

# Large NaCl-effect on the Decomposition Rate of Chlorate Ions in HCl-containing Brine Solutions and Its Consequences for the Chlor-alkali Industry

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## Abstract

The decomposition rate of chlorate ( $\text{NaClO}_3$ ) in aqueous solutions (brines) containing initially 6:1 mol/mol  $\text{HCl}:\text{NaClO}_3$  is studied at 90°C at various NaCl contents experimentally. A strong positive effect of NaCl addition is shown on the decomposition rate of chlorate. It is found more reasonable in the chlor-alkali industry first to saturate the brine by sodium chloride and only then to eliminate from it the chlorate by adding HCl (before the solution is transferred into the electrolysis cell to be protected from the chlorate ions).

## Keywords

brine solution, chlorate decomposition rate, HCl, effect of NaCl

## 1 Introduction

Unwanted chlorate ions form as a side-product in chlor-alkali membrane electrolysis cells [1–3]. Therefore, reduction and elimination of chlorate from brines is of high industrial importance [4–9]. For this reason many papers have been devoted to study chlorate-chloride reactions [10–17]. The chlorate content of the brine should be kept below an acceptable level, as its presence is detrimental for the membrane in the electrolytic cell. This is possible only if the chlorate is decomposed /eliminated/ reduced in each production cycle.

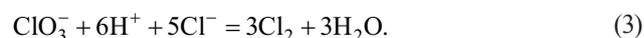
One of the ways to decompose chlorate dissolved in brine is to add acids to it, such as HCl. In this case, the following two major chemical reactions take place [18–22]:



The relative rates of the two parallel reactions (Eqs. (1) and (2)) depend on the  $\text{HCl}:\text{NaClO}_3$  mole ratio, on the pH of the solution, on temperature and on the salt (NaCl) content of brine. Chlorine dioxide is a strong oxidizer, and this property can be used in different industries [23–25].

For the same reason chloride dioxide is toxic [26, 27], and thus for safety reasons its formation in the chlor-alkali industry should be kept to minimum. This is achieved with applying high  $\text{HCl}:\text{NaClO}_3$  molar ratios, as follows from the stoichiometries of reactions (Eqs. (1) and (2)).

It is more correct to write reaction (Eq. (2)) in a partly ionic form, as some of the components of this reaction are highly dissociated in water:



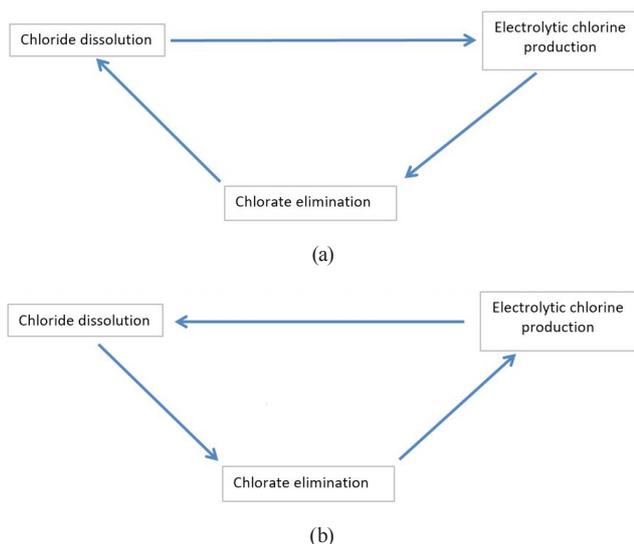
This ionic form of the chemical reaction was used also to explain kinetic measurements at both laboratory [18] and industrial [20] scales. However, in these publications [18, 20] experimental details and primary experimental results are not provided in sufficient detail. The experimental findings of Dotson are presented only in the form of the following semi-empirical kinetic equation [18]:

$$-\frac{d[\text{ClO}_3^-]}{dt} = 1.83 \times 10^{18} \times \exp\left(-\frac{35056}{RT}\right) \times \exp\left([\text{Cl}^-]\right) \times [\text{ClO}_3^-] \times [\text{H}^+]^2, \quad (4)$$

where  $[X]$  is the concentration of component  $X$  in brine in g-mol/litre,  $T$  is absolute temperature in  $K$  and  $t$  is time in minutes. Eq. (4) is valid in the following parameter ranges [18]: (0 ... 4.4) mol/litre NaCl; (1 ... 18) mol/mol  $HCl:ClO_3^-$  and (70 ... 105) °C = (343 ... 378) K. However, it is not clear how many experimental points are behind Eq. (4) and how well Eq. (4) reproduces those experimental results (the primary experimental data are not available nor in tabular, neither in graphical format in [18]).

In this work the findings of Dotson will be checked by careful experiments, providing all primary experimental data. In this study the molar ratio of  $HCl:ClO_3^-$  will be fixed at 6:1, i.e. at the stoichiometry of Eqs. (2) and (3), and temperature will be kept at a constant value of 90°C = 363 K. The goal of the present paper is to study the salt effect at high salt content-range on the rate of decomposition of the chlorate.

In addition to scientific interest, this question is of high interest for the chlor-alkali industry. In this industry chlorate is usually decomposed right after electrolysis (see in Fig. 1(a)), which is a clever choice if the rate of chlorate decomposition decreases with increasing the NaCl content. However, Fig. 1(b) is also possible (see Fig. 1), when chlorate is decomposed after the brine is re-saturated by the salt and right before it is transported for electrolysis, which is a clever choice if the rate of chlorate decomposition increases with increasing the NaCl

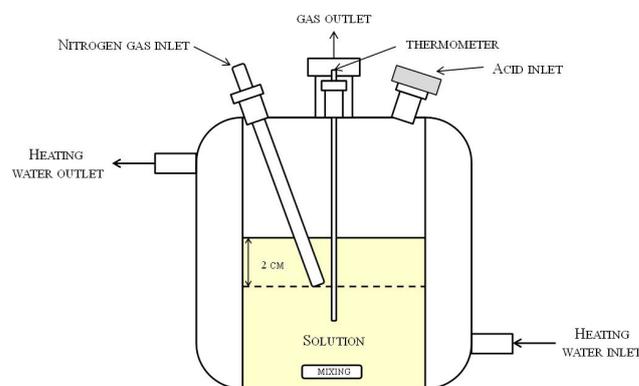


**Fig. 1** Schematic of the chlor-alkali process showing only the three major processes involved. According to part (a) the chlorate is eliminated right after the electrolysis, i.e. when the brine contains the lowest amount of NaCl, while according to part (b) the chlorate is eliminated right after the re-saturation by NaCl, i.e. when the brine contains the highest amount of NaCl

content. By the end of this paper it will be clear which of the parts of Fig. 1 is more preferable. It will be shown that the results of Dotson [18] and the patent based on it [20] are basically correct. However, some further details will be clarified in this paper.

## 2 Experiments

The schematic of the apparatus used to study the decomposition rate of sodium chlorate according to reactions (Eqs. (2) and (3)) is shown in Fig. 2. The aqueous solutions containing the controlled amounts of sodium chlorate and sodium chloride are kept in a double-walled beaker. Temperature is established at 90°C using heating water and is monitored during the experiment. Temperature variations during all experiments are within  $\pm 0.5^\circ C$ . Nitrogen gas is let 2 cm below the surface of the solution with a constant flow rate of 11 L/h. The bottom of the solution is mixed by a magnetic mixer with a rotation speed of 400 rpm (= rotation per minute). When steady state is established from point of view of solution flow, nitrogen flow and temperature, HCl is added in the amount of 6:1 (mol:mol)  $HCl:NaClO_3$ . The escaping nitrogen gas containing some chlorine gas according to reactions (Eqs. (2) and (3)) is bubbled through a NaOH solution. The moment when the HCl acid is added to the solution is taken as time zero for the reaction (it takes less than half a minute to add all the acid to the solution). Time to time a small sample is taken from the solution through the "acid inlet" neck (see Fig. 2). Each such sample is subdivided into two sub-samples and is analyzed for its chlorate content by iodo-metric titration. The two sub-samples are analyzed independently and the average analytical result is accepted if the difference between them is smaller than 5 rel %.



**Fig. 2** Schematic of the experimental setup to study the decomposition rate of chlorate according to reactions (Eqs. (2) and (3))

### 3 Experimental results

#### 3.1 Preliminary experimental results

First the importance of the presence of HCl was checked. For this, a blank experiment was run with zero amount of HCl under all other parameters kept constant. No decomposition of the chlorate was found in absence of HCl within 60 minutes at 90°C (see the 0-0 point in Fig. 3). It means that for the decomposition of chlorate some acid is indeed needed as expected from reactions (Eqs. (1) and (2)).

Second, in the presence of HCl the formation of a chlorine gas was confirmed in agreement with reactions (Eqs. (2) and (3)) by observing during the reaction the light-green color-change of both the solution and the gas above it.

Third, the importance of the nitrogen flow was checked in several experiments. In standard experiments nitrogen was bubbled into the solution with the flow rate of 11 L/h. As reactions (Eqs. (2) and (3)) lead to the formation of 3 moles of Cl<sub>2</sub> gas per 1 mole of decomposed chlorate, the nucleation of chlorine bubbles might be a rate limiting step of the whole process, which can be eliminated if nitrogen is bubbled through the solution. Therefore additional experiments were run when the nitrogen flow of the same flow rate was led above the solution and even when the nitrogen flow was absent. Although the conversion rate of chlorate somewhat decreased in both cases, this decrease was not significant. Further, the nitrogen flow rate was increased by about 5 times (to 50 L/h) while nitrogen was bubbled into the solution. Although this led to some increase in the conversion rate of the chlorate, this effect was not significant, either. Therefore nucleation of the chlorine bubbles is not a rate limiting step of reactions (Eqs. (2) and (3)).

As will be shown below, the increase in the NaCl concentration significantly enhanced the conversion rate of chlorate decomposition. In some experiments additional NaCl was added to the saturated solution. It was found that increasing the amount of NaCl above its saturation limit did not influence the conversion of chlorate above the level reached using the saturation concentration of NaCl (see the last points in Fig. 3). Thus, the decomposition of chlorate is a homogeneous chemical reaction and the presence of a solid NaCl phase does not have any influence on it.

#### 3.2 The decomposition rate of chlorate as function of NaCl-content

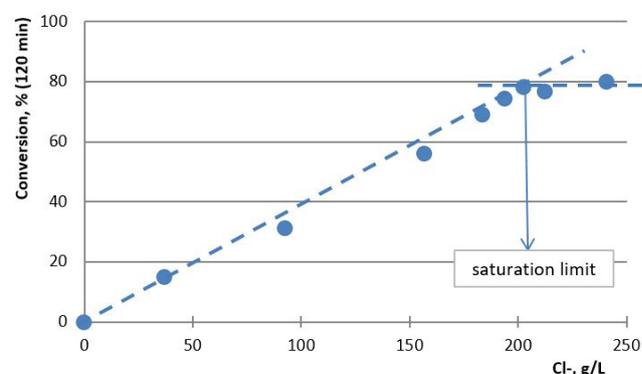
The primary results of the experiments are shown in Table 1. In Table 1 the measured concentrations of NaClO<sub>3</sub> (g/L) are shown as function of time in the interval 0 ... 120 min at different NaCl contents in the interval 0 ... 330 g/L at constant

temperature of 90°C, at constant HCl:NaClO<sub>3</sub> = 6:1 mol/mol ratio and at constant nitrogen flow of 11 L/h (nitrogen is bubbled through the brine solution). In the second row of Table 1 the initial chloride ion content is calculated, supposing that both the HCl and NaCl molecules are fully dissociated. In the last line of Table 1 the conversion (%) of chlorate is calculated after 120 min compared to its initial concentration. In Fig. 3 the conversion % of the chlorate is shown as function of the Cl<sup>-</sup> ion content of the solution. As follows from Fig. 3, all measured points are situated along an approximated straight line starting from the origo, at least until the saturation limit. Above the saturation limit the conversion becomes independent on the concentration.

Based on Table 1 and Fig. 3 it is evident that the chlorate conversion considerably increases with the increase in the NaCl-content of the brine solution from 99 g/L to its saturated value of about 270 g/L. Thus, from the technological

**Table 1** Primary experimental results: measured NaClO<sub>3</sub> concentrations in g/L as function of reaction time at different NaCl contents at 90°C and HCl:NaClO<sub>3</sub> = 6:1 mol/mol with nitrogen gas bubbled into the 250 mL solution with flow rate of 11 L/hour

NaCl, g/L	0	99	200	240	255	270	284	330
Cl <sup>-</sup> , g/L	37.2	92.9	157.0	183.9	194.0	202.7	212.8	241.1
0 min	18.6	16.4	17.8	19.1	19.6	19.4	20.2	20.4
10 min	16.3	15.3	12.5	10.9	9.5	8.3	8.2	7.0
20 min	16.2	14.7	11.5	9.2	8.0	6.9	7.1	5.9
30 min	16.2	14.5	10.3	8.3	8.4	5.9	6.6	5.4
40 min	16.1	13.6	9.9	7.8	6.8	5.7	6.2	5.1
50 min	16.0	13.3	9.3	7.4	6.4	5.5	5.8	4.9
60 min	15.6	13.1	9.1	7.1	6.2	5.2	5.5	4.7
90 min	15.9	12.1	8.1	6.2	5.5	4.7	5.1	4.3
120 min	15.8	11.3	7.8	5.9	5.0	4.2	4.7	4.1
conversion, %	15.1	31.3	56.2	69.1	74.5	78.4	76.7	79.9



**Fig. 3** Dependence of chlorate conversion on the chloride ion content of the solution, according to Table 1 (90°C, HCl:ClO<sub>3</sub><sup>-</sup> = 6:1 mol/mol, N<sub>2</sub> flow = 11 L/hour, 250 mL of solution, measured after 120 min, the last points are taken in over-saturated solutions)

point of view Fig. 1 (b) is preferred in Fig. 1, i.e. the elimination of chlorate from the brine should be performed when the brine is saturated in NaCl.

#### 4 Conclusions

It is more reasonable in the chlor-alkali process first to re-saturate the brine by sodium chloride and only then to purify it from sodium chlorate by adding HCl before the solution is added into the electrolysis cell again (see Fig. 1(b)). This finding re-confirms the previous findings of Dotson et al [18, 20], but in this paper further experimental details are added (see Fig. 4).

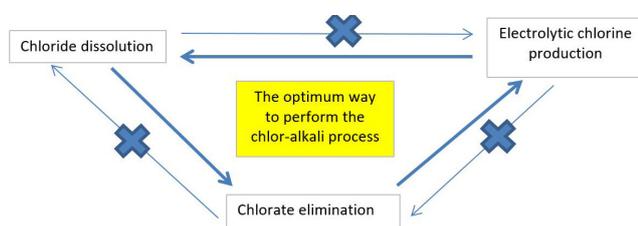


Fig. 4 Graphical abstract

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- *Ethics*: There are no ethical issues about this research, as it is done only on inorganic, not living objects.
- *Data accessibility*: All data are collected in Table 1 of this manuscript.
- *Authors contributions*: LF designed the study. AJN and DS carried out the measurements including analytical chemistry and collected the primary experimental data. DS designed Fig. 2. GK produced Figs. 1, 3 and 4 and wrote the manuscript. All authors gave final approval for publication.
- *Conflict of interest*: The authors declare no competing interest.
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