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TECHNICAL COMMUNICATION

In-lake Neutralization of East German Lignite Pit Lakes: Technical History and New Approaches from LMBV

Friedrich-Carl Benthaus[1] · **Oliver Totsche**[1] · **Ludwig Luckner**[2]

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Abstract

The Lausitzer und Mitteldeutsche Bergbau Verwaltungsgesellschaft (LMBV), a state-owned company, is the responsible partner for remediation of East Germany's lignite mining areas. This includes the obligation to create ecological and economically sustainable pit lakes. LMBV currently opts for in-lake treatment as the more reasonable alternative to classical discharge treatment in terms of environment and economics. LMBV has neutralized more than 20 highly acidic pit lakes and keep them in neutral conditions by regular follow up neutralization. Techniques especially adapted for the needs of East German pit lakes were developed. Of note has been the development and construction of the mobile treatment vessel "Klara", which combines a high daily neutralization agent input with a high efficiency factor. Some whole lake experiments with in-lake treatment plants for buffering pit lakes with CO_2 were also carried out. These techniques are quite costly, but under long term conditions, the buffering can be necessary to prevent re-acidification when the continuous addition of a neutralization agent is not possible, for instance under an ice cover.

Keywords Acid mine water treatment · Lake liming · Mobile treatment plants · Neutralization agents · Buffer systems

Background

Lignite was mined from opencast mines of East Germany in the Lusatian and central German areas for over 150 years. In total, an area of 130,000 km^2 was affected by lignite mining in Eastern Germany. The seams were located 20–80 m below ground, covered by unconsolidated sand and clay layers (Benthaus et al. 2014; Schreck and Glässer 1998; Seifert et al. 1993). To allow safe mining in these geological conditions, the aquifers were dewatered around the mines to a depth up to 100 m, leaving a water depression of ≈ 13 billion m^3. The groundwater drainage as well as the relocation of overburden initialized oxidation of minerals, e.g. pyrite, leading to deterioration of groundwater quality at a regional scale (Geller et al. 1998, 2013). Recent LMBV monitoring shows that run-off mine waters have a pH of 2.5–8.0, elevated concentrations of sulfate (up to 3000 mg/L), iron (up to 360 mg/L), aluminum (up to 40 mg/L), and other metal(loid)s.

Lignite mining in the area ceased partly at the end of the 1990s, and the LMBV, a state-owned company, took over all of these unreclaimed, mined-out premises in 1995. Also mines that had operated in socialist times and could no longer be operated economically were closed and reclaimed. Because of the vast mass deficit resulting from lignite mining, the resulting pits were flooded using nearby rivers and creek waters. The LMBV thus became responsible for almost 100 pit lakes in Lusatia alone (Fig. 1).

The aquifers surrounding the mining sites recovered by natural groundwater recharge, which resulted in dissolution of sulfate and iron elements. The acidified groundwater that resulted continues to cause acidification of the pit lakes. However, the quality of surface and ground water

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This paper is an extended version of an IMWA conference paper (Totsche et al. 2018) based on an online LMBV document about in-lake neutralization (Luckner and Totsche 2017).

✉ Oliver Totsche
oliver.totsche@lmbv.de

Friedrich-Carl Benthaus
FC.Benthaus@lmbv.de

Ludwig Luckner
lluckner@gfi-dresden.de

[1] Lausitzer und Mitteldeutsche Bergbau Verwaltungsgesellschaft mbH (LMBV), Knappenstr.1, 01968 Senftenberg, Germany

[2] GFI Grundwasser-Consulting-Institut GmbH Dresden, Meraner Str. 10, 01217 Dresden, Germany

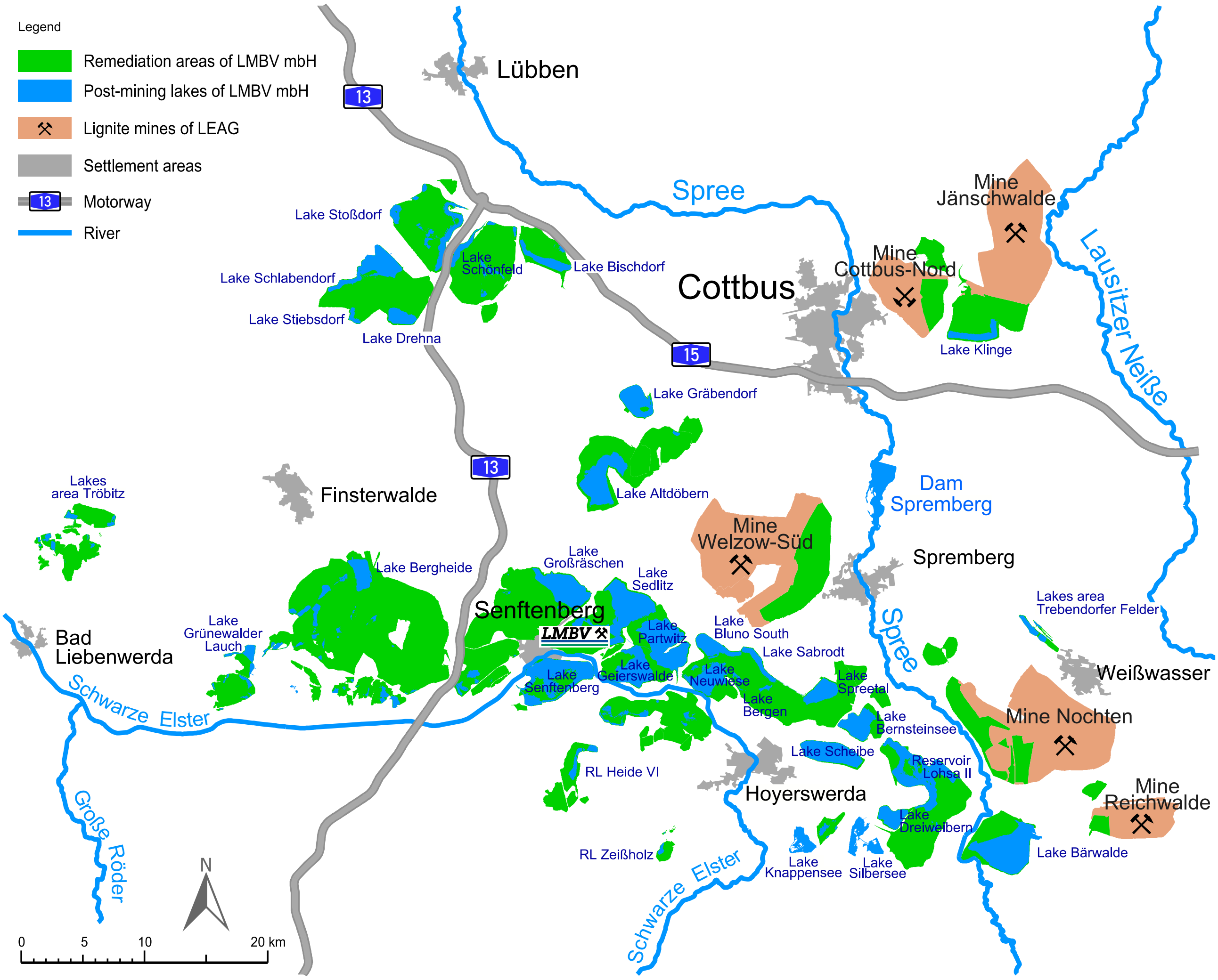


Fig. 1 Lignite mining area in Lusatia with the present state of operating mines (brown), already closed mines (green), and resulting pit lakes (image provided by LMBV)

must not be deteriorated by any activities, such as mining or industry, in order to comply with German water regulations as well as Article 1 of the European Water Framework Directive (European Commission 2000).

Pit lakes, as artificial water bodies, do not have to meet the high standards of natural water bodies, but the discharge of the pit lakes must not deteriorate the receiving rivers and streams. Thus, either the discharge or the whole pit lake must be treated to prevent the acidic discharge of the lakes from deteriorating the receiving waters with respect to pH, ammonium, iron, aluminum, and other metal(loid)s. Neutralization causes precipitation and flocculation of iron, aluminum, and most other metal(loid) ions. Ammonium concentration is reduced in neutral waters by nitrifying bacteria. Sulfate, although not considerably reduced by neutralization, is usually limited by gypsum ($CaSO_4 \cdot 2H_2O$) precipitation.

In-Lake Neutralization

The international mining industry's preferred way to handle acidic mine water is to treat the contaminated discharge waters by active water treatment (Wolkersdorfer 2020). Stationary water treatment plants can be automated to a large extent and thus operated and monitored remotely. This is a suitable solution when continuous, fairly steady treatment is required for a long time.

The alternative, in-lake neutralization of the entire lake, requires substantially larger quantities of neutralizing agent. It requires treatment of the entire water body, acidic lake sediment and erosion materials, in addition to the water run-off the lake. However, LMBV usually opts for in-lake treatment (Ulrich et al. 2012) as the more reasonable alternative in terms of environmental and economic feasibility. There are some advantages that in-lake technology offer: (1) The option of designing the capacity of the neutralization technology based on the mean, not the peak, requirement. This reduces the costs somewhat because treating the peak discharge, which can easily exceed some cubic meters per second under Eastern German soft rock conditions, can be avoided. The amount of discharge water does not matter, because it is neutral already. The lake itself acts as an alkalinity buffer. (2) There is no need for an ammonium treatment. Ammonium is degraded by microbes in open water and at the sediment–water interface. This degradation does not occur in acid water. If the ammonium concentration is too high, a separate cleaning stage for ammonium is required when treating just the discharge. (3) In stationary treatment plants, the iron sludge formed during neutralization has to be disposed of. Using in-lake technology, this is not necessary, because the iron precipitates on the lake bottom. (4) The positive effect of neutral lake water seeping into the aquifer is an advantage, allowing the mine-induced contamination of the aquifer to gradually recover. (5) Finally, from a social-economic perspective, neutral pit lakes have a much wider range of potential uses than acidic ones. Nevertheless, outflow neutralization continues to be relevant in those post-mining areas, often characterized by historic mining activity, where there are numerous minor pit lakes.

Buffering of Acidic Pit Lakes in Eastern Germany

The pH is the parameter specified in regulatory discharge permits as the relevant neutralization target. It is an intensity parameter and shows the concentration of acids dissolved in the water. Acidity, however, considers both acids and buffers present. It is therefore the relevant parameter when determining the neutralization agent requirement, and is usually given as the base neutralization capacity until a pH of 4.3, $K_{B4.3}$, i.e. the quantity of base that must be added to raise the pH to 4.3.

In a project examining acidic pit lake water from the ‘Plessa 111’ pit lake in East Germany, chemical and mineralogical analysis as well as hydrochemical modelling revealed that acidic lake water usually passes through three buffering systems during the neutralization process (Fig. 2; Totsche et al. 2003).

(I) The first buffering stage (pH 2–3) is the hydrogen sulfate buffer, during which aqueous HSO_4^- is transformed into aqueous SO_4^{2-}. If the neutralization agent is added gradually, it will not result in any precipitation and therefore no turbidity (photograph P1 in Fig. 2).

(II) In the range of the ferric iron buffering stage (pH 3–4), dissolved ferric iron is precipitated as orange-brown iron hydroxides (photographs P2–P5 in Fig. 2), which colors the water (Fig. 3). This buffer is usually the strongest buffer in acidic lignite pit lakes in Eastern Germany.

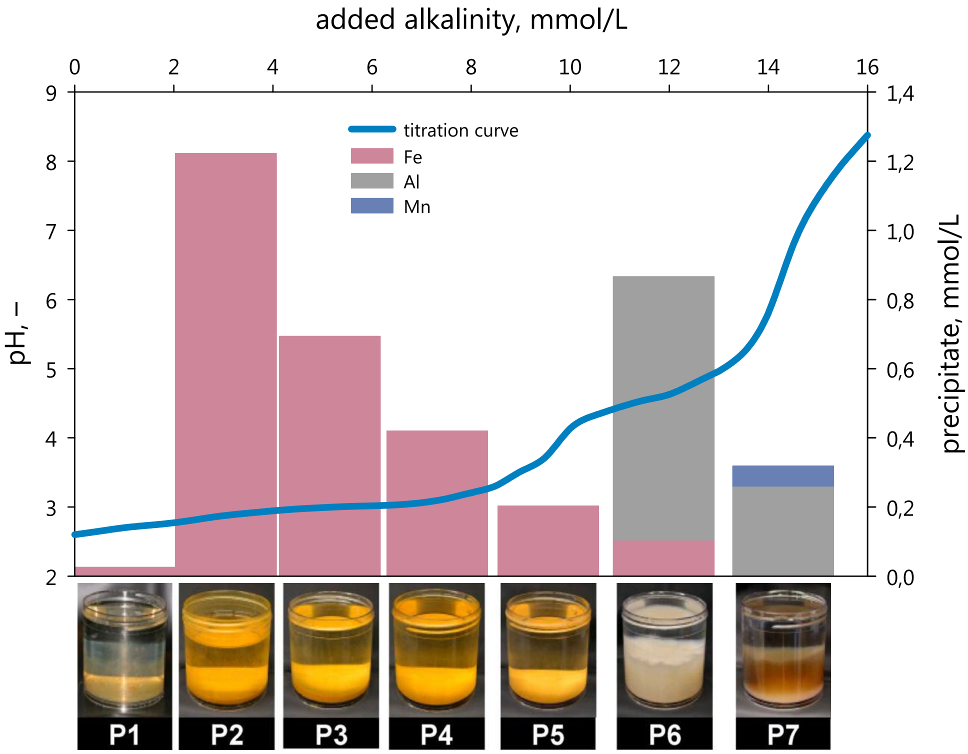


Fig. 2 Titration curve of typical water from an acidic pit lake in Eastern Germany (modified after Totsche et al. 2003)

Fig. 3 Water treatment at Lake Partwitz showing brown colored water due to iron buffering (image provided by LMBV)

Consequently, during lake neutralization, turbidity from iron precipitation continues for a very long time without any decisive pH change.

(III) The aluminum buffer (pH 4–5) is usually much weaker than the iron buffer and is characterized by white aluminum hydroxide precipitates (photograph P6 in Fig. 2). During this stage, most lakes become turquoise-colored (Boehrer 2013; Fig. 4).

Above pH 7, manganese oxide, also known as pyrolusite, may precipitate (see photographs P7 in Fig. 2). Because of the low Mn concentration in the Eastern German lignite mining pit lakes, the effect of this buffer can usually be ignored. However, in some lakes, a dark brown layer of suspended matter can be seen above the sediment, indicating the presence of this buffering process.

Choosing the Suitable Neutralizing Agent

The choice of neutralization agent is important for in-lake treatment. The different agents have specific chemical properties and therefore different technical possibilities. Quicklime (CaO, also known as caustic lime), calcium hydroxide ($Ca(OH)_2$), pulverized limestone ($CaCO_3$), and soda (Na_2CO_3) are the most frequently used neutralizing agents.

Quicklime has a high neutralization equivalent, up to 35 mol/kg, and a reasonable specific price of ≈ 0.3 Euro cents per Mole of alkalinity. Quicklime is characterized by a high neutralization equivalent and high reactivity. At the same time, even minor overdosing can rapidly result in a $pH > 9$. Usually, for ecological reasons, the authorities require that the pH of a neutralized lake be between 6 and 8.5. Also, in the vicinity of the injection area, the pH can exceed the healthy or ecologically tolerable levels, even if the lake water pH is still far from neutral.

Fig. 4 Water treatment at Lake Partwitz showing a turquoise color due to aluminum buffering (image provided by LMBV)

To check whether these locally elevated pH values represent the source of a relevant hazard, LMBV analyzed the pH distribution behind a water treatment vessel adding quicklime (Luckner and Totsche 2017). The tests showed that in an acidic lake (pH ≈ 2.8), the pH assessed as being potentially hazardous (pH > 9), only occurs immediately behind the vessel. In contrast, in a neutral lake, pH > 9 can still be identified 700 m behind the vessel and spreading some 400 m laterally. The main reason for this substantial difference lies in the fact that in acidic lakes up to a pH of ≈ 4, the dissolved iron and aluminum in the lake water precipitate as hydroxides when alkalinity is added. This means that in an acidic environment, the pH reduction is primarily brought about by chemical reactions, while in the neutral range, it is mainly due to the commingling with less alkaline water. Calcium hydroxide has similar characteristics as quicklime, but a lower neutralization equivalent, up to 27 mol/kg and a higher specific price. Therefore, quicklime is usually the preferred alternative.

Pulverized limestone has a substantially lower neutralization equivalent as well as less reactivity than quicklime. As a result, about twice the volumen of pulverized limestone than of quicklime is required to achieve the same neutralization effect. On the other hand, an excessively high pH cannot occur using pulverized limestone for neutralization as it will only react up to a pH of ≈ 7.5. Also, because of its carbonate component, pulverized limestone can buffer the lake water against reacidification.

The reactivity of the limestone particles depends on their size and density. While large particles, with a diameter ≥ 20 µm sink quite rapidly, particles with a diameter of < 10 µm remain long time in suspension. Chalk is an efficient form of pulverized limestone (Merkel et al. 2016); it is fine-grained (3–5 µm) and has a large inner surface area. Pulverized limestone has a relatively low neutralization equivalent (≤ 20 mol/kg) but a reasonable price: ≈ 0.3 Euro cents per mol of alkalinity.

Because of its carbonate component, soda can provide buffering in a similar manner to pulverized limestone. Unlike limestone, however, soda remains very soluble, even at a high pH, when potentially hazardous pH values may be reached. On the other hand, at a pH > 8, the bicarbonate (also referred to as hydrogen carbonate) buffer is precipitated as calcite, which limits the soda's buffering characteristics. Soda is also ecologically not ideal as it increases salinity (i.e. elevated sodium level). Soda has also a relatively low neutralization equivalent, and a high specific price.

Although the specific prices per mole of alkalinity of quicklime and of pulverized limestone are very similar, quicklime is usually the more cost-effective option, as substantially more mass of pulverized limestone must be discharged to achieve the same neutralizing effect. The technology costs thus are inevitably higher for pulverized limestone than they are for quicklime. Quicklime would be preferred wherever neutralization does not require alkaline buffering. Thus, the focus of initial neutralization is quicklime, while follow-up neutralizations focus on pulverized limestone to avoid the hazard of locally high pH values.

Early In-Lake Treatments (1970–2010)

When neutralization of the first pit lake in soft rock conditiones in East Germany became necessary, there was no standard technology available in the mining industry (Benthaus and Uhlmann 2006). Some early treatment efforts had been made on a trial and error basis. The two general approaches were to spread limestone into the pit lakes, using either mobile floating treatment vessels, which cover most of the lake surface during the liming period, or stationary treatment plants, which spread the limestone into the lake with pipes.

Treatment of Lake Senftenberg

The first full-scale in-lake neutralization in the East German mining area performed at Lake Senftenberg (volumen 80 million m^3). The former Niemtsch lignite pit operated from 1940 to 1966; remediation followed until 1970. Flooding of the former mine started in 1967 and lasted till 1972. While the pit was flooded with 75 million m^3 water from Schwarze Elster River, 22 million m^3 of acidic ground water inflow influenced the pit lake water. To neutralize the water body, ≈ 11,000 t of coarsed ground limestone and 3000 t of caustic soda were spread into the lake using hopper vessels. Most of the limestone particles sank rapidly from the hopper vessels to the lake bottom in clumps, without dissolving; thus, this method had little effect in reducing the acidity of the lake water. Later, the limestone particles were shown to be inert due to precipitation of gypsum on the particles in the sulfate-rich lake water.

Another approach was tested 2004 and 2005 in Lake Geierswalde (92 million m^3), formerly the Koschen mining pit. In the 1990s, lake sediments with a high limestone content were formed by the inflow of a nearby water treatment plant. These limestone particles also did not react because of a passivating gypsum surface. To reuse the alkalinity inside the limestone particles, these sediments were collected from the lake bottom by a suction dredger. The resulting slurry had a solid content of 1.9% by mass and was subsequently spread across the lake surface by a pipeline of 2.4 km length and 10 large sprinklers (Fig. 5). This reuse of the formerly inert limestone particles contributed to the neutralization of Lake Geierswalde by lowering the acid neutralization capacity ($K_{A4.3}$) from 1.6 to 0.9 mmol/L (Geller and Schultze 2013).

Fig. 5 Lake Geierswalde with sprinklers to distribute the suspended lime sediments (image provided by ETA/LMBV)

This project further demonstrated that wind and density driven convection in the lake also contributes to dissolution of limestone particles. This enhanced mixing and distribution of the reaction products and provided the basis for the later development of stationary in-lake liming plants.

The Application of Soda to Lake Bockwitz

The Bockwitz mining pit, south of Leipzig, was operated from 1982 to 1992. After closing, the open pit was surrounded by dump areas containing highly acidic material. The pit lake filled with groundwater until 2004. The initial water body (18 million m^3) had a pH value of 2.7, a $K_{B4.3}$ of 4.5 mmol/L, and an iron concentration of 55 mg/L. To improve the water quality of Lake Bockwitz as well as its discharge water, neutralization with soda started in 2004, with follow-up neutralization from 2007 to 2011.

The pulverized soda was delivered by silo vehicles directly to the lakeshore, where it was pumped pneumatically as a mixture of soda particles and air to a floating barge into the water body, below the surface (Fig. 6). As a result, a temporary pH (up to 7.7) was achieved with weak buffering (up to $K_{A4.3} \approx 0.4$ mol/L). Due to its high solubility, no further technical installations were necessary. Therefore, the application costs were very low. However, given the price of soda rose on global markets since then, the use of soda today is only economically feasible when the demand of neutralization agent is very low.

Knowledge Transfer from Scandinavian Lake Neutralization Experience

Since liming with hopper vessels was not effective at Lake Senftenberg, another approach was tested, taking advantage of Scandinavian experiences with acid rain-affected lakes (Dickson and Brodin 1995). However, the Scandinavian soft lake waters are far less acidic than Eastern Germany's post-mining lakes. Some Scandinavian lakes are limed by vessels that have been purposely built for this task. One such water treatment vessel was used for the first time on an Eastern German post-mining lake in 2008. The vessel was loaded with the neutralization agent from a silo vehicle by hose. The dry-bunkered pulverized limestone on the vessel was mixed on board with a flow of lake water generated by the vessel's pumping system. The suspension was spread across the lake surface by two water guns (Fig. 7). Only small quantities of pulverized limestone (37 t) were needed in 2008 to prevent re-acidification of the already neutral Lake Haselbach. In the following year, Lake Bernstein was the next post-mining lake to be neutralized using this type of water treatment vessel. 11,000 t of pulverized limestone were used to reach pH = 5, which was followed by 1000 t of calcium hydroxide to reach neutral water conditions.

Fig. 6 Soda application to Lake Bockwitz (image provided by LMBV/Detlef Stremke)

Fig. 7 Scandinavian water treatment vessel on Lake Haselbach and together with its trailer on Lake Burghammer (image provided by LMBV)

The advantage of these small Scandinavian water treatment vessels is that they can easily be transported by road on a trailer. From this, they can be launched, and subsequently recovered from a lake with relatively ease. They are therefore very flexible and can be rapidly deployed in post-mining lakes, though the low bunker volume of 11 m^3 was inconvenient, requiring many trips to refill during operation, which reduced their economic efficiency. A further disadvantage was the substantially poor efficiency of the relatively coarse-grained limestone powder used, in contrast to the Scandinavian soft water lakes, where it worked well. Using quicklime instead was considered potentially dangerous due to the formation of highly caustic aerosols in the air above the surface of the lake water.

Developing New In-lake Neutralization Technologies 2010–2020

The early treatments had some benefits, but also had some drawbacks. Therefore, many new ideas and demonstration projects have been submitted to LMBV during the last decade by engineering companies and scientific institutions. Many of these proposals had already been tested in the laboratory scale and needed to be evaluated on a larger scale. LMBV's "Scientific and Technical Advisory Board for Water Management," an independent committee composed of recognized water experts apart from LMBV. They have reviewed the projects for efficiency, sustainability, and transferability to other mining sites to select the most promising proposals for pilot and demonstration projects.

Considerable improvements were achieved for both mobile treatment by ship and stationary in-lake treatment by pipes. One of the 'new' treatments was an in-lake treatment plant at Lake Zwenkau. This pit lake had to be treated due to a sustained inflow of acidic groundwater. In 2011, the initial water body (85 million m^3) was acidic, with a pH = 2.8, high sulfate concentrations of ≈ 1.7 g/L, and typical iron concentrations of 16 mg/L. At this site, there was no need for a special input system. As the lake was being flooded with water from the nearby Profen open-cast mine, a quicklime suspension could be added to the flooding water on-shore. There, the flooding pipeline worked as a tube reactor in which the quicklime suspension effectively mixed with the flooding water (Fig. 8). The in-lake treatment plant could thus be constructed economically with a minimum of technical installations because this form of quicklime input exploits the kinetic energy already present in the flooding water. The current carrying the suspended quicklime descends into the deep area of Lake Zwenkau, with further distribution provided by wind- and density-driven currents.

The water quality in Lake Zwenkau during neutralization developed in several phases (Fig. 9). During the initial neutralization (phase 1), the alkalinity came from three sources: the water from the nearby Profen lignite mine, which untreated had an alkalinity of 168 · 10^6 mol, water from the Weiße Elster River, with an alkalinity of 78 · 10^6 mol, enriched by the neutralization treatment plant, which added 35,000 t of quicklime. In this phase, the lake's pH value rose to 2–2.5 and Al concentrations decreased from 3 to less than 0.8 mg/L.

In phase 2, the water treatment was carried out using a modified Scandinavian water treatment vessel; to meet LMBV's safety standards, the quicklime suspension dispersal system was changed from overwater to underwater. In this second phase, the pH rapidly increased to above 7.5. Phase 3 was an intermediate phase without alkali application, where the pH dropped from a maximum of 7.5–6.5. In phases 4 and 5, Lake Zwenkau was flooded with

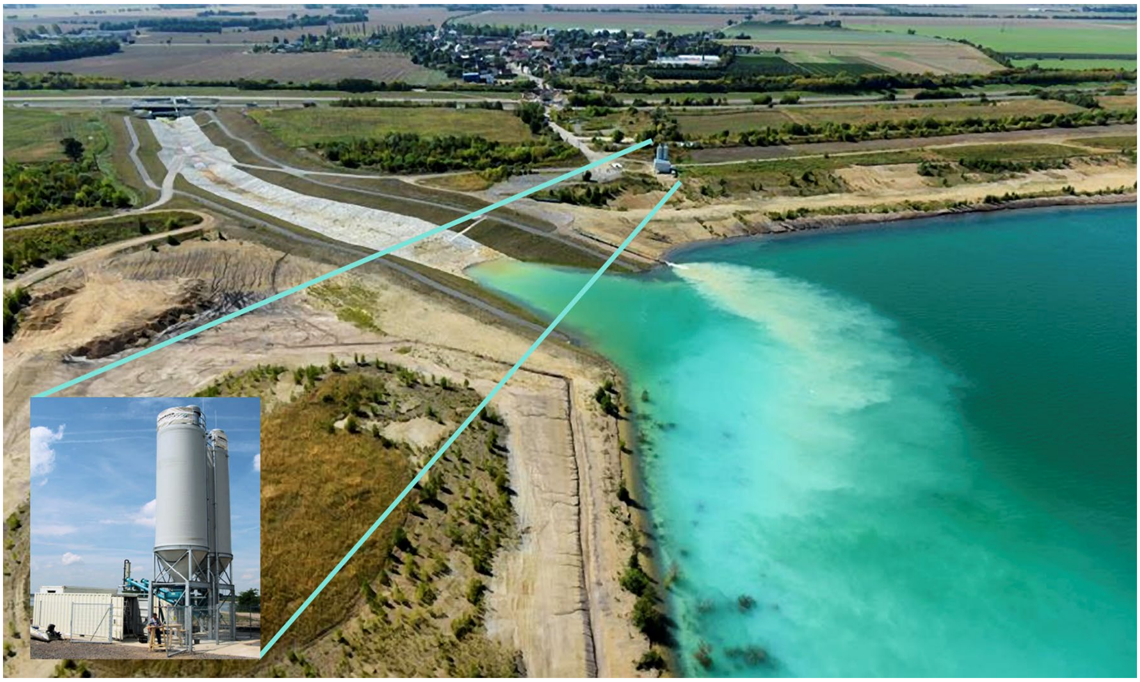


Fig. 8 Stationary neutralization plant on Lake Zwenkau and the lime plume spreading into the water body (image provided by LMBV)

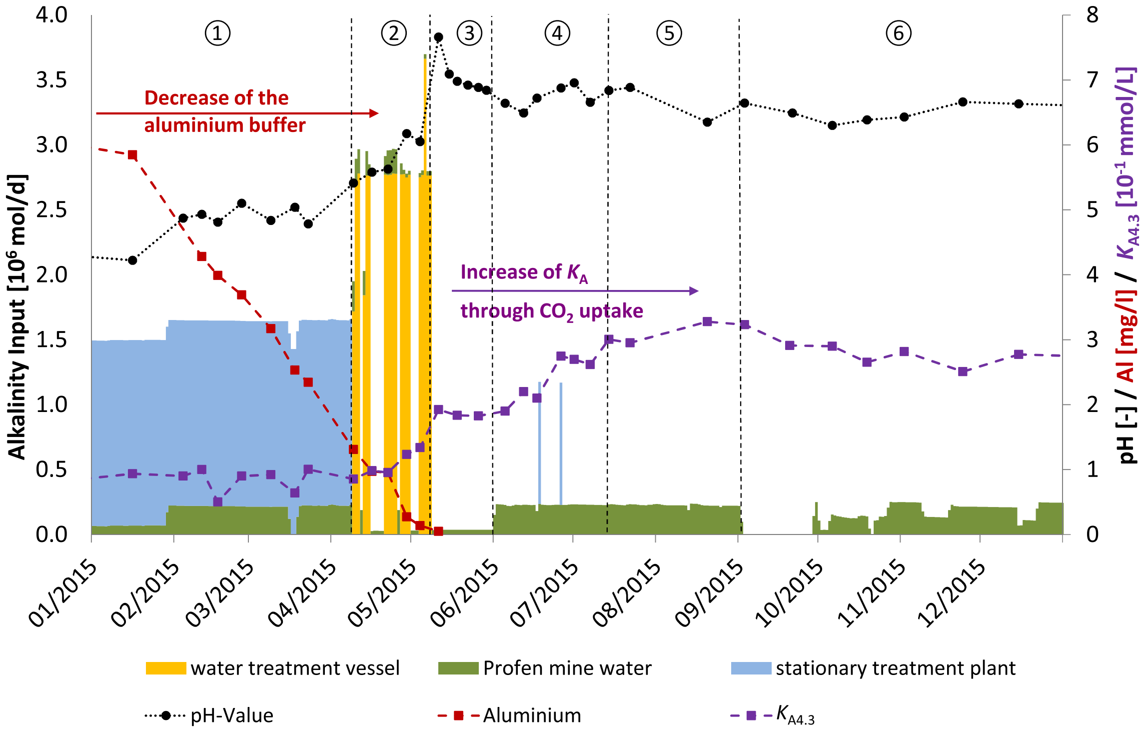
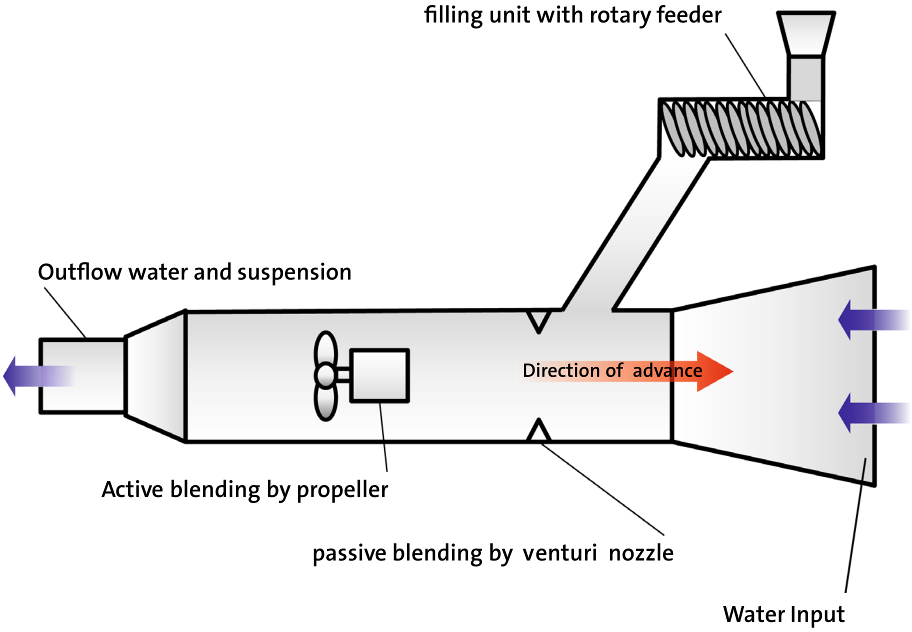


Fig. 9 Development of initial neutralization at Lake Zwenkau (data provided by GFI); 1: initial neutralization; 2: water treatment; 3: intermediate phase; 4 and 5: Lake Zwenkau flooded; 6: Water from Profen mine discharged into Lake Zwenkau

well-buffered water with a high level of bicarbonate from the nearby Profen mine. Consequently, the $K_{A4.3}$ rose from 0.5 to nearly 2 mmol/L. In the second half of 2015, the pH largely stabilized without any new quicklime input, as 35,000 m^3/d water from Profen mine at pH ≥ 6 and $K_{A4.3} \approx 0.3$ mmol/L was supplied in phase 6 to Lake Zwenkau.

Despite the successful modification of the Scandinavian vessels, more innovation was needed to improve the dilution and the horizontal spread of the neutralizing agent. Therefore, a new input system tailored to conditions in the acidic pit lakes was developed, based on dry liming using here a submerged tube mixer as a technical reactor and highly

Fig. 10 Sub-water input system (modified after patent DE102010019510A1)



turbulent delivery of the suspension (Fig. 10). This system is particularly suitable because it combines high performance with high dilution rates, which leads to high efficiency. In collaboration with Brain GmbH, LMBV has filed a patent application (DE102010019510A1) for this input system.

Brain GmbH built the water treatment vessel “Barbara”. This vessel is a catamaran with two of the tube mixers mounted between the twin hulls (Fig. 11). The vessel has two lime bunkers, each with a capacity of 12 m^3. In 2012, LMBV has operated the water treatment vessel “Barbara” on Lake Lichtenau within the framework of a pilot and demonstration project. The subsurface application of the neutralization agent resulted in a rapid intermixing with a great volume of lake water. Because of the high throughput of water, the percentage of solid matter in the suspension was 0.6% by mass of pulverized limestone and ≈ 0.2% by mass of calcium hydroxide ($Ca(OH)_2$). Although the material is spread over a width of some 12 m, the quantities needed per unit area, 0.07 kg $Ca(OH)_2/m^2$, were relatively low. The good handling of the vessel and effective use of the quicklime and pulverized limestone were positive aspects. Since 2013, the “Barbara” has worked at Lake Schlabendorf, the LMBV pit lake with the highest alkalinity demand.

The newest development is the construction of a vessel for the “Lausitzer Seenland” (Lusatian Lake Land). The Lusatian Lake Land in Eastern Germany consists of nine former mining pits, which are connected by navigable canals (Fig. 12). Between the towns of Senftenberg in the west and Spremberg in the east, the entire Lusatian Lake Land covers a surface area of 55 km^2 with a volume exceeding 800 million m^3. The lakes are surrounded by soft rock strata with groundwater layers and dump areas. This volume of lake water as well as the acidic groundwater inflow will require treatment for decades.

Due to the acidic groundwater, all lakes suffer reacidification and a treatment plant was needed for each of the nine lakes. To avoid this expense, the water treatment vessel “Klara” was constructed in 2016 to treat all nine lakes. “Klara” was designed and built specifically for the conditions in the Lusatian Lake Land, with dimensions that allowed to pass through all of the canals, bridges, and locks. The “Klara” consists of a push boat and two floating vessels with silos (Figs. 3, 4, 13). The engine, electric generator, and ship-bridge are on the push boat. There are two quicklime silos on each vessel and two discharge units have been mounted between the catamaran twin hulls of each vessel. An advantage of the discharge unit arrangement on the “Klara” is that while the first vessel is on the lake with the push boat, discharging the neutralization agent, the second vessel can be loaded with more neutralization agent. This reduces the time between treatment cycles to about 5 min for changing the vessels, rather than 60 min for loading the quicklime onto the vessel. The “Klara” uses the same subsurface input system as the “Barbara” and can distribute quicklime, pulverized limestone, or calcium hydroxide. The vessel can deliver the neutralization agent very efficiently and reaches high levels of dilution in the lake water by boosting the agent using the push boat’s propellers. The

Fig. 11 Water treatment vessel “Barbara” in operation–showing the input system between the vessel’s hulls (image provided by LUG/LMBV)

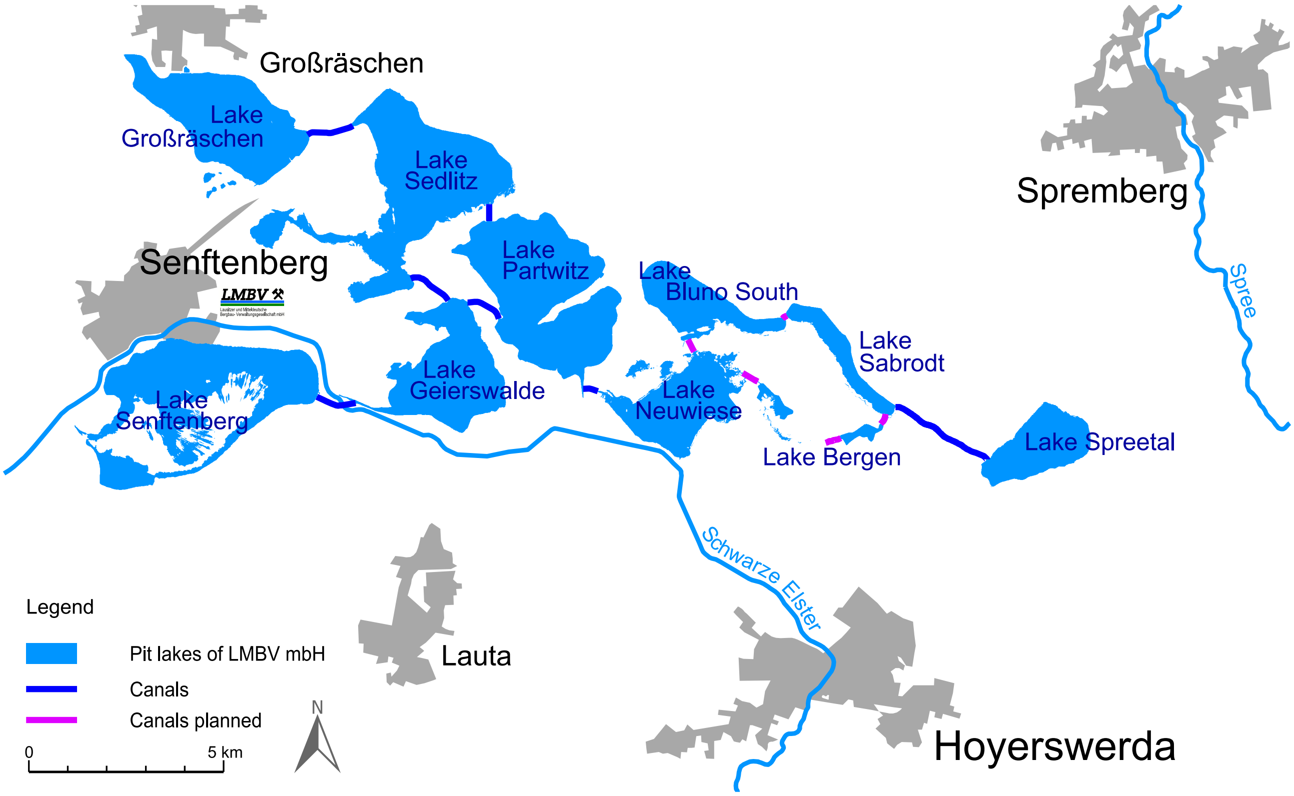


Fig. 12 "Lausitzer Seenland" (Lusatian Lake Land): nine interconnected post-mining lakes (image provided by LMBV)

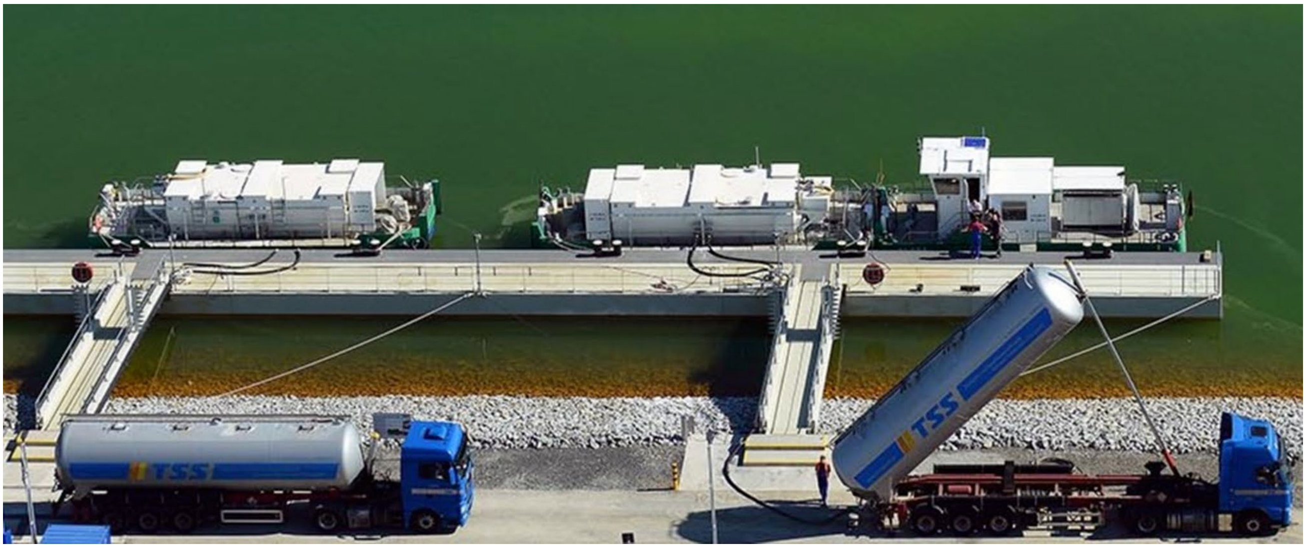


Fig. 13 LMBV water treatment vessel Klara during vessel change (image provided by LMBV)

system is fitted for the discharge of ≈ 40,000 t of neutralization agent per year. The "Klara" is therefore able to carry out both initial neutralization as well as follow-up treatment for the entire Lusatian Lake Land.

The operation of the in-lake neutralization at Lake Partwitz has been quite successful. The volume of 123 million m^3 water in Lake Partwitz was characterized initially by a pH = 2.8 and a $K_{B4.3} = 4.0$ mmol/L. Because "Klara" came straight from the dockyard to Lake Partwitz, the first phase was a trial run with three different neutralization agents: 1200 t of pulverized limestone, 1200 of quicklime, and 500 t of calcium hydroxide were added to the lake (Fig. 14). During the second phase, the initial neutralization started with the distribution of 15,300 t of quicklime, although the distribution had to be interrupted in February, when the lake was covered with ice (Fig. 14). At pH 4, the initial neutralization was finished with 6000 t of pulverized limestone. The neutralization agent was changed to avoid local hazardous pH values for the water tourists. The third phase, the follow up neutralization, started at pH 7. Up to December 2017, 10,900 t of pulverized limestone had been distributed in the lake and the $K_{A4.3}$ had risen to 0.6 mmol/L. Monitoring shows that ≈ 87% of the quicklime discharged achieved the above effects. It is assumed that the remaining 13% of the quicklime primarily neutralized the lake sediment.

CO_2 gas buffering: the future of in-lake treatments?

As previously described, the use of pulverized limestone provides some buffering because part of the alkalinity is retained in the water as dissolved hydrogen carbonate (HCO_3^-). This has a buffering effect during the reacidification phase. But in the pit lakes of Eastern Germany, this effect is limited to about 0.4–0.6 mmol/L. To achieve still greater buffering, CO_2 must be added to the water (Merkel 2005). This can be achieved per Eq. (1):

$$Ca(OH)_2 + CO_2 \rightarrow Ca^{2+} + OH^- + HCO_3^- \quad (1)$$

Hydrogen carbonate buffering is a useful follow-up treatment due to its ecological and economic advantages. The buffering is ecologically feasible because it stabilizes the pH during the treatment phase, preventing sudden pH fluctuations from 6 to 8, which is disadvantageous for sensitive aquatic organisms. Whether buffering is economically feasible or not is site specific, because it can delay follow-up treatments substantially. Although this can reduce plant costs, the expenses for the materials and agents used increase, as the costs of the CO_2, currently ≈ 120 €/t, must be considered as well.

In 2015, Lake Scheibe, a hydrogen carbonate buffer was developed using turbulent jet technology. The pulverized limestone and carbon dioxide were injected by a stationary free jet plant (Fig. 15). With pulverized limestone as a neutralization agent, half the alkalinity was delivered as a base, and half as hydrogen carbonate, per Eq. (2):

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + OH^- + HCO_3^- \quad (2)$$

When ground limestone was used, less CO_2 was required compared to using calcium hydroxide or quicklime to

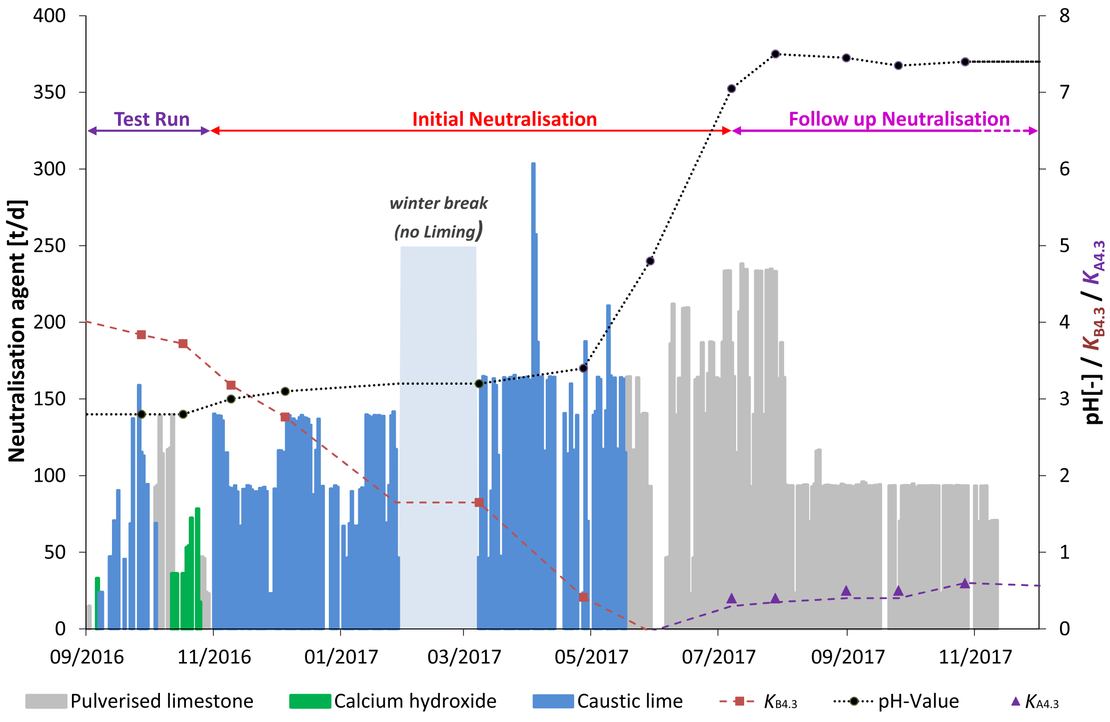


Fig. 14 Neutralization of Lake Partwitz, performed with the "Klara" water treatment vessel (image provided by GFI)

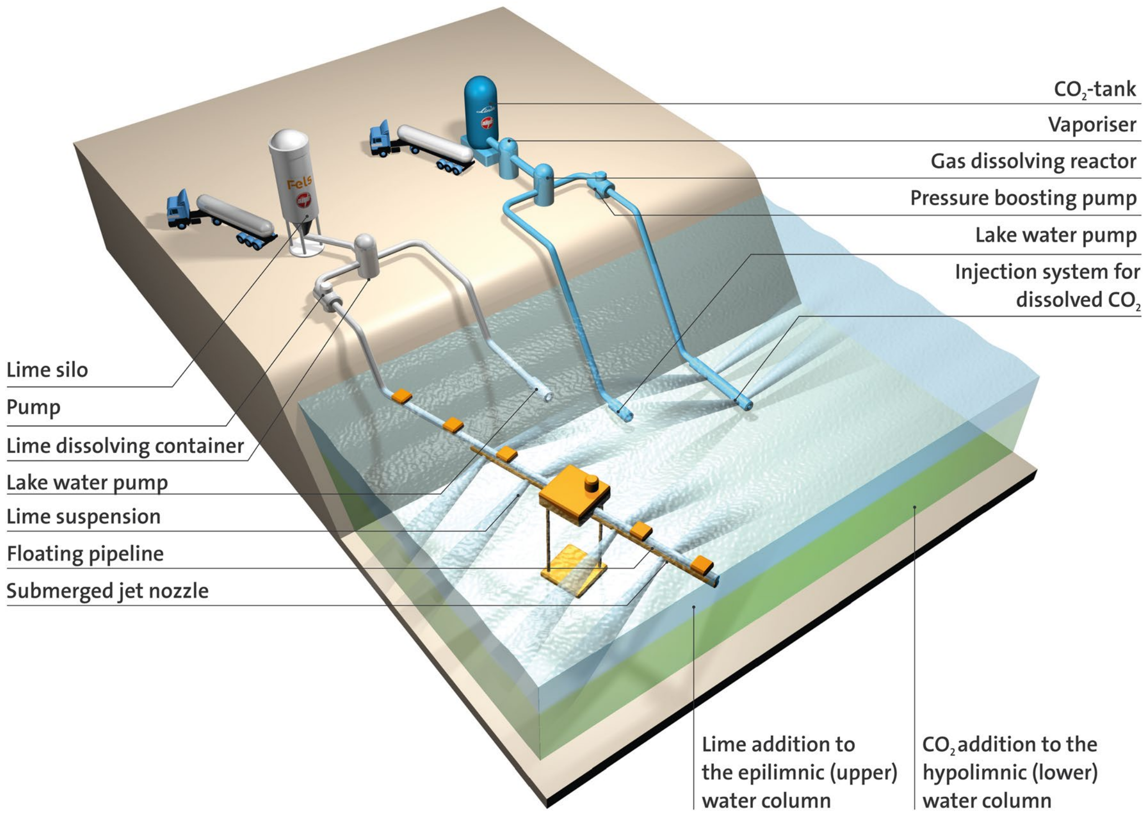


Fig. 15 Stationary neutralization plant with pulverized limestone (left) and CO$_2$ (image provided by GMB)

develop the same alkaline buffer quantity. The input of 11,000 t of pulverized limestone and 5000 t of CO$_2$ to Lake Scheibe in 2015 caused the $K_{A4.3}$ to rise from ≈ 0.1 mmol/L to ≈ 0.9 mmol/L, which equals an alkalization effect of some 87 · 10^6 mol.

Another buffer-related test project using CO$_2$ was performed from 2014 to 2016. A closed technical reactor generated hydrogen carbonate from quicklime as well as CO$_2$ gas and delivering it to the water of Lake Drehna at a hydrogen carbonate concentration of 25–30 mol/m^3 and a pH < 6. As the reactor operates with a high density of the reactants CO$_2$ and quicklime in a fluidized bed, it was designated a ‘high density hydrogen carbonate reactor’ (HDHC Reactor; Fig. 16).

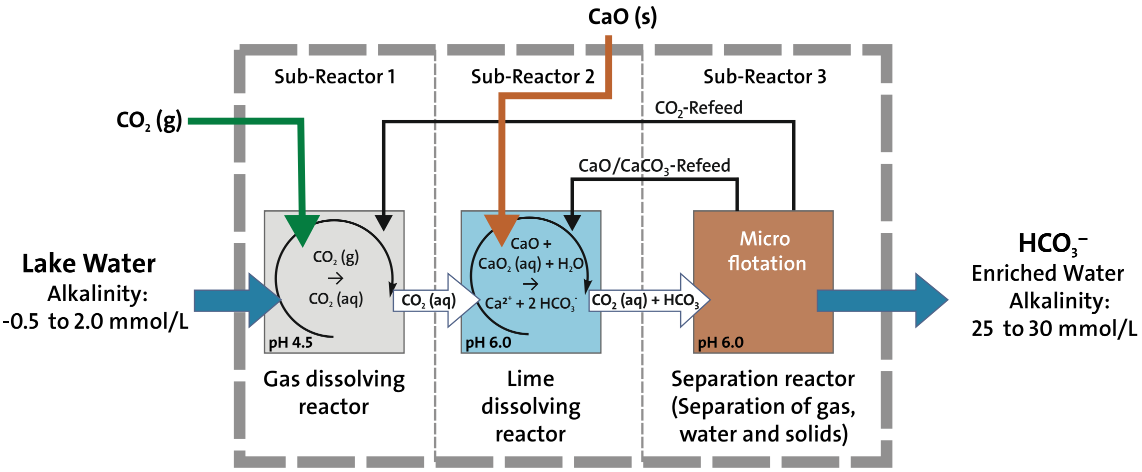


Fig. 16 Operation diagram of the high-density hydrogen carbonate (HDHC) reactor (image provided by GFI)

The HDHC reactor enriches the lake water with dissolved hydrogen carbonate (HCO_3^-), which can injected to the lake via a similar turbulent jet technology as used in Lake Scheibe. The objective of this reactor's development had been to enable high conversion rates by returning undissolved CO_2 (gas) to the gas-dissolving sub-reactor. The undissolved quicklime is refed into the solids sub-reactor inside the closed reactor, thus avoiding degassing and sedimentation losses in the HDHC-reactor. Another objective was to discharge only the dissolved HCO_3^- into the lake that was to be neutralized and buffered and to maintain the pH of this buffered discharge water at a pH ≈ 7.

Within this project, trials with different lime products were carried out and assessed between 2014 and 2016. In the lake, the trial with pulverized limestone caused an $K_{A4.3}$ of 0.9 mmol/L and with quicklime a $K_{A4.3}$ of 1.1 mmol/L. With an annual alkalinization to $K_{A4.3} \geq 1$ mmol/L, it is expected that the follow-up cycle in the surface water of Lake Drehna can be limited to three months of alkalization and nine months of reacidification. This will prevent annual acidification during the winter when the lakes freeze over.

Before starting the CO_2 projects, there had been an intensive discussion with the authorities on the potential risks of gas input to the lake's waters. The input of pulverized limestone to the epilimnion is safe, if the concentration of dissolved CO_2 near the lake surface does not exceed 1 mg/L. Furthermore, the physiological effect of CO_2 on 'legally protected subjects' such as the human workforce and aquatic fauna must be appropriately observed and limited. Above all, the zooplankton in the hypolimnion and the zoobenthos on the lake floor must not be endangered. The use of CO_2 will remain of interest in the future, especially to prevent the pH from dropping by reacidification.

Conclusions for In-lake Water Treatment

To date, LMBV has neutralized more than 20 acidic pit lakes and keeps them in neutral conditions by regular follow up neutralization. To enhance the existing in-lake techniques, every LMBV neutralization project involves two stages: (1) evaluation of the technical and economical results of the new approach, including intensive monitoring, and (2) hydrological and geochemical balancing of the neutralization project to prove the results. Efficiency is assessed by a third partner using hydrogeochemical models to prove the degree of efficiency of any new neutralization measure.

LMBV learned that the efficiency of a new technique and new agent primarily depends on the input technology, the concentration of the suspension, and the techniques of producing the turbulence. Another important parameter is the nature of the neutralization agent, above all its chemical composition, but also particle size and active surface area. The third important parameter is the composition of the lake water, whereas pH, sulfate concentration, and ionic strength are the most relevant parameters therein. Because of the large number of influential factors, it is difficult to assign each procedure an unambiguous degree of efficiency. General qualitative comparisons are still possible, and the results can then be considered for subsequent procedures.

The "Klara" is the most powerful water treatment vessel built to date. Other large treatment vessels such as the "Barbara" are suitable for pit lakes with relatively high demands for neutralization agents. They have proved their usefulness. However, hauling these large water treatment vessels from one lake to another by road is challenging. They also require suitable areas for launching the vessel and to add neutralization agents. Small water treatment vessels such as the Scandinavian ones can easily be launched and hauled without requiring a heavy-load transport.

For initial neutralization, quicklime tends to be the most cost-efficient neutralization agent. For follow-up neutralization, finely ground limestone usually is the preferred agent due to health and ecological reasons. Under certain conditions, the buffering of neutralized waters by the addition of CO_2 gas can also be appropriate.

Today, the in-lake neutralization toolbox is well filled because of a special funding program that allowed LMBV to test new approaches in pilot and demonstration projects. Although LMBV has at its disposal the appropriate tools and service providers, the technology must continuously be assessed, enhanced, and extended.

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