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ORIGINAL ARTICLE

Carbon dioxide treatment of low density sludge: a new remediation strategy for acidic mining lakes?

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Abstract Acid mine drainage (AMD) is treated at several points in the Lausitz lignite mine district (Saxony, Germany) in treatment plants. The remaining alkaline low density sludge (LDS) was deposited in acidic mining lakes without having an impact on the lake water quality. Batch experiments show that alkalinity can be raised using LDS from acid mine drainage treatment plants together with CO_2. Batch experiments were conducted using lake water and deposited LDS from the mining lake Spreetal-Nordost with varying concentrations of CO_2. Also the duration of gas contact as well as the LDS–water ratio was changed in the batch experiments. The gas contact time and the partial pressure of CO_2 are the relevant parameters controlling the alkalinity in the lake water at the end of the experiments. The Ca and Mg concentrations of the pore water are relevant for higher pH values. Therefore, dissolved CO_2 can form bicarbonate or carbonate complexes, thus alkalinity rises. A second factor for alkalinity gain is the calcite content of the sludge, because CO_2 triggers the dissolution of carbonates. Therefore, unused calcite in the sludge can raise the alkalinity more effectively by the application of carbon dioxide. Furthermore, it was shown that remobilization of trace elements will not affect the water quality.

Keywords Acidic mining lake · Low density sludge · Carbon dioxide · Lausitz · Alkalinity

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Introduction

In the Lausitz area (Saxony, Germany), many open lignite pits were operating from the 1950s to the 1980s, most of which were closed after the German reunification. Like in other mining areas, the oxidation of sulfide minerals (e.g. pyrite, marcasite) associated with lignite leads to acid mine drainage (AMD). Therefore, many lakes in this area are characterized by low pH values, high concentrations of sulfate and iron and a low acid neutralization capacity. Until now, investigations mainly focused on AMD neutralization, i.e. enhancement of active treatment plants (e.g. Watten et al. 2005; Kuyucak et al. 1999; Dey et al. 2007) or passive treatment systems (e.g. Cravotta 2003; Cravotta and Trahan 1999; Hedin et al. 1994; Watzlaf et al. 2000; Nairn and Mercer 2000; Hedin 2008; Ziemkiewicz et al. 2003). Different methods for neutralizing lake water have been investigated, such as chemical treatment by the addition of alkaline substances such as lime or fly ash (Cirmo et al. 2000; Gubala and Driscoll 1991; Loop et al. 2003; Castro and Moore 2000), stimulation of sulfate reduction (e.g. Koschorreck et al. 2002; Koschorreck and Tittel 2007; Brugam et al. 1995; Castro and Moore 2000) or controlled eutrophication (Fyson et al. 2006).

Another option available for mining lakes, receiving sludge from AMD treatment plants or with a treatment plant nearby, is investigated in this study. Sludge from AMD treatment plants (e.g. treatment plant Schwarze Pumpe) is deposited in some of the mining lakes in the Lausitz area. The AMD of still active open pits is treated in the plant "Schwarze Pumpe" by intensive aeration and addition of hydrated lime. The produced low density sludge (LDS) with a solid content of 0.5–1.5 mass%, is pumped into the nearby mining lake Spreetal-Nordost (Fig. 1).

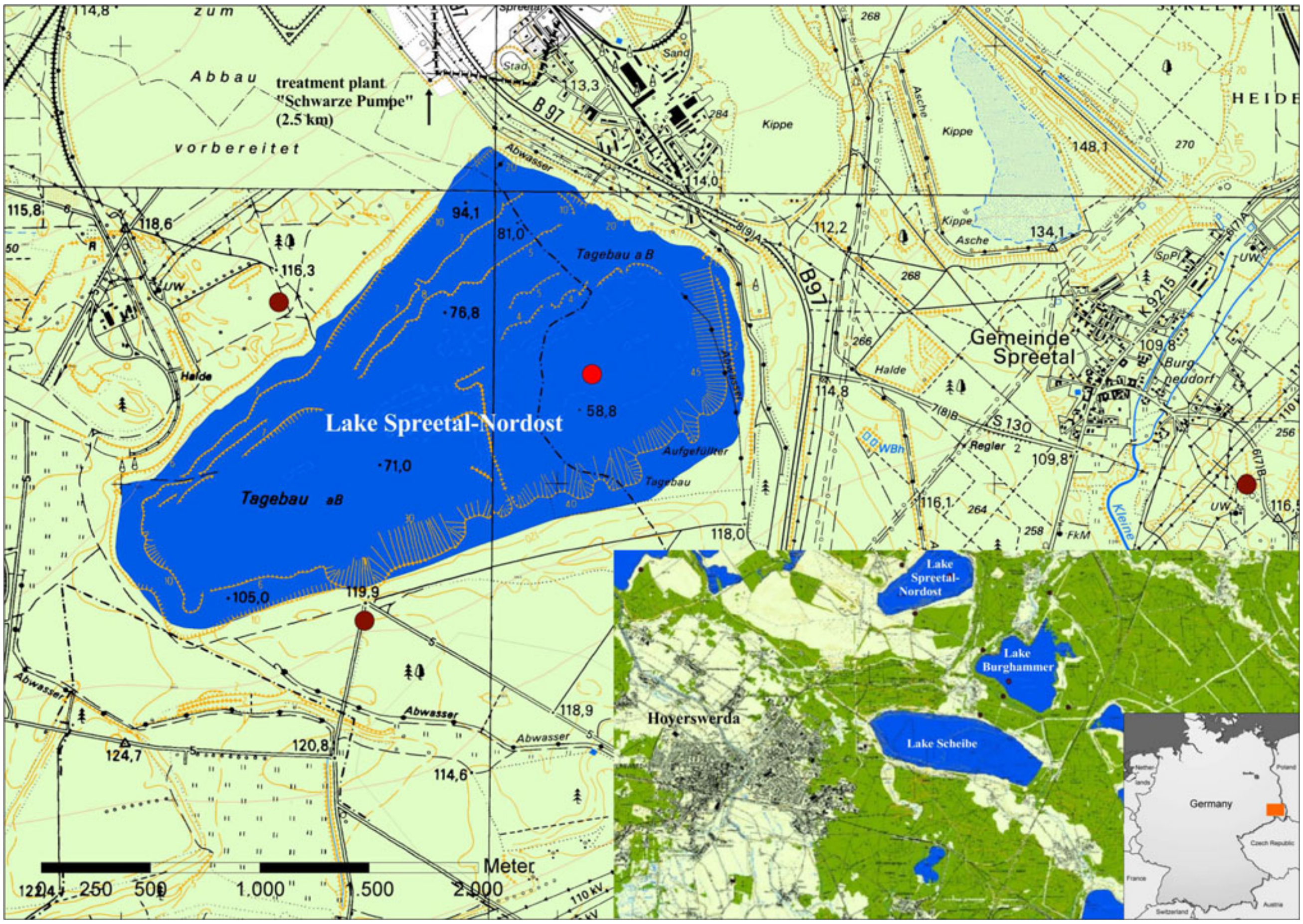

Fig. 1 Map of the investigation area (oriented to north; data provided by Saxon State Office for the Environment and Geology)

Spreetal-Nordost is located north-east to the city Hoyerswerda in the Lausitz. The open pit Spreetal was closed in 1991. Since 1997 the lake is flooded and currently flooding reached 87% (103.7 m NN) of the estimated end level of 108 m NN. Spreetal-Nordost will have a volume of 96.9 million m^3 with a mean water depth of 30.9 m after flooding (BTU Cottbus 2003). Hydrochemical data (Table 1) at the water surface and at the base show no evidence for a chemical stratification in Spreetal-Nordost. Since 1998 lake Spreetal-Nordost receives sludge from the AMD treatment plant "Schwarze Pumpe". This plant is located about 2,500 m to the north of lake Spreetal-Nordost.

This study investigates if alkaline cations in both the deposited sludge and the porewater can be used to improve the alkalinity in the lake water, when carbon dioxide is added (Eqs. 1, 2).

$$CO_2 + H_2O \leftrightarrow CO_3^{2-} + 2H^+ \tag{1}$$

$$(Ca, Fe)_2OH + CO_3^{2-} \leftrightarrow (Ca, Fe)CO_3 + OH^- \tag{2}$$

After Stumm and Morgan (1996) alkalinity is defined as follows:

Table 1 Comparison of main hydrochemical parameters in surface and in deep water from lake Spreetal-Nordost (unpublished data of the lake owner)

Parameter	Surface water	Deep water
Conductivity (μS/cm)	1,930	1,900
pH (–)	3.8	4.2
Ca (mg/L)	350	340
Mg (mg/L)	73	70
Na (mg/L)	19.2	21
K (mg/L)	9.1	8.1
SO_4 (mg/L)	1,165	1,100
Cl (mg/L)	24.2	27.0

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{3}$$

Thereby the concentration of bicarbonate and carbonate depends not only on total C concentration in the solution, but also on the pH value. The higher the pH value the more bicarbonate and carbonate complexes become the main species of C. The Ca concentration of the LDS is relevant for higher pH values. A second factor for alkalinity gain is the calcite content of the sludge, because CO_2 triggers the dissolution of carbonates. This CO_2-enhanced dissolution of carbonates is used and investigated in AMD remediation by limestone beds (e.g. Sibrell et al. 2006; Watten et al. 2004, 2007; Hedin et al. 1994).

The neutralization of AMD by addition of lime in treatment plants removes dissolved metals by the precipitation of metal hydroxides (SENES 1994). Therefore, it was investigated if these metal hydroxides together with CO_2 can be sequestrated within the LDS as carbonates. For mineral trapping Ca as well as Fe may react with CO_2 to form carbonates (Eqs. 1, 2). As expressed in Eq. 2, ferric iron has to be reduced to ferrous iron prior to the reaction with CO_2.

The reduction of ferric iron to ferrous iron was realized in the batch experiments by addition of zerovalent iron (RNIP–10AP) which was obtained from ALSTOM Power Environmental Consult GmbH (Stuttgart, Germany). The application of zerovalent iron (ZVI) in water produces pure hydrogen (Eq. 4; Liang et al. 2000), which may act as reducing agent for ferric iron (Eq. 5).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad (4)$$

$$2Fe(OH)_3 + 3H_2 \leftrightarrow 2Fe^{2+} + 6H_2O \qquad (5)$$

By nature LDS binds metal species present in the treated AMD (Zinck 2000). Thus, depending on the AMD chemistry, LDS contains different metal(oid)s (e.g. As, Zn, Cd, Pb, Co, Cr). The metal(oid)s are often precipitated as metal hydroxides or co-precipitated with iron hydroxides (SENES 1994). Application of CO_2 into the LDS and reduction of LDS will change sludge chemistry (e.g. dissolution of carbonates and iron hydroxides), therefore metal(oid)s may be remobilized. Metal(oid)s, which are present in higher concentrations in LDS and thus may relevant for remobilization, were identified by leaching tests. Therefore, water samples were taken before and after experiments and analyzed for the relevant metal(oid)s As, Zn, Co, Ni, Ba, Ce, and U.

Materials and methods

LDS characteristic

Low density sludge samples were collected from Lake Spreetal-Nordost by a gravity corer (Uwitec, Austria). The sampled cores were sliced into 5 cm pieces, transported in PE bottles into the laboratory and frozen in the same bottles. For mineralogical and chemical analyses frozen samples were freeze-dried. An aliquot of the freeze-dried samples was pulverized by a micronizing mill (McCrone, UK) to less than 10 µm. The samples were milled with corundum in an ethanol suspension. Mineralogical analyses were conducted by qualitative X-ray powder diffraction (Philips, Germany) with CoKα radiation. Quantitative analyses were not possible, because of the high content of amorphous ferric iron hydroxides.

Aqua regia leaching in a microwave (MLS, Germany) was conducted to identify metal(oid)s with increased concentration in the LDS. Aqua regia (1.2 mL of 65% HNO_3, 3.6 mL of 32% HCl and 0.5 mL deionized water) was added to an aliquot of the freeze-dried samples. After microwave digestion, samples were filtered through 0.2-µm cellulose acetate filters and filled up to 50 mL with deionized water. The leachates were analyzed for Li, Mg, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cs, Ba, La, Ce, W, Pb, and U by ICP-MS (VG Elemental Winsford, UK).

Batch experiments

The batch experiments were conducted in a Plexiglas column with a maximum volume of 1,260 mL (Fig. 2). The base and the cap of the column were removable and could be closed gastight by a rubber seal. All experiments were conducted in the dark to minimize reduction by microorganisms. Temperature, pH, Eh, and electrical conductivity were measured continuously by a laboratory measurement unit (LM 2000, Meinsberg, Germany). Oxygen was detected by an optical O_2 sensor probe obtained by Oceanoptics (Dunedin, FL, USA). All sensors were calibrated previous to each experiment. Water sampling and addition of ZVI was realized through a gastight septum integrated into the reactor wall. Hydrochemical analyses of the water samples (filtered through 0.2 µm cellulose acetate filters) were performed by liquid chromatography (Eppendorf-Biotronik Hamburg, Germany; for main anions), HPLC (Merck Hitachi, Tokyo, Japan; for main cations) and ICP-MS (VG Elemental Winsford, UK; for

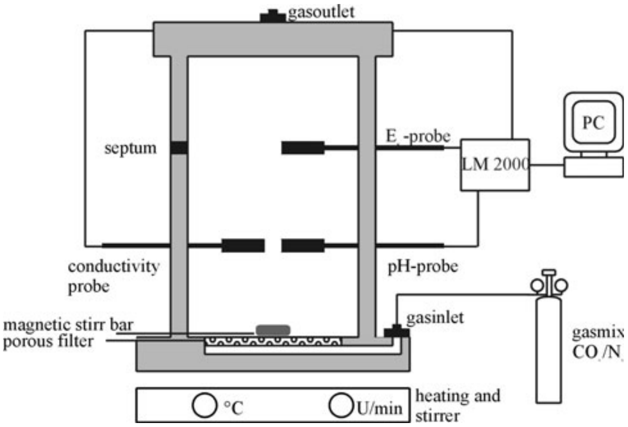

Fig. 2 Sketch of the batch reactor (Unger-Lindig and Merkel 2008)

Table 2 Parameters and modifications in the batch experiments

Parameter	Modification
Gas mixture CO_2 content	100, 50, 30, 10, 5% per volume
Solid amount	3 bis 11 g dry weight
LDS–water ratio	1:249 bis 1:482

trace elements). Alkalinity and acidity were measured by a processor controlled titrator (Metrohm AG, Germany). Total inorganic carbon (TIC) was determined by a TIC/TOC analysator (elementar Analysensysteme GmbH, Germany) also for the solid samples from the experiments.

Preliminary tests were conducted to determine optimal conditions for LDS reduction with ZVI. In these tests distilled water was used instead of lake water and no CO_2 gas exposure was realized. Preliminary tests were divided into the following three phases:

Phase 1 addition of 3 g LDS into 1 L distilled water; experiments with pH <3, were acidified with nitric acid.
Phase 2 addition of ZVI (4–65 mg);
Phase 3 reduction phase.

LDS was suspended in distilled water with a stirrer. ZVI was added after electrical conductivity reached constancy. At the end of the tests water samples (filtered through 0.2 μm cellulose acetate filters) were analyzed for ferrous and total iron by photometry (Hach Lange Duesseldorf, Germany). Ferrous and total iron analyses were performed by 1,10-phenanthrolin method after Eaton (1995). Fe concentration at the end was analyzed twice.

In this study, 48 experiments (29 experiments with reduction, 19 without reduction) were carried out. LDS and acidic lake water from the epilimnion of lake Spreetal-Nordost were used for the experiments. The LDS–water ratio averaged 1:360 according to the ratio in the mining lake Spreetal-Nordost (Table 2). Dry weight of the LDS varied between 3 and 11 g. The applied gas mixtures consisted of carbon dioxide (5, 10, 30, 50 and 100 Vol.%) and nitrogen. The gas mixture was added through a porous filter (pore size 10–30 μm) integrated into the bottom of the batch reactor with a mean flow rate of 30 mL/min. Most of the experiments were conducted both without and with reduction of the LDS. Ferric iron present in the sludge was reduced to ferrous iron by nanoscale ZVI, which was added in suspension via a syringe into the septum. The maximum gas exposure time in the experiments was 90 min.

Hydrogeochemical modeling was performed for all experiments with the program code PhreeqC (Parkhurst and Appelo 1999) using the Wateq4F-database. Thermodynamic data for ZVI are not available in this database, thus the data from Hummel et al. (2002) were used.

Results

LDS composition

The sludge from the plant "Schwarze Pumpe" mainly consists of amorphous ferric iron hydroxides. In addition to this, calcite and quartz could be detected by X-ray powder diffraction (XRD). Ferric iron hydroxides could not be identified exactly by XRD, because of the amorphous structure. However, based on the conditions (pH about 8) in the AMD treatment plant, ferric iron hydroxide is ferrihydrite. Bigham et al. (1996) showed that precipitates formed at pH 6.5 or higher are composed of ferrihydrite. Ferric iron ($\approx$31 mass%) and calcium ($\approx$5 mass%) represent the main cations in the sludge (Table 3).

Preliminary tests

Several tests were performed using various amounts of nanoscale ZVI. Initial pH values varied between 3 and 9. These preliminary tests showed that LDS reduction is pH dependent (Table 4). Initial acid conditions result in a more effective LDS reduction. Similar observations were reported by Chang (2005) for chromium reduction by ZVI.

In these tests, pH variations were also observed during the reactions. According to Eq. 4, reduction by ZVI will increase the pH value. Results of the preliminary tests show such an increasing of the pH value (Table 4). This increase depends on the initial pH value. For initial acid conditions, pH value increased from 3 to 6 in one experiment and from 4.2 to 7 in another one. However, for initial alkaline conditions the pH value increased only slightly (e.g. from 8.7 to 9). Therefore, LDS reduction by nanoscale ZVI seems to be more effective for lower initial pH values.

Alkalinity improvement

The hydrochemical composition found in the lake water from Spreetal-Nordost is given in Table 5. As a first step, LDS was added to the lake water, resulting in increasing pH values (6–8) in the suspension.

The alkalinity as well as the TIC increased in all experiments by addition of CO_2 and LDS to the lake water (Table 5). The alkalinity was increased up to 7 mmol/L using pure CO_2 and a gas exposure time t of 60 min. Resulting from the fewer number of experiments, it seems that the treatment with a 30 Vol.% CO_2 gas mixture reaches a more constant alkalinity, compared to pure CO_2. More experiments could not be conducted, due to problems with supply of gas mixture with 30 Vol.% CO_2. The gas exposure time in the experiments with 30 Vol.% CO_2 are also more constant than in the other experiments. Furthermore, the heavily fluctuant values in Table 5 are

Table 3 Cation concentration in the LDS (determined by aqua regia digestion, number of analyzes: 30)

Element	Min	Max	Mean	Median	Unpolluted soils	Reference
Ca (mg/g)	7.19	114.6	51.95	53.43	1–12 (noncarbonatic soils)	Scheffer and Schachtschabel (2002)
Fe (mg/g)	225.7	367.9	308.4	308.6	2–50	Scheffer and Schachtschabel (2002)
K (mg/g)	0.37	2.28	1.06	1.08	2–33	Scheffer and Schachtschabel (2002)
Mg (mg/g)	2.56	7.36	4.82	4.76	0.5–5	Scheffer and Schachtschabel (2002)
Mn (mg/g)	0.46	6.39	4.28	4.53	0.04–1 (9)	Scheffer and Schachtschabel (2002); Kabata-Pendias and Mukherjee (2007)
As (μg/g)	54.07	141.7	73.54	70.89	0.1–30	Kabata-Pendias and Mukherjee (2007)
Ba (μg/g)	53.60	159.5	92.13	94.60	84–960	Kabata-Pendias and Mukherjee (2007)
Ce (μg/g)	7.16	80.24	34.20	34.54	15–100	Kabata-Pendias and Mukherjee (2007)
Co (μg/g)	94.37	484.6	286.8	270.7	4.5–12	Kabata-Pendias and Mukherjee (2007)
Cr (μg/g)	3.37	21.89	11.41	11.18	2–350	Kabata-Pendias and Mukherjee (2007)
Cs (μg/g)	0.18	1.37	0.57	0.46	0.8–30	Kabata-Pendias and Mukherjee (2007)
Cu (μg/g)	5.53	17.26	8.89	8.50	8–80	Kabata-Pendias and Mukherjee (2007)
La (μg/g)	5.68	42.14	19.72	19.28	8–35	Kabata-Pendias and Mukherjee (2007)
Li (μg/g)	2.76	14.48	6.09	5.04	5–175	Kabata-Pendias and Mukherjee (2007)
Mo (μg/g)	0.40	1.28	0.58	0.55	0.1–7	Kabata-Pendias and Mukherjee (2007)
Ni (μg/g)	198.1	564.4	357.1	338.1	0.2–450	Kabata-Pendias and Mukherjee (2007)
P (μg/g)	178.5	873.9	339.8	315.1	<100–800	Scheffer and Schachtschabel (2002)
Pb (μg/g)	2.91	9.39	4.85	4.24	15–28 (80)	Kabata-Pendias and Mukherjee (2007); Scheffer and Schachtschabel (2002)
U (μg/g)	1.87	2.94	2.30	2.30	0.8–11	Kabata-Pendias and Mukherjee (2007)
W (μg/g)	0.04	0.38	0.12	0.11		
Zn (μg/g)	521.2	9,892	1,190	845.4	10–300	Kabata-Pendias and Mukherjee (2007)

Table 4 Concentration of iron in samples from preliminary tests, conducted with specified initial pH values and addition of nanoscale iron particles

Initial pH	Final pH	Quantity of Fe^0 (mg/L)	$Fe^{2+}_{initial}$ (mg/L)	Total $Fe_{initial}$ (mg/L)	Fe^{2+}_{end} (mg/L)	Total Fe_{end} (mg/L)
8.7	9.0	7.8	<0.02	<0.02	0.05 ± 0.0	2.45 ± 0.035
8.8	8.9	4.8	<0.02	0.06	0.02 ± 0.001	0.46 ± 0.007
8.8	8.8	16.8	<0.02	<0.02	0.07 ± 0.0	0.84 ± 0.0
8.8	9.7	64.8	<0.02	<0.02	0.18 ± 0.007	2.63 ± 0.530
3.0	4.6	4.8	1.13	9.00	31.9 ± 0.0	100 ± 0.0
3.0	6.4	9.6	1.13	9.00	29.8 ± 2.70	92.0 ± 2.00
4.2	6.7	4.8	0.03	0.17	17.0 ± 0.0	27.0 ± 0.0
4.2	7.0	9.6	0.03	0.17	12.1 ± 1.62	14.3 ± 1.25
4.6	6.0	4.8	0.09	2.70	4.60 ± 0.0	11.1 ± 0.0
4.6	7.7	9.6	0.09	2.70	19.4 ± 1.45	39.5 ± 14.50

c_{end} (double analyses; mean values ± standard deviation)

caused by the difference in the gas exposure time. Experimental results indicate that the gas exposure time is a main parameter for alkalinity improvement. Another important parameter is the concentration of CO_2 in the gas mixture as can be seen in Fig. 3. Alkalinity and gas exposure time show a logarithmic correlation for a defined CO_2 concentration in the gas mixture in the form $y = a \ln x + b$ (Table 6). Since only three experiments were conducted with a concentration of 30 Vol.% CO_2, a logarithmic correlation could not be determined. Because of the behavior of the variables a and b in the correlation it was tested if these variables depend on pCO_2. It was determined that a and b correlate linear with pCO_2, thus a and b can be substituted as follows: $a = 0.019pCO_2 + 0.21 (R^2 = 0.97)$;

Table 5 Hydrochemical data of untreated and treated lake water analyzed after batch experiments

	Untreated	CO_2 concentration in the gas (Vol-%)				
	Lake water	5	10	30	50	100
Number of experiments		16	11	3	8	9
Gas exposure time (s)		17–5,400	32–3,660	6,180–10,080	15–3,600	12–3,600
pH (–)	4.2	6.0–7.5 (6.9)	6.1–6.8 (6.4)	6.6 (6.6)	5.0–5.9 (5.5)	5.5–6.0 (5.9)
Conductivity (mS/cm)	1.5	1.2–1.7 (1.5)	1.0–2.0 (1.7)	1.9–2.3 (2.0)	1.6–1.8 (1.7)	1.6–2.2 (1.8)
E_H (mV)	230	230–240 (230)	230–240 (230)	−150–90 (−40)	130–250 (190)	220–230 (230)
Ca^{2+}	340	216–372 (267.9)	159–405 (286.3)	396–500 (440.6)	293–306 (300)	208–458 (269)
Mg^{2+}	70	47.5–86.8 (66.5)	37.0–63.0 (53.7)	74.9–102 (91.0)	61.3–67.1 (64.3)	65.1–72.8 (64.4)
Na^{+}	21	17.0–28.8 (20.3)	15.7–22.5 (19.0)	24.2–29.6 (26.5)	17.8–19.6 (18.7)	17.4–33.3 (23.1)
K^{+}	8	7.8–17.2 (11.9)	8.3–12.2 (9.6)	13.9–20.7 (17.6)	10.8–14.6 (12.8)	4.4–13.6 (10.7)
Fe^{2+}	0.2	<0.02–18.0 (3.2)	<0.02–17.5 (3.6)	0.15–42.9 (24.6)	<0.02–17 (8.8)	<0.02–25.5 (6.5)
Fe^{3+}	1.4	<0.02–7.9 (1.6)	<0.02–8.7 (2.4)	2.4–21.6 (11.4)	0.97–57.5 (30.1)	<0.02–6.5 (1.1)
SO_4^{2-}	1,100	716–1,220 (860)	517–1,240 (873)	1,100–1,450 (1,225)	1,020–1,030 (1,025)	790–1,500 (876)
Cl^{-}	27	18.2–39.2 (27.7)	20.1–25.4 (23.6)	31.3–44.2 (39.2)	28.5–30.8 (29.7)	28.4–36.3 (33.7)
TIC	0.3	2.3–32.3 (11.9)	5.8–72.9 (29.2)	101.5–108.6 (104.5)	17.6–151.1 (86.4)	34.1–294.7 (87.5)
Alkalinity (mmol/L)	−0.49	0.07–1.36 (0.82)	0.48–3.64 (1.58)	7.14–7.39 (7.27)	0.38–3.48 (2.0)	1.13–7.17 (2.90)

Results given in mg/L unless otherwise noted. Brackets: mean values

$b = 0.011p\mathrm{CO}_2 + 0.17 (R^2 = 0.95)$. Based on these data, alkalinity (alk) in mmol/L is determined by the following empirical equation:

$$\mathrm{alk} = 0.019p\mathrm{CO}_2 \ln(t) + 0.21 \ln(t) + 0.011p\mathrm{CO}_2 + 0.17 \qquad (6)$$

with alk—alkalinity in mmol/L, $p\mathrm{CO}_2$—CO_2 concentration in the gas mixture in Vol.%, and t—gas exposure time in minutes.

This equation applies to a gas exposure time below 90 min, without reduction of iron hydroxide. The initial LDS dry weight in the experiments was also varied, but it seems that these changes have no influence on alkalinity (Fig. 4). Based on this, that more reactive material is available when more LDS is used, it would be expected that alkalinity depends on the LDS dry weight. However, as can be seen in Fig. 5, carbonates are not consumed completely, even when smaller amounts of LDS are used. Therefore, the relative small changes in initial LDS dry weight do not influence the alkalinity within this experimental setup.

In 29 experiments ferric iron was reduced to ferrous iron prior gas exposure. This reduction leads to a further improvement of the alkalinity in the lake water. Along with that, pH values were higher in the solution with reduction at the end of the batch experiment. The alkalinity in experiments with reduction of LDS is about two times higher than in experiments without reduction (Fig. 6; Table 7).

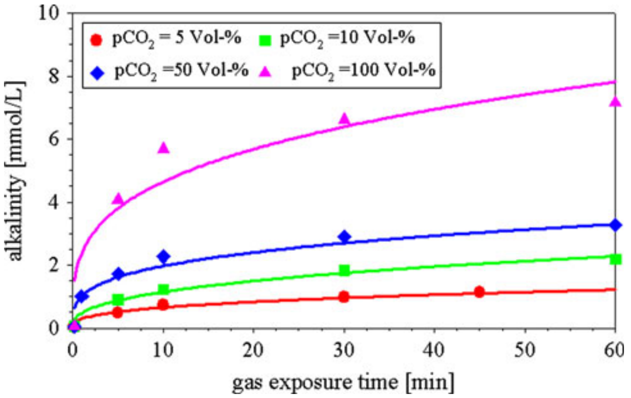

Fig. 3 Alkalinity depending on gassing time and CO_2 partial pressure in batch experiments without iron reduction

CO_2 storage

To minimize anthropogenic emissions of the greenhouse gas CO_2, a variety of capture and storage concepts are under investigation. Mineral carbonation is a more sustainable way to sequestrate CO_2 than injection into the underground (e.g. Holloway 2005; Bachu and Adams 2003; Stevens et al. 1999) or into the ocean (e.g. Marchetti 1977; Herzog et al. 1991).

Therefore, a second aspect of this study was the mineral storage of carbon dioxide as siderite. CO_2 together with two valent metal cations contained in LDS may form carbonates. Since carbonates are formed during CO_2 treatment, carbon concentration in the LDS will increase. However, a comparison of the total carbon (TC) concentrations in the LDS before and after CO_2 exposure shows a decrease in TC in almost all experiments (Fig. 5). It is assumed that decrease in TC is caused by dissolution of calcite as a consequence of increasing $p\mathrm{CO}_2$.

Table 6 Correlation between alkalinity (alk) and gas exposure time (t) for a defined CO_2 concentration in the gas mixture (pCO_2)

pCO_2 (Vol.-%)	Logarithmic correlation	Coefficient of determination R^2
5	Alk = 1.2815*ln(t) + 2.2075	0.987
10	Alk = 0.5617*ln(t) + 0.9522	0.997
50	Alk = 0.3684*ln(t) + 0.5187	0.957
100	Alk = 0.2087*ln(t) + 0.3031	0.955

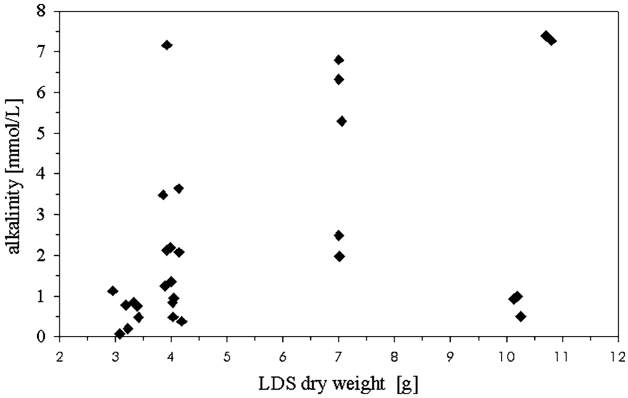

Fig. 4 Influence of LDS dry weight variations on alkalinity

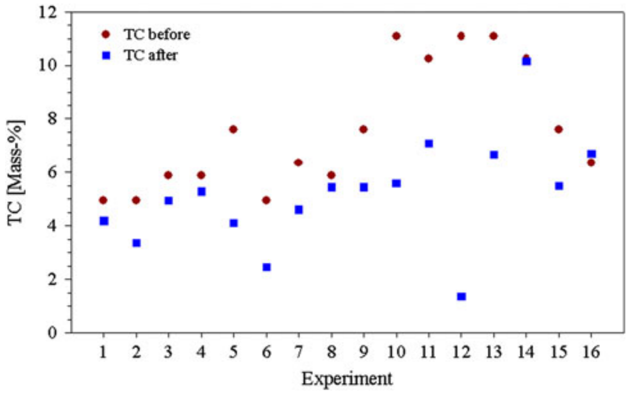

Fig. 5 Total carbon concentration before and after batch experiments (dry weight: experiments 1–7: 3 g LDS; experiments 8–12: 7 g LDS; experiments 13–16: 11 g LDS)

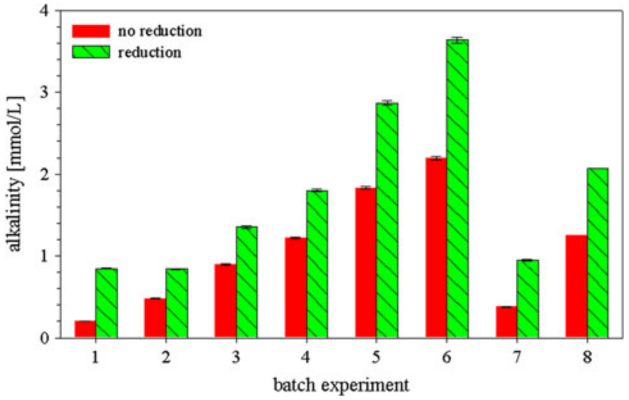

Fig. 6 Comparison of batch experiments with and without reduction of ferric iron (apart from that, same experimental conditions were applied)

Remobilization

Aqua regia leaching of the LDS showed that the LDS contains increased concentrations of the trace elements Zn, As, Co, and Ni. Therefore, these elements were analyzed before (c_0) and after the batch experiments (c_{end}) to preclude that these elements will be remobilized by treatment with CO_2. The trace elements Li, P, Cr, Mn, Cu, Mo, Cs, Ba, La, Ce, W, Pb, and U, which are also analyzed in the aqua regia leachate, showed concentrations like unpolluted soils (Table 3). Although, Ba, Ce, and U are contained in concentrations comparable with unpolluted soil, the laboratory conducting ICP-MS measurements analyzed these elements as well. Therefore, Ba, Ce, and U were also taken into account for investigation of remobilization. The key parameter for remobilization of trace elements is the pH value in the water after the batch experiments. For the elements Zn, Co, Ni, and Ba a critical value for the pH (pH_{crit}) was observed. This applies to experiments with as well as without reduction of LDS. Below this pH_{crit}, remobilization of the mentioned elements can occur (Fig. 7, Table 8). Cerium decreases in all experiments and thus shows no remobilization potential. The correlation coefficient R^2 for As and U is 0.29 and 0.1, respectively. Therefore, the determination of a significant pH_{crit} is not possible.

The most problematic trace element is Ni if the concentration is compared to drinking water limits (20 µg/L; TVO 2001). However, the lake water will not be used for drinking water purposes and the analyzed concentrations are below the mean nickel concentration (220 µg/L, unpublished data of the lake owner) in Lake Spreetal-Nordost. Furthermore, the maximum Ni concentration of 197.5 µg/L is below the Action threshold value suggested by the German Working Group on water issues (LAWA 1994; Table 9). A pH value of the solution above pH_{crit} should almost preclude the remobilization of Ni.

As can be seen in Table 8, the concentration of most trace elements decreased after the batch experiments, if LDS was reduced in the experiments. Only As and Ba increased slightly in most of these experiments. The maximum c_{end} was 0.0015 and 0.05 mg/L, respectively. The As concentrations are below the limits of 0.01 mg/L restricted in TVO (2001), for Ba exist no limit. US EPA (2008) mentions a maximum contaminant level of 2 mg/L for Ba, thus the increasing of As and Ba does not present a significant deterioration of the water quality. Co and U also

Table 7 Comparison of alkalinity for experiments with and without reduction

Experiment	Reduction	pCO_2 (Vol.%)	Gas exposure time (min)	LDS dry weight (g)	Alkalinity (mmol/L)	pH (−)	Factor
1a	No	5	0.3	3.2	0.206	6.0	
1b	Yes	5	0.6	3.3	0.846	7.5	4.11
2a	No	10	0.7	3.4	0.480	6.4	
2b	Yes	10	0.6	4.0	0.840	6.6	1.75
3a	No	10	5	4.0	0.897	6.0	
3b	Yes	10	5	4.1	1.354	6.2	1.51
4a	No	10	10	4.0	1.217	5.9	
4b	Yes	10	10	4.1	1.800	6.1	1.48
5a	No	10	30	4.0	1.833	6.0	
5b	Yes	10	30	4.1	2.869	6.2	1.57
6a	No	10	60	4.0	2.197	6.1	
6b	Yes	10	61	4.1	3.636	6.3	1.66
7a	No	50	0.3	4.2	0.380	5.0	
7b	Yes	50	0.5	4.0	0.950	5.9	2.50
8a	No	100	0.4	3.9	1.250	5.7	
8b	Yes	100	0.5	4.1	2.073	6.0	1.66

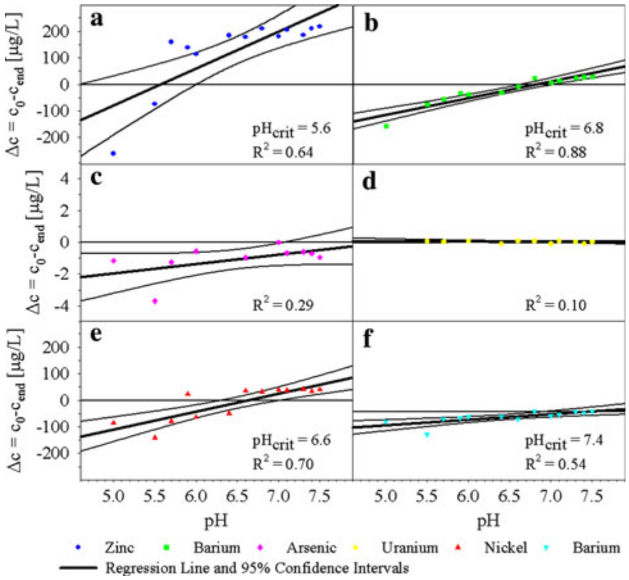

Fig. 7 Remobilization of trace elements depending on pH-value

increase in some experiments with LDS reduction with maximum c_{end} of 72.3 and 0.21 µg/L, respectively. For both elements the German Drinking Water Ordinance (TVO 2001) gives no limit. US EPA (2008) defines 30 µg/L as maximum contaminant level of U. Therefore, U seems to be no risk for water quality in the lake water.

Hydrogeochemical modeling

For modeling with PhreeqC, water analyses before and after the experiments as well as LDS composition were used. For modeling results comply with experimental results, CO_2 and calcite dissolution were varied. Results show that modeled CO_2 partial pressure is only 23.7% in average of the experimental partial pressure (Table 10). CO_2 dissolution rate dCO_2 resulting from gas exposure is calculated by hydrogeochemical modeling (Table 10).

Discussion

Improvement of alkalinity

The described results show that it is possible to improve alkalinity in acidic mining lakes by CO_2 treatment of deposited LDS. The relevant parameters that determine the alkalinity improvement are gas exposure time and CO_2 concentration in the gas. Variation of the LDS–water ratio shows no significant influence on alkalinity. The advantage of this treatment method is that material is used, which has no further utilization and is available for free. Carbon dioxide can be used either directly or after separation from combustion gases. AMD treatment produces large amounts of LDS in many mining areas. The most economical storage solution for LDS is disposal in pit lakes (Zinck 2006). Thus, LDS together with CO_2 might be an option for improving water quality in such mining lakes.

On the one hand, the rising of alkalinity as well as the concentration of TIC in the lake water is caused by dissolution of carbon dioxide in lake water and pore water and reaction with alkaline cations in the sludge (especially Ca and Fe), producing bicarbonate complexes, natural buffers.

Table 8 Concentrations of trace elements before and after the batch experiments in the lake water

Element	pH$_{crit}$	c_0 (µg/L)	c_{end} (µg/L) with reduction	c_{end} (µg/L) without reduction	Mean lake concentration (µg/L) (unpublished data of the lake owner)
Zinc	5.6	226.7	**9.3–87.7 (38.8)**	**16.7**–487.7 **(171.2)**	**260**
Arsenic	n.a.	0.5	**<0.25**–1.5 (1.1)	**<0.25**–4.2 (2.0)	**3**
Cobalt	6.8	40.2	**11.2**–72.3 **(32.0)**	**12.7**–197.2 (94.9)	n.a.
Nickel	6.6	56.4	**14.7–33.1 (20.6)**	**21.4**–197.5 (120.0)	**220**
Barium	7.4	19.8	**18.0**–52.3 (32.0)	25.4–119.4 (56.6)	n.a.
Cerium	–	1.96	**0.01–0.56 (0.24)**	**0.01–1.75 (0.57)**	n.a.
Uranium	n.a.	0.10	**0.03**–0.21 **(0.09)**	**0.04**–0.23 (0.13)	n.a.

Brackets: mean value (number of experiments: 13); bold: decreasing of concentration

Table 9 Inspection and action threshold values given by LAWA (1994) for analyzed trace elements, drinking water limits given by TVO (2001) and by US Environmental Protection Agency (US EPA 2008) in brackets

Element	Maximum c_{end} (µg/L)	Inspection value (µg/L)	Action threshold value (µg/L)	Drinking water limits (mg/L)
Zink	487.7	100–300	500–2,000	– (5)
Arsenic	4.2	2–10	20–60	0.01 (0.01)
Nickel	197.5	15–50	100–200	0.02 (–)
Barium	119.4	100–200	400–600	– (2)
Uranium	0.23	–	–	– (0.03)

Table 10 Experimental and modeled pCO_2

Experiment	pCO_2 (Vol.-%)	Modeled pCO_2 (Vol.-%)	Mod. pCO_2/pCO_2	dCO_2 (mmol/L)	SI$_{Siderite}$
1a	5	0.37	7.4	0.00	No reduction
1b	5	0.08	1.6	0.18	−0.61
2a	10	0.72	7.2	0.22	No reduction
2b	10	0.63	6.3	0.68	−0.16
6a	10	7.76	77.6	3.43	No reduction
6b	10	8.71	87.1	8.71	−11.62
7a	50	7.24	14.5	2.32	No reduction
7b	50	1.58	3.2	1.68	−0.92
8a	100	6.46	6.5	2.30	No reduction
8b	100	8.91	8.9	3.93	−0.37
9	5	1.38	27.6	0.44	−0.41
10	10	0.32	3.2	0.48	−1.57
11	5	0.16	3.2	0.45	0.18
12	5	0.14	2.8	0.26	−0.08
13	5	0.10	2.0	0.28	No reduction
14	100	10.0	10.0	3.45	No reduction
15	30	20.0	66.7	6.74	1.16
16	30	19.1	63.7	7.26	1.16
17	30	19.1	63.7	6.43	−1.11
18	100	10	10.0	3.60	−0.12

Figure 8 shows the correlation of modeled dCO_2 with analyzed TIC concentration after experiments (with and without LDS reduction). Based on the close correlation, CO_2 dissolution is responsible for 87% of the TIC concentration in the lake water after gas exposure. On the other hand, TIC increase originates from the dissolution of carbonates contained in the LDS. Adding CO_2 as gas leads to an increase of the partial pressure of CO_2 (pCO_2). A higher pCO_2 enhances the dissolution of calcites from the solid phase, i.e. LDS, and results in an improved alkalinity in the

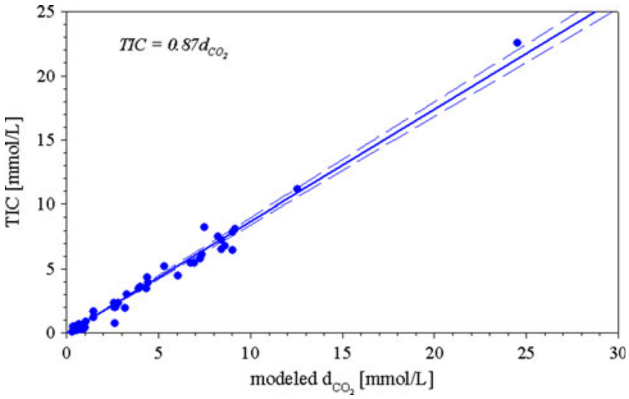

Fig. 8 Dissolved CO_2 fraction dCO_2 of the TIC concentration at the end of experiments

liquid phase, i.e. lake water (e.g. Sibrell et al. 2006; Watten et al. 2004, 2005, 2007; Hedin et al. 1994).

As described above, reduction of LDS by nanoscale ZVI leads to higher alkalinity and concentration of TIC in the treated lake water. One reason is that ferrous Fe, in addition to Ca and Mg, is made available to form bicarbonate complexes with CO_2. Therefore, more carbon dioxide can be dissolved and react in the water. On the other hand, preliminary tests showed that the addition of nanoscale iron particles raises the pH value, especially for lower initial pH values (Table 4), thus dissolved CO_2 exists mainly in form of bicarbonate and carbonate complexes.

Apart from the alkalinity improvement, the reduction has to be regarded. Nanoscale ZVI was used as chemical reducing agent in the laboratory, because of the easier handling. In the field scale, biological reduction with addition of organic material will be more cost effective. Fauville et al. (2004) tested pyruvate, glucose, succinic acid, lactate, ethanol, acetate, and various industrial by-products and Castro et al. (1999) used organic waste products (waste from a potato-processing plant and composted steer manure) to create anoxic conditions in bottle experiments and microcosm studies, respectively. Koschorreck et al. (2007) added Carbokalk and straw to enhance sulphate reduction by microorganisms and to neutralize acid mining lakes in field mesocosms.

Formation of siderite and CO_2 capturing

The concentration of TC in the sludge could not be increased in the batch experiments. Thus, probably only little or no siderite precipitates in the experiments; at least it does not exceed the dissolution of calcite. But in some of these experiments, hydrogeochemical modeling shows a supersaturation of siderite for equilibrium conditions (Table 10). Therefore, the kinetics of siderite precipitation has to be examined in further investigations. Since concentration of TC decreased in most experiments, carbon dioxide can be captured only as metal–bicarbonate complexes. These complexes mainly improve water quality in the acidic mining lakes, but CO_2 sequestration is less effective, compared to capturing as siderite (mineral carbonation). The mineral carbonation concept involves converting CO_2 to solid inorganic carbonates using chemical reactions (IPCC 2005). For the mineral carbonation process many different alkaline materials may be used. Teir et al. (2007, 2009), Haenchen et al. (2008), and Park et al. (2003) propose the precipitation of magnesium carbonates using Mg-bearing silicate rocks such as olivine or serpentinite. Uibu et al. (2009) investigated ash formed during oil-shale combustion, which contains free Ca and Mg oxides and could show that free CaO is the main CO_2-binding component in ash, but other components such as MgO and Ca-silicates may also participate in the carbonation process. Montes-Hernandez et al. (2009) propose the use of ash from coal combustion for mineral carbonation process. Stolaroff et al. (2005), Eloneva et al. (2008), and Huijgen et al. (2005) used $Ca(OH)_2$ and CaO from steel slag and concrete waste to react with CO_2 and to form stable carbonate minerals. Numerous computer simulations as well as experimental studies investigate glauconitic or iron-rich sandstones and dunites for their potential to sequestrate CO_2 in siderite and other carbonates (Palandri and Kharaka 2005; Palandri et al. 2005; Xu et al. 2004, 2005; Zerai et al. 2006; Andreani et al. 2009). Rau (2004) proposed the use of Fe/CO_2 fuel cells to sequestrate CO_2 and to produce hydrogen gas and/or electricity within in this reaction.

Remobilization of trace elements

Even though trace element concentrations in the lake water increase in some experiments, the maximum analyzed concentrations are below the action threshold values published by the LAWA (1994) as it is shown in Table 9. Thus, from that point of view, CO_2 gas exposure of LDS will not lead to a degradation of the lake water quality. On the contrary, water quality will be improved by the formation of a bicarbonate buffer. In experiments without reduction, remobilization of trace elements is more possible. In the laboratory experiments, this is caused by lower pH values at the end of the batch tests. As described above, in experiments with LDS reduction, the pH value increases by addition of ZVI.

As shown in Table 8 trace elements could be decreased in some experiments, especially in experiments with LDS reduction. Different mechanism for decreasing might be possible. Trace elements might be co-precipitated with newly formed minerals or are adsorbed by either LDS or ZVI particles in experiments with LDS reduction.

Based on the results from batch experiments, CO_2 treatment of reduced LDS seems to be a possible strategy to improve water quality (especially alkalinity) in acidic mining lakes. For pH values above pH_{crit}, remobilization of trace elements can be minimized. CO_2 can be captured in small quantities at least for a certain time as metal–bicarbonate complexes dissolved in water.

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