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Modelling of ClO_2-decomposition in Hot Water Systems

Recently an accumulation of corrosion failures of stainless steel equipment having to do with chlorine dioxide have led to increased interest in the topic of the disinfectant's corrosive properties. So far, studies have mostly focused on the corrsion risk of temporary disinfection steps as usually applied during CIP-processes. However, analyses of corrosion defects in the brewing industry show that a significant number of chlorine dioxide related failures occur in pipes and tanks of hot water circuits. In these areas, influences like high temperatures and stagnant flow conditions can favour pitting corrosion despite lower concentrations. But while electrochemical analysis can only reveal conditions at the time of sampling, these corrosion problems can only be understood if hydrochemical means are considered.

The aim of this study was to investigate the stability of chlorine dioxide in hot water distribution systems of brewery plants. For this purpose decomposition kinetics were analysed in laboratory experiments with brewing water and reverse osmosis water at 40 °C, 60 °C and 80 °C. Experimental data was modelled using a second order kinetic approach. Moreover the hydrochemical calculation program PHREEQC was used to simulate changes in water composition due to dosing and decomposition of chlorine dioxide.

Results showed that chlorine dioxide decomposition in reverse osmosis water was considerably slower than in brewing water and exhibited less temperature dependency of the reaction rate. Over a period of 48 h a decrease of only 25 % of initial ClO_2-concentration was observed in 80 °C hot reverse osmosis water. PHREEQC simulations revealed that dosage of acidic chlorine dioxide solution to the mostly unbuffered water caused pH to sink to 4.3 which inhibited decomposition. Because of the combination of constantly high redox potential and acidic pH-values chlorine dioxide treatment of decarbonized waters presents a potential corrosion risk to stainless steel equipment when heated and stored in water distribution networks.

Descriptors: chlorine dioxide, decomposition, water distribution systems, water treatment, PHREEQC, corrosion

1 Introduction

Due to its beneficial properties, e.g. pH stability, no formation of trihalomethanes [1, 2, 3, 4, 5], chlorine dioxide is widely used as a disinfectant in production systems of the brewing industry. However, conventional applications use the chlorite-/hydrochloric acid process which produces highly acidic chlorine dioxide solutions (pH < 1 [6, 7]) due to the fact that in order to be efficient a high surplus of HCl has to be used for the reaction.The combination of high oxidation potential, high chloride concentration and low pH values favours pitting corrosion of stainless steel equipment [8].

Recently, an extensive report on the corrosion risk for higher alloyed steels by newly developped disinfectants inluding chlorine dioxide was released by *Ahrens* and *Erning* [9]. Based on the results of electrochemichal polarisation tests, the authors concluded that 1.4301 or higher alloyed steels are unlikely to show pitting corrosion in disinfectant solutions containing under 10 mg/L ClO_2 for a contact time of up to 20 minutes and temperature under 20 °C. According to Ahrens and Erning, to prevent corrosion during disinfection steps of CIP-processes, the main objective is to keep chloride levels below 250 mg/L.

Besides the use for designated disinfection steps during production processes, chlorine dioxide is also utilized for water disinfection in distribution systems and storage tanks. In this case, hot water tanks and parts with stagnant flow conditions are particularly prone to corrosion attacks. As contact time and temperature, both crucial factors for pitting corrosion, are much higher, corrosion failures can occur despite much lower disinfectant concentrations [10]. Moreover outgassing chlorine dioxide can lead to corrosion in the headspace of hot water storage tanks and pipes when resolved in condensate water on the inner surface of containers [11].

To evaluate the influence on corrosion processes in hot water circuits, it is necessary to know the behaviour of chlorine dioxide in these systems. Physical and chemical properties of the disinfectant have been comprehensively described by *Gordon* et al. [12] and *Masschelein* and *Rice* [1]. The decomposition of ClO_2 (Eq.1) is known to be accelerated by high temperatures, high pH, exposition to light, and traces of water contamination.

$$2\,\mathrm{ClO_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{ClO_2}^- + \mathrm{ClO_3}^- + 2\,\mathrm{H}^+ \qquad \textbf{Eq. 1}$$

However, existing results of kinetic studies have only been conducted in model waters and cannot be adapted to the conditions

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in hot water distribution systems because they either describe the reaction under the presence of light [12, 13] or only at lower temperatures [14]. Moreover the outgassing of chlorine dioxide in containers comprising headspace and the influence of the decomposition reaction in the gas phase (Eq. 2) have not been described in these studies.

$$2\,\mathrm{ClO_2} \longrightarrow \mathrm{Cl_2} + 2\,\mathrm{O_2}$$ **Eq. 2**

In this study the decomposition kinetics of chlorine dioxide were examined at three different temperatures (40 °C, 60 °C, 80 °C) in two typical waters used in breweries, reverse osmosis water and brewing water. The tests were carried out in gas tight containers with different filling levels to evaluate the influence of the gas phase volume on decomposition.

2 Materials and methods

2.1 Experimental

Chlorine dioxide decomposition kinetics were analysed in two different media (brewing water, reverse osmosis water) at three different temperatures (40 °C, 60 °C, 80 °C). Tested media were taken from a reverse osmosis unit of a brewery. The chlorine dioxide stock solution was obtained from a convential automated chlorite-/hydrochloric acid ClO_2-production unit. Properties are shown in table 1.

Test solutions were adjusted to 1.0–1.3 mg/L chlorine dioxide concentration and filled into 20 mL glass flasks that were sealed with gas tight aluminium crimp caps (gas chromatography flasks). During the time of the experiment the flasks were put in a drying cabinet in which the temperature was regulated. In order to analyse the influence of headspace as present in not entirely filled pipes and tanks, test series with 10 mL and 20 mL filling volume were carried out for each combination of media and temperature. The small amount of headspace in the samples with 20 mL filling volume was considered negligible. Analysed parameter combinations are shown in table 2.

Table 1 Composition of tested waters and chlorine dioxide stock solution (* could not be measured due to low conductivity in reverse osmosis water)

parameter	unit	brew-ing water	reverse osmosis water	ClO_2 solution
pH	[ ]	7.3	( )*	2.0 – 2.3
chlorine dioxide (ClO_2)	[mg/L]	0	0	100 – 120
conductivity	[µS/cm]	126.4	12.1	
total hardness	[°dH]	3.06	0.24	
alkalinity	[mmol/L]	1.1	0.1	
sodium (Na^+)	[mg/L]	5.0	1.6	
potassium (K^+)	[mg/L]	0.5	0.2	
calcium (Ca^{2+})	[mg/L]	14.0	1.2	
magnesium (Mg^{2+})	[mg/L]	4.8	0.3	
chloride (Cl^-)	[mg/L]	3.6	0.3	500 – 600
sulfate (SO_4^{2-})	[mg/L]	4.4	0.2	
nitrate (NO_3^-)	[mg/L]	1.7	0.5	

Table 2 Tested variations of experimental conditions

parameter	variation
medium	brewing water, reverse osmosis water
chlorine dioxide concentration [mg/L]	1.0 – 1.3 mg/L
temperature [°C]	40, 60, 80
filling level [mL]	10, 20
Time [h]	0, 1, 2, 4, 6, 8, 24, 48

ClO_2-concentration was analysed at seven points over a total time of 48 h using a photometric DPD-method (Nanocolor Chlor/Ozon 2, Macherey-Nagel GmbH & Co. KG, Düren, Germany). As the applied DPD-method not only detects chlorine dioxide but oxidising agents in water like free chlorine and ozone in general, measured values were slightly higher than actual ClO_2 concentrations. However, it was observed in preruns with ClO_2 masking reagent (Nanocolor Chlordioxid 5, Macherey-Nagel GmbH & Co. KG, Düren, Germany) that deviation to the regular method was below 0,1 mg/L. To ensure gas tightness sample volumes were taken with a syringe and put in prepared cuvettes. Because of the fugacity of chlorine dioxide and its instability when exposed to light, it was important to work efficiently. To prevent losses due to contamination, all glass ware was pre-rinsed with test solution. The accuracy of the method was measured in preruns by threefold tests in which the average standard deviation was ± 0.05 mg/L.

2.2 Reaction kinetic modelling

Experimental data was modelled by a reaction kinetic approach. As presented by *Böhler* et al. [14] the disproportion reaction that describes the decomposition of chlorine dioxide (Eq. 1) can be regarded as

$$2\,\mathrm{A} \longrightarrow \mathrm{C} + \mathrm{D}$$ **Eq. 3**

with C and D representing chlorite and chlorate. Thus, the decomposition reaction can be described by a second order time law [14]:

$$-\frac{1}{2} \cdot \frac{d[ClO_2]}{dt} = k_{decomposition} \cdot [ClO_2]^2$$ **Eq. 4a**

$$\frac{1}{[ClO_2]_t} = 2k_{decomposition} \cdot t + \frac{1}{[ClO_2]_0} = k \cdot t + \frac{1}{[ClO_2]_0}$$ **Eq. 4b**

The integrated form (Eq. 4b) shows the linear relation between $1/[ClO_2]_t$ and the reaction time t for which the velocity constant k marks the slope and $1/[ClO_2]_0$ the y-intercept. For developping the model, linear functions were obtained by linear regression for each test series.

In order to model the temperature dependency of the chlorine dioxide decomposition in the two tested waters, the Arrhenius-equation

$$k(T) = k_0 \cdot e^{\frac{-E_A}{R \cdot T}} \qquad \text{Eq. 5}$$

was implemented to describe the velocity constant k in equation 6:

$$\frac{d[ClO_2]}{dt} = k_0 \cdot e^{\frac{-E_A}{R \cdot T}} \cdot [ClO_2]^2 \qquad \text{Eq. 6}$$

The required constants E_A and k_0 were obtained individually for both reverse osmosis water and brewing water by plotting the logarithmic k-values against the inverted temperature in Kelvin as described by the logarithmised form of equation 7:

$$lnk = -\frac{E_A}{R} \cdot \frac{1}{T} + lnk_0 \qquad \text{Eq. 7}$$

E_A and k_0 were calculated from the linear regression function.

2.3 PHREEQC simulations

For further analysis of hydrochemical conditions during chlorine dioxide disinfection, simulations on change of pH, outgassing and decomposition were performed using the program PHREEQC (v. PhreeqcI 3.3.5.10806) [15].

PHREEQC is a hydrogeochemical calculation tool written in the C and C++ programming language which can simulate chemical reactions and transport processes in natural, experimental or industrial waters. Performed calculations are based on equilibrium chemistry, hence the acronym PHREEQ which stands for pH-Redox-Equilibrium. Thermodynamic data is defined in databases and different processes are described by specific keywords.

PHREEQC was particularly useful for determining the pH of reverse osmosis water, which could not be measured due to the low conductivity. Also, it could be used to graph the development of chlorine dioxide decomposition at different temperatures based on the forumlated kinetic model.

3 Results and Discussion

3.1 Influence of gas phase volume

The tests with different filling levels show that transfer of chlorine dioxide into the headspace of containers does not have an influence on decomposition.

The graphs of 10 mL and 20 mL experiments generally have the same form, but are shifted parallel. As depicted in figure 1 for brewing water and temperatures of 40 °C and 80 °C, no significant tendency for increase or decrease of decomposition velocity is noticeable because of the headspace in half filled flasks. As this is observed in every analysed media-temperature combination, further analysis and modelling was exclusively performed using data from the 20 mL test series.

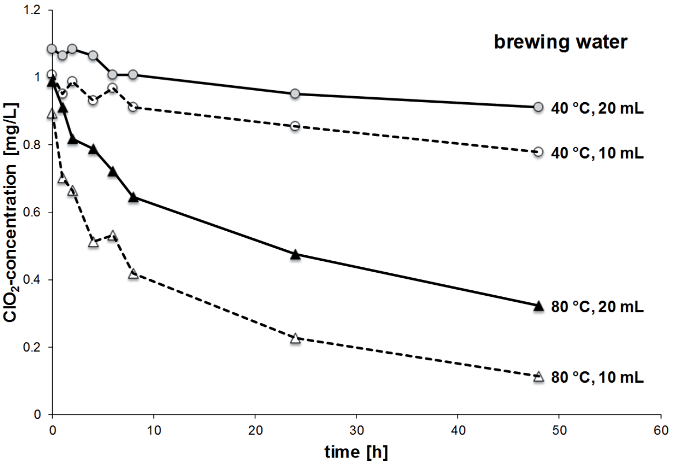

Fig. 1 Influence of filling volume on ClO_2-decomposition in brewing water at 40 °C and 80 °C

Table 3 Difference between ClO_2-concentration in 10 mL and 20 mL samples in mg/L

$\Delta C_t(ClO_2) = c_t^{20mL}(ClO_2) - c_t^{10mL}(ClO_2)$

	brewing water			reverse osmosis water		
	40 °C	60 °C	80 °C	40 °C	60 °C	80 °C
mean	**0.10**	**0.17**	**0.21**	**0.08**	**0.13**	**0.24**
SD	0.032	0.041	0.043	0.026	0.047	0.044

Only between 0 h and 1 h the 10 mL plots show an abrupt decrease, because the 0 h samples were taken before they were temperated in the drying cabinets and thus analysed at room temperature. As gas solubility in the fluid phase decreases with rising temperature, the difference between ClO_2-concentration in 10 mL and 20 mL samples is measurably higher at 80 °C than at 40 °C after temperature adjustment.

Test results indicate that in comparison to the fluid phase reaction (Eq. 1) decomposition of chlorine dioxide in the gas phase (Eq. 2) plays a minor role. Based on the evaluation of the measured difference between 10 mL and 20 mL trials (Table 3), it seems probable that the lower ClO_2-concentrations in half filled flasks are predominantly a result of outgassing due to solubility euqilibrium adjustment. The equilibrium distribution in fluid and gas is reached quickly as differences between 10 mL and 20 mL samples are already measurable at 0 h.

3.2 Influence of media type

Test results show that decomposition rates in brewing water are much higher and more temperature dependent than in reverse osmosis water.

During the observed reaction time of 48 h 70 % of initial chlorine dioxide decays in brewing water at 80 °C, whereas at 40 °C the proportion amounts only 15 %. In reverse osmosis water ClO_2-decomposition is low at all observed temperatures and does not exeed 25 %.

The higher stability of chlorine dioxide in these test series can be explained by the lower pH-values that resulted from the addition of the acidic stock solution (pH 2) to the mostly not buffer capable reverse osmosis water. Although pH could not be measured due to

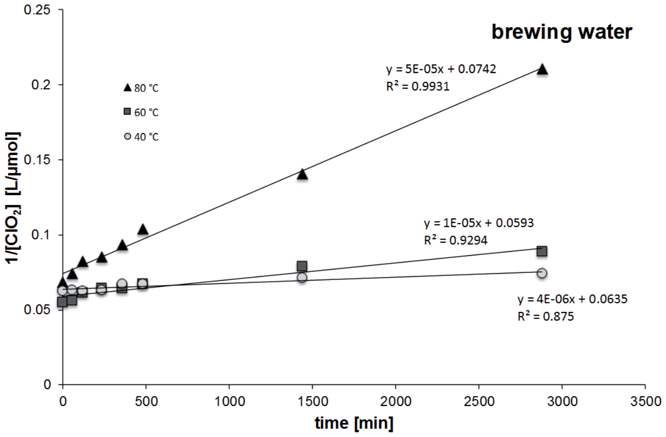

Fig. 2 ClO_2-decomposition kinetics in brewing water plotted by a second order time law

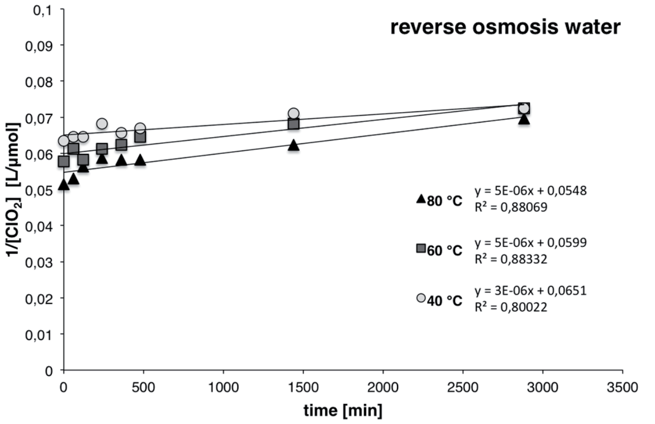

Fig. 3 ClO_2-decomposition kinetics in reverse osmosis water plotted by a second order time law

the low conductivity, simulations performed with the hydrochemical calculation program PHREEQC predicted a reduction to pH 4.2–4.7. The inhibiting effect of neutral and acidic pH is well known [1, 12, 13] and was also observed by Böhler et al. [14].

3.3 Reaction kinetic modelling

In both tested media types decomposition kinetics of chlorine dioxide can be described by a second order reaction kinetic model (Fig. 2 and 3).

Reaction constants k and correlation factors R^2 of the analysed media-temperature combinations are illustrated and compared with the results by Böhler et al. in table 4.

Correlation between experimental data and the linear regression function is generally better for the brewing water test series. However, all test series on which modelling was performed show correlation factors over 0.8.

Table 4 Comparison of chlorine dioxide decomposition reaction constants k at different pH and temperature (* pH in reverse osmosis water estimated by simulation)

data series	temperature	pH	reaction order	k [L µmol^{-1} min^{-1}]
brewing water	40 °C	7.3	n = 2 (R^2 = 0.8750)	$4 \cdot 10^{-6}$
brewing water	60 °C	7.3	n = 2 (R^2 = 0.9294)	$1 \cdot 10^{-5}$
brewing water	80 °C	7.3	n = 2 (R^2 = 0.9930)	$5 \cdot 10^{-5}$
reverse osmosis water	40 °C	4.7*	n = 2 (R^2 = 0.8002)	$3 \cdot 10^{-6}$
reverse osmosis water	60 °C	4.6*	n = 2 (R^2 = 0.8833)	$5 \cdot 10^{-6}$
reverse osmosis water	80 °C	4.3*	n = 2 (R^2 = 0.8807)	$5 \cdot 10^{-6}$
Böhler et al. (2003)	20 °C	8.3	n = 2	$4 \cdot 10^{-4}$
Böhler et al. (2003)	20 °C	5.4	n = 2	$5 \cdot 10^{-5}$

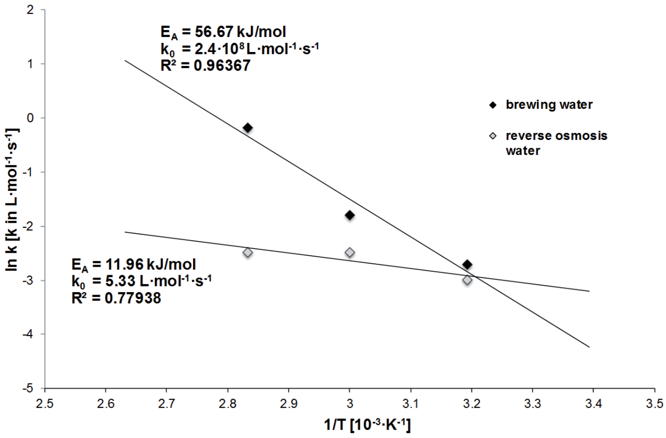

Fig. 4 Arrhenius-plot showing activation energy and preexponential factors of the ClO_2-decomposition reaction in brewing water and reverse osmosis water

Despite different experimental conditions, reaction constants are distinctly lower compared to the results by Böhler et al.. At a temperature of 20 °C and a inhibiting pH of 5.4 the k-value determined by Böhler et al. is more than ten times higher than in brewing water at 40 °C and pH 7.3. As specific experimental conditions (exposure to light, attrition, outgassing) are not indicated by Böhler et al., it cannot be discussed which influences were responisble for the divergent results in this study.

For both media, reaction constants for the three examined temperatures could be used to determine activation energy and preexponential factor of the decomposition reaction (Fig. 4). Surprisingly the determined activation energy was higher in the brewing water test series and the lower overall reaction rate in reverse osmosis water is only caused by the much lower k_0-values in these test series.

Like with the determination of the reaction constants, linear regression provided better results for the brewing water test series. This can be explained by the low overall decomposition in reverse osmosis water, on which deviations by the applied analysis method (SD = 0.05 mg/L) had a greater impact.

3.4 PHREEQC simulations

PHREEQC proved as a helpful tool to evaluate corrosive properties during chlorine dioxide disinfection, as induced changes in water composition can be simulated for different process conditions. Decisive parameters are the alkalinity of the water and the pH of the chlorine dioxide solution which is dependent on the HCl-surplus used for the ClO_2-production process.

If properties of the raw water and dosed chlorine dioxide solution are defined, the change of pH resulting from a specific dosing amount can be predicted by PHREEQC. Because acid-base reactions are well described by equilibrium calculations [16] as used by PHREEQC simulations, it can be assumed that results are applicable to practical uses. Thus, PHREEQC can help to design disinfection steps in a way that critical pH reductions are avoided.

As depicted in figure 5 for a pH 0.5 ClO_2-solution, a minimum raw water alkalinity of 0,5 mmol/L is needed to keep pH above 6.5 (minimum pH required by the German drinking water law [17]) at a dosing of 0.4 mg/L (maximum dosing by the German drinking water law [17]).

With integration of the kinetics in PHREEQC it is also possible to simulate the decomposition of chlorine dioxide and its influence on water composition and gas phase concentration at variable temperatures and times. Simulation results show, that at the low concentrations applied during water disinfection the decomposition reaction itself has very little effect on pH even in soft waters. This is illustrated in figure 6 for a simulated container half filled with reverse osmosis water after dosing of 1 mg/L ClO_2.

Although after one week at 80 °C ClO_2-concentration decreases by 0,25 mg/L, pH alteration is marginal. This also applies for chloride concentration (not shown in Fig. 6) which is not increased by more than 1 mg/L. Gas phase concentration of chlorine dioxide changes according to Henry's Law.

4 Conclusion

Results provide insights to the stability of chlorine dioxide when used as a disinfecting agent in pipes and storage tanks that supply different water qualities at brewery plants. For treated reverse osmosis water, it was shown that even at temperatures up to 80 °C ClO_2 decomposes very slowly. It can be assumed that reduction of pH resulting from dosage of the acidic chlorine dioxide solution is the inhibiting factor to the decomposition reaction in the almost entirely unbuffered water.

Regarding corrosive properties in hot water distribution systems, the higher stability of chorine dioxide in such waters means a higher redox potential at elevated temperatures and acidic pH values. As these factors generally favour pitting corrosion [10, 18], it can be concluded that chlorine dioxide treatment of decarbonized waters, which cannot sufficiently buffer the dosed disinfectant solution, increases corrosion probability of stainless steel equipment.

In order to reduce the corrosion risk in these cases, it is necessary to plan water treatment steps in a way that pH is maintained neutral after dosage of chlorine dioxide. Hydrochemical calculation programs like PHREEQC can be used for this purpose. As the performed simulations show, even low concentrations within the German drinking water law limit of 0.4 mg/L can cause critical pH reductions if the buffer capability of raw waters is low.

However, besides media composition, corrosion risk always depends on multiple factors (e.g. material, suface quality, flow conditions, etc.) which need to be considered. While chlorine dioxide concentrations tested during this study and usually used in disinfection of water circuits are relatively low compared to CIP-processes, the permanent exposure to oxidizing solutions and lower flow velocities can be initiating factors to pitting corrosion.

An important factor on which litte has been published yet is corrosion due to outgassing of chlorine dioxide, which can affect upper sections of hot water tanks [11]. As determined in this study, the transfer of ClO_2 into the headspace of containers has no influence on decomposition kinetics. Yet, the corrosivity of outgassing chlorine dioxide itself or influencing factors were not analysed.

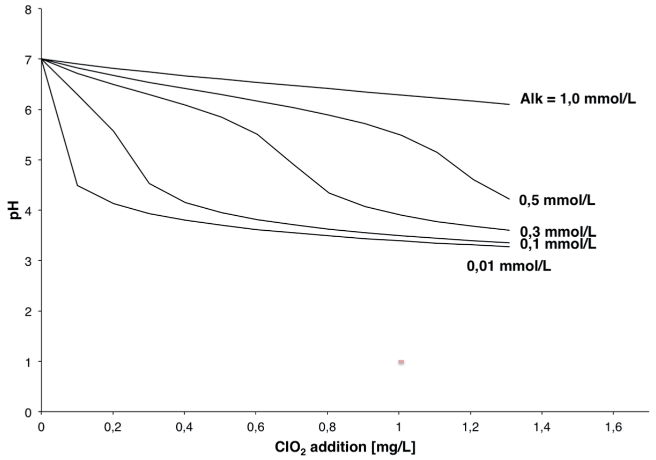

Fig. 5 Calculated change of pH by addition of ClO_2-solution (0,1 g/L ClO_2; pH 0,5) to waters with different alkalinities at a temperature of 25 °C

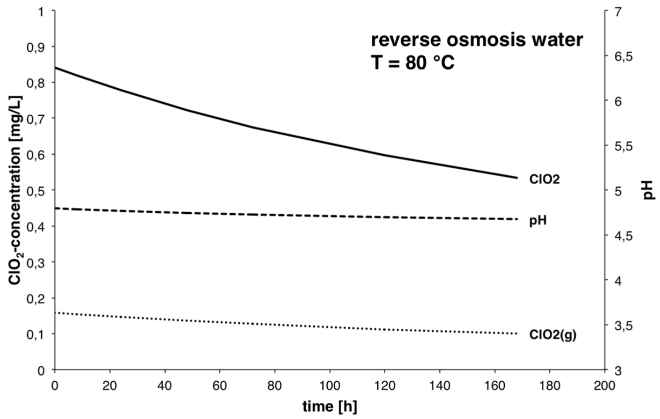

Fig. 6 Simulation of ClO_2-decomposition in reverse osmosis water at 80 °C and its influence on pH and gas phase concentration

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