

# Kinetic aspects of different procedures for the adjustment of the pH-value: steps against acidification and for buffering of drinking water and dam water bodies

Thomas Striebel and Thomas Willuweit

## ABSTRACT

A new treatment method for acidic and aggressive water is presented. This method evades high pH-values and the difficulties in the prediction of the end-pH-values. Most of the kinetic problems of other treatment methods are not relevant here.

Difficulties in the prediction of end-pH-values are caused by the fact that phase transitions are not considered sufficiently. Even under evaluation of these transitions the predicted end-pH-values are not attained, because kinetic aspects are ignored.

Base addition and calcite treatment influence mainly the pH. Calcite saturation frequently appears at  $\text{pH} > 9$ . Then, new solution of  $\text{CO}_2$  causes decreasing pH and new calcite aggression. Often, solution kinetics of calcite are too slow to establish saturation.

In most cases the new treatment method with mixed salts (the CarbonAdd principle) enables a predictable rise in both pH-value and buffer capacity. The saturation index of calcite is adjustable without negative effects on the saturation state of  $\text{CO}_2$ . Thus, no new  $\text{CO}_2$  solution will influence the treated water. The result is a well buffered, stable water with an adjusted calcite saturation index and a pH-value around 8.

**Key words** | acidification, buffer capacity, dam water treatment, drinking water treatment, kinetic aspects, pH adjustment

**Thomas Striebel** (corresponding author)  
Söll,  
Schleizer Straße 105,  
D-95028 Hof  
Present Address: Geo-Applica,  
Ahornweg 3,  
D-95445 Bayreuth  
Tel: +49 921 460 07 99  
Fax: +49 1212 6 787 43 235  
E-mail: [striebel@seensanierung.de](mailto:striebel@seensanierung.de)

**Thomas Willuweit**  
Söll,  
Schleizer Straße 105,  
D-95028 Hof  
E-mail: [willuweit@soelltec.de](mailto:willuweit@soelltec.de)

## INTRODUCTION

The paper presents a new treatment method for acidic and aggressive water bodies and a comparison with some other methods. The experiments and calculations have been carried out with acid raw water from the Falkenstein dam water body, Erzgebirge, Germany (Ulrich & Paul 2000; Ulrich *et al.* 2000). The new method evades high pH-values and the difficulties in the prediction of the end-pH-values. Most of the kinetic problems of other treatment methods are not relevant here.

There are different reasons for the requirement of measures for water treatment in order to adjust the pH-value or to affect the system of calcium carbonate and carbonic acid. Frequently, raw water that is too acidic or aggressive must be treated and must be hardened for drinking water purposes. Water undersaturated in calcite

must be saturated. Acidic drinking dam water bodies are treated with the aim of raising the pH-value and the buffer capacity.

Difficulties in an exact prediction of the end-pH-values are frequently caused by the fact that phase transitions (solution and degassing of  $\text{CO}_2$ , solution and precipitation of calcite) are not sufficiently considered. Even under exact evaluation of these transitions by difficult thermodynamic calculations the predicted end-pH-values are not necessarily attained, because the kinetic aspects are not taken under consideration. Therefore, problems caused by slow reactions are important disadvantages of some treatment methods and should be avoided by the choice of better methods.

## SODA OR BASE TREATMENT METHODS

Treatments like addition of soda ( $\text{Na}_2\text{CO}_3$ ) or base ( $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ ) influence only the pH-value, but not the hardness and buffer capacity. The pH-value can be raised significantly and rapidly with only a small input of material. However, a very precise dosage and a good mixing is required; this cannot be guaranteed in every case. The disadvantage of these substances is that calcite saturation frequently appears at pH-values above 9.

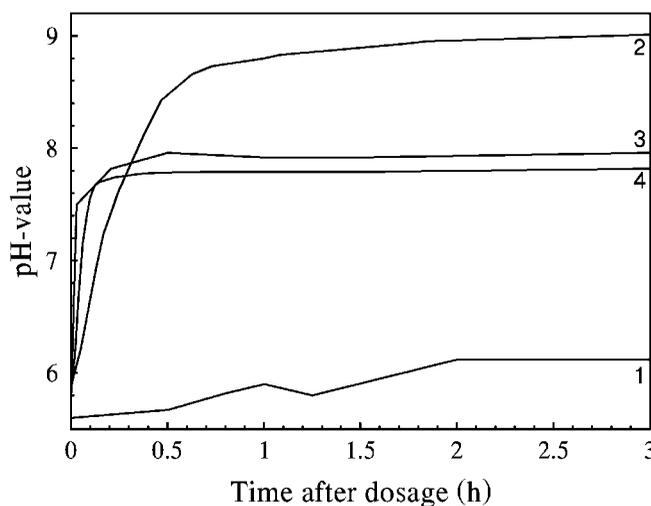
A distinct undersaturation of  $\text{CO}_2$  frequently results from such a treatment. Thus, the water is unstable. With decreasing pH-values due to the solution of  $\text{CO}_2$  a new calcite aggressivity will result. Then the water no longer meets drinking water regulations.

## CALCITE TREATMENT

Treatment with calcite for hardening will also raise buffer capacity and pH-value. The solution kinetics of calcite are very slow, however, especially if only a slight undersaturation exists (Plummer *et al.* 1978; Dreybrodt 1988). When the turbulence or residence time is sufficient the speed of calcite solution may be satisfactory. However, acidified waters frequently show a low  $\text{CO}_2$  content. Not much calcite can be dissolved in such water bodies, even when the equilibrium state is reached. An addition of calcite can raise the pH-value, therefore, to values around 9, without the solution of considerable quantities of calcite. The buffer capacity is raised only insignificantly.

Due to the jump in the pH-value,  $\text{CO}_2$  is undersaturated after the treatment. Further solution of  $\text{CO}_2$  causes a gradual decrease in pH-value. Then the water shows calcite aggressivity again. It is hard to predict the speed of this phase transition and the end-pH-values. If calcite is no longer available due to sedimentation in the dam water body or filtration in the treatment facilities, compensation by way of new dissolution of calcite is not possible.

Consequently, the application of calcite is ineffective, the results can hardly be calculated and even less controlled. The buffer capacity can hardly be raised.



**Figure 1** | Dissolution experiments, calcite and reference mixture no. 1 (for numbering see text).

## THE NEW TREATMENT METHOD: MIXED SALTS

In most cases, treatment with mixed salts (CarbonAdd; Willuweit *et al.* 1995; for example  $\text{NaHCO}_3$  with  $\text{CaCl}_2$  and  $\text{CaCO}_3$ , 'SOCAL') enables a fast, problem-free and predictable rise in pH-value. Simultaneously, buffer capacity is raised. In special cases a decrease in pH-value can also be achieved, if necessary (Schuster *et al.* 1999). The saturation index of calcite is adjustable without an important effect on the saturation state of  $\text{CO}_2$ . The result is a well-buffered, stable water body with an adjusted saturation index of calcite and an ideal pH-value around 8.

## COMPARISON OF CALCITE TREATMENT WITH THE TREATMENT METHOD OF MIXED SALTS: KINETIC ASPECTS

Four experiments have been conducted in 60-l buckets filled with acid raw water from the Falkenstein dam water body. Figure 1 shows the results, with the numbering of the graphs corresponding to the numbering of the experiments.

In experiment no. 1 the water was treated with  $60 \text{ g m}^{-3}$  calcite powder. This charge is three times more than the necessary charge to establish calcite saturation. To simulate the absence of turbulent conditions in a dam water body, the water was not stirred. The quantities of calcite dissolving within 3 h are insignificant. Therefore, this treatment method is inefficient under such conditions.

In experiment no. 2 calcite ( $60 \text{ g m}^{-3}$ ) was again applied. The water body was slightly stirred to simulate turbulent conditions (e.g. in water treatment facilities or in river streams). Within 3 h, calcite dissolution occurs until the point of saturation and consequently the pH-value increases to 9. Calculations show that a distinct  $\text{CO}_2$  undersaturation is established under such conditions. There is no hint that dissolution of  $\text{CO}_2$  takes place in significant quantities within 3 h. Later dissolution of  $\text{CO}_2$  causes a distinct decrease in pH-value and new calcite aggressivity. Because the surplus calcite may no longer be available due to sedimentation or filtration, there is no compensating effect by further calcite dissolution.

In experiments nos 3 and 4 a mixture of three components, reference mixture no. 1 ( $\text{CaCl}_2$ ,  $\text{NaHCO}_3$ ,  $\text{CaCO}_3$ , 'SOCAL'), was applied at a dosage of  $880 \text{ g m}^{-3}$ . This dosage establishes a calcite oversaturation. Due to the calcite component, which works as seed crystal application, the oversaturation causes a rapid precipitation of the surplus calcium and carbonate. Experiment no. 3 was conducted without stirring, experiment no. 4 with stirring. There is no clear difference in the kinetics of pH adjustment, so the problem of turbulence is not relevant here.

### COMPARISON OF SOME TREATMENT METHODS: DOSAGE-DEPENDENT VALUES OF pH, $\text{CO}_2$ SATURATION INDEX AND ALKALINITY

For the acid dam water of Falkenstein, some computer dosage-effect calculations have been performed with the program 'KKG'. In Figures 2, 3 and 4, graphs are plotted for six different treatment methods from the starting point to the point of calcite saturation. The treatment methods are:

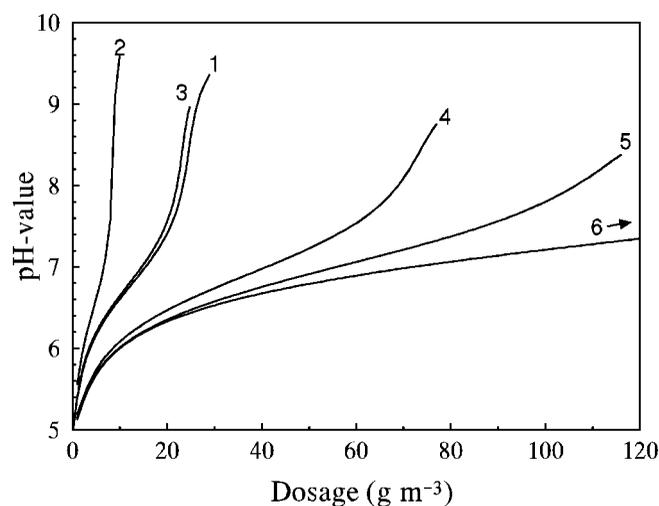


Figure 2 | Dosage-dependent values of pH (for numbering see text).

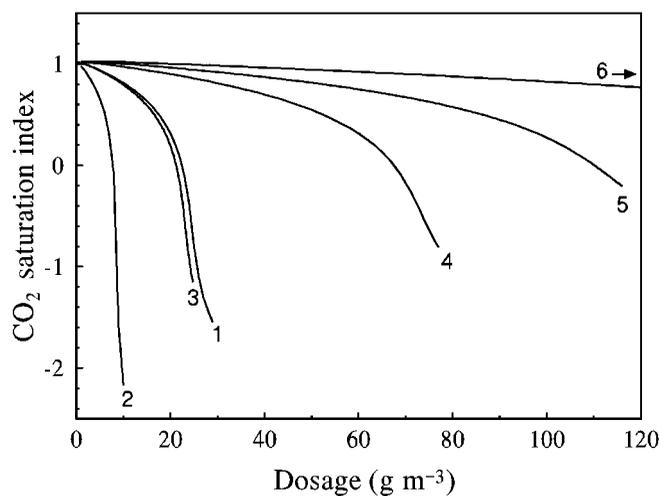


Figure 3 | Dosage-dependent values of the  $\text{CO}_2$  saturation index (for numbering see text).

1. soda ( $\text{Na}_2\text{CO}_3$ )
2. calcium hydroxide ( $\text{Ca}(\text{OH})_2$ , calculated as solid compound)
3. calcite ( $\text{CaCO}_3$ )
4. reference mixture 4 (four compounds:  $\text{CaCl}_2$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  (SOCAL); molar ratio of the sodium compounds 1:1.17)
5. reference mixture 7 (the same four compounds, molar ratio of the sodium compounds 2.5:1)

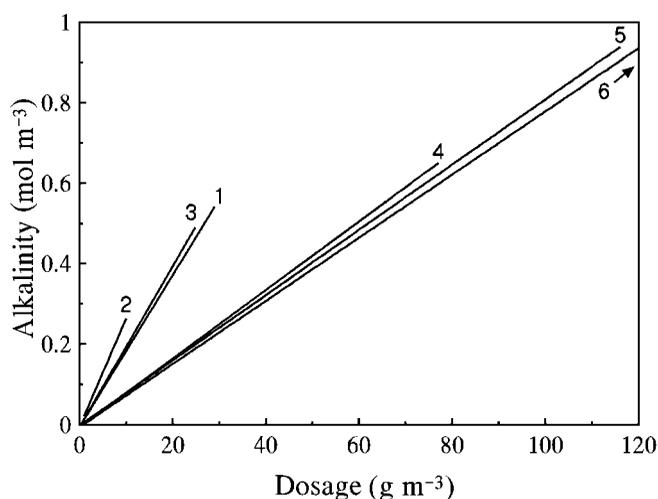


Figure 4 | Dosage-dependent values of alkalinity (for numbering see text).

6. reference mixture 1 (three compounds:  $\text{CaCl}_2$ ,  $\text{NaHCO}_3$ ,  $\text{CaCO}_3$  (SOCAL))

The calculations were conducted under the assumption that all components will dissolve.

Figure 2 shows the pH-values obtained. Treatment methods nos 1–3 result in values at or above 9. Treatment methods 4 and 5 are compromises between high pH-values and high dosages. Treatment method no. 6 requires a dosage of  $220 \text{ g m}^{-3}$  to obtain calcite saturation at a pH-value of 8.15. From the point of water chemistry, this would be the best solution, but the high dosage makes the method more expensive.

Figure 3 shows the  $\text{CO}_2$  saturation indices. A saturation index of 0 means saturation; positive values represent supersaturations in orders of magnitude, negative values represent undersaturations in orders of magnitude. Treatment methods nos 1–3 led to a distinct undersaturation of  $\text{CO}_2$  (negative values). This may cause instability with a latent potential of new calcite aggressivity. For method no. 4 this is valid to a smaller extent. Method no. 5 lowers the index from 1 to only slightly negative values, meaning virtual  $\text{CO}_2$  saturation. Method no. 6 does not influence the index significantly.

In Figure 4 the alkalinity is plotted as surrogate parameter for the buffer capacity. In method no. 2 the

increase in alkalinity is only due to the pH increase. In methods nos 1 and 3 the alkalinity gain results mainly from the increase in pH-value; the dissolution of carbonate compounds causes no considerable increase in the total carbonate content. Only methods nos 4–6 result in an increase in alkalinity, which consists of both the pH increase and the increase in total carbonate content.

## CONCLUSION

The disadvantages of the three traditional treatment methods (calcite, calcium hydroxide, soda) are: high pH-values,  $\text{CO}_2$  undersaturation, low gain of buffer capacity, problems with dissolution rates and the need for a very exact dosage. With the treatment with mixed salts (CarbonAdd) these disadvantages can be avoided: a stable pH-value of 8 can be obtained in a few minutes. The treatment does not significantly influence the  $\text{CO}_2$  saturation state. Buffer capacity can be raised distinctly. Because the best solution from the point of water chemistry needs a relatively high dosage, compromise solutions are offered by variations of the components of the CarbonAdd mixture.

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