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ORIGINAL PAPER

Chloride behaviour in electromembrane treatment of brine issued from desalination plants

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Abstract In this work, the chloride behavior through an electrochemical treatment of brines is examined using ion exchange membranes like in electrodialysis. All experiments have been performed using solutions of NaCl before an application on real brines issued from an Algerian desalination plant. After checking oxidation parameters of chloride oxidation by electrolysis, ion exchange membrane have been introduced to control both the pH and the species migrated. The effect of current density and the membrane nature has been studied. The electrochemical treatment described in this work allows transforming the brines in useful products as NaOH, HCl and Cl_2. The pH and the salt concentration are varied and the products obtained at the electrodes were identified and analyzed. It was shown that we can get chlorates according to the current density applied and the fixed pH. This fact gives rise to an economical process where valuable products can be obtained using only the chloride oxidation current. Results were linked to the Pourbaix diagram and allow the prediction of the process efficiency.

Keywords Brine · Chloride · Chlorate · Membrane · Electro-electrodialysis

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1 Introduction

In the output of a desalination plant, great quantities of brine are generated and cause an environmental problem. Effectively, brines cannot be rejected in the sea because it provokes an increase of the salt concentration which is hazardous to all marine life. It is a worried problem which is not well treated until now. On the other hand, the brine production gives rise to a real problem of storage like sludge in the output of surface industries.

Although the possibility of electrochemical scale removal has long been recognized, industrial application of this technique is rather limited and technical information in the literature is not important. Electrolytic scale removal is based on the generation of a high pH environment around the cathode by the cathodic reactions which produce OH^-. Thus, the alkaline environment promotes precipitation of both the calcium hardness in the form of $CaCO_3$ and the magnesium hardness in the form of $Mg(OH)_2$.

In the presence of chloride ions, authors [1] assume that only chlorine gas is released at the anode. Despite the commercial availability of such equipment, the use of electrolytic scale control methods is quite limited. The small number of laboratory studies [2–4] and the few publications dealing with commercial devices [5–7] provide very limited information on parameters affecting the performance of electrolytic scale removal installations. Recent publications [8–11] indicate a revived interest in the study of electrochemical precipitation of $CaCO_3$.

Electrochemical treatment is also proposed by Van Hege et al. [12] as a novel treatment strategy for RO membrane concentrate. Electro-oxidation has been successfully implemented for the abatement of hard-to-treat wastes such as landfill leachate [13, 14], textile effluent [15] and wastewater containing polyaromatic organic pollutants

[16]. Particularly with regard to RO brine, it has several advantageous features: first, the elevated salinity of RO concentrate ensures an excellent electric conductivity (EC) that could lower the energy consumption [17]. Second, the high chloride content could facilitate indirect bulk oxidation through the electrogeneration of strong oxidants such as hypochlorite [13]. Third, oxidation of recalcitrant organics can be accomplished concomitantly [14].

Maxhobandile Siguba [18] performed a comparative study of electrolysers using different anodic materials for the electrolysis of brine (sodium chloride) for the production of sodium hypochlorite as a source of available chlorine for disinfection of rural water supplies has been undertaken. The electrolyser design used was tubular in form, having two chambers, i.e. anode inside and cathode outside, separated by a tubular inorganic ceramic membrane. The anode was made of titanium rod coated with a thin layer of platinum and a further coat of metal oxide. The cathode was made of stainless steel wire. An assessment of these electrolysers was undertaken by studying the effects of some variable parameters, i.e. current, voltage and sodium chloride concentration. The cobalt oxide electrolyser has been shown to be superior as compared to the ruthenium dioxide and manganese dioxide electrolysers in terms of hypochlorite generation. Sodium chlorate was present but at concentration levels not hazardous for use in dosing water for drinking purposes.

Chlorate can be produced in undivided cells, where the overall reaction is sodium chloride and water forming sodium chlorate and hydrogen. The most common electrodes are ruthenium-based dimensionally stable anodes (DSAs) and cathodes of steel. The hydrogen bubbles formed in the cathode reaction (reaction 2) give rise to a gas-lift effect, which enhances mass transport of reactants to the electrode surfaces. Chlorine formed on the anode is dissolved in the electrolyte and reacts to form chlorate through a number of reaction steps.

Knowing that NaCl is the most important component in brine issued from a desalination plant, the aim of this work is to examine the behavior of the chloride ions during an electro-electrodialysis. The use of the ion exchange membranes is tested to allow the control of the pH. Current density effect is studied against the products obtained in the anodic side.

2 Experimental

2.1 Electro-electrodialysis

All electro-electrodialyses have been performed using a three compartment Plexiglas cell with a working membrane area of 16 cm^2 (Fig. 1). The two extreme compartments are composed by a graphite anode and a stainless steel cathode immersed in a solution where the pH is fixed. The central compartment (dilute compartment) contains NaCl solution at different concentrations. Experiments were followed by sampling the solution of both the central compartment and the two adjacent compartments (anolyte and catholyte) at regular intervals of time. The analyses are performed using ionic chromatography with conductimetric detector Dionex Quick Analyzer with AS12A 4 × 25 mm as anionic column and $NaHCO_3$ as eluent.

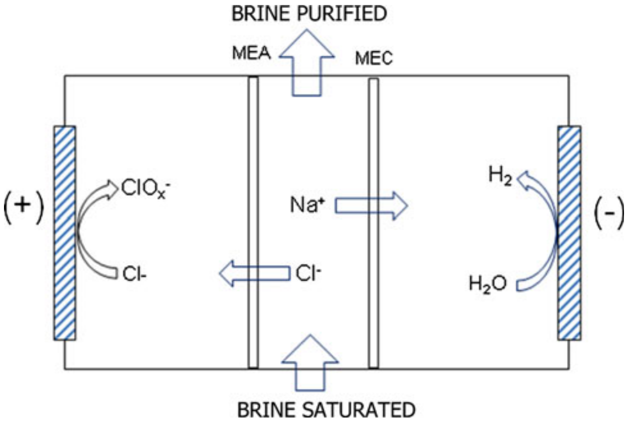

Fig. 1 Electro-electrodialysis cell scheme

The cation exchange membrane used was the CMX of exchange capacity 3.85 meq g^{-1}. The anion exchange membrane was the AMX of exchange capacity 1.25 meq g^{-1}. Before each electrodialysis, the cation exchange membranes were equilibrated in hydrochloric (or sulphuric) acid solution 2 N for 24 h whereas the anion exchange membranes were immersed for the same time in 2 M NaCl (or Na_2SO_4) solution.

The $i = f(E)$ curves have been obtained using a potentiostat–galvanostat Autolab with a specific software which get data (GPES, V. 4.9). The experiments have been performed using a Galvan dynamic mode with a rate of 0.1 mA s^{-1}.

3 Results and discussion

A direct electrolysis of brine gives rise to both chloride oxidation and water oxidation which produces hydroxides at the cathode and H$^+$ at the anode. Thus, these reactions modify continuously the pH which cannot be regulated. Figure 2 shows the effect of the concentration of NaCl on the chloride oxidation. It is noticed that oxidation is favored. That can be owed to the decrease of the NaCl dissociation and probably the concentration polarization is attained. However, this result shows that an electrochemical treatment of brine which contains NaCl between 25 and

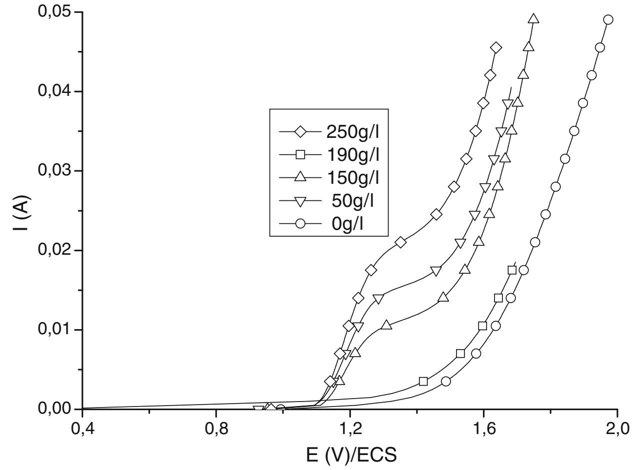

Fig. 2 Intensity–potential curves of chloride oxidation versus the NaCl concentration. Anode in graphite

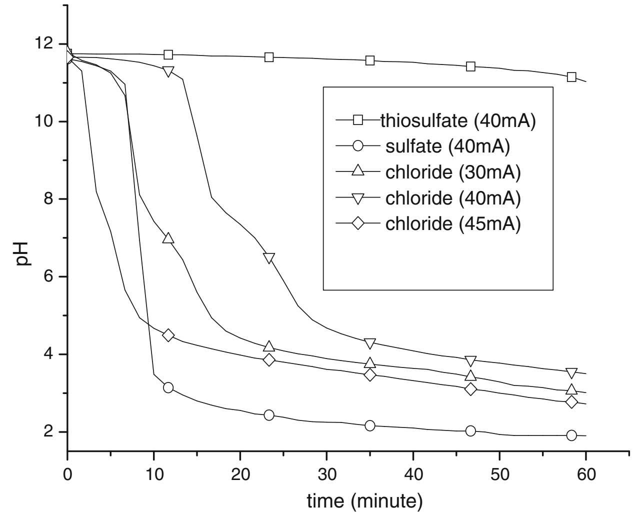

Fig. 3 pH variation of the anodic compartment during the oxidation of various anions using conventional electrolysis

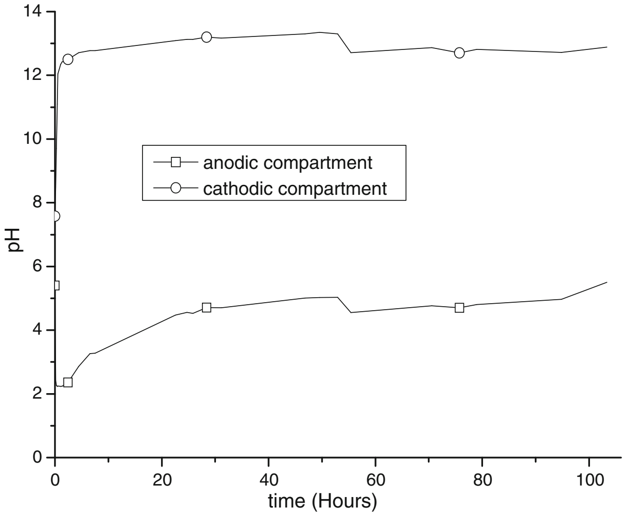

Fig. 4 pH variation of the anodic compartment during the chloride oxidation using electro-electrodialysis. Membranes CMX/AMX. NaCl 50 g L^{-1}. Current intensity 45 mA

190 g L^{-1} can be efficient. In Fig. 3, the pH variation during the chloride oxidation is examined. It is shown that a pH decreasing is observed as a function of time concerning the chlorides and sulfates. This phenomenon is not observed for the thiosulphates regarding their p*K*a. This instability of the pH provokes an instability of the chlorine formed and can perturb the chloride oxidation. In effect, the chlorine can exist under many oxidation states which are highly dependent of the pH. Cl_2 is stable under pH = 2 and this fact necessitates a high current density which enhances water oxidation too. To optimize the efficiency of the electrochemical treatment, the oxidation yield should reach 100%. Many parameters influence this yield, i.e. pH, current density, temperature and concentration. Knowing that the pH is the most important parameter, ion exchange membranes were introduced in our work to increase the selectivity and control the pH. The cell used (Fig. 1) allows the transport of Cl^- contained in the central compartment towards the anode across the anion exchange membrane while Na^+ moves similarly through the cation exchange membrane toward the cathode. This fact occurs like in conventional electrolysis, however, the advantage of the membranes is to maintain both H^+ and OH^- ions, produced by water splitting, inside the central compartment. Thus, results will depend on the permselectivity of the membranes. Electro-electrodialyses experiments have been carried out using 50 g L^{-1} of NaCl and a current intensity of 45 mA for different membranes and the optimized results have been obtained for the CMX/AMX ion exchange membranes. In effect, the pH was stabilized more than 80 h in this case as it is shown in the Fig. 4. This fact allows a control of the pH by adding an acid or a base. After the choice of the membrane, the current density effect is studied and the Fig. 5 shows that the oxidation yield increases until 100 mA. Above to this value, the amount of chloride transferred which is oxidized decreases. This is owed to the hydroxide transfer from the central compartment which both perturbs and competes the chloride oxidation. Using CMX and AMX membranes and a current intensity which vary between 50 and 100 mA, electro-electrodialyses of NaCl solution (50 g L^{-1}) were performed with the variation of the pH in the anolyte. To study the pH effect, the chloride oxidation was followed by adding of NaOH continuously inside the anolyte. The analyses by ionic chromatography are showing the nature and the amount of the species which are finally obtained. In effect, at first the chloride oxidation gives rise to chlorine

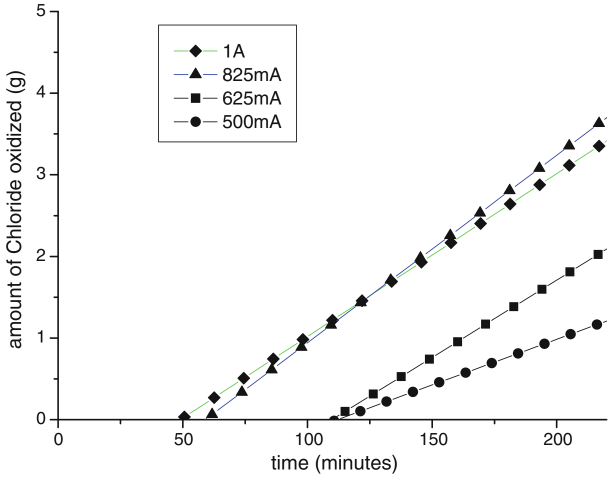

Fig. 5 Influence of the current intensity on the chloride oxidation during an electro-electrodialysis. Membranes AMX/CMX

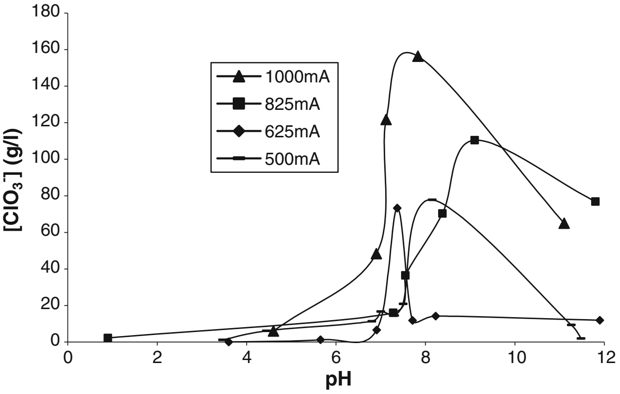

Fig. 6 Amount of chlorate produced by electro-electrodialysis as a function of pH and current intensity. Membranes AMX/CMX

gas (Cl_2) which is unstable at pH more greater than 2. When the pH increases, a dismutation of chlorine takes place and we get oxygenated compounds of chlorine, i.e. HClO, ClO^-, ClO_2 or ${ClO_3}^-$ with an amount of Cl^-. In alkaline solution, the most important species which is obtained is the chlorate as we can see on the Fig. 6 where the electro-electrodialyses were performed during 210 min for each current intensity. In effect, chloride is oxidized first as the following reaction:

$$6Cl^- \rightarrow 3Cl_2 + 6e^- \tag{1}$$

However, chlorine is not stable and gives rise to a dismutation as following:

$$3Cl_2 + 3H_2O \rightarrow 3HClO + 3Cl^- + 3H^+ \tag{2}$$

A part of HClO is converted hypochlorite ion as it is shown in the following equation:

$$HClO + H_2O \rightarrow ClO^- + H_3O^+ \tag{3}$$

Then, the pH increase allows the excess of HClO to interact with the produced ClO^- to give rise to a chlorate production according to the equation:

$$2HClO + ClO^- \rightarrow {ClO_3}^- + 2Cl^- + 2H^+ \tag{4}$$

On the other hand, a secondary oxidation of hypochlorite in the anodic compartment can take place producing chlorate ions too according to the equation:

$$6ClO^- + 3H_2O \rightarrow 2{ClO_3}^- + 4Cl^- + 6H^+ + 3/2O_2 + 6e^- \tag{5}$$

It is noticed that chloride ions are produced again in the oxidation process. This fact shows that the current efficiency for the chlorate production cannot attain 100%. To increase this yield, the secondary reaction should be avoided for the optimization of the current. These results are in accordance with the Pourbaix diagram represented on the Fig. 7. The diagram shows that in alkaline medium, chlorate is the predominate species which can be easily obtained by oxidation of the other species of chlorine. Final experiments of electro-electrodialyses of brines issued from an Algerian desalination plant sited at the west of Algiers have been carried out. The initial concentration of NaCl is 50 g L^{-1} and the experiments duration was fixed to 210 min. The pH was fixed to 10 by adding of NaOH. Both chloride and chlorate amount were followed using ionic chromatography. The results are reported on the Table 1. They are showing accordance with the previous simulated results and they confirm all hypotheses. The chloride migration is enhanced by the current increasing until 825 mA although the chlorate production is increased continuously according to the current intensity effect. The chloride oxidation is efficient and there is not a limitation due to the other anions while a slight effect is observed

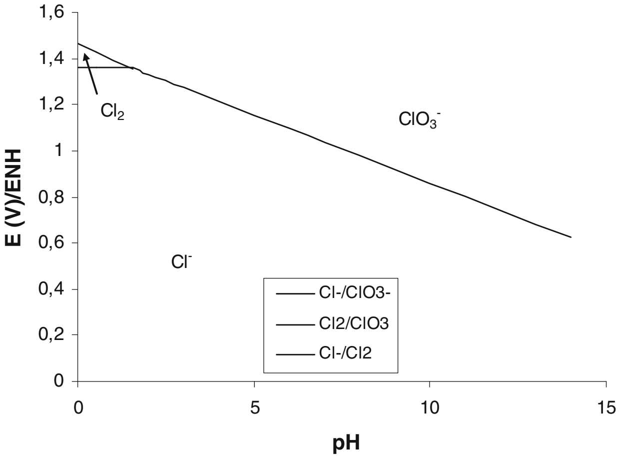

Fig. 7 Pourbaix diagram of chlorine and derivates species

Table 1 Chlorate production yield as a function of the current applied during electro-electrodialyses of brine solutions which contain NaCl (50 g L^{-1})

Current (mA)	Chloride migrated (%)	Chloride oxidized (%)	Chlorate produced (%)
1000	88.2	70.4	98.2
825	98.4	96.2	95.3
625	72.5	61.1	71.2
500	50.2	35.4	50.3

Time of experiments: 210 min

when the current intensity attains 1A. At this intensity, the water oxidation is more quantitative and the current is also consumed by OH^- which is transferred with chloride.

4 Conclusion

In this work, the behavior of Cl species after an electrochemical treatment of brines is examined. The important role of the pH in the oxidation of chloride is shown, thus, ion exchange membranes have been introduced to allow its control. Although electrolyses of NaCl solutions have been widely studied, the use of selective membranes gives rise to a more economical process where the chlorate production is observed. Knowing that chlorate is used in some industries, electro-electrodialyses allow its production using the same current which oxidize the chloride which migrate toward the anode. The fixation of the pH favors the production of chlorate as the principal compound with a relatively high purity. The process described was applied with success to the treatment of real brines. It represents an interesting alternative to solve the environmental problem of brine with the production of valuable byproduct: the chlorate.

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