Improving the efficiency of rapid sandfilters by adding small amounts of ferric salts ($\beta_{Fe} \leq 0.1 \text{ mg L}^{-1}$)

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Abstract Improved removal of suspended matter during the treatment of water from Lake Constance has been achieved by pre-ozonation ($\beta_{O_3} = 1 \text{ mg L}^{-1}$ corresponding to 0.8 mg O$_3$/mg DOC) and the addition of small quantities of iron salts ($\beta_{Fe} \leq 0.1 \text{ mg L}^{-1}$; “Fe(III)-assisted filtration”) followed by rapid sand filtration. As shown by investigations on a large-scale installation (bypass mode) over several years, this procedure reliably reduces particulate matter in the water by about 3 orders of magnitude in long-term use. However, the high efficacy of Fe(III)-assisted filtration cannot be explained on the basis of known coagulation mechanisms (adsorption-charge neutralization, co-precipitation). Instead, the essential step was found to be the conditioning of the filter medium by coating it with colloids containing Fe(OH)$_3$, and this “Fe coating” process only occurs in the presence of alkaline earth cations (especially Ca$^{2+}$). According to further experiments, the enhanced solid-liquid separation was ultimately traced to chemical interactions such as the formation of calcium-NOM bridges between the iron hydroxides and other solids.

Keywords Alkaline earth cations; ferric supported filtration; filter media conditioning; mechanism; particle removal; water treatment

Introduction

Along with disinfection, the removal of particulate matter (and thus microorganisms as well) is one of the most important steps in the purification of surface waters. The available methods include the use of membrane filtration units and/or the addition of coagulants before mechanical solid-liquid separation. Techniques of this sort can substantially increase the degree of particle retention, and thus further reduce the probability that potential infectious microorganisms (e.g. Cryptosporidium parvum or Giardia lamblia) will reach the consumer through the drinking water. However, economic and environmental factors also need to be taken into consideration when choosing a suitable method.

Investigations into the optimization of the rapid filtration of water from Lake Constance (Winzenbacher et al., 1998, 1999b; Winzenbacher, 2000; Schick, 2000) have shown that the addition of very small quantities of Fe(III) salts ($\beta_{Fe} \leq 0.1 \text{ mg L}^{-1}$; “Fe(III)-assisted filtration”) together with preceeding ozone treatment ($\beta_{O_3} = 1.0 \text{ mg L}^{-1}$) can be sufficient to achieve retentions of > 99% of particles ($d_p > 1 \mu$m), irrespective of the raw water quality. As this result can only be partly explained by known coagulation theories this work will describe the reliability and mode of action of Fe(III)-assisted filtration.

Theoretical aspects of the use of iron salts in the purification of drinking water

The term coagulation covers the processes by changing the surface properties of existing particulates so that they are able to form aggregates (primary effects) or by which new particulates are produced by precipitation reactions. This leads to a change in the effectiveness...
of the removal of solids in subsequent purification steps (secondary effects). The most commonly used (inorganic) coagulants are Fe^{3+} and Al^{3+} salts, which are employed at concentrations between 0.6 and 80 mg\cdot L^{-1} (Johnson and Amirtharajah, 1983; Petrusevski et al., 1995; DVGW, 1996; Mouchet and Bonnélye, 1998). The essential mechanisms known to be involved in coagulation by multivalent metal ions in natural aquatic systems are two destabilization processes (Johnson and Amirtharajah, 1983; Jekel, 1994): adsorption-charge neutralization and sweep coagulation (co-precipitation). In adsorptive charge neutralization the normally negative surface potential of natural suspended matter is modified by the adsorption of positively charged metal hydroxide complexes, reducing electrostatic repulsion between the particles to such an extent that the solids can adhere to each other or to the reactor wall, whereas sweep coagulation involves the formation of voluminous hydroxide precipitates which incorporate the natural particles. In terms of the amount which needs to be added, adsorption-charge neutralization is fundamentally the more favourable mechanism, particularly when relatively small quantities of suspended matter are present and dosages are low (Petrusevski et al., 1995).

Sedimentation, flotation, and deep-bed filtration have all been found to be successful methods for the removal of the (destabilized) suspended matter and the added coagulant. The last of these techniques can be carried out either as in-line filtration or as direct filtration. In the case of in-line filtration the coagulant is added immediately before the rapid filter, thus much of the aggregation occurs in the space above the filter bed and in the interstitial voids of the filter layer. This contrasts with direct filtration, where coagulation takes place in a separate step, and is largely complete before the actual removal of the solids on a filter bed. The procedure which should be chosen in a particular case depends on the operational requirements and on a large number of chemical and physical parameters.

One of the most important factors influencing the coagulation process, and thus the efficacy of particle separation, is the nature of the raw water. For example, when Fe(III) salts are used the adsorption of hydroxo complexes mainly takes place under acidic conditions, whereas precipitation of amorphous Fe(OH)\textsubscript{3} tends to dominate at pH values > 7.5 (Johnson and Amirtharajah, 1983). The presence of natural organic matter (NOM) can also have substantial effects on the coagulation process (Jekel, 1994). In particular, below a certain $\beta_{\text{coagulant}}/\text{DOC}$ ratio there may be massive disturbance due to formation of (genuinely) dissolved metal-NOM complexes (e.g. R-[COOFe(OH)\textsubscript{2}]) or to extensive specific surface complexation of organic substances on freshly precipitated metal hydroxides. The latter gives rise to electrosteric stabilization (Amirbahman and Olson, 1995) of very fine colloidal precipitation products, which are not adequately retained in a subsequent filtration step and which – together with the genuinely dissolved complexes – cause high residual coagulant levels in the filtrate. Another parameter is the level of the divalent cations which cause hardness, as they have the ability to bind coordinatively to the carboxyl and OH\textsuperscript{-} groups of humic substances, metal oxides/hydroxides, and clay minerals (Stumm and Morgan, 1981; Jekel, 1994). The complex-forming potential of alkaline earth ions can thus help counteract inactivation of the coagulant by NOM. Especially in alkaline medium, Ca\textsuperscript{2+} competes particularly well with Fe\textsuperscript{3+}-species (Schnitzer and Skinner, 1963; Petrusevski et al., 1995).

**Experimental set-up**

**Continuous filtration tests in a large-scale system**

The investigations on the reliability of the enhanced particle removal were carried out in a large-scale system operating in bypass mode. The raw water from Lake Constance (Table 1) was extracted from a depth of 60 m and was first passed through microstrainers (nominal mesh size: 15 µm) to remove larger algae and the remains of plankton. The
subsequent ozone treatment was carried out in spray towers with a counter-current of a mixture of ozone and oxygen or with an injector system employing static mixing elements. A reaction chamber taking at least 2 h to pass through was followed by a rapid filtration ($A = 111 \text{m}^2$) with filter rates between 5.7 and 9.3 m h$^{-1}$. The filter material was pumice (bed thickness: 20 cm; grain size: 1.2–1.8 mm) and quartz sand (bed thickness: 80 cm; effective grain size $d_W$ in the top 20 cm: 0.44 mm, uniformity coefficient $U$: approx. 1.35). TRIFLOC FeCl$_3$ solution (Giulini GmbH, Ludwigshafen, $\beta_{Fe} = 210 \text{g L}^{-1}$) was added in the filter inlet, the subsequent residence time in the excess head being at least 20 – 25 min. Once the pressure drop exceeded a certain level the filter was regenerated using a two-stage air/water backwash process.

**Experimental procedure for determining the influence of calcium and magnesium on Fe(III)-assisted filtration**

The effects of different levels of water hardness on particle removal optimized by the addition of Fe(III) were investigated using a small-scale test system. The alkaline earth ions had first to be removed from raw Lake Constance water without changing the other properties of the water (especially the particle concentration). This was done in a 15 L bead bed of the strongly acidic ion exchanger Lewatit S 100 (Bayer AG, Leverkusen) in the Na form, using the fluidized bed procedure described by Dorfner, 1970 (Figure 1). When ozone treatment was used the residual O$_3$ was stripped out with nitrogen immediately before the softening stage to prevent its reaction with the resin (polystyrene-sulfonic acid). The degree of softening using this procedure was over 99%, based on the sum of the Ca$^{2+}$ and Mg$^{2+}$ concentrations, and this could be maintained for an operating period of at least 20 h (about 400–450 times the exchanger bed volume).

The water was adjusted to the exact level of hardness required for the particular filtration test by the addition of CaCl$_2$ or MgCl$_2$ solution after passing through the ion exchanger. The actual removal of suspended matter was carried out in a filtration column made of transparent PVC (diameter: 10.5 cm), and again operated as an in-line filtration without a separate aggregation step (residence time between Fe addition and filter bed: approx. 26 min). The filter rate was 6.9 m h$^{-1}$ and the depth of the filter layer (quartz sand, $d_W = 0.54 \text{mm}$, $U$ = approximately 1.35) was 50 cm.

<table>
<thead>
<tr>
<th><strong>Parameter</strong></th>
<th><strong>Unit</strong></th>
<th><strong>Value</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>$\mu\text{S cm}^{-1}$</td>
<td>326</td>
</tr>
<tr>
<td>pH (8°C)</td>
<td>$-$</td>
<td>7.90</td>
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<tr>
<td>Alkalinity (up to pH = 4.3 at 20°C)</td>
<td>mmol L$^{-1}$</td>
<td>2.51</td>
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<tr>
<td>Total alkaline earths</td>
<td>mmol L$^{-1}$</td>
<td>1.58</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>mg L$^{-1}$</td>
<td>48.0</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>mg L$^{-1}$</td>
<td>8.0</td>
</tr>
<tr>
<td>Fe$_{total}$</td>
<td>mg L$^{-1}$</td>
<td>0.0059</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>mg L$^{-1}$</td>
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</tr>
<tr>
<td>Dissolved organic carbon, DOC</td>
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</tr>
<tr>
<td>Spectral absorption coefficient (254 nm), SAC$_{254}$</td>
<td>m$^{-1}$</td>
<td>2.8</td>
</tr>
<tr>
<td>Turbidity</td>
<td>FNU</td>
<td>0.35</td>
</tr>
<tr>
<td>Solid dry weight</td>
<td>mg L$^{-1}$</td>
<td>0.55</td>
</tr>
<tr>
<td>Particulate organic material (referred to solid dry weight)</td>
<td>$%$</td>
<td>30–40</td>
</tr>
<tr>
<td>Particle count, $d_p &gt; 1 \mu\text{m}$</td>
<td>$\text{ml}^{-1}$</td>
<td>approximately 10,000</td>
</tr>
<tr>
<td>Volume fraction of suspended solids</td>
<td>$-$</td>
<td>approximately $10^{-7}$</td>
</tr>
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</table>
Discontinuous tests on a laboratory scale

Additional experiments in a stirred reactor were used to investigate the influence of dissolved organic substances on Fe(III)-induced particle destabilization at different levels of water hardness. The water sample concerned (water from Lake Constance or ultrapure HCO₃⁻ water) was placed in a beaker (volume: 4.5 L) and sealed off with a floating Teflon lid. To prevent the – normally negatively charged – natural particles being immediately deposited on the walls of the reactor, all glass parts were rinsed with a sodium bicarbonate solution (cNa₂CO₃ = 2 mM) before the start of the experiment to render them alkaline. A cross-blade stirrer (also made of glass) was used to ensure rapid mixing of iron(III) chloride added through a plastic septum (mixing period: 30 s) and the achievement of exactly defined flow conditions (mean velocity gradient $G$ during mixing: 200 s⁻¹, otherwise: $G$ = 80 s⁻¹). The reactor was connected to the sensor of a particle counter via a small Teflon connector to permit continuous recording of the particle count and size distribution (on-line) after adding Fe(III) (Figure 2). The low sensor flow rates largely excluded distortion of the particle analysis in the connector system (smallest diameter: 3 mm) by flow and shear force induced changes of the composition of the dispersion.

Measurement techniques

The analyses necessary to determine the chemical and physical parameters of water quality (iron, calcium, and magnesium concentrations, SAK₂₅₄, etc.) were carried out on the basis of the appropriate DIN, ISO, or CEN standards. The efficacy of the filtration was characterized by determination of the particle count and size distribution ($d_p = 1–116$ µm) using a laser-optic particle counter, 9064/HRLD150.25, HIAC ROYCO Pacific Scientific, Leonberg (Schick et al., 1998) and parallel optical microscope investigations (Axiovert 135/dark-field microscope, Utermöhl type, Zeiss, Oberkochen). The effective surface potential of the dispersed solids was determined using a zeta-potential meter, Zetaphoremeter II, Particle Metrix, Herrsching, (Winzenbacher et al., 1999) which records migration of particles ($d_p = 0.1–50$ µm) in an electric field via computer-aided image analysis and a laser-optical microscope. Scanning electron micrographs of the surface of the
quartz sand taken from the filters were also recorded (ISI-DS 130, Elektronen-Optik-Service GmbH, Berlin). As well as visual analysis, it was possible to carry out elementary analysis of the sample surface (minimum cross-section: approximately 50 nm; penetration depth up to 500 nm) by examination of the characteristic X-rays. This non-destructive EDX microanalysis (EDR 288, Röntec GmbH, Berlin) could detect all elements with an atomic number > 4 (except Au and Pd), the limit of detection being about 8–500 µg/g of solid.

Results and discussion

Reliability of the Fe(III)-assisted filtration

The results of an investigation in a large-scale demonstration unit over two and a half years so far ($\beta_{O_3} = 1.0$ mg L$^{-1}$) have shown that the use of small quantities of iron salts ($\beta_{Fe} = 0.1–0.15$ mg L$^{-1}$) ensures a permanent increase in the efficacy of the removal of particulate matter from water ($d_p > 1$ µm) (Figure 3, top). Since the start of Fe(III) addition at the end of March 1997 the efficacy has been higher than conventional operation of the rapid sand filter, and has consistently been above 99%. Counting of phytoplankton cells under the microscope showed that their removal too became more efficient as a result of the use of the Fe(III)-assisted filtration (Figure 3, bottom). Although ozone pre-treatment only produced a relatively modest in filtration reduction in the total cell count, which depends upon the raw water quality, the reduction in the number of algal cells as a result of Fe addition was about 3 logs of ten. In this case total elimination resulting from disinfection (inactivation) and removal of intact phytoplankton algae was actually more than 99.95%.

Figure 4 explicitly compares the particle concentrations and total phytoplankton cell counts in the filtrate once again. Although the correlation between the two parameters does not seem to be very pronounced in the lower concentration regions the resultant log-log plot over the whole concentration range clearly confirms the association between particle
Figure 3  Improved particle removal in the large-scale unit at the Lake Constance waterworks by the use of Fe(III)-assisted filtration: top: change in the particle concentration; bottom: change in the phyto-plankton concentration. Long-term study in bypass mode; ozone pre-treatment: $\beta_{O_3} = 1.0 \text{mg L}^{-1}$

* Start of Fe addition

Figure 4  Relationship between particle concentration and total phytoplankton cell count in the filtrate of the rapid sand filtration (large-scale unit)
removal and the removal of microorganisms. Similar results have been obtained by Nieminski and Ongerth (1995) within the framework of the purification of river and reservoir water. The authors demonstrated a direct correlation between the degree of retention of *Giardia* and *Cryptosporidium* cysts and the reduction in particles in the size range between 7 and 11 µm and 4 and 7 µm respectively, confirming that particle counting can act as an indicator of the possible presence of pathogens.

**Investigations on the mode of action of the filtration process optimized by the iron addition**

As the results have shown so far, Fe(III)-assisted filtration is a reliable method for the removal of inorganic and organic particulate matter from water, at least in the purification of water from Lake Constance. To obtain further information about the general conditions under which this procedure can be used for the purification of water, it is essential to know its mechanism of action. The remainder of this paper will therefore examine more closely the processes triggered by the addition of small quantities of iron salts.

**Effect of Fe(III) addition on the surface properties of filter collectors.** According to earlier studies (Winzenbacher *et al.*, 1999a,b) the increased particle removal at Fe concentrations ≤ 0.1 mg L⁻¹ would not be anticipated on the basis of voluminous iron hydroxide formation (co-precipitation) or classical adsorption-charge neutralization. Rather, the addition of small quantities of Fe(III) to Lake Constance water led to a mixed population of natural particles and colloids containing iron hydroxide whose size was estimated – on the basis of ultrafiltration experiments – at dₚ = 100–800 nm. The colloid particles formed were at least partly coated with organic material and showed a great tendency to deposit on the surfaces of the filter grain material. Consequently, it can be assumed that a process resembling conditioning of the filtration medium is the decisive step in the improved particle removal. For example, the massive deposition of hydroxide colloids could increase the roughness of the collectors and thus improve the physical capture of particles (Gimbel, 1984), though reduced flow-related resuspension of particles already in contact with grains of filter material due to stronger chemical interactions is also conceivable (O’Melia and Stumm, 1967). It was therefore consequent to investigate these possibilities with the aid of scanning electron microscopy (SEM).

Figure 5 shows micrographs of samples of quartz sand taken from the top 10 cm of the filter bed during the filtration phase. The sand grains from a filter operated conventionally show a clearly structured surface with small sharp-edged elevations providing roughness. By contrast, collectors from a filter operated with the addition of low amounts of iron(III) salts (β_Fe = 0.1 mg L⁻¹) could be seen to have a coating with an irregular structure.

**Figure 5** Scanning electron micrograph (SEM) of the surface of (a) quartz sand from a filter operated without Fe(III) and (b) quartz sand from a filter operated with continuous addition of Fe(III) (β_Fe = 0.1 mg L⁻¹), each collected from the top 10 cm of the filter bed during the filtration phase.
Energy-dispersive X-ray microanalysis (EDX) confirmed that these deposits contain iron. It was also found that the iron-hydroxide-rich zones always contained calcium as well, although significant retention of calcium did not occur during the filtration process. A semi-quantitative evaluation of the elementary composition of the coating gave a \( \frac{c_{Fe}}{c_{Ca}} \) molar ratio of about 3.5. Bearing in mind that the \( \frac{c_{Fe}}{c_{Ca}} \) ratio in the water being filtered was only about 0.001 mol/mol, it is clear that the colloidal iron on the grains of filter material must have accumulated in association with calcium.

The small quantity of Fe(III) added thus actually does induce about a (reversible) change to the surface of the sand grains, apparently causing increased deposition of suspended matter in the presence of organic substances and calcium ions. Since, however, the surface structure of the “Fe coating” did not display substantially increased roughness, it seems that particle capture is less important than improved adhesion resulting from chemical or physical interactions.

Influence of alkaline earth cations on the efficacy of Fe(III)-assisted filtration. Other experiments were designed to investigate the role of alkaline earth ions (\( \text{Ca}^{2+}, \text{Mg}^{2+} \), etc.) on the enhanced particle removal (with or without pre-treatment with ozone). The small-scale investigations showed that both the nature and quantity of the alkaline earths present and their reactions with natural organic matter (NOM) have substantial effects on filter efficacy \( \eta_P \) (Figure 6).

![Figure 6](https://iwaponline.com/ws/article-pdf/2/1/191/408730/191.pdf)
Only 15% of the suspended matter in softened Lake Constance water was removed despite the addition of Fe ($\beta_{Fe} = 0.1 \text{ mg L}^{-1}$), and there was a high residual iron content in the filtrate (94% of the quantity added). The retention of iron and particulate matter increased only with increasing Ca$^{2+}$ concentration (up to $\eta = 85\%$ at $c_{Ca} = 1.4 \text{ mmol L}^{-1}$). The addition of MgCl$_2$ to softened water also increased the removal of particulate matter, but the highest efficacy, at $c_{Mg} = 1.4 \text{ mmol L}^{-1}$, was only 75%. Ozone treatment of water of various degrees of hardness before Fe(III)-assisted filtration (specific ozone dose: 0.8 mg O$_3$ per mg DOC) only produced an improvement in $\eta$ at the highest calcium levels – analogous to those of Lake Constance water. By contrast, at lower Ca$^{2+}$ concentrations (<1 mmol L$^{-1}$) or when Mg$^{2+}$ ions alone were used to harden the water, ozone treatment led to a deterioration in filtration efficiency. In unfavourable cases the oxidation of organic materials in the water had such adverse effects on the removal of suspended matter that retention was less than 50% of that achieved in non-ozonized samples.

The following possible explanations for the effects observed here were considered:

- **Hypothesis A:** The formation of (high surface affinity) Fe(OH)$_3$ colloids could be accelerated by the incorporation of calcium/magnesium species or crystallization nuclei, e.g. calcite (Stumm and Morgan, 1981)
- **Hypothesis B:** Complexation of the hardness formers by (dissolved) organic substances could prevent formation of genuine dissolved metal(III) complexes (no “masking” of the coagulant)
- **Hypothesis C:** The finest colloidal NOM-laden iron hydroxides will be destabilized electrostatically, sterically, or because of changes in hydrophobic properties by interacting specifically with alkaline earth cations (Dowbiggin and Singer, 1989; Beckett and Lee, 1990; Amirkahraman and Olson, 1995).
- **Hypothesis D:** Reactions between the divalent cations and hydroxide surfaces and organic (macro)molecules adsorbed on surfaces or in solution make improve the deposition of particles by bridge formation (Jekel and Ernst, 1981; Dowbiggin and Singer, 1989; Amirkahraman and Olson, 1995).

Hypothesis A was first investigated by calculating the saturation index SI of solid inorganic calcium phases for Lake Constance water using the chemical equilibrium modeling program MINEQL+ (Schecher and McAvoy, 1998). This produced positive SI values of $\log(c_{Ca}c_{CO_3}/K_{So,\text{CaCO}_3}) = 0.17$ and $\log(c_{Ca}^5c_{OH}c_{PO_4}/K_{So,\text{Ca}_5\text{OH(PO}_4\text{)}_3}) = 2.61$ for calcite (CaCO$_3$) and for hydroxyapatite (Ca$_5$OH(PO$_4$)$_3$) respectively, which indicates that the solubility product $K_{So}$ is exceeded, and thus that precipitation should theoretically occur. According to Stumm and Morgan (1981), however, calcite should be the kinetically preferred solid phase at the low phosphate concentrations, the relatively high HCO$_3^-$ levels, and the pH of 7.9–8.0 found in Lake Constance water. Optical microscopy with a polarizing filter nevertheless shows that the Fe(III)-assisted filtration of Lake Constance water does not appear to be accompanied by any significant involvement of precipitated calcites (in suspended form). This method visualizes calcite crystals > 0.45 µm in aqueous solution as

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* The filtration efficacies achieved in these experiments were generally a little bit lower than that achieved in the large-scale filtration. This is probably due the larger grain size used in the small-scale experimental unit.
† According to Stumm and Morgan (1981), Jekel (1994) and Petrusheski et al. (1995) it is quite conceivable that in natural aquatic systems with high concentrations of Ca$^{2+}$ ions (especially under alkaline conditions and after ozonation of organics compounds), Fe$^{3+}$ ions, although usually forming stronger complexes than Ca$^{2+}$, can be replaced by Ca$^{2+}$ ions.
‡ The electrosteric stability of the dispersion can also be influenced by the complexation of Ca$^{2+}$ by (dissolved) organic substances, thereby changing the adsorption tendency of calcium and (anionic) NOM constituents, respectively (Ali and Dzombak 1996; Chandrakanth and Amy, 1998).

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yellow luminescent particles. This was, for example, clearly visible in raw water samples artificially spiked with calcite crystals. By contrast, there were hardly any particles containing calcite in untreated Lake Constance water (\(c_{\text{Ca}} = 1.2 \text{ mmol} \cdot \text{L}^{-1}\)) or in softened water subsequently treated with CaCl_2 (\(c_{\text{Ca}} = 1.4 \text{ mmol} \cdot \text{L}^{-1}\)) (Figure 7).

Measurements of the Fe(III)-induced particle destabilization in water containing different amounts of NOM were used to determine the extent to which the higher Fe concentrations found in the filtrate, obtained from softened water, were due to the formation of genuine dissolved iron complexes with NOM (see hypothesis B). This was done by monitoring the changes in particle concentration resulting from Fe addition over a period of several hours (see Experimental Set-up). The resultant particle count-time curves show that – under the refined conditions – the formation of precipitation products > 1 µm was always observed after an appropriate reaction time, even at low Fe concentrations (\(\beta_{\text{Fe}} = 0.1 \text{ mg} \cdot \text{L}^{-1}\), essential formation time: at least 70 min). To quantify the kinetics of precipitation (an initial increase followed by a decrease in the particle count), the time of the maximum particle concentration \(t_{\text{P,max}}\) was then determined\(^\S\) as done by Jekel (1978) in a similar way.

The reciprocal of this value reflects the precipitation rate for the formation of particles in a physical sense. These calculations showed very low precipitation rates of between 0.0045 and 0.0052 min\(^{-1}\) for both softened Lake Constance water (DOC = 1.2 mg L\(^{-1}\)) and virtually NOM-free ultrapure HCO\(_3\) water (pH = 8.0; DOC = 0.1–0.2 mg L\(^{-1}\)) (Figure 8).

In both cases, however, the formation of at least a small amount of precipitation products > 1 µm was detected after about 4 h. Finally, an increase in the water hardness brought about a clear increase in the rate of the precipitation process, though substantially more Ca\(^{2+}\) ions were required in the presence of organic substances.

The presence of NOM thus seems to be only partly responsible for the absence of precipitation products, and a shortage of alkaline earth ions appears to be primarily responsible. Although inactivation of the iron by the formation of dissolved organic complexes cannot be excluded, it does not appear to play the dominant role. It is therefore assumed that the failure of collector conditioning with Fe(OH)\(_3\) in softened Lake Constance water is mainly due to electrosteric stabilization of the extremely fine Fe hydroxide colloids which are formed (hypothesis C).

\(^\S\) Exact determination of \(t_{\text{P,max}}\) was carried out by fitting the mathematical function

\[
N(t) = N_0 \left( \frac{t}{a \cdot t^2 + b \cdot t + c} + \frac{1}{t+1} \right)
\]

which includes the constants a, b and c, to the measured particle counts (noted N) using the least-squares method and differentiation of this equation with respect to time (noted t).
It was now necessary to investigate the specific influence of alkaline earth ions on the electrical repulsion forces between dispersed solids using zeta-potential analyses as a function of electrolyte composition. The electrophoretically determined potential values showed an ion-selective reduction in the negative surface charge with increasing Ca\(^{2+}\) or Mg\(^{2+}\) concentration (measurement time: approximately 30 min after Fe addition; \(\beta_{Fe} = 0.1\) mg·L\(^{-1}\)). Even small quantities of calcium (< 0.2–0.4 mmol·L\(^{-1}\)) were sufficient to bring about a large shift in the potential in the direction of neutrality. By contrast, compensation of the negative charge on the particles by divalent cations was less pronounced after ozone treatment (\(\beta_{O_3} = \) approximately 1.0 mg·L\(^{-1}\)) of the softened water samples. In these samples the specific direct reaction of ozone with NOM (introduction of functional groups, cleavage of macromolecules (Jekel, 1981; Dowbiggin and Singer, 1989) could, therefore, have led to such negative charge densities on solid surfaces (natural particles, Fe(OH)\(_3\) colloids, filter collectors) that an ozone-induced deterioration of \(\eta_P\) occurred because of the high electrostatic repulsion.

This relationship between particle charge and the concentration of alkaline earths suggests that ion-specific “charge screening” is a necessary prerequisite for successful particle removal. However, electrostatic effects alone cannot be responsible for the increase in efficiency of the Fe(III)-assisted filtration following the addition of Ca\(^{2+}\)/Mg\(^{2+}\). This was made clear by a quantitative comparison of the measured \(\zeta\)-values and the corresponding filter efficacy at different levels of hardness (Figure 9). At most, there was a correlation between particle charge and filter efficacy at low calcium concentrations (up to approximately 0.4 mmol·L\(^{-1}\)), and there was no correlation after the addition of larger quantities of Ca\(^{2+}\). The large increase in filter efficacy in hard water – especially above the observed threshold Ca\(^{2+}\) concentration of 0.4 mmol·L\(^{-1}\) – must, therefore, relate to other chemical processes (e.g. Ca\(^{2+}\)-NOM bridge formation, see hypothesis D).

**Proposed mechanism of Fe(III)-assisted filtration.** According to the results of this work, the fundamental mechanism of Fe(III)-assisted filtration can be described as follows (Figure 10): Following the addition of a small quantity of Fe(III) salts, colloidal iron...
hydroxide is formed during the reaction time available in the space above the filter \((d_p = 100–800\, \text{nm})\). The colloids formed are largely deposited on the filter collectors, leading to the formation of an “Fe coat”. In the presence of divalent alkaline earth ions (especially \(\text{Ca}^{2+}\)) the filter medium conditioned in this way induces improved retention of the suspended material covered with natural organic matter in water from Lake Constance. The individual effects which are probably involved are hardness-associated electrostatic effects (charge screening) and the formation of \(\text{Ca}^{2+}\)-NOM bridges (Amirbahman and Olson,

Figure 9 Relationship between the surface charge of particles dispersed in Lake Constance water (about 30 min after addition of \(\text{Fe}\)) and filter efficacy (small-scale experimental unit) at various levels of water hardness. Squares = no ozone pre-treatment; circles = after ozone pre-treatment \((\beta_{\text{O}_3} = 1.0\, \text{mg}\cdot\text{L}^{-1})\)

Figure 10 Mechanism of the \(\text{Fe(III)}\)-assisted filtration \((\beta_{\text{Fe}} = 0.1\, \text{mg}\cdot\text{L}^{-1})\) of Lake Constance water
The conditioning of the filter sand itself in water containing NOM is presumably also encouraged by chemical interactions between quartz sand, Fe hydroxides and Ca$^{2+}$.

Ozone pretreatment can further increase the efficiency of Fe(III)-assisted filtration, as long as there is a certain minimum level of hardness in the raw water. Again, specific reactions between Ca$^{2+}$ ions and the ozonated organic substances are assumed to play an important role in this ozone-induced destabilization of both the Fe hydroxides formed in-situ and the natural particles.

**Summary and conclusions**

Fe(III)-assisted filtration is an efficient method for the enhanced removal of particulate matter. It is characterized by simple operation and is also suitable for ensuring reliable removal of potential dangerous microorganisms in the long term, despite seasonal changes in raw water quality. Unlike the use of membrane filtration units, which in this case would lead to very high investment and operating costs, the addition of small quantities of iron salts leads to an optimal cost-benefit relationship. However, there are also certain prerequisites to the success of optimization of the filtration process by this method. The essential factor of relevance here is the need for the raw water to contain a certain minimum concentration of calcium ions, this minimum level depending in particular on whether or not the filtration is preceded by oxidation of the organic substances with ozone. Detailed clarification of the role of the NOM and their ability to react with alkaline earths and the Fe species formed during Fe(III)-assisted filtration, however, would require further studies.

**References**


