Liming of acid surface waters: Effect of water constituents and material impurities on calcite dissolution kinetics

Mandy Schipek and Broder J. Merkel

TU Bergakademie Freiberg, Chair of Hydrogeology, Gustav-Zeuner-Str. 12, 09599 Freiberg, Germany, mandy.schipek@geo.tu-freiberg.de

Abstract

Using limestone instead of soda or lime as neutralizing product during lake water treatment has additional economic and ecological benefits. Dissolution kinetics of pure calcite is well investigated. However the composition of natural carbonates as well as the constituents in mine waters have strong influence on solution kinetics and may inhibit dissolution processes during lake remediation. 25 different neutralisation products were tested and investigated by XRF and SEM-EDX. The reactivity of synthetic marble powder and two industrial products (KSM Beroun, CC20) was investigated in a free-drift batch-experiment by adding different amounts of inhibiting ions.

Based on the elemental contents, no significant difference between synthetic marble powder and industrial products was found. Significant deviations from the theoretical model after Plummer et al. (1978) were noticeable during kinetic experiments with limestone in pure water. Additionally, ions typical for acid mine drainage (e.g. Mn^{2+}, Cd^{2+}, Fe^{3+}, SO_4^{2-}) can have different effects on the kinetics of carbonate dissolution. Manganese concentrations typical for acidic mining lakes (8.98×10^{-4} mmol/L) inhibit calcite dissolution and result in 66.4% of dissolved calcium compared to the experiments without inhibitor. Supplying excess calcite (20 times excess instead of 5 times with respect to calcite carbon dioxide equilibrium) results in 92.7% of the equilibrium concentration and a significant time-shift in reaching equilibrium. Cadmium has also a significant influence on the dissolution and kinetics. Only 58.2% of the calcium concentration was reached with cadmium as inhibitor (7.65×10^{-6} mmol/L) compared to the dissolution of pure water. Using 20 times more carbonate revealed a slightly higher dissolution reaction (63.8%).

Material impurities and water constituents significantly affect the dissolution kinetics of limestone. Thus, both should be considered if there are ambitious efforts to remediate acidic mining lakes by in-lake liming.

Keywords: in-lake liming, acid mine drainage, inhibition, lime, kinetics

Introduction

Experiences in direct liming of lakes over more than three decades can be found mainly in Sweden, Norway and Finland. In Northern European lakes, the acidic load originates mainly from the atmosphere and is not influenced by pyrite weathering. Since more than 30 years, direct liming in catchment areas, or of lakes by boat or helicopter, was applied (Henrikson et al. 1995, Sverdrup 1985). A number of publications exists dealing with the properties of the neutralizing agents and their influence on the success of the remediation strategy (Nyberg and Thornelof 1988). Positive effects resulted not only in terms of water quality aspects but also for the whole ecosystem (Driscoll et al. 1996, Guhrén et al. 2007, Iivonen et al. 1995). Furthermore, there are some experiences in the rehabilitation of mining lakes by liming, in the United States (Castro and Moore 2000, Dowling et al. 2004), Finland (Ahtiainen et al. 1983). Despite considerable research only little information is available in international literature for acidic lakes in Germany (Bozau et al. 2007, Hemm et al. 2002, Koschorreck et al. 2007, Pust et al. 2010). In order to optimize direct liming of acidified surface water lab and field experiments have been conducted with acid mine water form pit lakes (Merkel et al. 2010, Schipek et al. 2011).

According to Svensson and Dreybrodt (1992) natural limestone contains impurities that accumulate at the mineral surface during the dissolution process and interact with Ca^{2+}/HCO_3^- ions absorbed from the solution on the surface. Numerous publications deal with the study of solutions kinetics of synthetic, highly pure calcite. These results are not applicable to natural systems as natural limestone differs in its solution behavior (Svensson and Dreybrodt 1992). Furthermore a great variance between natural carbonate rocks exists (Eisenlohr et al. 1999). The composition of investigated calcite materials has a strong influence on the solution kinetics (Arvidson et al. 2006, Cubillas et al. 2005, Vinson et al. 2007). Natural lime products often contain trace ions such as magnesium, aluminum, silicates, phosphate, strontium, and iron. These ions are often bound by sorption on the surface of carbonates, and thus inhibit the solution of the limestone.

Additionally constituents in natural waters have a strong influence on the solution kinetics by changing the saturation state of the solution or by sorption processes on the mineral surface. Buhmann and Dreybrodt (1987) describe ionic-pairing effects, ionic-strength effect, common-ion effect, acid effect, and base effect. Important mining-related water constituents include sulfate, manganese, cadmium, and iron. Only little information regarding the effect of dissolved sulfate on the dissolution kinetic of calcite is available. The results of different authors (Akinfiev and Diamond 2003, Dreybrodt and Gabrovsek 2000, Edenborn et al. 1986) provide inconsistent evidence for the inhibition of the dissolution by sulfate ions. Other authors (Lea et al. 2001, Vinson et al. 2007) describe the inhibition by manganese and strontium.

Methods

X-ray fluorescence analysis was performed on powder samples (< 63 microns). A XEPOS (Spectro) device was used to determine the elements K to U (mass number 39 to 238). Matrix effects were taken into account by the Turbo Quant method. The excitation of the elements was performed by using different targets (K - V: HOPG Target; Cr - Zn, Pr - U: Mo secondary target, Y - Ce: Barkla-Al_2O_3-target). The morphology of the liming agents (calcite, dolomite) was investigated by SEM-EDX using a JEOL JSM 7001F (Zeiss AG) and Esprit was used for data evaluation.With an energy-dispersive X-ray probe the chemical composition of special sample areas was investigated.

Furthermore, experiments were carried out taking into account the inhibition of dissolution kinetics by water constituents typically for AMD affected waters. We used powdered samples in free-drift experiments particularly with regard to the technical application on a remediation ship used in liming campaigns. The batch system consisted of a 5-L beaker, filled with 4 L distilled water. CO_2 partial pressure and temperature was kept constant during the experiment. The amount of reactive material used in all experiments exceeded the solubility capacity 5 times or 20 times, so that a rather constant particle surface to water ratio can be assumed over the entire time of an experiment. Turbulent flow conditions were generated using a stirrer (700 rpm) and calcium and other metal concentrations were determined with an ICP-MS (Thermo Fisher Scientific).

Results and Discussion

Geochemical characterization

A total of 25 different neutralization products of different manufacturers (calcite / dolomite / mixed products) had been investigated for their elemental contents. Main constituents of liming material used in kinetic and/or column experiments are listed in Table 1. For kinetic experiments, marble powder and the limestone KSM Beroun were used. Chemical composition seems quite similar. The synthetic chemical marble powder contained small amounts of impurities (like magnesium, silicon, aluminum, iron, etc.). KSM Beroun is a limestone that was already used in liming of mining lakes (Pust et al. 2010, Schipek et al. 2011). Therefore, the content of minor constituents and trace metals is relevant to estimate a possible release into lake water. Other limestone products (e.g. Borna KSM 90) had significantly lower calcium concentrations (30.3 wt.-%), but higher concentrations of magnesium (3.52 wt.-%) and silicon (5.65 wt.-%). Contents of trace metals like aluminum, iron, strontium and manganese were observed at higher concentrations than in KSM Beroun. Besides limestone, also dolomitic products were used in columns experiments in order to estimate the neutralization efficiency of these products. They seem to be cheaper in production, so they may be an alternative for limestone. 2 dolomites were tested: DSM Ostrau and Borna DSM 90. Main constituents of both products were calcium and magnesium with 22.42 / 25.04 wt.-% and 12.46 / 9.98 wt.-% respectively. Additionally, higher concentrations of silicon, aluminum, iron, and manganese were observed in these materials. Contents correlate with SEM-EDX results. High reactive CaO and $Ca(OH)_2$ was tested in column experiments, too. Both, rich in calcium (65.72 wt.-% for CaO, 51.1 wt.-% for $Ca(OH)_2$) contained only small amounts of minor constituents (magnesium, silicon, strontium, …). Results observed by X-ray fluorescence correlate with data obtained by SEM-EDX.

Figure 1 and Figure 2 show SEM images of particles of synthetic marble powder and a limestone powder (KSM Beroun) from Rheinkalk GmbH (Germany) with the typical rhombohedral structure of the particles. Moreover, the surface of the synthetic product is smoother than that of the industrial product. Visually, the geometry of industrial product particles seems to be entirely different from that of the synthetic material. A significantly larger surface of the material can be estimated.

Kinetics

Figure 3 shows the development of the calcium concentration within kinetic experiments. Using marble powder and KSM Beroun equilibrium was reached after about 15,000 minutes, significantly later than modeled after Plummer et al. (1978). CC20 used in 5-times excess showed within the first 20 minutes of the experiment a faster kinetic than KSM Beroun and marble powder. This can be reasoned by the finer particle size (CC20: > 90% < 6 µm).

Differences between the different amounts of liming agents (5 vs. 20 times excess of reactive material) and the resulting increased calcium concentrations can be explained by a relatively larger particle surface that is not inhibited by minor constituents of the liming agents. Furthermore, a significant difference between the EC (data not shown) and the calcium concentration compared to the modeled data can be seen.

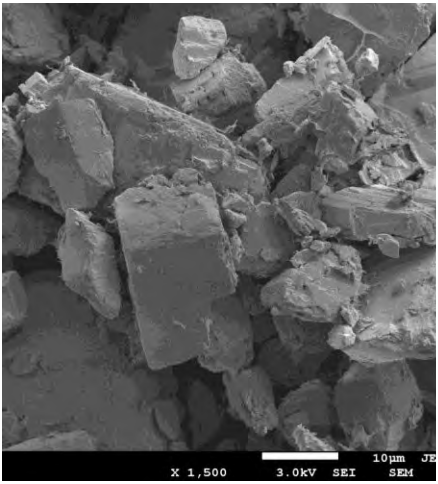

Figure 1 *SEM image of marble powder.*

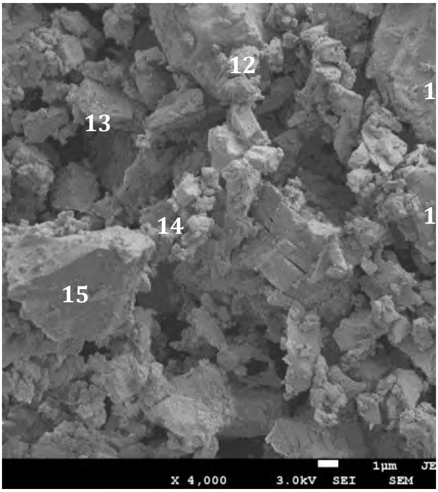

Figure 2 *SEM image of KSM Beroun. 11-18 indicate mainly Ca-rich phase (CaO_{calc} 97.8 wt.-%). Minor constituents contain Si ($SiO_{2, calc}$ 0.85 wt.-%), Mg (MgO_{calc} 0.53 wt.-%), Sr (SrO_{calc} 0.50 wt.-%), Al ($Al_2O_{3, calc}$ 0.26 wt.-%) and Fe (Fe_{calc} 0.07 wt.-%).*

Table 1 *Elemental contents(selection) of investigated liming agents. Contents are given in wt.-%.*

	Marble powder	**KSM Beroun**	**KSM CC20**	**DSM Ostrau**	**Borna DSM 90**	**Borna KSM 90**	**CaO_ 02/11**	**$Ca(OH)_2$_ 02/11**
Ca	39.10	39.40	36.87	22.42	25.04	30.30	65.72	51.10
Mg	0.2497	0.2747	0.2994	12.46	9.982	3.518	0.4563	0.4367
Si	0.0878	0.0558	2.997	1.005	4.842	5.648	0.2454	0.0424
Al	0.0376	0.0139	0.6562	0.4061	0.7719	0.9508	0.081	< 0.002
Fe	0.0201	0.0198	0.2986	0.4909	0.5045	0.5293	0.0784	0.0055
Sr	0.0155	0.0155	0.0822	0.0085	0.0208	0.0311	0.0252	0.0194
Mn	0.0070	0.0052	0.0230	0.2083	0.0331	0.1212	0.0077	0.005
Ba	0.0029	< 0.0002	0.0135	0.0018	0.0058	0.0033	0.0041	< 0.00020
P	0.0013	0.0032	0.0288	0.0120	0.0118	0.0119	0.0054	0.0026
Sn	0.0012	0.0015	0.0010	< 0.0003	< 0.0003	0.0005	0.0045	0.0028
Sb	0.0010	0.0016	0.0010	< 0.0003	< 0.0003	0.0003	0.0042	0.0032
Mo	0.0010	0.0009	0.0006	0.0004	0.0006	0.0007	0.0022	0.0016
Zn	0.0008	0.0009	0.0052	0.0334	0.0050	0.0445	0.0015	0.0012
Th	0.0003	0.0003	0.0001	0.0005	0.0002	0.0002	0.0005	0.0003
Pb	0.0003	0.0004	0.0004	0.0464	0.0007	0.0007	0.0006	0.0003
Cu	0.0002	0.0002	0.0005	0.002	0.0007	0.0007	< 0.00005	< 0.00005
K	< 0.001	< 0.001	0.126	0.122	0.096	0.201	< 0.001	< 0.001
S	< 0.0002	0.0014	0.0750	0.0419	0.0541	0.0422	0.0840	0.0136

This might be due to the performance of batch experiments in free-drift mode by using calcite powder. Electrical conductivity was measured in the solution with undissoluted calcite particles.

Based on the elemental contents of the two liming agents KSM Beroun and marble powder no significant difference between the synthetic marble powder and the industrial products appeared. The final concentrations in equilibrium state for marble powder was measured with 19.44 ppm and 22.06 ppm; the final concentration of KSM Beroun was 17.57 ppm (- 11.72 % / + 0.15 % / -20.21 % compared to the modeled results (Plummer et al. 1978)). Thermodynamical modeling showed consistence (wateq4f.dat: 22.02 ppm, llnl.dat 21.544 ppm). In addition to occurring inhibition by minor constituents of natural lime products kinetic experiments spiked with Mn and Cd were carried out. Dissolved (metal) ions typical for AMD do have different effects on the kinetic of carbonate dissolution. Figure 4 illustrates the influence of manganese ions on carbonate dissolution.

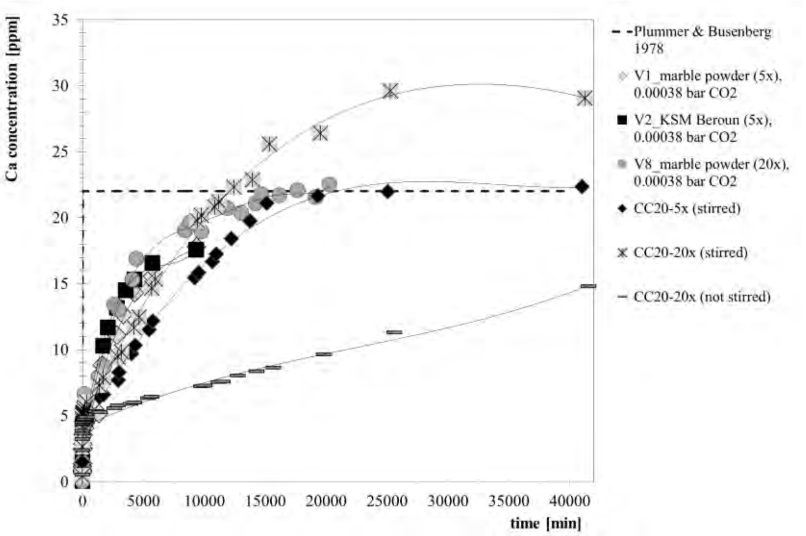

Figure 3 *Development of the calcium concentration over time. Boundary condition: pure water,* p_{CO2} *3.8 ×*10^{-4}*bar.*

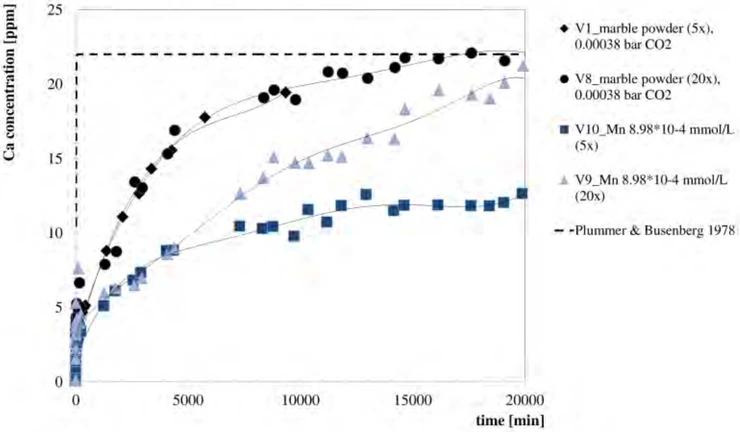

***Figure 4** Development of the calcium concentration in kinetic experiment influence by manganese ions (c_{Mn2+} = 8.98×10^{-4} mmol/L. Boundary condition: pure water, p_{CO2} 3.8×10^{-4}bar, 5-times / 20 times saturated. Plotted curves represent best-fit curves (polynomial).*

The dissolution rates of the marble powder were inhibited by manganese ions in the solution. In comparison with Figure 3, the finally reached concentration of calcium was calculated by 66.4 % compared to the experiment without addition of manganese ions (5-times excess). The experiment with 20-times excess and the addition of manganese as inhibitor showed a time shift until equilibrium was reached (20,000 min instead of 12,000 minutes). The fitted curves of the experiments, however, differ significantly.

As can be seen in Figure 5 the effect of cadmium ions in water has significant influence on carbonate dissolution kinetics. Compared with the general results of calcite dissolution, the final concentration of calcium under consideration of cadmium as inhibitor reached only 12.81 ppm (5-times excess). This equals approximately 58.2% compared to the dissolution in pure water. 20-times excess solution showed a slight higher dissolution reaction. Finally, 14.04 ppm calcium was reached in equilibrium which equals 63.8%. The orange squares in Figure 5 represent calcium concentrations of the experiment (Cd as inhibitor, 5-times excess). It can be seen that the final equilibrium concentration can be reached much faster compared to marble powder in pure water. The curve fits almost the modeled one; without considering the reached equilibrium concentration. The experiment with 20-times saturated conditions is quite different. Here equilibrium seems to be reached within the same period like calcite dissolution in pure water.

Conclusions

As can be seen by the shown examples, water constituents might affect the dissolution rates of possible liming agents. So water composition should be considered if there are ambitious efforts to remediate acidic mine lakes by in-lake liming.

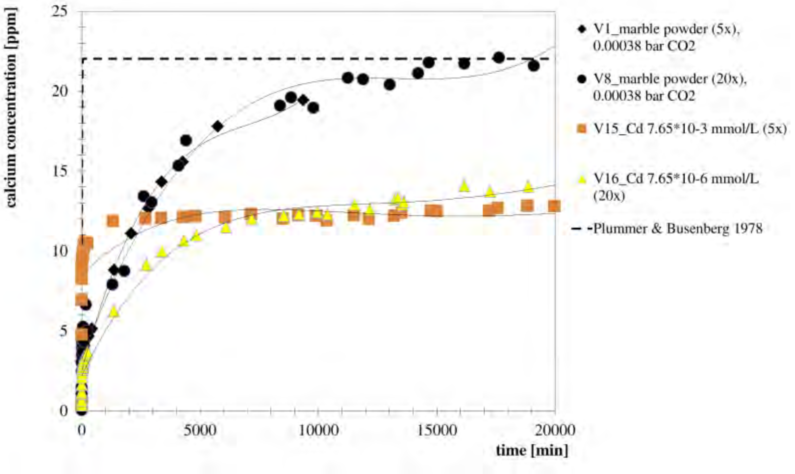

Figure 5 *Development of the calcium concentration in kinetic experiment influence by cadmium ions (c_{Mn2+} = 7.65 × 10^{-6} mmol/L. Boundary condition: pure water, p_{CO2} 3.8 ×10^{-4}bar, 5-times / 20 times saturated. Plotted curves represent best-fit curves (polynomial).*

References

Ahtiainen M, Sandman O & Tynni R (1983) Sysmajarvi - a Lake Polluted by Mining Waste-Water. *Hydrobiologia,* 103, 303-308

Akinfiev Nn & Diamond Lw (2003) Thermodynamic description of aqueous nonelectrolytes at infinite dilution over a wide range of state parameters. *Geochimica et Cosmochimica Acta,* 67, 613-629

Arvidson Rs, Collier M, Davis Kj, Vinson Md, Amonette Je & Luttge A (2006) Magnesium inhibition of calcite dissolution kinetics. *Geochimica et Cosmochimica Acta,* 70, 583-594

Bircumshaw Ll & Riddiford Ac (1952) Transport Control in Heterogeneous Reactions. *Quarterly Reviews,* 6, 157-185

Bozau E, Bechstedt T, Friese K, Frömmichen R, Herzsprung P, Koschorreck M, Meier J, Völkner C, Wendt-Potthoff K, Wieprecht M & Geller W (2007) Biotechnological remediation of an acidic pit lake: Modelling the basic processes in a mesocosm experiment. *Journal of Geochemical Exploration,* 92, 212-221

Buhmann D & Dreybrodt W (1987) Calcite Dissolution Kinetics in the System H_2O-CO_2-$CaCO_3$ with Participation of Foreign Ions. *Chemical Geology,* 64, 89-102

Castro Jm & Moore Jn (2000) Pit lakes: their characteristics and the potential for their remediation. *Environmental Geology,* 39, 1254-1260

Cubillas P, Kohler S, Prieto M, Causserand C & Oelkers Eh (2005) How do mineral coatings affect dissolution rates? An experimental study of coupled $CaCO_3$ dissolution - $CdCO_3$ precipitation. *Geochimica et Cosmochimica Acta,* 69, 5459-5476

Dowling J, Atkin S, Beale G & Alexander G (2004) Development of the Sleeper pit lake. *Mine Water and the Environment,* 23, 2

Dreybrodt W & Gabrovsek F (2000) Comments on: Mixed transport/reaction control of gypsum dissolution kinetics in aqueous solutions and initiation of gypsum karst by Michael A. Raines and Thomas A. Dewers in Chemical Geology 140, 29-48, 1997. *Chemical Geology,* 168, 169-172

Driscoll Ct, Cirmo Cp, Fahey Tj, Blette Vl, Bukaveckas Pa, Burns Da, Gubala Cp, Leopold Dj, Newton Rm, Raynal Dj, Schofield Cl, Yavitt Jb & Porcella Db (1996) The experimental watershed liming study: Comparison of lake and watershed neutralization strategies. *Biogeochemistry,* 32**,** 143-174

Edenborn Hm, Mucci A, Belzile N, Lebel J, Silverberg N & Sundby B (1986) A Glove Box for the Fine-Scale Subsampling of Sediment Box Cores. *Sedimentology,* 33**,** 147-150

Eisenlohr L, Meteva K, Gabrovsek F & Dreybrodt W (1999) The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous H_2O-CO_2 solutions. *Geochimica et Cosmochimica Acta,* 63**,** 989-1001

Guhrén M, Bigler C & Renberg I (2007) Liming placed in a long-term perspective: A paleolimnological study of 12 lakes in the Swedish liming program. *Journal of Paleolimnology,* 37**,** 247

Hemm M, Schlundt A, Kapfer M & Nixdorf B (2002) Beispiele für Neutralisierungsversuche am Steinberger See (Bayern) und Zieselsmaar (Nordrhein-Westfalen) - aus der UBA-Studie „Tagebauseen in Deutschland“. Conference Proceedings, Biogene Neutralisierung, 37-42

Henrikson L, Hindar A & Thornelof E (1995) Freshwater liming. *Water Air and Soil Pollution,* 85**,** 131-142

Iivonen P, Jarvenpaa T, Lappalainen A, Mannio J & Rask M (1995) Chemical, biological and socio-economic approaches to the liming of Lake Alinenjarvi in southern Finland. *Water, Air, and Soil Pollution,* 85**,** 937-942

Koschorreck M, Bozau E, Froemmichen R, Geller W, Herzsprung P & Wendt-Potthoff K (2007) Processes at the sediment water interface after addition of organic matter and lime to an acid mine pit lake mesocosm. *Environmental Science and Technology,* 41**,** 1608

Lea As, Amonette Je, Baer Dr, Liang Y & Colton Ng (2001) Microscopic effects of carbonate, manganese, and strontium ions on calcite dissolution. *Geochimica et Cosmochimica Acta,* 65**,** 369-379

Levich V (1962) Physicochemical Hydrodynamics. Longman Higher Education, 700

Merkel B, Schipek M, Scholz G & Rabe W (2010) Optimierung der Kalkung von Tagebauseen. *Wissenschaftliche Mitteilungen,* 42**,** 51 - 59

Nyberg P & Thornelof E (1988) Operational liming of surface waters in Sweden. *Water, Air, and Soil Pollution,* 41**,** 3

Plummer Ln, Wigley Tml & Parkhurst Dl (1978) Kinetics of Calcite Dissolution in CO_2-Water Systems at 5-Degrees-C to 60-Degrees-C and 0.0 to 1.0 Atm CO_2. *American Journal of Science,* 278**,** 179-216

Pust C, Schüppel B, Merkel B, Schipek M, Lilja G, Rabe W & Scholz G (2010) Advanced Mobile Inlake Technology (AMIT) - An efficient Process for Neutralisation of Acid Open Pit Lakes. Conference Proceedings, International Mine Water Association Symposium - Mine Water and Innovative Thinking, Sydney, Nova Scotia, Canada, 175 - 179

Schipek M, Rabe W, Scholz G, Clauß D, Merkel B & Lilja G (2011) Recent results of the research project OILL (Optimizing In-Lake Liming) Conference Proceedings, 11th IMWA Congress, Aachen, Germany, 457-462

Sjoberg El (1976) Fundamental Equation for Calcite Dissolution Kinetics. *Geochimica et Cosmochimica Acta,* 40**,** 441-447

Sjoberg El & Rickard D (1983) The Influence of Experimental-Design on the Rate of Calcite Dissolution. *Geochimica et Cosmochimica Acta,* 47**,** 2281-2285

Svensson U & Dreybrodt W (1992) Dissolution Kinetics of Natural Calcite Minerals in CO_2-Water Systems Approaching Calcite Equilibrium. *Chemical Geology,* 100**,** 129-145

Sverdrup Hu (1985) Calcite dissolution kinetics and Lake neutralization. Lund Institute of Technology, 170

Vinson Md, Arvidson Rs & Luttge A (2007) Kinetic inhibition of calcite (104) dissolution by aqueous manganese(II). *Journal of Crystal Growth,* 307**,** 116-125