Suppressed oxygen evolution during chlorate formation from hypochlorite in the presence of chromium(VI)

Balázs Endrődi, a, b* Staffan Sandin, a Mats Wildlock, c Nina Simic c and Ann Cornell a*

Abstract

BACKGROUND: Chromium(VI) is a crucial electrolyte component in industrial chlorate production. Due to its toxicity, it urgently needs to be abandoned and its functions fulfilled by new solutions. In the industrial production of sodium chlorate, homogeneous decomposition of the hypochlorite intermediate to chlorate is a key step. As a competing loss reaction, hypochlorite can decompose to oxygen. How chromium(VI) affects these reactions is not well understood.

RESULTS: This work shows, for the first time, that chromium(VI) selectively accelerates the chlorate formation from hypochlorite both in dilute and concentrated, industrially relevant solutions. The effect of the ionic strength and the specific contribution of different electrolyte components were systematically studied. By simultaneously measuring the concentration decay of hypochlorite (UV−vis spectroscopy) and the oxygen formation (mass spectrometry), both the rate and the selectivity of the reactions were evaluated.

CONCLUSION: In the presence of chromium(VI) the hypochlorite decomposition is described by the sum of an uncatalyzed and a parallel catalyzed reaction, where oxygen only forms in the uncatalyzed reaction. When removing chromium(VI), the homogeneous oxygen formation increases, causing economic and safety concerns. The need for a catalyst selective for chlorate formation is emphasized.

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INTRODUCTION

About 95% of the sodium chlorate produced worldwide is used in kraft pulp bleaching. 1 As the use of different paper products is increasing, the demand for sodium chlorate is still growing. The annual production was about 4 million tons in 2017. 2 This amount is almost exclusively produced by the electrolysis of concentrated brine solutions (Eqn (1)), making the chlorate production one of the major electrochemical industrial processes of today.

\[ NaCl + 3H_2O \xrightarrow{\text{Electrical energy}} NaClO_3 + 3H_2 \]  

Chromium(VI) is an essential component in the chlorate electrolyte, ensuring high hydrogen evolution selectivity on the cathode. 3–5 As all chromium(VI) species are classified as carcinogenic, mutagenic and reprotoxic (CMR), it has been included in Annex XIV of REACH, and is aimed to be phased out from industrial use. An authorization must now be granted by the European Commission for continued industrial use in Europe and a search for alternatives 6 to chromium(VI) in the chlorate process. 5 Even though the effect of chromium(VI) on the cathode reactions has been extensively studied, 7–11 less is known about its role in the homogeneous decomposition of hypochlorite, and most importantly, the losses due to oxygen formation has not been clarified yet.

* Correspondence to: B Endrődi, Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary, E-mail: endrodib@chem.u-szeged.hu; or A Cornell, Applied Electrochemistry, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, Stockholm, Sweden. E-mail: ann.cornell@ket.kth.se

Balázs Endrődi and Staffan Sandin contributed equally to this work.

a Department of Chemical Engineering, Applied Electrochemistry, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, Stockholm, Sweden
b Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary
c AkzoNobel Pulp and Performance Chemicals, Bohus, Sweden
During the electrolytic process, chlorine produced on the anode dissolves and forms hypochlorite ions and hypochlorous acid (for simplicity, in what follows the term ‘hypochlorite’ will be used as a general expression for the sum of these species). The chlorate product is formed from hypochlorite according to the overall stoichiometry shown in Eqn (2). The kinetics of the reaction in the absence of chromium(VI) was investigated earlier, and a complex reaction mechanism was proposed.13 Most importantly, the model describes a fast initiation step between two HClO molecules (or HClO and ClO\(^{-}\)). The third molecule (either ClO\(^{-}\) or HClO) reacts in a subsequent, rate-determining reaction step. This model satisfactorily describes the experimentally found third-order kinetics (Eqn (3), where \(C_{t}=\left[H\text{ClO}\right]+\left[\text{ClO}^{-}\right]\) and \(k\) is the third-order rate constant). Note that in the equations expressed with \(C_{t}\) (instead of [HClO] and [ClO\(^{-}\)]) \(k\) is the experimental third-order rate constant, which contains the value of pH and \(pK_{a}\) as detailed in the Supporting information in File S1.

\[
2\text{HClO} + \text{ClO}^{-} \rightarrow \text{ClO}^{-}_{2} + 2\text{Cl}^{-} + 2\text{H}^{+} \quad (2)
\]

\[
\frac{dC_{t}}{dt} = -k \left[\text{HClO}\right] \left[\text{ClO}^{-}\right] = -k_{1} C_{t}^{2} \quad (3)
\]

\[
2\text{ClO}^{-} \rightarrow \text{O}_{2} + 2\text{Cl}^{-} \quad (4)
\]

\[
2\text{HClO} \rightarrow \text{O}_{2} + 2\text{Cl}^{-} + 2\text{H}^{+} \quad (5)
\]

Similarly to the chlorate formation reaction, the decomposition of hypochlorite to oxygen (Eqn (4) and (5)) has been shown to follow third-order kinetics in dilute solutions at pH = 6.5.13 Its rate is pH dependent, having its maximum at the same pH as the chlorate-forming reaction. It was therefore proposed that these reactions share an intermediate, which can decompose to either oxygen or chlorate.13 In the absence of catalytic species in the solution, the preferred reaction path is the chlorate formation, and only a minor portion of hypochlorite decomposes to oxygen. The relative rate of these reactions is however strongly affected by the presence of different impurities in the solution.13–15 Note, that an increased oxygen formation is not only an efficiency loss but also a safety hazard, as when it exits the electrolyzers with chlorine gas. The electrolyte composition can greatly affect the reaction path and oxygen formation. It may have a very strong influence on the reaction path, and pH-dependent oxygen formation was observed.22,24

**METHODS**

**Chemicals**

Commercially purchased chemicals were used as received, without further purification. NaClO (0.5 mol dm\(^{-3}\) solution in 0.1 mol dm\(^{-3}\) NaOH, containing 0.5 mol dm\(^{-3}\) NaCl), NaClO\(_3\cdot\) H\(_2\)O (ACS grade), NaOH (analytical reagent), acetic acid (GPR Rectapur) and HCl 37% solution (Emsure) were purchased from WVR International, Spånga, Sweden while KI (pro analysi) and Na\(_2\)Cr\(_2\)O\(_7\) (pro analysi) were from Merck, Stockholm, Sweden and anhydrous sodium acetate (>99% FCC) from Sigma-Aldrich, Stockholm, Sweden. The sodium chlorate used in our experiments was provided by AkzoNobel and was purified by recrystallization. Commercially available buffer solutions of pH = 4.00 and 7.00 from Metrometh (Metrohm 827 pH lab instrument or Metrometh 907 Titrator titrator equipped with a Unitrode with Pt 1000 combined pH and temperature sensor) prior to each experiment. MilliQ grade \((\rho = 18.2 \text{M} \Omega \cdot \text{cm})\), produced by a Millipore Direct–Q3 UV instrument water was used for preparing all aqueous solutions.

The salts (sodium chlorate, sodium chloride) were dissolved in the reaction chamber at T = 80 °C. Subsequently, the hypochlorite (50 cm\(^{-2}\)) was added to the solution to make a total volume of V = 320 cm\(^3\). The sodium perchlorate solutions were prepared similarly, based on literature data.25

**Quantifying the formed oxygen amount**

The measurements were performed in a custom-designed setup (see Fig. 1) in which the pH was continuously monitored and regulated (Metrohm 907 Titratior, using 6 mol dm\(^{-3}\) HCl and 2 mol dm\(^{-3}\) NaOH solutions, equipped with a Unitrode Pt 1000 combined pH and temperature sensor). In this study, ‘pH’ is defined as the reading from the instrument, after its calibration to the above mentioned commercial buffer solutions. Note that in the very concentrated electrolytes the activity of H\(^{+}\) may have a very different value. The temperature of the solution was measured with the same electrode and was regulated by circulating water from an external heater bath in the jacket of the cell. The concentration of hypochlorite in the solution was followed by taking liquid aliquots and analyzing them by UV–vis spectroscopy (Expe- deon VersaWave type instrument). The molar absorbance value of \(ε_{292\text{nm}} = 350 \text{dm}^{3}\text{mol}^{-1}\text{cm}^{-1}\) was used for the calculations, which was confirmed by our own calibration experiments (see details in Supporting information in Figure S1 – S3 in File S1).26 The
sodium chlorate concentration of the solution was not analyzed in this work, as the precision of any applicable analytical method (titration, ion chromatography) is not high enough to reliably detect the small changes in the concentrated solutions (5.2 mol dm$^{-3}$ NaClO$_3$) used in this study (maximum 80/3 mmol dm$^{-3}$ increase, as dictated by the stoichiometry of the hypochlorite decomposition reaction, shown in Eqn (2), and by the initial concentration of hypochlorite, $C_{i} = 80$ mmol dm$^{-3}$). Note that in previous work$^{13}$ it was shown, that the mass balance during hypochlorite decomposition can be reliably given based on measuring only oxygen or chlorate production rate in relation to hypochlorite concentration decay. The closed reaction vessel (Fig. 1) was continuously purged with argon carrier gas, and the cell off-gas was fed to a mass spectrometer (Hiden HPR-20 type benchtop mass spectrometer, equipped with a quartz capillary inlet) where it was continuously analyzed by monitoring the typical m/z values of the species present.

For a typical measurement, the hypochlorite-containing solution was first heated to 80°C, while its pH was kept at pH $\approx 12$ to minimize the decomposition rate of hypochlorite. During this time, three samples were taken for UV–vis analysis to reliably quantify the initial hypochlorite concentration. Subsequently, the reaction was initiated by adding a predetermined volume of 6 mol dm$^{-3}$ HCl to reach pH $= 6.5$, which was then kept constant during the measurements. Further details can be found in the Supporting information in File S1).

**RESULTS AND DISCUSSION**

**The effect of chromium(VI) on hypochlorite decomposition in dilute solutions**

The rate and selectivity of hypochlorite decomposition was first studied in dilute solutions (80 mmol dm$^{-3}$ hypochlorite $+ 80$ mmol dm$^{-3}$ NaCl) without any further additives. The oxygen formed was quantified by continuously analyzing the cell off-gas using mass spectrometry (Fig. 2(A)), while the concentration of hypochlorite in the solution was monitored by UV–vis spectroscopy (Fig. 2(B)). At the beginning of the recorded oxygen evolution rate curve a delay time of 2 – 3 min was observed. This can be attributed to the geometry of the setup, as a dead volume is formed by the headspace over the solution and by the volume of the tubing connecting the cell to the mass spectrometer. Although this makes it difficult to extract kinetic information from the oxygen evolution curves, it does not affect the quantification of the total amount of formed oxygen.

The kinetics of the hypochlorite decomposition reaction was analyzed from the hypochlorite concentration decay curves (Fig. 3(A)) calculated from the UV–vis measurements (Fig. 2(B)). In good agreement with our previous results, under these conditions the decomposition reaction follows third-order kinetics with respect to hypochlorite as indicated in Eqn (3) (in the model $k_1 = k_m = k_2 \frac{p_{CH}^{-1}p_{Cl}}{(p_{OH}^{-1}p_{Cl}^{2})^{\frac{1}{2}}}$, further explained in the Supporting information in File S1).$^{13}$ The fitted experimental rate constant of
the reaction is \( k_1 = 0.38 \text{ dm}^6 \text{mol}^{-2} \text{s}^{-1} \). Using the acid dissociation constant of hypochlorous acid (p\( K_a \) = 6.93), \( k_1 \) was calculated to be 2.6 \( \text{dm}^6 \text{mol}^{-2} \text{s}^{-1} \), which coincides well with earlier results.\(^{13} \)

When adding 6 \( \text{g dm}^{-3} \) \( \text{Na}_2\text{Cr}_2\text{O}_7 \) to the solution, a large increase in the reaction rate was observed (Fig. 3(A)). Importantly, the decomposition rate no longer follows the third- order kinetic model, involving only hypochlorite species as reactants. Instead, in agreement with previous literature data,\(^{22,24} \) the hypochlorite decomposition rate \( \left( r = -\frac{dC_H}{dt} \right) \) can be described by the sum of an uncatalyzed third-order reaction \( (r_1 = k_1C_H^2) \), and a parallel catalyzed reaction \( (r_2 = k_2C_H) \) (Eqn (6), further detailed in the Supporting information in File S1). Using this model, the experimental data was fitted to give a partial order of \( \alpha = 2 \), with respect to hypochlorite species, in the second term.

\[
\frac{dC_H}{dt} = -(k_1C_H^2 + k_2C_H) = -(r_1 + r_2)
\]  

The total amount of oxygen formed during the reaction was calculated by integrating the oxygen evolution rate curves (Fig. 2(A)). To evaluate the selectivity of the reaction, this amount was divided by the total amount of decomposed hypochlorite (Fig. 3(B), columns with hatched pattern). As shown in Fig. 3(B), the oxygen formation ratio is decreased by c. 70% upon the addition of chromium(VI). Beyond its effect on the overall reaction rate, the presence of 6 \( \text{g dm}^{-3} \) \( \text{Na}_2\text{Cr}_2\text{O}_7 \) in the solution hence also leads to an increased selectivity towards chloride formation. After fitting the \( k_1 \) and \( k_2 \) values, the contribution of the two competing reaction paths to the overall hypochlorite decomposition can be calculated (see Supporting information Fig. S8A in File S1). The ratio of the total formed oxygen amount and the hypochlorite amount decomposed in the uncatalyzed reaction (Fig. 3(B), columns without pattern) agrees well with what was measured in the absence of the chromium(VI) additive. In other words, the total amount of the formed oxygen can be accounted for by assuming that oxygen is formed only in the uncatalyzed reaction, in the same ratio as in the additive free case. This indicates that in the chromium(VI) catalyzed reaction no, or a negligible amount of oxygen is formed.

**The effect of ionic strength on hypochlorite decomposition**

The effect of the ionic strength on the rate and selectivity of hypochlorite decomposition was studied by gradually increasing the NaCl and/or NaClO\(_3\) concentration until reaching a composition close to the industrial chlorate electrolyte (5.2 \( \text{mol dm}^{-3} \) (550 \( \text{g dm}^{-3} \)) \( \text{NaClO}_3 \) + 1.9 \( \text{mol dm}^{-3} \) (110 \( \text{g dm}^{-3} \)) \( \text{NaCl} \)) (Fig. 4(A)). In accordance with what is reported in the scientific literature,\(^{19–21} \) the decomposition rate of hypochlorite increases with increasing ionic strength. Comparing the hypochlorite concentration decay curves at the same ionic strength set by the two different salts (NaClO\(_3\) or NaCl) no significant differences can be observed. This suggests that these salts have no catalytic effect on the reaction, the increased decomposition rate is caused only by the higher ionic strength.

Just as in the case of the dilute hypochlorite solution, the decomposition follows third- order kinetics. This can be seen from the linearity of the data when \( C_H^{-2} \) is plotted as a function of time, according to the integrated form of the third-order kinetic expression. The fitted third-order rate coefficients (\( k_1 \)) can be found in Supporting information Table S1 in File S1. It is important to note that these values are only valid for the experimental conditions used in this study, as these depend on both the pH of the solution and the deprotonation constant of hypochlorous acid.\(^{13} \) Using the literature value of p\( K_a \) = 6.79 measured in high temperature high ionic strength solutions, the value of \( k_1 \) was calculated from \( k_1 \) (as detailed in the Supporting information in File S1), and good agreement was found between our result and those reported earlier for \( \sim 7 \text{mol dm}^{-3} \) ionic strength solutions (12.8 vs 13.1 \( \text{mol}^2 \text{dm}^{-6} \text{s}^{-1} \)).\(^{22} \)

The selectivity of the reaction is also affected, as a more pronounced oxygen evolution can be observed in solutions of higher ionic strength (Fig. 4(B)). Again, the ratio of the evolved oxygen to the decomposed hypochlorite amount is the same (within experimental error) for the different solutions with the same ionic strength.

Experiments using NaClO\(_4\) resulted in similar conclusions, namely that both the rate of hypochlorite decomposition (Supporting information Fig. S7A in File S1), and the oxygen formation ratio (Supporting information Fig. S7B in File S1) increase with ionic strength. The fitted third-order rate constants are however
significantly higher when the same ionic strength is set by NaClO₄ instead of NaClO₃ and/or NaCl (Fig. 5 and supporting information Table S1 in File S1). This is indeed a very interesting effect, especially since NaClO₄ is an unwanted by-product in the process.¹⁸ The reason behind this increased reaction rate is not fully understood yet. Note however, that contrary to ClO₄⁻, both Cl⁻ and ClO₃⁻ ions are products in the hypochlorite decomposition reaction (Eqn (2)). Any equilibrium reaction steps before the rate limiting step in the reaction scheme involving Cl⁻ and/or ClO₃⁻ may influence the reaction rate. Another source of this difference might be found in the different interaction of the perchlorate and chlorate ions with water. Both the chlorate and perchlorate are weakly hydrated ions, while chloride has a larger hydration shell due to its stronger hydrogen bonds to water.²⁷ As the ionic strength is getting very high, there might be a significant difference in available water in chlorate/chloride electrolyte compared with perchlorate electrolyte, where ion pairing might play an important role. In reaction (2) more species form (ClO₃⁻, Cl⁻, H⁺) than react (HClO, ClO⁻) requiring larger amounts of water for the hydration.

Hence a limited access to available water may have an inhibiting effect on the rate of this reaction.

The effect of chromium(VI) on hypochlorite decomposition in concentrated solutions

The effect of Na₂Cr₂O₇ addition was studied in 5.2 mol dm⁻³ NaClO₃ + 1.9 mol dm⁻³ NaCl solutions (Fig. 6). The decomposition rate increases with increased amount of chromium(VI) in the solution (Fig. 6(A)). Similarly to the case of the dilute solution, the decomposition curve in the presence of Na₂Cr₂O₇ cannot be fitted by a single third-order term including hypochlorite species only. This is readily seen from the deviation of the data from the linear trend when C₂H⁻ is plotted as a function of time (according to the integrated form of the third-order kinetic expression). Instead, the previously shown kinetic model, (Eqn (6)), describes the curve satisfactorily. For these fittings the k₁ value from the measurements without chromium(VI) addition was used, while k₃ was fitted. Just as in the case of the dilute electrolyte, a ≈ 2 was found from the fittings, and therefore this value was used to calculate the curves presented in Fig. 6(A). Plotting the logarithm of the fitted k₂ values as a function of the logarithm of the Na₂Cr₂O₇ concentration (Supporting information Fig. S6 in File S1), a partial order of ≈1.5 was determined for Na₂Cr₂O₇.

As seen from the decreasing ratio of oxygen formed to the total amount of decomposed hypochlorite (Fig. 6(B), columns with hatched pattern), the selectivity of the reaction towards chlorate formation increases continuously with increasing concentration of Na₂Cr₂O₇. At the typical industrial concentration of 6 g dm⁻³, the total formed oxygen amount is 0.8% of the decomposed hypochlorite amount, a 70% decrease compared with the chromium(VI)-free case (2.7%). Calculating the contribution of the two competing reaction paths, the amount of hypochlorite decomposed in the uncatalyzed reaction was quantified (supporting information Fig. S8B,C in File S1). The ratio of this and the total amount of formed oxygen (Fig. 6(B), columns without pattern) agrees well at all concentrations with what was measured in 5.2 mol dm⁻³ NaClO₃ + 1.9 mol dm⁻³ NaCl containing solutions, in the absence of the chromium(VI) additive. Again, this indicates that in the chromium(VI) catalyzed reaction no, or a negligible
the rate-determining reaction (Eqn (7)) proceeds via a transition state complex, formed by a hypochlorite ion and an intermediate in the reaction scheme during or after the rate-determining reaction. This corroborates our previous hypothesis, namely that the hypochlorite decomposition to chlorate or oxygen share an intermediate in the reaction scheme during or after the rate-determining step. A Cl₂O₂·H₂O molecule. In the reaction scheme suggested by Kalmár24 for the catalyzed case (Eqn (8)), chromate takes the place of the hypochlorite ion in the transition state. In a chromium(VI)-containing electrolyte the uncatalyzed and catalyzed reactions proceed in parallel. Hence, we assume, that in the presence of chromium(VI) both transition state complexes form in a concentration ratio dependent on the chromium(VI) concentration. The contribution of the uncatalyzed reaction path, and the formation of oxygen decreases simultaneously with the increasing chromium(VI) concentration. This suggests that the oxygen formation proceeds only through the complex formed in Eqn (7), as summarized in Scheme 1.

**Industrial impact of the results**

In industrial chlorate electrolytes the Na₂Cr₂O₇ concentration is typically kept in the range 3–8 g dm⁻³ and, according to industrial experience, the steady-state hypochlorite concentration in the electrolyzer remains in the range of 1–3 g dm⁻³ (25–40 mmol dm⁻³). As shown in Fig. 7, calculated from the experimentally determined rate constants (Supporting information Table S1 in File S1), with decrease of the hypochlorite concentration and/or increase in chromium(VI) concentration the contribution of the catalyzed route (r₂) to the overall decomposition rate (r = r₁ + r₂) of hypochlorite becomes increasingly important. At industrially relevant conditions the chromium(VI) catalyzed decomposition of hypochlorite is dominant. As no oxygen seems to be formed in this step, the chromium(VI) additive in the solution contributes to the overall efficiency of the chlorate synthesis by lowering the homogeneous formation of the oxygen by-product. Also, the low steady-state hypochlorite concentration leads to moderate anodic oxygen formation from hypochlorite.

In the absence of chromium(VI) the decomposition rate will decrease, and the steady-state hypochlorite concentration will therefore increase. This will cause an increased formation of oxygen from anodic reactions in addition to the important homogeneous oxygen formation. As earlier mentioned, the overall hypochlorite decomposition and both the oxygen and chlorate formation reactions are of third order with respect to hypochlorite species. This implies that the selectivity between oxygen and chlorate formation in the homogeneous reactions is independent of hypochlorite concentration.

Hypochlorite and hydrogen forms in the same rate in a chlorate cell, as shown by the cathodic and anodic half-cell reactions and the hydrolysis equilibrium of chlorine (Eqns (9)–(11)).

\[ \text{H}_2	ext{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (9) \]

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad (10) \]

\[ \text{Cl}_2 + \text{H}_2\text{O} = \text{HOCI} + \text{HCl} \quad (11) \]

During the steady-state operation there is no hypochlorite accumulation, the rate of hydrogen production and hypochlorite decomposition are equal. The constant oxygen formation to hypochlorite decomposition ratio would thus mean that the uncatalyzed homogeneous decomposition of hypochlorite may contribute to the O₂ content of the off-gas with up to 2.7 V/V%, as dictated by the formed oxygen/decomposed hypochlorite ratio of 0.027. In the currently applied cell configurations the oxygen content of the off-gas is typically 2–3 V/V% in the presence of chromium(VI), where the majority of hypochlorite decomposes through the catalyzed reaction (Fig. 7). According to our results,
this oxygen is not formed during hypochlorite decomposition, but most probably comes from the anodic reaction. In the absence of chromium(VI) all hypochlorite would decompose through the uncatalyzed reaction, which could, depending on the process configuration, increase the oxygen level of the cell off-gas above the explosion limit.

As the chromium(VI) additive must be replaced in the chlorate process according to the decision of the European Commission, finding a catalyst selective for chlorate formation is crucial for the safe and sustainable operation of the current chlorate producing plants. As our results emphasize - for the first time - the homogeneous oxygen formation must be taken into consideration when evaluating the potential candidates to replace chromium(VI).

CONCLUSIONS

In this study the decomposition of hypochlorite was investigated in solutions of different ionic strength and Na$_2$Cr$_2$O$_7$ concentration. By simultaneously measuring the concentration decay of hypochlorite (UV–vis spectroscopy) and the formed oxygen amount (mass spectroscopy), both the rate and the selectivity of the reaction was evaluated.

In the absence of Na$_2$Cr$_2$O$_7$, the decomposition reaction follows third-order kinetics with respect to hypochlorite, irrespective of the ionic strength of the solution. When adding Na$_2$Cr$_2$O$_7$ to the solution, the decomposition can however no longer be described by this model. Instead, the competition between two reactions (a catalyzed, involving chromium(VI) as a reactant, and an uncatalyzed, involving only hypochlorite species) is proposed in agreement with the results of previous works. The rate of decomposition increases both with ionic strength and chromium(VI) concentration. The increased ionic strength leads to a more pronounced oxygen formation, and hence to increased losses in the industrial process. When the ionic strength is set by NaClO$_4$, the increase in reaction rate is significantly higher than when using NaClO$_3$ and/or NaCl. On the other hand, the selectivity of the reaction is the same at any given ionic strength for these two background electrolytes. The Na$_2$Cr$_2$O$_7$ addition increases the rate of hypochlorite decomposition and leads to a significantly increased selectivity towards chlorate formation. Analyzing the contribution of the two parallel reactions in the Na$_2$Cr$_2$O$_7$ containing solutions, the results indicate that no, or a negligible amount of oxygen is formed in the chromium(VI) catalyzed decomposition reaction.

Because of the increasing health and safety concerns, the chromium(VI) additive must soon be removed from the industrial process. This would lead to increased oxygen formation, in particular from homogeneous hypochlorite decomposition, which would not only affect the process efficiency but would also constitute a safety hazard due to risk of explosions. Finding a selective catalyst for chlorate formation from hypochlorite decomposition is highly important for a chromium(VI)-free chlorate process.

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Supporting Information

Supporting information may be found in the online version of this article.

REFERENCES

1. Suhr M, Klein G, Kourti I, Gonzalo MR, Santonja GG, Roudier S et al., Best available techniques (BAT) Reference document for the production of pulp, paper and board, Publications Office of the European Union, Luxembourg (2015).
2. Beraud SSL, Gao A and Davis S, Sodium Chlorate - IHS Chemical Economics Handbook. IHS (2015). Available: https://ihsmarkit.com/products/sodium-chlorate-chemical-economics-handbook.html
3. Hardee KL and Mitchell LK, The influence of electrolyte parameters on the percent oxygen evolved from a chlorate cell. J Electrochem Soc 136:3214 (1989).
4. Karlsson RKB and Cornell A, Selectivity between oxygen and chlorine evolution in the chlor-alkali and chlorate processes. Chem Rev 116:2982 – 3028 (2016).
5 Endrődi B, Simic N, Wildlock M and Cornell A, A review of chromium(VI) use in chlorate electrolysis: functions, challenges and suggested alternatives. Electrochim Acta 234:108 – 122 (2017).
6 Endrődi B, Sandin S, Smulders V, Simic N, Wildlock M, Mul G et al., Towards sustainable chloride production: the effect of permanganate addition on current efficiency. J Clean Prod 182:529 – 537 (2018).
7 Cornell A, Lindbergh G and Simonsson D, The effect of addition of chromate on the hydrogen evolution reaction and on iron oxidation in hydroxide and chlorate solutions. Electrochim Acta 37:1873 – 1881 (1992).
8 Ahlberg Tidblad A and Lindbergh G, Surface analysis with ESCA and GD-OES of the film formed by cathodic reduction of chromate. Electrochim Acta 36:1605 – 1610 (1991).
9 Lindbergh G and Simonsson D, Inhibition of cathode reactions in sodium hydroxide solution containing chromate. Electrochim Acta 36:1985 – 1994 (1991).
10 Lindbergh G and Simonsson D, The effect of chromate addition on cathodic reduction of hypochlorite in hydroxide and chlorate solutions. J Electrochem Soc 137:3094 (1990).
11 Tidblad AA and Martensson J, In situ ellipsometric characterization of films formed by cathodic reduction of chromate. Electrochim Acta 42:389 – 398 (1997).
12 Adam LC, Fabian I, Suzuki K and Gordon G, Hypochlorous acid decomposition in the pH 5–8 region. Inorg Chem 31:3534 – 3541 (1992).
13 Sandin S, Karlsson RKB and Cornell A, Catalyzed and uncatalyzed decomposition of hypochlorite in dilute solutions. Ind Eng Chem Res 54:3767 – 3774 (2015).
14 Lister MW, Decomposition of sodium hypochlorite: the catalyzed reactions. Can J Chem 34:479 – 488 (1956).
15 Kim K-W, Lee E-H, Chung D-Y, Moon J-K, Shin H-S, Kim J-S et al., Manufacture characteristics of metal oxide–hydroxides for the catalytic decomposition of a sodium hypochlorite solution. Chem Eng J 200–202:52 – 58 (2012).
16 Yoon Y, Cho E, Jung Y, Kwon M, Yoon J and Kang J-W, Evaluation of the formation of oxidants and by-products using Pt/Ti, RuO₂/Ti, and IrO₂/Ti electrodes in the electrochemical process. Environ Technol 36:317 – 326 (2015).
17 Neodo S, Rosestolato D, Ferro S and De BA, On the electrolysis of dilute chloride solutions: influence of the electrode material on faradaic efficiency for active chlorine, chlorate and perchlorate. Electrochim Acta 80:282 – 291 (2012).
18 Kreysa G, Ota K and Savinell RF eds, Encyclopedia of Applied Electrochemistry. Springer New York, New York (2014).
19 Adam LC and Gordon G, Hypochlorite ion decomposition: effects of temperature, ionic strength, and chloride ion. Inorg Chem 38:1299 – 1304 (1999).
20 Lister MW, Decomposition of sodium hypochlorite: the uncatalyzed reactions. Can J Chem 34:465 – 478 (1956).
21 Lister MW, The decomposition of hypochlorous acid. Can J Chem 30:879 – 889 (1952).
22 Wanngård J and Wildlock M, The catalyzing effect of chromate in the chlorate formation reaction. Chem Eng Res Des 121:438 – 447 (2017).
23 Spasojević M, Marković D, Trišović T and Spasojević M, Mathematical model of the catalytic effect of chromium(VI) on hypochlorite disproportionation in chlorate electrolysis. J Electrochem Soc 165:E8 – E19 (2018).
24 Kalmár J, Szabó M, Simic N and Fábián I, Kinetics and mechanism of the chromium(VI) catalyzed decomposition of hypochlorous acid at elevated temperature and high ionic strength. Dalt Trans 47:3831 – 3840 (2018).
25 Miller ML and Doran M, Concentrated salt solutions. II. Viscosity and density of sodium thiocyanate, sodium perchlorate and sodium iodide. J Phys Chem 60:186 – 189 (1956).
26 Yan Y, Wang S, Liu Z, Wang H and Huang D, CdSe-ZnS quantum dots for selective and sensitive detection and quantification of hypochlorite. Anal Chem 82:9775 – 9781 (2010).
27 Eklund L, Hofer TS and Persson I, Structure and water exchange dynamics of hydrated oxo halo ions in aqueous solution using QMCF MD simulation, large angle X-ray scattering and EXAFS. Dalt Trans 44:1816 – 1828 (2015).