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The catalyzing effect of chromate in the chlorate formation reaction

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ABSTRACT

Electrolyte used in the manufacturing process of sodium chlorate contains chromate primarily to inhibit cathodic loss reactions. Chromate also accelerates the chlorate formation reaction which reduces the concentration of hypochlorite species in the chlorate cell leading to enhanced anodic current yield, reduced risk of oxygen explosions and reduced cost for the purification of the cell gas.

Laboratory scale trials show that the rate of chlorate formation can be described as an 'uncatalyzed' third order reaction with respect to hypochlorite species and a parallel chromate catalyzed reaction of apparent reaction order 2.2. Validation is presented based on data from electrolysis trials in pilot plant and bench scale at technically relevant conditions. If the dichromate concentration is increased from 0 to 5 g/L, more than 50% of the chlorate may be formed via the chromate catalyzed path and the apparent reaction order changes from 3 to about 2.4. The kinetic effect of the chromate species also lowers the optimum reaction pH below that of the uncatalyzed reaction. Furthermore, anionic hypochlorite does not seem to be necessary to generate chlorate via the chromate catalyzed path.

Other hypochlorite consuming reactions such as anodic and homogeneous oxygen formation as well as cathodic reduction and desorption of chlorine species in the cell gas only have a marginal effect on the hypochlorite concentration in the chlorate cell.

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1. Introduction

Electrochemical production of chlorates began in the 1890s driven by demands from the match industry, weed killing and perchlorate manufacture. Today, the dominating use is in the manufacture of chlorine dioxide being the principal bleaching agent for environmentally friendly ECF bleaching of chemical pulp. The global production capacity of sodium chlorate exceeded 4 Million tons 2012 (Sodium Chlorate, Chemical Engineer's Handbook, 2012). Comprehensive reviews describing the process and its chemistry have been compiled by Vogt et al. (2010), Colman and Tilak (1995) and Ibl and Vogt (1981), for instance.

Chlorate is produced in an electrolyte that besides the main constituents chloride and chlorate also contains small amounts of hexavalent chromium, Cr(VI). These species exist as chromate, hydrogen chromate and dichromate and the total chromium concentration is generally expressed as the equivalent concentration of sodium dichromate. The main purpose of adding Cr(VI) is to inhibit reduction losses of hypochlorites and chlorate at the cathode. However, Müller (1899) discovered that dichromate additions also accelerate chlorate formation. This attractive feature can be used to reduce the concentration of hypochlorite species in the electrolyser offering some important advantages such as improved current yield, reduced risk for cell gas explosion and reduced consumption of caustic and hydrochloric acid. Therefore, chlorate electrolyte generally contains as much as 3–8 g/L sodium dichromate (Vogt et al., 2010; Colman and Tilak, 1995) while only about 0.3 g/L is sufficient to efficiently suppress the cathodic loss reactions and attain cathodic current yields close to 100% (US Pat 3.535.216).

In a chlorate cell electrolyte circulates between the electrodes and a reaction volume. Chlorine is formed at the anode while hydroxide and hydrogen gas are formed at the cathode:

$$2Cl^- \rightarrow 2e^- + Cl_2(aq) \quad E^0 = 1.39\ V \tag{1}$$

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$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad E^0 = -0.82V \tag{2}$$

Unless explicitly mentioned, all standard potentials E^0 in this paper are given vs SHE at 25 °C.

The chlorine is rapidly absorbed in the electrolyte and hydrolyses to hypochlorous acid which partially dissociates to hypochlorite:

$$Cl_2 + H_2OHClO + Cl^- + H^+ \quad [HClO]\,[Cl^-]\,/\,[Cl_2] = 10^{pH-pK_{hy}} \tag{3}$$

$$HClO \leftrightarrow ClO^- + H^+ \quad [ClO^-]\,/\,[HClO] = 10^{pH-pK_h} \tag{4}$$

In the reaction volume, generally confined in direct connection to the electrodes, the major fraction of the hypochlorite species disproportionate to chlorate according to the commonly accepted stoichiometry (Vogt et al., 2010; Colman and Tilak, 1995; Ibl and Vogt, 1981):

$$2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \tag{5}$$

However, the disproportionation kinetics has never been studied in detail in the presence of dichromate. Finally, the overall reaction for chlorate formation

$$Cl^- + 3H_2O \rightarrow ClO_3^- + 3H_2 \tag{6}$$

can be derived by combination of the forward Reactions (1)–(5) and taking the water formation of released protons neutralizing cathodically generated hydroxide into account.

A minor fraction of the hypochlorite species decomposes to oxygen and chloride in the bulk solution

$$2uHClO + 2(1-u)\,ClO^- \rightarrow O_2 + 2Cl^- + 2uH^+ \tag{7}$$

where $0 < u < 1$ depending on the actual pH according to Eq. (4).

Hypochlorite is also consumed on the anode or/and in the anode boundary layer. Much attention has been paid to the so-called Foerster reaction (Ibl and Landholt, 1968; Landholt and Ibl, 1970; Jaksić et al., 1969b, 1972; Czarnetzki and Janssen, 1992) which can be regarded as an electrochemical reaction with simultaneous formation of oxygen and chlorate in the stoichiometric relations

$$6ClO^- + 3H_2O \rightarrow 1.5O_2 + 2ClO_3^- + 4Cl^- + 6H^+ + 6e^- \quad E^0 = 0.69V \tag{8a}$$

$$6HClO + 3H_2O \rightarrow 1.5O_2 + 2ClO_3^- + 4Cl^- + 12H^+ + 6e^- \quad E^0 = 1.14V \tag{8b}$$

originally written on alkaline form but later also on acid form taking a low pH in the anode boundary layer into account. Studies on platinum show that hypochlorite is oxidized to hypochlorite radicals (Djordjević et al., 1973; Czarnetzki and Janssen, 1988; Minhová Macounová et al., 2015) that may initiate reactions with oxygen and chlorate as possible end products. Reaction (8) has mainly been studied in laboratory scale at low temperatures and in alkaline media.

However, oxygen is also anodically generated by water oxidation

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23V \tag{9}$$

lowering the chlorine yield of Reaction (1). The loss becomes particularly significant at low chloride concentrations (Krstajić et al., 1991) and at low anode potentials (Karlsson and Cornell, 2016). The coating composition is also of high importance (Krstajić et al., 1986). Despite its lower reversible potential, Reaction (9) is efficiently suppressed in industrial chlorate manufacture by use of highly selective DSA anodes and by keeping the sodium chloride concentration above 100 g/L (Karlsson and Cornell, 2016).

Kotowski and Busse (1986) found that the ratio between formed oxygen and chlorate in chloralkali electrolysis was higher than predicted by Reaction (8). They also found that the byproduct distribution depends on the type of anode coating due to their different selectivity properties. After an extensive analysis, they proposed an additional reaction for electrochemical oxygen formation as an explanation to the observed byproduct distributions viz.

$$HClO + H_2O \rightarrow O_2 + Cl^- + 3H^+ + 2e^- \quad E^0 = 0.97\,V \tag{10}$$

also judged realistic in chlorate electrolysis (Colman and Tilak, 1995; Hardee and Mitchell, 1989; Byrne et al., 2001; Karlsson and Cornell, 2016).

In a chlorate cell the oxygen formation is the principal yield loss. The cell gas generally contains about 2.0–2.5% oxygen with respect to dry hydrogen (Vogt et al., 2010). This corresponds to a current efficiency loss of 4–5% while the total current efficiencies are reported to be 95–96% (Vogt et al., 2010). Consequently, the cathodic losses of hypochlorites and chlorates

$$ClO^- + H_2O + 2e^- \leftrightarrow Cl^- + 2OH^- \quad E^0 = 0.89\ V \tag{11}$$

$$ClO_3^- + \quad 3H_2\,O + 6e^- \leftrightarrow Cl^- + 6OH^- \quad E^0 = 0.63\,V \tag{12}$$

are very small and can often be disregarded in practice except at start up when the chromium oxide film on the cathode is not fully developed (Wulff and Cornell, 2007).

The kinetics of Reaction (5) has so far been described as a third order reaction with respect to hypochlorous acid and anionic hypochlorite (Colman and Tilak, 1995) provided that the concentration of hypochlorite ion does not exceed about 60 mM (Adam et al., 1992):

$$r_{ClO_3^-} = k_{ClO_3^-}\,[HClO]^2\left[ClO^-\right] \tag{13}$$

This expression is, however, insufficient for process applications since the ever-present accelerating effect of chromate species shown by Müller (1899) is left out. The purpose of the present paper is to experimentally demonstrate how the disproportionation kinetics, at conditions of industrial relevance, is related not only to the chlorate and chloride concentrations, temperature and pH but also to the chromate concentration. The results are validated with data from bench scale and pilot plant trials. In this connection, mass balance components for a chlorate cell are discussed also including a comparison between the Foerster and Kotowski–Busse stoichiometries.

In order to accomplish buffer calculations and speciation related to the nominal dichromate concentration, the dissociation constants of hypochlorite and Cr(VI) species (pK_h, pK_d and pK_c) defined in Eqs. (4), (14) and (15) must be known:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \quad \left[HCrO_4^-\right]^2 / \left[Cr_2O_7^{2-}\right] = 10^{-pK_d} \tag{14}$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \quad \left[CrO_4^{2-}\right] / \left[HCrO_4^-\right] = 10^{pH-pK_c} \tag{15}$$

However, no data of these equilibrium coefficients at relevant temperatures and electrolyte compositions are found in the literature. A limited number of measurements have therefore been made in relevant electrolyte matrices and with the same measuring technique as in the trials in which the coefficients are utilized.

2. Materials and methods

The kinetic studies were made in laboratory scale while validations were made using data from pilot plant and bench scale trials as described below.

2.1. *Laboratory scale studies*

2.1.1. *Chemicals*

Electrolyte was prepared using technical grade sodium chlorate (AkzoNobel), sodium chloride (Scharlau), sodium dichromate (Sigma–Aldrich) and de-ionized water (DIW). About 2.3 mol/L technical grade hypochlorite (Brenntag) was

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