Chemical Engineering Journal 253 (2014) 427–437

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

One-flow feed divided electrochemical reactor for indirect electrolytic production of hypochlorite from brine for swimming pool treatment-experimental and theoretical optimization

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HIGHLIGHTS

- Optimization of an electrochemical chlorinator for swimming pool.
- Divided asymmetric electrochemical continuously stirred reactor.
- Convective transfer of the anolyte across the separator to the cathodic compartment.
- The brine (5 M NaCl) conversion reaches 50% under 3 kA m^{-2} with a faradic yield of 80%.
- Correlation of current density versus chloride concentration for concentrated brine.

ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form 29 April 2014
Accepted 1 May 2014
Available online 22 May 2014

Keywords:
Swimming pool treatment
Continuously stirred electrochemical reactor
Chlorine

ABSTRACT

A 'two-compartment' asymmetric electrochemical reactor, operating without electrodes polarity inversion, was designed and optimized for the chlorination of swimming pools. Gaseous chlorine, produced at the anode and absorbed in the alkalinized catholyte, provides the hypochlorite solution. Empiric equations providing the chloride concentration dependence on the initial current density magnitude were established. Experimental optimization of the effect of the various operating parameters allows a chloride conversion close to 50% with faradic yields higher than 80%, and a chlorine production of 1 kmol/day/m^2 to be achieved. Macroscopic mass balance, was performed and the obtained theoretical results correlate with the experimental ones ($X_{\text{theor.Cl}^-} - X_{\text{exper.Cl}^-} < 10\%$).

1. Introduction

Gaseous chlorine was produced at industrial scale by electrolysis of concentrated brine solution. Several studies focus on the production of chlorine, involving new material or processes, that enable saving electrical energy; thus the field is important to industrial production [1–7]. Furthermore, several commercial devices (chlorinators) exist that produce chlorine or hypochlorite, used for treating swimming pool water. Diluted brine solutions (NaCl < 30 g L^{-1}), were electrolyzed using an undivided mono/bi polar electrochemical reactor, continuously supplied by swimming pool water.

DSA Ti/TiO_2/RuO_2, is the anodic material used for chloride oxidation to chlorine [8–10]. Titanium (or stainless steel) was used as the cathodic material.

Due to the neutral pH of the electrolyte, chloride oxidation directly produces hypochlorite (Table 1, R1) used in swimming pools. In fact, gaseous chlorine produced by electrolysis is transformed into hypochlorite following the disproportionation reaction (11 or 12, Table 1) by the action of soda [11,12]. Note that concentrated (50%) hypochlorite solutions were also produced by action of gaseous chlorine and soda.

Chlorinators can operate as a function of the geographical area for long periods; the main problem of these systems was due to the limescale which can deposit on the electrodes, mainly the Ti or steel cathodes (because of alkalinization of the interface); indeed, during electrolyses the limescale cumulates on the electrode surface leading to short circuits and damage to the electrodes, so the system becomes inoperative.

Several devices have been patented in order to overcome the limescale deposit growth [12–14]. For automated chlorinators, one possibility consists of alternating the polarity of the electrodes [14]. A slight acidification of the interface of the cathode during the short anodic polarization causes dissolution of the limescale

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http://dx.doi.org/10.1016/j.cej.2014.05.001
1385-8947/

Table 1
Various possible reactions during electrolysis of a brine solution (1–12) depending on the operating conditions (pH, T°C, $[Cl^-]$,…). The reaction (13) corresponds to the hypochlorite potentiometric titration.

Electrode	Main/acidic media pH < 3	N°	Side/slight acidic or neutral media pH > 5	N°
Anode	$Cl^- \rightarrow 1/2\ Cl_2 + e^-$	(1)	$Cl^- + 2OH^- \rightarrow ClO^- + 2e^-$	(2)
	$H_2O \rightarrow 1/2\ O_2 + 2e^- + 2H^+$	(3)	$OH^- \rightarrow 1/4O_2 + e^- + 1/2H_2O$	(4)
Cathode	$H^+ + e^- \rightarrow 1/2\ H_2$	(5)	$H_2O + e^- \rightarrow 1/2H_2 + OH^-$	(6)
	$ClO^- + 2e^- + 2H^+ \rightarrow Cl^- + H_2O$	(7)	$ClO^- + 2e^- + H_2O \rightarrow Cl^- + 2OH^-$	(8)
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	(9)	$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$	(10)
Cl_2 disproportionation	(pH$\sim \geqslant 4$) $Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+$	(11)	(pH$\sim \geqslant 7$) $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$	(12)
Hypochlorite titration	$ClO^- + SO_3^{2-} \rightarrow SO_4^{2-} + Cl^-$	(13)		

deposit enabling activation of the electrode. Even if this system appears efficient, after several 'electrodes polarity' inversions, the catalytic layer (Ru/Ti oxides) is damaged; hypochlorite production then drastically decreases and requires the electrodes to be changed.

The goals of this study are to design and optimize an electrochemical reactor dedicated to supplying active chlorine/hypochlorite for swimming pool. The main criteria that govern the design of this device are indicated below:

- it must operate without polarity inversion (to avoid destruction of the catalytic coating) to maximize the duration of the electrode material.
- as with the existing devices, the new proposed reactor has to operate automatically for the required duration (3–4 months), implying that it is supplied by a concentrated brine (sodium chloride $\sim$300 g L^{-1}; $\sim$5 mol L^{-1}), reducing the volume used.

To reach this goal, this study aims to design and optimize a divided electrochemical cell, continuously supplied in the anodic compartment by brine in slightly acidified (pH < 3), demineralized water. The electrolytic compartments are separated by a porous ceramic diaphragm allowing convective transfer of the anolyte to the cathodic compartment. Acidification of brine allows gaseous chlorine production; simultaneously, water (or H^+) reduction to H_2 leads to alkalinization of the catholyte and the production of soda. Absorption of gaseous chlorine in the catholyte (in the outlet of the cathodic compartment) leads to the production of hypochlorite.

Experimental and theoretical optimization of the various operating parameters (applied current density, electrolyte flow, pH adjustment of the solutions,…) for chloride conversion and chlorine converted to hypochlorite production, constitutes the main points involved below.

2. Experimental section: chemicals-analytical procedure and devices

Deionised water was used for all solutions. Chemicals were supplied by WVR. A divided electrochemical cell of a volume of 50 cm^3 per compartment, was used to carry out the electrochemical kinetics studies. The electrolytic compartments were separated by a ceramic diaphragm of porosity 5. Current potential curves were plotted using a Potentiostat–Galvanostat (PGZ 100-Voltalab of Radiometer Analytical, and a VoltaMaster 4 software). The working electrode used was a chlorine/DSA® plate (24 mm^2) e.g. titanium grids covered by a catalytic layer of metallic oxides from Ru/Ti/In-DSA® from ELTECH. A platinum rod was used as auxiliary electrode and the reference electrode was a silver/silver chloride (Ag/AgCl/KCl saturated).

Divided electrochemical cells with volume ratio ($V_{anolyte}/V_{catholyte} \sim 2$) were used to carry out preparative electrolyses. The electrolytic compartments were separated by a ceramic diaphragm of porosity 2–3. As anode, the same ELTECH-chlorine/DSA® was used as previously and the cathodic material was Ti made. Various surface ratios ($1 < S_{anode}/S_{cathode} < 4$) are involved for the preparative electrolyses, carried out using a constant current electrochemical supplier (lamvda 60 V/30A). The anolyte was supplied by solutions of (i) Brine (NaCl 300 g L^{-1}) and (ii) an acidic solution (HCl or H_2SO_4 6 mol L^{-1}, according to the experiments, to maintain the anolyte pH < 3). A 'two push-syringes' device (model A-99 from Fischer Scientific) was used to supply these solutions at constant volumetric flow.

According to the operating conditions (pH, temperature, Cl^- concentration,…) various reactions could take place (1–12, Table 1).

Hypochlorite potentiometric titration was performed using an anhydrous sodium sulfite Na_2SO_3 (97%) according to the method described by Adam and Gordon [15]: reaction (13), Table 1.

By monitoring the zero current potential of a platinum electrode versus a $Ag/AgCl/KCl_{saturated}$ reference electrode, the required volume of the sulfite solution to neutralize the hypochlorite and to access its concentration C_{ClO^-} can be determined.

The overall conversion X of the chloride ions for an electrolysis duration t (versus all the used volume of brine), as well as the corresponding Faradic yield y_f were calculated respectively by Eqs. (14) and (15):

$$X = \frac{\text{mol of Cl}^- \text{ transformed by electrolysis}}{\text{mol of Cl}^- \text{ (initial + introduced brine and acid)}}$$

$$X = \frac{2 * C_{ClO^-} * V_p}{(C_{NaCl} * V_{anolyte})^{\circ} + t * (Q_{acid} * C_{acid} + Q_{brine} * C_{brine})} \tag{14}$$

$$y_f = \frac{\text{produced mole number of OCl}^-}{\text{theoretical mole number of OCl}^- \text{ produced}} = \frac{C_{ClO^-} * V_p}{\frac{I_{applied} \cdot t}{2 * F}} \tag{15}$$

where: V is the volume; V_p is the volume of the NaOH trapping solution of the produced gaseous chlorine (see corresponding section); C is the concentration; Q is the volumetric flow; I is the applied current and t the electrolysis duration.

3. Results

3.1. Electrochemical kinetics

To determine the appropriate current density to apply in order to carry out electrolyses in optimal conditions (no oxygen, no chlorate), current potential curves were plotted (Fig. 1) for various concentrations of sodium chloride (curves 1–4), with (a) and without (c) an electrolyte.