Electrochemical production of perchlorates as a way of valorize the rejection streams of the SWRO process

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1 INTRODUCTION

MANAGEMENT OF SWRO BRINE

DISPOSAL

CONCENTRATION

VALORIZATION

ENERGY RECOVERY

CLEANING

INDUSTRY

AGRICULTURE

A) Pressure retarded osmosis

Pretratamiento
INTRODUCTION

1. Oxidants

- Bleaching agents
- Detergents
- Explosives
- Organic synthesis

2. Oxidants for water treatment
- Disinfection

3. Oxidants for soil treatment
**Introduction**

**Boron Doped Diamond (BDD) Electrodes**

- Metaestable form of carbon at room pressure and temperature
- Electrical insulator
  - Positive doping
  - Negative doping
  - High thermal conductivity
  - High electrochemical stability
  - Wide electrochemical window

Production of high concentration of hydroxyl radicals, available to perform electrochemical reactions.
1 INTRODUCTION

MANAGEMENT OF SWRO BRINE. VALORIZACION

\[
\begin{align*}
\text{Cl}^- + \cdot \text{OH} & \rightarrow \text{ClO}^- + \text{H}^+ + \text{e}^- \\
\text{ClO}^- + \cdot \text{OH} & \rightarrow \text{ClO}_2^- + \text{H}^+ + \text{e}^- \\
\text{ClO}_2^- + \cdot \text{OH} & \rightarrow \text{ClO}_3^- + \text{H}^+ + \text{e}^- \\
\text{ClO}_3^- + \cdot \text{OH} & \rightarrow \text{ClO}_4^- + \text{H}^+ + \text{e}^-
\end{align*}
\]

BDD ELECTROLYSIS

PRODUCTION OF PERCHLORATE
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To develop a process for the electrochemical production of perchlorate by BDD electrolysis from highly-concentrated NaCl solutions (typical of SWRO brines)

- To evaluate the general behaviour of the electrolysis of NaCl solutions (from 1M to 5M, 58.5 to 292.5 g dm$^{-3}$) by BDD electrolysis
- To determine the influence of the initial concentration of NaCl and current density
- To estimate the power consumption and cost of energy for the production of perchlorate
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Boron doped diamond (BDD): anode
- Stainless steel: cathode
- Coating: (boron content: 500-700 ppm, sp$^3$/sp$^2$ ratio: 220 ± 5%, thickness: 2.7 µm ± 10%)
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RESULTS AND DISCUSSION

PRODUCTION OF CHLORINE DERIVATES

1 M NaCl; V = 1 L
- • 1000 A m⁻²; ▲ 1500 A m⁻²; ■ 2000 A m⁻²

Hypochlorite and Chlorate coexist within the first part of the test.
RESULTS AND DISCUSSION

PRODUCTION OF CHLORINE DERIVATES

1 M NaCl; V = 2 L
• 1000 A m\(^{-2}\); ▲ 1500 A m\(^{-2}\); ■ 2000 A m\(^{-2}\)

\[
\begin{align*}
\text{Cl}^- + \cdot \text{OH} & \rightarrow \text{ClO}^- + \text{H}^+ + \text{e}^- & \text{(1)} \\
\text{ClO}^- + \cdot \text{OH} & \rightarrow \text{ClO}_2^- + \text{H}^+ + \text{e}^- & \text{(2)} \\
\text{ClO}_2^- + \cdot \text{OH} & \rightarrow \text{ClO}_3^- + \text{H}^+ + \text{e}^- & \text{(3)} \\
\text{ClO}_3^- + \cdot \text{OH} & \rightarrow \text{ClO}_4^- + \text{H}^+ + \text{e}^- & \text{(4)}
\end{align*}
\]

HIGH CONVERSION. MINIMUM CHARGE FOR PERCHLORATE PRODUCTION
RESULTS AND DISCUSSION

INFLUENCE OF NaCl CONCENTRATION

2 M NaCl; V = 1 L
• 1000 A m⁻²; ▲ 1500 A m⁻²; ■ 2000 A m⁻²

SIMILAR BEHAVIOR WITH 2M NaCl
RESULTS AND DISCUSSION

INFLUENCE OF NaCl CONCENTRATION

Full symbols: conversion; Empty symbols: current efficiency

- ● 1000 A m\(^{-2}\);
- ▲ 1500 A m\(^{-2}\);
- ■ 2000 A m\(^{-2}\)

✓ HIGHEST CONVERSION REPORTED
✓ HIGH CURRENT EFFICIENCY
✓ NEGLIGIBLE INFLUENCE OF CURRENT DENSITY AND CONCENTRATION
RESULTS AND DISCUSSION

Anode

\[ \text{Anode} \]

\[ \text{Interphase} \quad \text{Electrolyte} \]

\[ nF \]

\[ I \]

\[ r \]

\[ 1 \]

\[ (\text{full availability of raw material}) \]

For high Cl\(^-\) concentration

High value of \( r_2 \)

\( r_2 \geq r_1 \)

Negligible influence of working variables

Electrochemical reaction

\[ r_1 = \frac{I}{nF} \]

Mass transport

\[ r_2 = kA(C_b - C_e) \]
RESULTS AND DISCUSSION

HIGHER Cl\(^-\) CONCENTRATION

3500 MILLION DOLLARS FOR 10000 STUDENTS

NO MASS TRANSFER LIMITATIONS

LOWER Cl\(^-\) CONCENTRATION

250 MILLION EUROS FOR 20000 STUDENTS

MASS TRANSFER LIMITATIONS DEPENDING ON WORKING PARAMETERS
SIMILAR EVOLUTION OF CELL VOLTAGE AND POWER CONSUMPTION

POWER CONSUMPTION OF 26.14 kWh kg\(^{-1}\) FOR 2 M & 1000 A m\(^{-2}\)
### Results and Discussion

#### Influence of NaCl Concentration. Power Consumption

<table>
<thead>
<tr>
<th>$j$ (A m$^{-2}$)</th>
<th>$[\text{NaCl}]_0$ 1 M</th>
<th>2 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>3.70</td>
<td>2.93</td>
</tr>
<tr>
<td>1500</td>
<td>3.49</td>
<td>2.99</td>
</tr>
<tr>
<td>2000</td>
<td>6.28</td>
<td>4.78</td>
</tr>
</tbody>
</table>

- COST OF ENERGY* FROM 2.93 € kg$^{-1}$ TO 6.28 € kg$^{-1}$ *

* EUROSTAT cost of energy for non-household users (2017)
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The production of perchlorate with BDD from high-salinity effluents (typical of the brine of SWRO processes) is technically viable and efficient.

- High conversions and current efficiency.

- A very limited influence of initial NaCl concentration and current density

- Perchlorate is not produced until a value of applied electric charge.

- Specific energy consumption of 26.14 kWh kg\(^{-1}\)
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INTRODUCTION

Oxidants:
- Chlorine-based oxidants
- Hydrogen peroxide
- Potassium permanganate

Substances:
- Peracetic acid
- Perchlorate
- Peroxodisulphate
- Ferrate
- Peroxophosphate
- Perbromate
INTRODUCTION

ELECTROCHEMICAL TECHNOLOGY

MAIN ADVANTAGES

✓ It is **not necessary** to add additional chemical reagents. The \( e^- \) es the main “reagent”

✓ **Minimization** in the production of waste streams

✓ **Room** temperature and pressure

✓ **Easy automation** of the process
1 INTRODUCTION

**Industria cloro-alcalina**

\[ 2 \text{NaCl(aq)} + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaOH(aq)} + \text{Cl}_2 + \text{H}_2 \]

- Electrólisis con celda de mercurio
- Electrólisis con celda de diafragma
- Electrólisis con celda de membrana

**PRINCIPALES PROCESOS ELECTROQUÍMICOS DE SÍNTESIS DE OXIDANTES**

**Producción de peroxodisulfatos**

\[ 2 \text{H}_2\text{SO}_4 - 2 \text{e}^- \rightarrow \text{S}_2\text{O}_8^{4-} + 4 \text{H}^+ \]

**Producción de permanganato de potasio**

\[ 2 \text{MnO}_2 + 6 \text{KOH} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{K}_3\text{MnO}_4 + 3 \text{H}_2\text{O} \]

\[ 2 \text{K}_3\text{MnO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{K}_2\text{MnO}_4 + 2 \text{KOH} \]

\[ 2 \text{MnO}_2 + 2 \text{KOH} + 3/2 \text{O}_2 \rightarrow 2 \text{KMnO}_4 + \text{H}_2\text{O} \]