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# A Reacidification Model for Acidified Lakes Neutralized With Calcite

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In lake liming operations in Sweden, acidified lakes are reclaimed by neutralization with calcite powder. The amount added is intended to neutralize the water column as well as to delay the reacidification. The reacidification of limed lakes is dependent on the dilution of the dissolved calcium carbonate with time and, for a limited period of time, the dissolution of calcite from the lake sediments. Calcite on the lake bottom will, in addition to being covered by sedimentation, become inactivated by precipitates of humus and clay minerals clogging the calcite surfaces. A model has been developed to calculate the reacidification of a limed lake which includes the following mechanisms: (1) the dissolution of calcite and a subsequent neutralization of acid water, (2) owing to the increase in *p*H value, occurrence of precipitation of humus and dissolved metals onto the calcite surface and inhibition of the dissolution of calcite (3) reversible sorbtion of calcium from the water column by sediments not covered with calcite, and (4) diffusive transport through a boundary bottom layer to the water column. In a first approach the lake was modeled as a continuously stirred tank. The equations were derived from a mass balance and the dissolution kinetics for calcite to describe the long-term development of *p*H, alkalinity, and calcium concentration in the lake. The differential equations describing the mechanisms were solved with the help of a computer code. The model accurately describes the reacidification and the mass balances observed in several limed lakes.

## INTRODUCTION

Thousands of lakes and rivers in Scandinavia and North America located on low weathering bedrock or surrounded by soils with a low calcite content are suffering from the effects of acid rain. In Norway and Sweden waters in the southern parts of the countries, an area of almost 200,000 km$^2$, will have critical *p*H values during some time of the year. Nearly 40,000 lakes are affected in addition to countless kilometers of rivers and brooks.

The measure most frequently taken is liming of the river or lake affected. This is in fact the only large-scale remedy available until emissions of $SO_2$ and $NO_x$ have been reduced drastically on the European continent. In Sweden, large programs for liming of lakes and running waters are in progress and about $20,000,000 (U.S.) will be spent each year in the final program. It is quite obvious that it is of great importance to use the resources as efficiently as possible.

Acidified lakes in Sweden are reclaimed by distributing calcite powder in the lakes. This neutralizes the acid and restores the alkalinity. A large fraction of the calcite dissolves during sinking, and the rest precipitates on the bottom. This study concerns the dissolution of calcite from the bottom and the modeling the process of reacidification.

In earlier works we have studied several aspects of liming, such as the dissolution of calcite in acidic solution [*Sverdrup and Bjerle*, 1982], calcite dissolution and lake liming [*Sverdrup and Bjerle*, 1983; *Sverdrup*, 1983*a*, *b*; *Warfvinge et al.*, 1984], the transport of substances from the sediments in lakes [*Warfvinge et al.*, 1983], liming of running waters [*Sverdrup et al.*, 1984*a*], a simple model for the reacidification of limed lakes [*Sverdrup et al.*, 1983, 1984*b*; *Sverdrup and Warfvinge*, 1984*a*], integrated mass balances for limed lakes [*Sverdrup and Warfvinge*, 1984*b*], and soil liming [*Warfvinge and Sverdrup*, 1983]. One earlier attempt to make a reacidification model is known to us [*Dillon*, 1984]. However, this model did not take any reaction with residual calcite or any sediment-water interaction into account and therefore failed to simulate the observed results.

## DISSOLUTION OF CALCITE IN LAKES

The dissolution of calcite in dilute acidic aqueous solution can be described as a heterogeneous solid-liquid reaction controlled by diffusion. The chemical reactions involved are

$$CaCO_3(s) + H^+ > Ca^{2+} + HCO_3 \qquad (R1)$$

$$CaCO_3(s) + H_2O + CO_2 > Ca^{2+} + 2HCO_3 \qquad (R2)$$

$$CaCO_3(s) + H_2O > Ca^{2+} + HCO_3 + OH^- \qquad (R3)$$

In natural waters with *p*H values below 5.5 and a carbon dioxide partial pressure less than 0.3 atm, (R1) will dominate, and the dissolution rate will be proportional to the hydrogen ion concentration, while at higher *p*H values, (R3) will dominate. If the carbon dioxide partial pressure exceeds 0.3 atm, (R2) will contribute to the dissolution rate, and it may be increased as much as one order of magnitude [*Bjerle et al.*, 1982].

The backward reaction rate can be shown to be dependent on the hydrogen bicarbonate concentration, and the dissolution rate may be described with the general expression [*Plummer et al.*, 1978]

$$R = k_1(H^+) + k_2(CO_2) + k_3(H_2O) + k_B(Ca^{2+})(HCO_3) \quad (\text{kmol/m}^2\text{s}) \qquad (1)$$

In natural lakes, acidic or limed, the carbon dioxide partial pressure will usually be much less then 0.3 atm, and the expression for the dissolution rate at *p*H values below 5.5 may be simplified to

$$R = k_1(H^+) \quad (\text{kmol/m}^2\ \text{s}) \qquad (2)$$

and at *p*H values between 5.5 and 8,

$$R = k_1(H^+) + k_W - k_B(Ca^{2+})(HCO_3^-) \quad (\text{kmol/m}^2\ \text{s}) \qquad (3)$$

where the last term takes the backward reaction at high alkalinities into account, and $k_w$ accounts for the effect of the reaction with water and carbon dioxide. In open systems this may be approximated as a constant factor.

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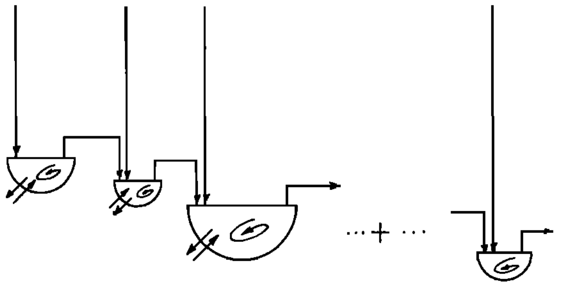

Fig. 1. A simple model may simulate a series of lakes as a series of stirred tank reactors with variable flow and chemical reaction on the tank walls.

Several coupled mechanisms will influence the dissolution rate of calcite from the bottom: (1) the dissolution of calcite and a subsequent increase in the *p*H value due to the neutralization of the acid, (2) owing to the increase in *p*H value, occurrence precipitation of humates and metal complexes on the calcite surfaces and inhibition of the dissolution of calcite, and (3) owing to the increase in the calcium concentration in the water column, entrance of calcium into ion exchange with hydrogen ions in the sediments.

The dissolution rate for calcite in the lake sediment may be expressed as

$$-(dm/dt) = R\ A\ B(t) \quad \text{(kmol/s)} \qquad (4)$$

where $R$ is the reaction rate and $A$ the available mineral surface area for dissolution and $B(t)$ the deactivation function. If the area is expressed as a fraction of the lake bottom area, for the simple case where the reaction takes place far from calcite saturation, we may use a truncated form of equation (3) to obtain

$$-(dm/dt) = (k_1\text{H}^+ + k_W)A_LPB(t) \quad \text{(kmol/s)} \qquad (5)$$

The sorption of calcium to the sediments will be diffusion limited, and the exchange rate can be described by

$$-(dS/dt) = k_A A_S(\text{Ca}^{2+}) - k_S S \quad \text{(kmol/s)} \qquad (6)$$

where $k_A$ is the adsorption rate coefficient and $k_S$ the desorption rate coefficient. The area active in sorption is $A_S$, the sediment surface area without calcite cover.

### HYDROLOGY OF CHEMICAL LAKE REACTORS

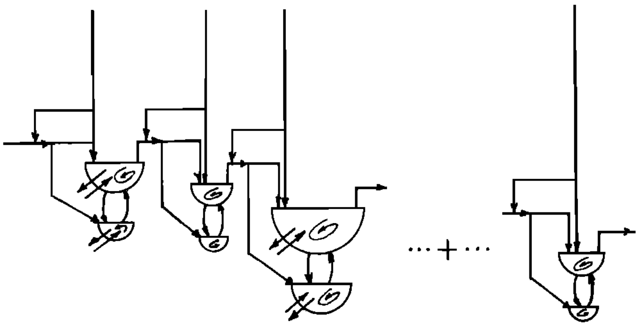

Fig. 2. A more complicated structure is needed when the stratification of lakes are to be considered. Each lake is modeled as two-tank reactors during the stratification period which are merged at every turnover.

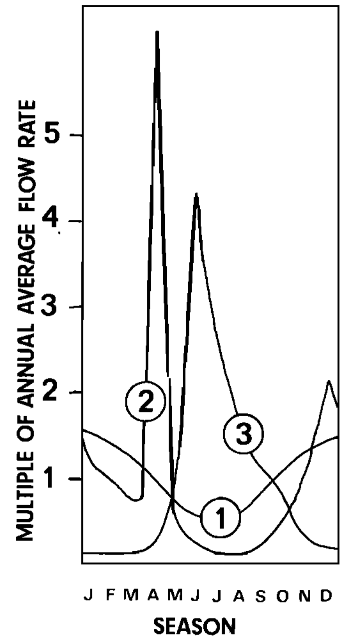

Fig. 3. The three seasonal variation types used in the model is a simplification of classifications introduced by *Gottschalk et al.* [1979]. They apply for 1, coastal regions; 2, inland regions; and 3, mountain regions. The location of these regions in Scandinavia are shown on the map in Figure 4.

The hydrology of most lakes varies substantially with the seasons. The two main reasons for this are the seasonal variations in the tributary flow rate and the thermal stratification of lakes.

The stratification may in shallow lakes reach such a depth that the volume under the thermocline, the hypolimnion, becomes small compared to the total lake volume. In such a case the stratification of the lake will have little influence on resi-

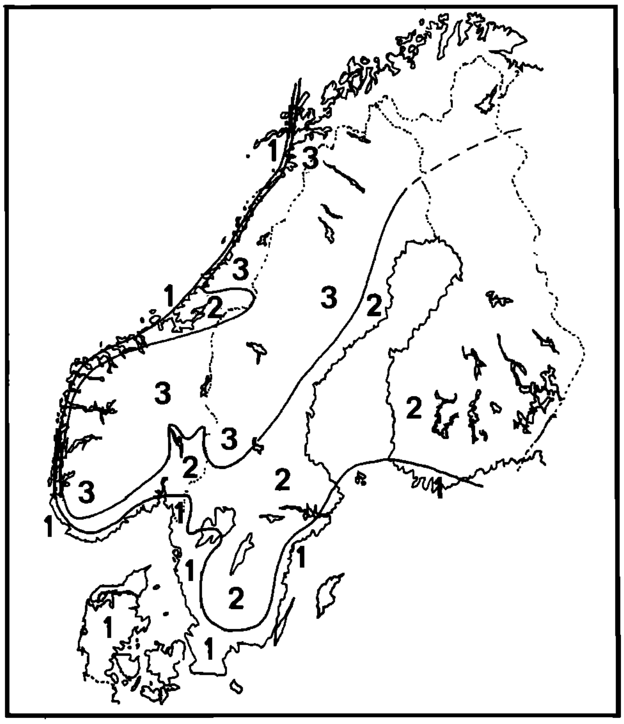

Fig. 4. The map shows to which region the different runoff variation types used in the model apply. They are 1, coastal regions; 2, inland regions; and 3, mountain regions.

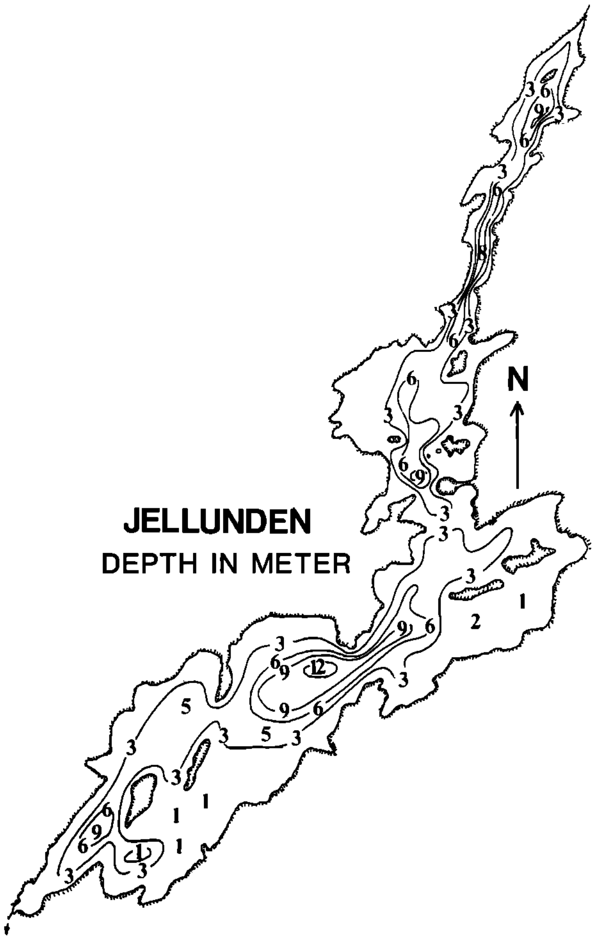

Fig. 5. Bathymetric map of the lake Jellunden in the province of Halland. The map is based on 97 shots in the lake.

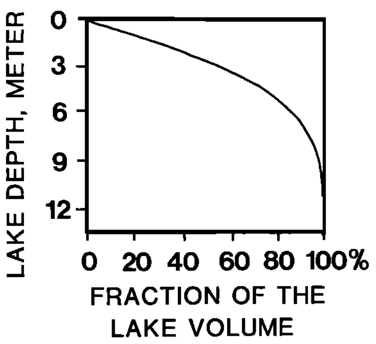

Fig. 6. Hypsographic curve for the lake Jellunden based on the bathymetric map. It may be seen that the volume beneath the 6 m line is very small, making the hypolimnion of the lake less than 10 percent of the total volume.

dence time variations in relation to the influence caused by the tributary flow rate variation. Such a system may well be modeled as a stirred tank reactor with variable flow rate.

The residence time distribution will be influenced by both the stratification and the flow variations in deeper lakes with short residence times. A two-tank reactor model will be able to describe the system in which the two tanks are merged at every turnover and the flow rate varies with the seasons.

In deeper lakes where the residence time is considerably longer than each stratification period, the lake may be considered to be fairly well mixed during one residence time period. Accordingly, the lake may be modeled with a one-tank model with variable flow rate. Stagnant zones or separated basins generally contain a very small fraction of the lake volume or the water exchange is not sufficiently restricted over the actual time periods involved.

## MODEL STRUCTURES

On the basis of the considerations discussed above, two model structures of different complexity were designed in order to model the lake reacidification process after liming. The first and the simplest structure is shown in Figure 1 and models each lake in a system as a stirred tank with variable inlet flow.

The more complex structure is shown in Figure 2 and accounts for the stratification by modeling each lake as two stirred tanks with variable inlet flow rate. The model is reduced to a one-tank model at every turnover when the lake is completely mixed. The model will calculate the position of the thermocline, and the water is exchanged across it.

The seasonal runoff variations may be divided into different classes. The classification of *Gottschalk et al.* [1979] was simplified into three types of seasonal runoff regimes: (1) variations typical of coastal regions, (2) variations typical of inland regions, and (3) variations typical of mountain regions. All three types are shown in Figure 3, and the geographical region to which they apply is shown on the map in Figure 4.

## MASS BALANCES USED

For each tank in the model structure a complete mass balance is made for the components to be calculated. The inlet

TABLE 1. Input Data Used in Model Calculation of the Reacidification of the Lakes Jellunden and Nedre Sernamannasjön

| Data | Jellunden | Nedre Sernamannasjön |
|---|---|---|
| Initial *p*H after liming | 6.5 | 6.7 |
| Average *p*H in the tributary | 5.0 | 5.1 |
| Calcium concentration after liming | 6.0 mg/L | 3.6 mg/L |
| Calcium concentration in the tributary | 2.8 mg/L | 0.4 mg/L |
| Lake volume | $37.5 \times 10^6$ m$^3$ | $0.66 \times 10^6$ m$^3$ |
| Lake depth | 4.4 m | 2.0 m |
| Residence time | 1.45 years | 0.3 years |
| Amount calcite on the bottom | 1000 tons | 20 tons |
| Fraction of the bottom covered by calcite | 7% | 5% |

The data are actual physical and chemical data estimated from the records kept at the Swedish National Board of Fisheries and the Swedish Environmental Protection Agency.

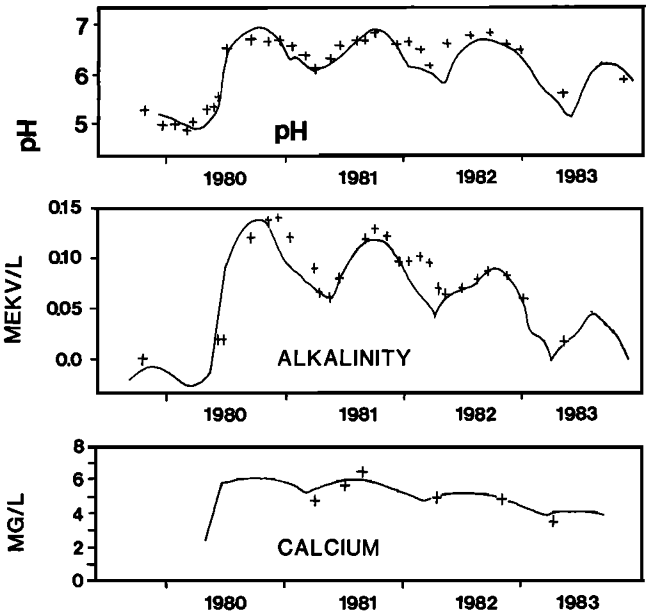

Fig. 7. The model calculation for the reacidification of Jellunden is shown by the bold line, together with the observed data (crosses).

flux from the tributaries plus the amount dissolved or neutralized ($dm/dt$) is balanced by the accumulation in the lake volume $V$ plus the amount sorbed to the sediment ($dS/dt$) plus the outlet flux:

$$(Q_iC_i) + (dmdt) = V(dC/dt) + (dS/dt) + Q_uC \quad \text{(kmol/s)} \qquad (7)$$

where the sum of the discharge of $n$ tributaries is assumed to be equal to the outlet flow:

$$\sum_{i=1}^{n} (Q_i) = Q_u \quad (\mathrm{m^3/s}) \qquad (8)$$

The lake volume is assumed to be constant, which is nearly true for deeper lakes and more approximate for shallow lakes. Each tank is assumed to be well mixed, and the concentration in the lake is assumed to be equal to the concentration at the outlet.

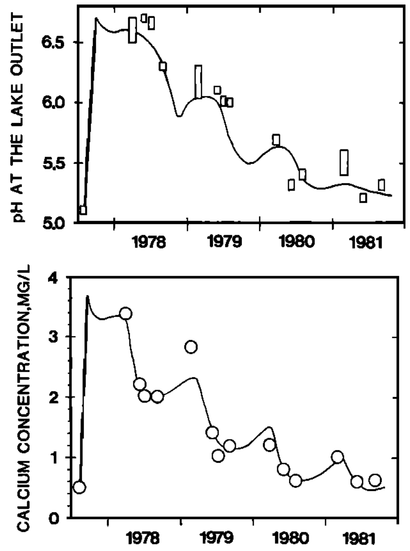

Fig. 8. The calculated $p$H and calsium concentrations for Nedre Sernamannasjön (solid curve) shown together with the observed values (open circles). The residence time for the lake is approximately 0.3 years. The bars indicate inaccuracies in the measurements.

The mass balance may be rephrased to a differential equation:

$$(dC/dt) - [(dm/dt) - (dS/dt)]/V + \left(C - \sum_{i=1}^{n} C_i\right)Q_u/V = 0 \quad \text{(kmol/m s)} \qquad (9)$$

where the dissolution ($dm/dt$) is given by (5) and the sorption ($dS/dt$) by (6). The calcite deactivation function is usually approximated with an exponential expression [*Sverdrup et al.*, 1984*a*]. It was chosen to work with the mass balaces for hydrogen ion and calcium, to calculate the alkalinity from a titration curve, to assume that the carbonate system is approximately at equilibrium in the water column, and to consider the alkalinity as dependent on the concentrations of the hydrogen ion and calcium. The lake was also assumed to be an open system to the atmosphere with respect to carbon dioxide.

## NUMERICAL CALCULATIONS

A computer code was written to solve the differential equations numerically with the Runge-Kutta algorithm and calculate the reacidification of a limed lake. The code was written for a small personal computer to facilitate model availability.

The simple model structure will need the following input data which are among those usually provided in Swedish lake liming projects or may be easily estimated from the following: (1) initial $p$H in the lake after liming, (2) annual average $p$H in the tributary, (3) initial calcium concentration after liming (in milligrams per liter), (4) average calcium conc in the tributary (in milligrams per liter), (5) amount of calcite on the bottom of the lake (tons), (6) fraction of the bottom covered by calcite (in percent), (7) mean lake depth (in meters), (8) lake volume (in $10^6$ m$^3$), and (9) average residence time (in years). For all Swedish lake liming projects, plans are made that describe the total amounts of calcite to be spread and its spatial distributions over the lake surface. The amount on the bottom may be estimated from the total amount distributed and the amount instantly dissolved. The fraction of the bottom fully covered by calcite may be estimated from the spatial distribution of calcite powder over the lake surface and the amount on the lake bottom [*Sverdrup et al.*, 1984*a*].

TABLE 2. Input Data Used for Model Calculation for Lake Lysevatten

| | Value |
|---|---|
| $p$H in the epilimnion after liming | 7.4 |
| $p$H in the hypolimnion after liming | 5.0 |
| $p$H in the tributary | 4.9 |
| $p$H of the precipitation | 4.2 |
| Calcium concentration in the epilimnion after liming | 7.4 mg/L |
| Calcium concentration in the hypolimnion after liming | 1.7 mg/L |
| Calcium concentration in the tributaries | 1.6 mg/L |
| Calcium deactivation rate | 0.8 yr$^{-1}$ |
| Mean lake depth | 4.7 m |
| Maximum lake depth | 17.0 m |
| Lake volume | 1.9 × $10^6$ m$^3$ |
| Lake surface as fraction of the watershed | 33.0% |
| Amount calcite on the bottom | 30 tons |
| Fraction of the epilimnic bottom covered by calcite | 25% |
| Fraction of the hypolimnic bottom covered by calcite | 0% |

The data are actual estimates from *Hultberg and Andersson* [1982].

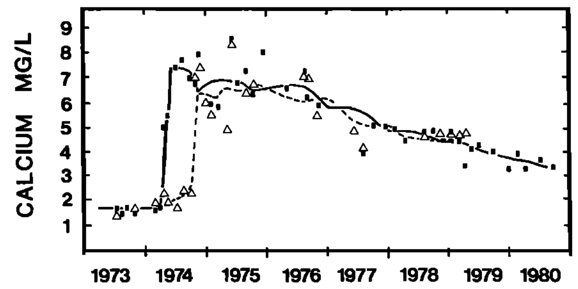

Fig. 9. The initial stages after liming in the lake Lysevatten on the Swedish west coast. The lake was limed in the littoral zones only, neutralizing the epilimnion but not the hypolimnion. The figure shows the calculated calcium concentration (solid curve) and the observed data for the epilimnion (solid squares) and in the hypolimnion (dashed curve and triangles).

In addition, the tributary flow variation type is indicated with a number that can be read from the map in Figure 4: (10) tributary flow variation type. If whole series of lakes are to be modeled the modeler needs to know the fraction of the tributary input coming from an upstream modeled lake (as in data). The deactivation rate for calcite on the bottom and the sorption rate were kept constant internally in the model. The deactivation rate has been determined from large amounts of lake liming data [*Sverdrup and Bjerle*, 1983; *Sverdrup et al.*, 1984*a*, *b*; *Bengtsson et al.*, 1981] and was set at 0.6 $y^{-1}$.

## Calculations for the Lakes Jellunden and Nedre Särnamannasjön

The model was used to calculate the reacidification of lake Jellunden in the province of Halland in southwest Sweden [*Sverdrup et al.*, 1984*a*]. The lake was limed in 1980 with 1800 tons of calcite powder classified as 0–0.2 mm; 1400 tons were spread in the lake, mostly in the littoral zone; the rest was spread as coarse gravel in a tributary. Experiences from the Swedish Experimental Liming Program [*Bengtsson et al.*, 1981] indicate that liming with coarse gravel seldom works, and accordingly it was assumed that the gravel had no significant effect on the lake chemistry.

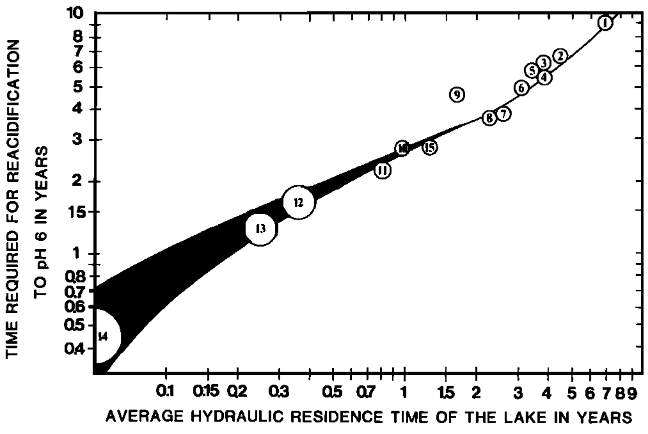

Fig. 10. The time required for an average limed lake to reacidify to *p*H 6.0 may be read as dependent on the residence time for the lake. The diagram was calculated for a lake with a volume of 1.5 × $10^6$ $m^3$ and 5 m average depth with the model. The numbered circles represent observed reacidification times for the lakes: 1, Hornasjön; 2, Övre Bolsjön; 3, Lysevatten; 4, Smedvatten; 5, Ski tjern; 6, Blomman; 7, Södra Blötevatten; 8, Bredvatten; 9, Stensjön; 10, Grytsjön; 11, Ekelidvattnet; 12, Nedre Sernamannasjön; 13, Tarmlången; 14, Kolabodasjön; 15, Jellunden. The lake volume in the lakes vary from 0.4 to 37.5 × $10^6$ $m^3$ and the depth from 2 to 15 m. Lake liming will hardly produce a stable result in lakes with residence times shorter than half a year. In such lakes strategies for liming running waters may be more successful. Lakes with residence times longer than 3 years will have their reacidification rate mostly determined by the flushing rate. The diagram applies to a bottom cover of calcite, *P* from 0.05 to 0.30 and a bottom residual of calcite between 0.2 and 0.8 ton/ha.

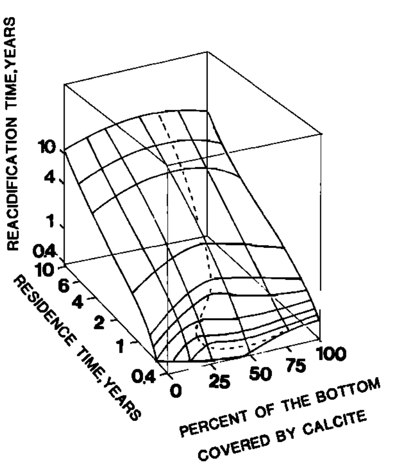

Fig. 11. The response surface for the reacidification time in terms of hydrological residence time and fraction of the bottom with calcite cover after liming (*P*).

The bathymetric map of Jellunden, based on 97 measurements (Figure 5), was used to make the hypsographic curve in Figure 6 for the lake. It indicates that the volume of an eventual hypolimnion will be small compared to the total lake volume if it is assumed that the thermocline reaches a depth of 6–8 m. This allowed us to use a one-tank model for the calculation.

The data needed for the calculation are listed in Table 1. The lake was monitored by the local authorities from the date of liming till the reliming in late 1983. These data for *p*H, alkalinity, and calcium are shown together with the calculated values in Figure 7.

Lake Nedre Sernamannasjön is a mountain lake in the province of Dalarna, Sweden. It is rather small and has a short residence time, 0.3 years. The lake was limed in October 1977 with 44 tons of a coarse calcite powder classified as 0–1 mm. Half the amount was spread in the lake, and the rest was spread on land around the lake. The lake chemistry was monitored by the Swedish Environmental Protection Agency after the liming of the lake [*Sverdrup et al.*, 1984*c*].

The input data used for the calculation of the reacidification are found in Table 1. The observed *p*H and calcium concentrations are shown together with the calculations in Figure 8. It can be clearly seen that the calculations follow the observations accurately.

## Stratification Model

The more complicated model structure shown in Figure 2 may be used to calculate the reacidification of a stratified lake. This model structure requires some additional data in order to work: (1) *p*H in the epilimnion after liming, (2) *p*H in the hypolimnion after liming, (3) calcium concentration in the epilimnion after liming (in milligrams per liter), (4) calcium concentration in the hypolimnion after liming (in milligrams per liter), (5) average *p*H in the tributary, (6) average calcium concentration in the tributary (in milligrams per liter), (7) amount of calcite on the lake bottom (in tons), (8) fraction of the epilimnic bottom covered by calcite (in percent), (9) fraction of

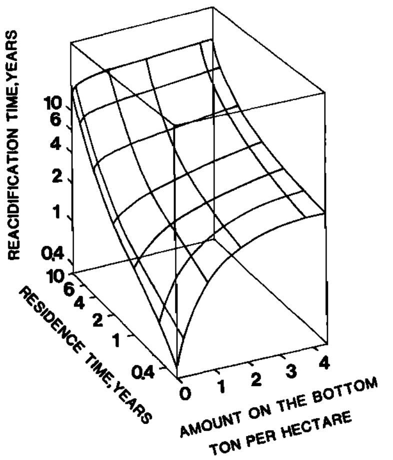

Fig. 12. The responce surface for the reacidification time in terms of hydrological residence time and amount calcite on the bottom after liming.

the hypolimnic bottom covered by calcite (in percent), (10) mean lake depth (in meters), (11) maximum lake depth (in meters), (12) lake volume (in $10^6 m^3$), (13) residence time (in years), (14) lake surface area as a fraction of the watershed area, and (15) tributary flow variation type. This model does not have the same practical applicability in operational liming as the simpler model, as the complete set of input data needed is available only in a few special liming projects. The model was used to calculate the initial stages after the liming of the lake Lysevatten near the city of Göteborg on the Swedish west coast. It is a clear water lake of medium size, an average depth of 4.7 and a maximum depth of 17.

Lysevatten was limed in May 1984 with 60 tons of "T-slag", an industrial waste product composed of different calcium silicates. The dissolution kinetics of "T-slag" appear to be similar to the kinetics of calcite [*Sverdrup*, 1983*a*]. The lake was limed mainly in the littoral zone, which caused neutralization of the epilimnion only. The hypolimnion remained acidic from the liming in May 1974 until the turnover in the fall the same year. The chemistry of the lake was carefully monitored by *Hultberg* [1982] of Institute for Water and Air Pollution (IVL) in Göteborg from 1973 until present.

A calculation for the lake was done, using the data in Table 2. The stratification becomes less important for the later stages of the reacidification as the residence time of the lake, 3.7 years, spans over several turnover times. The calculation for the calcium concentration after liming is shown in Figure 9 together with the observations. The transport across the thermocline was modelled as turbulent diffusion across a boundary layer [*Warfvinge et al.*, 1983]. It can be seen that the concentrations in the epilimnion and the hypolimnion will converge after approximately one residence time.

The sediments not receiving calcite consumed calcium and alkalinity from the water column, as only a small fraction of the lake bottom was covered with calcite. In Lysevatten it may be calculated that the sediments consumed approximately 0.2 tons calcite per hectare, which is in good agreement with what can be observed in other lakes [*Sverdrup and Warfvinge*, 1984*b*].

## DISCUSSION

The simple model structure gives rather accurate predictions for the reacidification of limed lakes. It may be used to relate the residence time of a lake to the time required to reacidify a limed lake to *p*H 6.0, which the Swedish authorities define as the point for reliming [*Bengtsson et al.*, 1981]. Figure 10 indicates the observed reacidification time for limed lakes. The curve is valid for bottom dosages in the range 0.2–1.3 ton calcite per hectare.

By doing a sensitivity analysis for the different parameters, those with the strongest influence on the reacidification rate may be identified. The four most important factors determining the reacidification rate may be identified as hydrological residence time, amount of calcite on the bottom, fraction of the bottom with calcite cover, and acicity of the tributaries. Other important parameters are stratification, sediment ion exchange, calcite deactivation rate, and supply of acidic organic matter with the tributaries. These are of lesser importance compared with the first four or do not vary very much between the different limed lakes.

Figure 11 is a drawing of the response surface for the reacidification in terms of hydrological residence time and the fraction of the bottom with calcite cover. It can be seen that there is a maximum in reacidification time. Optimally, the fraction of the bottom with calcite should be 0.25–0.50. It can be seen that to limit the calcite distribution to the littoral zone only, which leads to a calcite bottom cover in the range 0.05–0.10, is far from optimal.

An indication of the importance of the amount of calcite on the bottom is given by Figure 12. It shows the response surface for the reacidification time in terms of hydrological residence time and amount of calcite on the bottom.

Studies of limed lakes with the model and a survey of data from lake limings allow us to divide the diagram in Figure 11 into three zones. In lakes with residence times longer than 3 years, the residence time will be substantially longer than the deactivation time for calcite on the bottom. Accordingly, the time required for reacidification will be mainly determined by the flushing rate and calcite dissolving from the bottom will be of less importance.

Residence times between 3 years and 1/2 year will be of approximately the same order of magnitude as the calcite deactivation time. For such lakes the dissolution will be able to prevent reacidification the first year after liming, after which the flushing rate will be the main determining factor for the reacidification rate.

For lakes with residence times shorter than 1/2 year, lake liming does not necessarily produce a stable result. The *p*H shocks may break through in the system at periods with high flow and ruin the liming result. Such lakes are often more

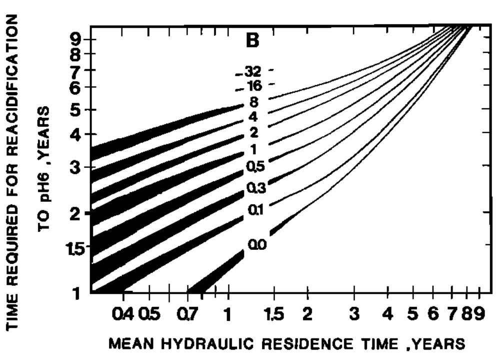

Fig. 13. General diagram to estimate the reacidification time. The factor *B* combines the effect of the residual amount calcite on the bottom after liming, the fraction of the bottom area with calcite cover and sediment–lake water interactions. *B* is defined as $(M_B/A_L)$ $(P/0.20)$ and expressed as ton calcite per hectare.

adequately treated with methods for the liming of running water.

Studies of integrated mass balances for limed lakes [*Sverdrup and Warfvinge*, 1984*b*] together with model studies indicate the 1–2.0 tons of calcite per hectare lake bottom will be able to dissolve before the deactivation virtually brings the dissolution to a halt. This stresses the fact that it is of no use to pile large amounts of calcite on the lake bottom or in narrow littoral zones and hope it will dissolve. The limited amount of wave actions in the littoral zone of a lake is far from enough to prevent the deactivation to take place [*Sverdrup et al.*, 1984*a*].

It is important that the model works with physical parameters that can be easily determined. No calibrations or "rubber parameters" are needed. This strengthens the general applicability of the model.

Having identified the most important parameters for the reacidification rate, the model may be used to make a general diagram for predicting the approixmate time required for reacidification of a lake. In Figure 13 an attempt has been made to combine some of the most important parameters. The time for reacidification may be read from the diagram as a function of the hydrological residence time and the calcite load factor $B$, defined as

$$B = (M_B/A_L)(P/0.20) \quad \text{ton/ha}$$

where $M_B$ is the amount of calcite on the bottom, to the lake surface area, and $P$ is the fraction of the bottom area with calcite cover.

## NOTATION

| | |
|---|---|
| $\sum_{i+1}^{n} a$ | sum of all elements from $a_1$ to $a_n$; $a_1 + a_2 + \cdots + a_2$. |
| $A$ | calcite surface area, m. |
| $A_L$ | lake bottom area, $m^2$. |
| $A_S$ | lake bottom participating in sorption, $m^2$. |
| $B(t)$ | deactivation function. |
| $C$ | concentration, $kmol/m^3$. |
| $C_i$ | concentration in tributary $i$, $kmol/m^3$. |
| $i$ | index. |
| $K_1$ | mass transfer coefficient for hydrogen ion, m/s. |
| $K_2$, $K_3$ | mass transfer related reaction rate coefficients. |
| $K_A$ | adsorption coefficient, m/s. |
| $K_D$ | desorption coefficient, m/s. |
| $K_B$ | dissolution back reaction coefficient, $m^4$/kmol s. |
| $K_W$ | reaction rate coefficient for the reaction of calcite with water, $kmol/m^2$ s. |
| $m$ | mass. |
| $M_B$ | amount calcite on the bottom after liming, ton. |
| $n$ | number of tributaries. |
| $P$ | calcite surface area as fraction of the lake bottom surface area. |
| $Q_i$ | flow rate in the tributary $i$, $m^3/s$. |
| $Q_u$ | flow rate at the lake outlet, $m^3/s$. |
| $R$ | reaction rate, $kmol/m^2$ s. |
| $S$ | sorbed amount, kmol. |
| $t$ | time, s. |
| $V$ | lake volume, $m^3$. |

Differentials

| | |
|---|---|
| $dC/dt$ | concentration change with time, $kmol/m^3$ s. |
| $dm/dt$ | dissolved mass with time, kmol/s. |
| $dS/dt$ | sorbed mass with time, kmol/s. |

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## REFERENCES

Bengtsson, B., et al., Kalkning av sjöar och vattendrag 1977-1981. Information från Sötvattenslaboratoriet, *Drottningholm, 1981*, 4, 1981.

Bjerle, I., G. Rochelle, and H. Sverdrup, Limestone dissolution in acid lakes, *Vatten, 38*, 156–163, 1982.

Dillon, P. J., The use of mass balances and mass balance models for the quantification of the effects of anthropogenic activities on lakes near Sudbury, Ontario, in *Environmental Impacts by Smelters*, edited by J. Nriagu, pp. 283–347, John Wiley, New York, 1984.

Gottschalk, L., J. Jensen, D. Lindquist, R. Solantie, and A. Tollan, Hydrological regions in the Nordic countries, *Nord. Hydrol., 10*, 273–286, 1979.

Hultberg, H., and I. Andersson, Liming of acidified lakes: Induced long term changes, *Water Air Soil Pollut., 18*, 311–331, 1982.

Plummer, L. N., T. M. L. Wigley, and B. L. Parkhurst, The kinetics of calcite dissolution in $CO_2$-water systems at 5°C to 50°C and 0.0 to 1.0 atm $CO_2$, *Am. J. Sci., 273*, 179–216, 1978.

Sverdrup, H., Lake liming, *Chem. Scr., 22*, 12–18, 1983*a*.

Sverdrup, H., Calcite dissolution and acidification mitigation strategies, paper presented at the International Symposium on Lake and Reservoir Management, EPA/Tennessee Valley Authority, Knoxville, Tenn., Oct. 18–20, 1983*b*.

Sverdrup, H., and I. Bjerle, Dissolution of calcite and other related minerals in acidic aqueous solution in a *p*H-stat, *Vatten, 39*, 59–73, 1982.

Sverdrup, H., and I. Bjerle, The calcite utilization efficiency and the long term effect on alkalinity in several Swedish lake liming projects, *Vatten, 39*, 41–54, 1983.

Sverdrup, H., and P. Warfvinge, Omsettningstidens innflytelse på resultatet av en sjökalkning, *Vatten, 40*, 10–17, 1984*a*.

Sverdrup H., and P. Warfvinge, Integrerte massebalanser for kalkede sjöer, *Vatten, 40*, 369–382, 1984*b*.

Sverdrup, H., et al., Kalkning av rinnande vatten, paper presented at symposium, Alvesta, Sweden, Sept. 13, 1983. (Translated into English in 62nd Bimonthly report, Battelle Memorial Institute, Columbus, Ohio, 1983.)

Sverdrup, H., R. Rasmussen, and I. Bjerle, A simple model for the reacidification of limed lakes, taking the simultaneous deactivation and dissolution of calcite in the sediments into account, *Chem. Scr., 23*, 199–208, 1984*a*.

Sverdrup, H., P. Warfvinge, and I. Bjerle, Modellberegning og igjenforsurningsprognose for sjöen Jellunden, kalket i 1980 og 1984, *Vatten, 40*, 164–176, 1984*b*.

Sverdrup, H., P. Warfvinge, and I. Bjerle, Modellberegning for Nedre Sernamannasjön, *Vannet Norden, 1*, 16–25, 1984*c*.

Warfvinge, P., and H. Sverdrup, Soil liming and runoff acidification mitigation, paper presented at the International Symposium on Lake and Reservoir Management, EPA/Tennessee Valley Authority, Knoxville, Tenn., Oct. 18–20, 1983.

Warfvinge, P., H. Sverdrup, and I. Bjerle, Mass transfer from sediments treated with chemicals, *Vatten, 40*, 337–345, 1983.

Warfvinge, P., H. Sverdrup, and I. Bjerle, Dissolution of calcite powder sinking in an acidic solumn of water in relation to a theoretical lake liming model, *Chem. Scr., 24*, 67–74, 1984.

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