one is the use of a closed system, which is described in this paper.

In Germany and Sweden the application of alkaline solids for lake water treatment is mainly achieved by distribution of the reactants on the lake surface by small or medium sized boats or ships. Technologies that uses submerged jets were only tested in the last 5-10 years and show promising results, since the energy for mixing the reactants into the water body is more efficiently used, compared to the application of the reactants on the water surface. Since process efficiencies are higher and specific costs are lower, a submerged jet based units was chosen for the distribution of the process water discharge to the lake.

A variety of alkaline solids such as lime (CaO), hydrated lime ($Ca(OH)_2$) or limestone ($CaCO_3$) can be used to achieve neutral pH-values in acidic pit lakes. Due to the lack of inorganic carbon or kinetic constraints, the aforementioned materials are limited in the production of the aquatic species HCO_3^-..

This paper presents a closed treatment system that uses lime (phase 1) and limestone (phase 2) in combination with CO_2 with the aim to significantly increase the alkalinity of the lake chosen as a test site.

Methods

Study area

The pit lake Drehnaer See has a volume of about 13 Mio. m³. The bathymetry of the lake and the cross sections A-A' and B-B' are shown in figure 1. Coal mining at the site produced long trenches in the northern and southern part of the lake, which are accompanied by a shallow area in its centre.
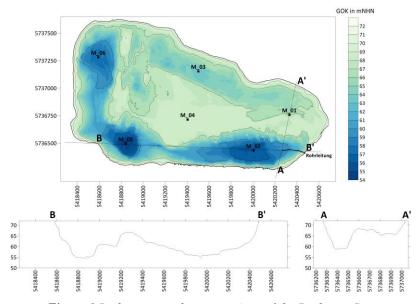

Figure 1 *Bathymetry and cross sections of the Drehnaer See.*

Lake water quality

The lake water quality before the treatment was typical for pit lakes in Germany. Measurements were conducted at six sampling points (M_01 to M_06 in figure 1) in varying water depths. The low pH-values (2.99 and 3.12) and high values of electrical conductivity (1660 µS/cm and 1670 µS/cm) derived from acid mine drainage. The corresponding lake water acidities were determined by titration and yielded values between 3.4 and 4.1 mol/m³. The acidity is mainly connected to iron (31.6 to 32.5 mg/L), aluminium (5.81 to 6.58 mg/L) and manganese (1.14 to 1.27 mg/L) as well as ammonia (1.5 to 1.6 mg/L). Low values for total organic (0.58 to 1.0 mg/L) and total inorganic carbon (0.2 to 1.1 mg/L) are characteristic for acidic pit lakes in Germany too.

Experimental design

The treatment test had several steps. First, the initial neutralisation was achieved by the application of a lime suspension. The pH-values of the lake water were increased from around 3.0 to 8.0 and higher. In a second step alkalinity was injected into the lake using the developed closed reactor system, which allows for intense chemical reactions between the solid phase ($CaO/(Ca(OH)_2$ or $CaCO_3$) and the gas phase CO_2 to produce the aquatic species HCO_3^-. After the successful increase of alkalinity re-acidification was monitored. In this period pH-levels decreased to values below 4, before test phase 2 was started. For the subsequent neutralisation limestone was used followed by test phase 2, were $CaCO_3$ and CO_2 were applied to increase alkalinity.

Closed reactor system

The applied treatment technology in a closed reactor system was developed in the GFI laboratory. The main aim of the research was to develop a technology that produces alkalinities above 20 mol/m³. The industrial scale reactor (figure 5 and 6) was designed based on successful tests with a batch reactor (figure 3) and in a small scale pilot plant (figure 4). In the small scale reactor alkalinities as HCO_3^- of up to 48 mol/m³ were repeatedly produced. Figure 2 shows the heterogeneous reactions and the components of the tested technology that were considered in the design.

The industrial scale reactor has several modules (figure 2 and 5). The modules can be operated semi-automatically on site or even from a smartphone. Module one (K1, K2a, K2b) is a standard lime slaking technology, module two is a carbon dioxide dissolution reactor (C2), module three is an alkalinity producing reactor (HCO_3-reactor), that was developed at the GFI Grundwasser-Consulting-Institut GmbH (GFI 2012). Comparable tests are described in Watten et. al (2007). The fourth module is a gas recovery reactor (GRR) and the fifth module is an injection system based on free, submerged buoyant jets (momentum discharge), that was applied to distribute the alkaline water in the entire water body from a single point close to the bank of the lake.

Sampling – lake water

The lake water was closely monitored fortnightly. At each of the six monitoring points vertical profiles for pH, specific conductance, temperature, O_2-concentration and turbidity were recorded. Further, water samples in 1, 8, 10, 13 and 15 m water depth were taken. The following parameters were determined: acidity/alkalinity, total Fe, dissolved Fe, Fe(II), Fe(III), Al, Mn, Ca, Mg, NH_4-N, NO_2-N, NO_3-N, SO_4, TOC, TIC.

Sampling – process water / closed reactor

During the process all relevant flow rates and mass fluxes were recorded. Water samples were tested for the same parameters as the lake water (see above). Sampling points were installed before and after the HCO_3^--producing rector (figure 6) as well as after the gas recovery reactor.
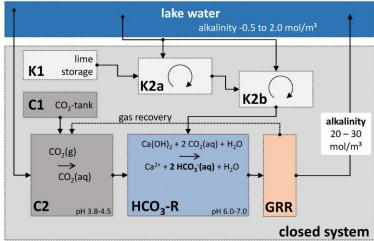
Figure 2 Closed reactor system and heterogeneous reactions.
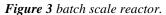

Figure 3 batch scale reactor.

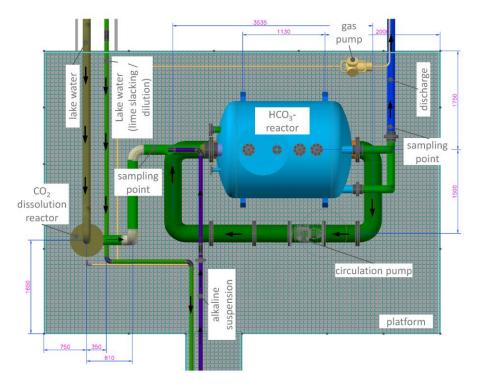*Figure 4* small scale reactor.

Figure 5 industrial scale reactor.

Figure 6 flow directions of the closed system and location of sampling points.

Results and discussion

The tested treatment process is influenced by multiple factors, e. g. the pH value in the HCO_3-reactor or the ratio of TIC flux to mass flux of the used alkaline solid (TIC/alk_{solid}). Further, the efficiency of the process is closely linked to the degree of calcite oversaturation and the CO_2-concentration of the water that enters the HCO_3-reactor. The experiments on the large scale reactor showed that the alkalinity produced by the process strongly depends on the energy input (mixing) and the reaction time. During a total of 52 tests alkalinities between 9.4 und 30.4 mol/m³ (see figure 7, phase 1, CaO / CO_2) respectively between 11.4 und 18.05 mol/m³ in 18 tests (see figure 8, phase 2, $CaCO_3$ / CO_2) were measured.
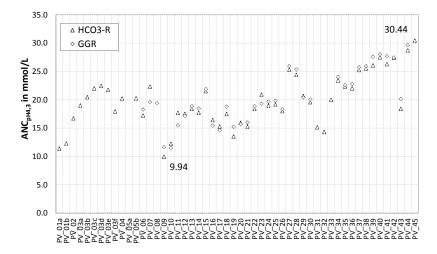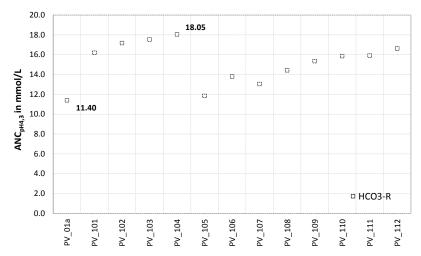

Figure 7 Measured ANC downstream of the HCO_3- reactor and the GRR in phase 1 (CaO / CO_2)

Figure 8 *Measured ANC downstream of the HCO₃- reactor in phase 2 (CaCO₃ / CO₂).*

reactor

The overall alkalinity production of the system was limited by the capacity of the CO_2-mass flux. With a maximum capacity of 340 kg/h and the flow rate of the system (108 m³/h) the CO_2-concentration could not exceed 71.5 mol/m³. As a result of the small scale reactor tests (see figure 4) a stoichiometric ratio TIC/alk$_{CaO}$ of > 1.8 needs to be specified to produce alkalinities around 50 mol/m³. Based on these findings the maximum achievable alkalinity is 39.7 mol/m³. All measured alkalinity values were below this level. Table 1 sums up the capacities of the installed technological units.

Table 1 *Capacities of the technological units.*

unit	unit is limited by	range	notes
system flow rate	pressure at desired flow rate	86-108 m³/h	max. CO_2-dissolution is determined by system pressure
CO_2-mass flux	water flux over CO_2-dissolution reactor	0-400 kg/h	limited by pressure of system
	evaporator unit	0-340 kg/h	max. CO_2-mass flux was limited by capacity of evaporator unit, design mass flux was not reached, installed capacity was not high enough
Energy input	circulation pump	0-550 m³/h	determines turbulence in HCO₃-reactor
HCO₃-reactor	pressure	1.0-4.5 bar	for safety < 5 bar
resulting HCO₃-producing capacity		*39.7 mol$_{Alk}$/m³*	*max. alkalinity at DIC/alk$_{CaO}$ ratio of (GFI 2012)*

mass concentration of suspension

The test results showed that with increasing mass concentration up to a value of 2.5 % (phase 1) and 8 % (phase 2) the HCO₃-concentration was increased too. Above the aforementioned values an alkalinity increase in the aquatic phase was not observed. These threshold values were caused by the CO_2 limitations of the installed unit (see table 1).

mixing energy

A set of tests were conducted to optimise the input of mixing energy into the HCO₃-reactor. During the these tests the parameters c_{CO2} (54.7 ± 1,5 mol/m³), c_{Alk_solid} (58,8 ± 0,2 mol/m³) and the mass

concentration of the suspension ($1{,}35 \pm 0{,}1$ Ma%) were fixed. The energy input was varied between 39.6 and 316.9 W/m³. The results of the tests PV_3a to PV_3f revealed, that increasing the energy input up to 250 W/m³ increase the alkalinity output. Higher inputs of mixing energy not necessarily increased the alkalinity of the discharge.

calcite saturation

All discharges were calcite oversaturated. The degree of oversaturation ranged between $0.05 < SI < 0.65$. With increasing saturation indices (SI) the observed alkalinities increased as well. The interesting fact is, that despite the oversaturation, calcite precipitation was hardly noticed in the system, when flushing intervals were implemented as part of the process control.
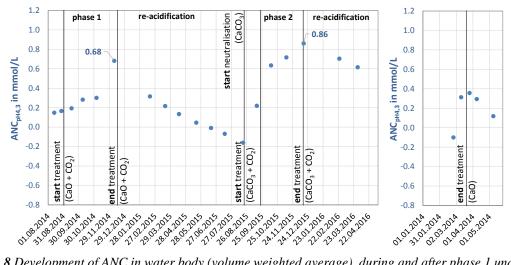
efficiency of the process

The process efficiency was defined by the ratio of filtered to unfiltered alkalinity in the process water downstream the HCO_3-reactor. Both were determined by titration. The unfiltered sample sums the alkalinity in the aquatic and in the solid phase. Determined efficiencies were between 5.3 and 50.5 %. Due to the fact that the closed system was limited to an alkalinity maximum of 39.7 mol/m³ by the CO_2 capacity, the process efficiency regarding the installed units are higher and ranged between 24.9 and 76.5 %.

The CO_2-limitation of the process proved an important point. The closed system can be operated with a stoichiometric ratio TIC/alk$_{solid}$ of around 1 without severe calcite precipitation in the HCO_3-reactor. The application of this ratio significantly reduces the process efficiency, but increases the alkalinity load drastically while the pH values in the discharge stayed in the neutral range. Further, the particle size of the used alkaline solids is reduced, which is an advantage for the ongoing reactions that take place in the lake.

pit lake water quality

The development of the lake water alkalinity (ANC - acid-neutralising capacity) is shown in figure 8. The pH values during the course of the tests are presented in figure 9. For comparison both figures show the values during and after phase 1 und 2 (CO_2 application) as well as the values after the neutralisation (no CO_2 used).

Figure 8 *Development of ANC in water body (volume weighted average), during and after phase 1 und 2 (left), after neutralisation (right).*

After phase 1 an ANC volume weighted average of 0.68 mol/m³ and after phase 2 of 0.86 mol/m³ was determined. Due to problems with the CO_2 unit, the treatment process in phase 1 only worked properly in the last third of the test period and limited the alkalinity.

The comparison of ANC and pH development after the tests with the period after the initial neutralisation of the lake shows that without the application of CO_2 and the related increase in alkalinity, pH values dropped below 6 in less than two months (figure 9, right). The alkalinity increase extended this period

by roughly 6 months in phase 1. Three months after the end of phase 2 the pH values were still around 7 (figure 9, left). The pH values are expected to stay on that level over a period of 6-8 months.
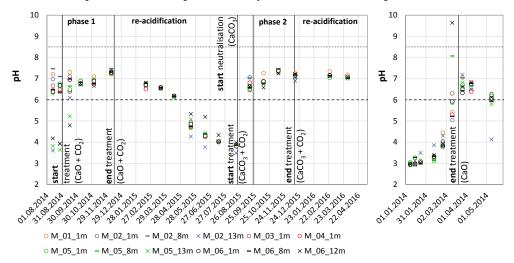

Figure 9 pH values at sampling points during and after phase 1 und 2 (left) and after neutralisation (right)

Conclusions

In the described tests it was shown that alkalinities of around 30 mol/m³ and 18 mol/m³ in the aquatic phase can be achieved using CaO or $CaCO_3$ in combination with CO_2 respectively. Higher alkalinities between 40 and 50 mol/m³ are possible using CaO and CO_2, but were not achieved in the tests due to limitations in the CO_2 supply unit. By application of $CaCO_3$ the alkalinity was limited around 20 mol/m³ due to smaller reactions rates of $CaCO_3$ compared to CaO.

The system can run in an oversaturated state for the mineral calcite, but needs to be automatically controlled, especially regarding the specified flushing cycles and pH values in the HCO_3-reactor. To run the process stable, with regard to the prevention of calcite precipitation and associated blocking of process units, pH values around 6.5 need to be maintained in the HCO_3-reactor.

If the process is used to treat a pit lake, the water body can and should function as a second reactor, where the additional reaction time can enhance the overall process efficiency. A direct application of CO_2 and alkaline solids is not favourable, since high CO_2 concentrations in the lake force a high degree of degassing and therefore the loss of a reactant. Due to the closed system approach the CO_2 loss to the atmosphere was minimised.

The process can be applied to other applications in which high alkaline water is needed. Depending on the application the gas recovery reactor can even function as a microflotation unit to reduce the amount of particles in the discharge to a minimum.

Acknowledgements

References

GFI (2012) Labor- und Technikumsversuche zur Entwicklung eines schiffsgestützten Reaktor- und Eintrags-systems zur bedarfsangepassten alkalischen Konditionierung von Tagebaufolgeseen, Z.169.001.012, project report

Watten BJ, Lee PC, Sibrell PL, Timmons MB (2007) Effect of temperature, hydraulic residence time and elevated pCO2 on acid neutralisation within a pulsed limestone bed reactor. Water Research, Vol. 41, 1207-1214