Development of the electrochemical scale removal technique for desalination applications

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Abstract

The possibility of alkaline scale precipitation and removal by electrolytic devices has long been recognized. The scale removal principle of the electrochemical technique is based on the creation of a high pH environment around the cathode by water and oxygen reduction reactions which release hydroxyl ions. The alkaline environment induces precipitation of the calcium hardness in the form of CaCO$_3$ and of the magnesium hardness, in the form of Mg(OH)$_2$. Despite the commercial availability of such equipment, the use of electrochemical scale control methods is quite limited. Currently, the main field of application of electrolytic devices is for reducing the hardness of water recirculating in cooling towers. The lack of authoritative technical information on electrochemical scale removal reflects the paucity of research and development efforts in a technology which holds considerable promise for expanding the rather limited scope of viable scale control techniques. The objectives of this research project are to evaluate the potential of the electrochemical technique for RO desalination processes in general and for increasing water recovery levels in particular. The paper summarizes results of the first phase of the research. Models describing cell resistance in the absence and in the presence of a deposit on the cathode are presented. The effects of several parameters on the deposition rate and on the electric energy consumption are investigated. Results show that the higher the water hardness, the higher the scale precipitation rate and the lower the specific energy consumption. An increase in the flow velocity augments the scale deposition rate. Analysis of the velocity effect data indicates that the scale precipitation reaction is mass transfer controlled. The main optimization parameter is the current density. As may be anticipated, a low specific electrical energy is consumed when the electrolyzed solution is exposed to a large electrode surface and a high specific energy is consumed when the solution is exposed to a small electrode surface. The energy consumption can be rather low. For instance, in the electrolysis of a typical concentrate stream of a brackish desalination plant at a current density of 25 A/m$^2$, the energy consumption is of the order of 4 kWh per kg of precipitated CaCO$_3$ and the scale precipitation rate is of the order of 25 g CaCO$_3$/h m$^2$. Finally, a flow scheme

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is presented indicating the possibility of beneficial increase of the water recovery level in brackish water RO desalination, by partial recycle of the concentrate after electrochemical precipitation of the scale forming ions held in solution by the anti-scalant.

**Keywords:** Electrolytic precipitation; Cell modeling; CaCO₃ precipitation kinetics; Energy consumption; Electrode area

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### 1. Introduction

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 scant. Electrolytic scale removal is based on the generation of a high pH environment around the cathode by the following cathodic reactions:

\[
2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \quad (1)
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)
\]

(main cathode reaction)

The alkaline environment promotes precipitation of the calcium hardness in the form of CaCO₃ and of the magnesium hardness in the form of Mg(OH)₂ according to the reactions:

\[
Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 \downarrow + H_2O \quad (3)
\]

\[
Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow \quad (4)
\]

In the presence of chloride ions, chlorine gas is released at the anode by the reaction:

\[
2Cl^- \rightarrow Cl_2 \uparrow + 2e^- \quad (5)
\]

Despite the commercial availability of such equipment, the use of electrolytic scale control methods is quite limited. The small number of laboratory studies [1–4] and the few publications dealing with commercial devices [5–9] provide very limited information on parameters affecting the performance of electrolytic scale removal installations. Recent publications [11–14] indicate a revived interest in the study of electrochemical precipitation of CaCO₃.

The objectives of the present project are to evaluate the potential of the electrolytic technique for RO desalination processes in general and for increasing water recovery levels in particular. This paper summarizes results of the first phase of the research. Models characterizing cell resistance in the absence and in the presence of a deposit on the cathode are presented. Effects of several parameters on the deposition rate and energy efficiency are explored. Finally the possibility of precipitating effectively CaCO₃ on the cathode in the presence of an anti-scalant is demonstrated.

### 2. Experimental

Electrolytic deposition of CaCO₃ scale was investigated in two experimental systems: a continuous flow pilot system and a bench-scale system.

#### 2.1. Continuous flow system

The continuous flow system (Fig. 1) consisted of a set of feed vessels and dosage pumps enabling preparation of feed water of a desired hardness by mixing tap water with NaHCO₃ and CaCl₂ solutions and adjusting the pH by controlled CO₂ bubbling. The system allowed feed flows up to 5 L/min. The cylindrical cell serving as the cathode of the electrolytic device was made of stainless steel. Its height was 850 mm and its
The anode was a centrally located cylindrical rod, having a diameter of 30 mm and an immersed length of 850 mm. The anode was made of a corrosion-resistant titanium alloy. This so-called dimensionally stable anode (DSA) was supplied by Whizzo Science & Technology Co., China.

Each test lasted several days. The rate of electrolytic scale precipitation was evaluated by two techniques: measurement of the difference in water hardness between the water entering and leaving the electrolytic device and determination at the end of the run of the total amount of precipitated CaCO$_3$. The second technique provided the more accurate data. Most of the precipitate deposited on the cathode; a small amount released to the flowing water was collected in trap vessels.

2.2. Bench-scale system

The electrolytic cell of the bench-scale system (Fig. 2) was constructed from a stainless steel tube having an internal diameter of 56.1 mm serving as a cathode and a central titanium rod of 25.3 mm diameter, serving as a dimensionally stable anode. The cell was immersed in a 2 L glass beaker. Tests were carried out by recycling a solution held in a 10 L vessel. The solution entered the top of the annular passage of the electrolytic cell, drained into the 2 L glass beaker and overflowed into the 10L recycle vessel. The
pumping system enabled flow rates of up to 2.2 L/min. Each test lasted a few hours. The tests were conducted at room temperature (25–28°C). The scale deposition rate was determined by periodic analyses of the recycling solution. The parameters monitored included pH, Ca concentration, total alkalinity, solution conductivity and temperature.

3. Modeling the electrolytic cell

3.1. Analysis of solution resistance in cylindrical cell geometry

The total voltage $V_T$ imposed on an electrolytic cell system is consumed in various elements [15]:

$$V_T = E_D + \eta_A + (-\eta_C) + I \cdot R_T$$

(6)

where $E_D$ is the decomposition potential, $\eta_A$ and $\eta_C$ are the over-voltage at the anode and the cathode, respectively, and $I \cdot R_T$ is the ohmic voltage drop. The total resistance $R_T$ is due to several factors:

$$R_T = R_W + R_A + R_C + R_{Solution} = R_S + R_{Solution}$$

(7)

where $R_W$, $R_A$ and $R_C$ are the resistances of the wires, the anode and the cathode respectively, and $R_{Solution}$ is the solution resistance.

Solution resistance for cylindrical cell geometry is obtained by integration of the basic differential equation:

$$R_{Solution} = \frac{1}{k} \int_{r_0}^{r_1} \frac{d r}{A(r)} = \frac{1}{k} \frac{\ln r_1 - \ln r_0}{2 \pi L}$$

(8)

where $r_1$ is the internal radius of the cathode, $r_0$ is the radius of the centrally located cylindrical anode, $L$ is length of the electrodes and $k$ is the conductivity (i.e. specific conductance) of the solution.

The solution resistance may be conveniently expressed using a geometrical factor $R_g$ [1/cm] defined by:

$$R_{Solution} = \frac{R_g}{k}$$

(9)

The total applied voltage $V_T$ is composed of a current dependent part, $I \cdot R_T$, related to the ohmic resistance and a constant, current independent part, $V_0$, related to the decomposition potential and to the electrodes over-voltage:

$$V_T = V_0 + I \cdot R_T$$

(10)

Values of $V_0$ and $R_T$ may be determined from the linear plot of total voltage $V_T$ versus current intensity $I$. The total resistance $R_T$ is related to the cell geometrical factor $R_g$ and to the solution conductivity $k$ by:

$$R_T = R_S + \frac{R_g}{k}$$

(11)

The value of $R_g$ can be determined by measuring $R_T$ at various solution conductivities. A linear relationship is expected between $R_T$ and $1/k$.

3.2. Investigation of edge effects

Eqs. (7) and (8) rest on the assumption of a sufficiently long cylinder for which end effects may be neglected. The presence of a small but not negligible edge effect was evident from measurements carried out on the electrolytic cell of the pilot system.

Results presented in Fig. 3 show a good linear relationship between total resistance $R_T$ and
Fig. 3. Total resistance as a function of solution resistivity.

The experimental value of $R_g$ obtained from the slope of the line is $7.46 \times 10^{-4}$ cm$^{-1}$. The theoretical value of $R_g$ calculated from Eqs. (8) and (9) is:

$$R_g = \frac{(\ln r_1 - \ln r_0)}{2\pi L} = \frac{(\ln 25.8 - \ln 15)}{2 \cdot \pi \cdot 85} = 10.15 \times 10^{-4}$$

The most plausible explanation for the difference between the experimental value of $7.46 \times 10^{-4}$ and the theoretical value of $10.15 \times 10^{-4}$ is that edge effects were not negligible. This hypothesis was verified by carrying out measurements of $R_g$ for immersed electrode lengths varying from 4.2 to 21.5 cm.

Fig. 4 shows measured values of $R_g$ versus immersed electrode length and also compares theoretical and experimental results. It is seen that the difference between calculated and experimental values of $R_g$ is progressively reduced as the immersed length is increased. The theoretical value is experimentally realized at an electrode length of 21.5 cm, i.e. when $L/r_i$, the ratio of electrode length to cathode diameter, exceeds the value of 3.8. Since the energy consumption of an electrolytic scale removal process increases with $R_g$, the practical importance of the above result is that electrolytic cells should be designed with a sufficiently high ratio of $L/r_i$.

3.3. Modeling the resistance imposed by a cathodic scale layer

The formation of scale layer on the cathode wall imposes an additional resistance to the electrolytic system which augments the specific energy consumption. For a cathodic surface covered by a scale layer of thickness $\Delta x$ and uniform porosity $\varepsilon_s$ (Fig. 5), the increase in the geometric factor is assumed to be governed by the magnitude of the tortuous path ($\Delta x \cdot \tau$) available for electrical conduction, where $\tau$ is the tortuosity factor. In this case, it may be shown that the solution resistance in the presence of a scale layer is given by:
Section of the cathodic tube covered with a scale layer of thickness $\Delta x$.

\[
R_{\text{Solution}} = \frac{\ln r_2 - \ln r_0}{2\pi Lk} + \frac{\ln (r_2 + \Delta x\tau) - \ln r_2}{2\pi L\varepsilon g k}
\]

where $R_{gs}$ is the geometric factor in the presence of a scale deposit.

Order of magnitude calculations indicate that the first term of Eq. (13) representing solution resistance is negligibly small compared to the second term, which represents the resistance stemming from a restricted solution path within the scale layer. The validity of the above model was investigated by measurements carried out on a simulated scale deposit, using the bench scale electrolytic system.

A cylindrical Perspex pipe, 3 mm thick ($\Delta x = 3$ mm), perfectly matching the inner side of the cathode tube, was perforated throughout its surface by uniformly spaced holes. The cylinder dimensions were: $r_1 = 24.0$ mm, $r_0 = 12.65$ mm and $L = 206$ mm. For this simple simulated scale geometry, the tortuosity factor $\tau = 1$. The electrical resistance imposed by the reduced cathode area was measured in three insert configurations characterized by:

- 180 evenly spread holes, diameter of 1.5 mm and surface porosity of about 1%.
- 180 evenly spread holes, diameter of 3.3 mm and surface porosity of about 5%.
- 348 evenly spread holes, diameter of 3.3 mm and surface porosity of about 10%.

The cell properties were determined, as before, by measuring total voltage versus current with several solutions of NaCl covering the conductivity range of 1 to 3 mS/cm. The slopes of the lines relating total resistance with solution resistivity provided measurements of the geometric factor.

Fig. 6 displays measurements obtained with a bare cathodic surface and with the Perspex insert perforated with 180 holes of 1.5 mm diameter, providing a surface porosity of about 1%. The data for the bare cathodic surface indicate a geometric factor of $5.0 \times 10^{-3}$ cm$^{-1}$, which is virtually identical to the theoretically calculated value of $4.95 \times 10^{-3}$ cm$^{-1}$. The resistance imposed...
by the Perspex insert of 1% porosity increased considerably the geometrical factor, from $5.0 \times 10^{-3}$ cm$^{-1}$ to $131.3 \times 10^{-3}$ cm$^{-1}$. Results obtained with the three perforate Perspex configurations (Table 1) confirm that Eq. (13) provides very good predictions of $R_{gs}$ for the tested geometrical configuration.

A geometrical configuration approaching a real scale deposit is a uniform porous structure. In this case, it is anticipated that Eq. (13) will hold, but with a value of $\tau$, which depends on the scale porosity $\varepsilon_s$.

### 4. Effect of various parameters on electrolytic precipitation

#### 4.1. Effects of current intensity and hardness level

Initial exploratory experiments were carried out in the pilot system in order to gather information on the effects of major operational parameters. Most experiments were carried at a current of 1.5 A and a voltage of 3.5 V with Technion tap water at a feed flow rate of 1.0 L/min ($Re = 325$). The conductivity of the tap water was around 1000 µS/cm, the pH about 7.5 and the temperature varied in the range of 20 to 30°C. Total alkalinity was around 3 m-equiv/L, Ca$^{2+}$ around 1.5 m-mole/L and Mg$^{2+}$ around 1.0 m-mole/L. The main results of these experiments may be summarized as follows.

- The pH on the cathode surface was estimated by withdrawing a very small stream of drops from a tiny perforation on the cathode tube. The plot of pH versus the rate of drops withdrawal was extrapolated to zero leakage to give an estimate of the pH on the cathode surface. The pH values measured with tap water at a current of 1.5 A and a voltage of 3.8 V were in the range of 10.5 to 11.0.

- At such high pH values, both CaCO$_3$ and Mg(OH)$_2$ are highly supersaturated and are prone to precipitation. However, analysis of the deposits showed that they consisted mostly of CaCO$_3$, mixed with a minor amount of Mg(OH)$_2$ (less than 16% by weight).

- The effect of current intensity at constant flow velocity and solution composition was explored over the range of 0.5–3.0 A. The chlorine release and CaCO$_3$ precipitation increased with current intensity. The maximum total chlorine concentration was 23 ppm. The maximum specific energy consumption was 20 kWh per kg CaCO$_3$.

- The effect of the Ca$^{2+}$ hardness level was explored at a current of 1.5 A over the range of inlet concentrations of 160 to 610 mg/L as CaCO$_3$. As anticipated, the CaCO$_3$ deposition rate increased as hardness intensity was augmented, with a concomitant decrease in the energy consumption, from 8.7 to 2.2 kWh/kg CaCO$_3$.

#### 4.2. Effect of the flow velocity

A systematic series of experiments was carried out in the continuous flow pilot system (Fig. 1) to measure the effect of flow velocity on the specific energy consumption and on the CaCO$_3$ deposition rate. The mean composition of the tap water used in these experiments was: pH = 7.6, Ca$^{2+}$ = 1.3 m-mole/L, total alkalinity = 2.6 m-equiv/L, Mg$^{2+}$ = 1.0 m-mole/L, conductivity = 1050 µS/cm. The

<table>
<thead>
<tr>
<th>Insert porosity, $\varepsilon_s$ (%)</th>
<th>Measured geometric factor, $R_{gs}$ (cm$^{-1}$)</th>
<th>Theoretical geometric factor, $R_{gs}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$131 \times 10^{-3}$</td>
<td>$107 \times 10^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>$23 \times 10^{-3}$</td>
<td>$25 \times 10^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>$11 \times 10^{-3}$</td>
<td>$14 \times 10^{-3}$</td>
</tr>
<tr>
<td>Bare cathodic surface</td>
<td>$5.0 \times 10^{-3}$</td>
<td>$4.95 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
The specific energy data displayed in Fig. 7 show that the electrical energy consumption (kWh per kg CaCO\textsubscript{3}) in electrolytic scale removal can be significantly reduced by operating at high Reynolds numbers. Another important parameter is the solution conductivity. Energy consumption is reduced at high salinities. The energy consumption in experiments carried out with solutions simulating desalination plant concentrates was as low as 2.2 kWh/kg CaCO\textsubscript{3}.

A most interesting result was observed in the measurement of the CaCO\textsubscript{3} precipitation rate as a function of Reynolds number. The data, plotted in Fig. 8 on log-log coordinates, are seen to fall on a straight line indicating that the precipitation rate increases with \text{Re}^{0.4}. As discussed below, the observed Re exponent of 0.4 is close to the theoretical value of 0.33 for mass transfer in laminar flow \cite{Eq. (14)}, indicating that the deposition process is mass transfer controlled. This result inspired derivation of the theoretical CaCO\textsubscript{3} electro-precipitation model presented in Sec. 4.3 which successfully correlated the data of Fig. 8.

To confirm the validity of the proposed model, a second series of experiments was carried out with a solution of increased calcium and carbonate concentrations. The experiments were carried out using the bench scale system (Fig. 2) which enabled more convenient and more accurate experimentation. The solution initial composition was as follows: pH = 6.8, $\text{Ca}^{2+} = 5.5$ m-mole/L, total alkalinity =4.3 m-equiv/L, conductivity = 9700 µS/cm. The velocity effect was investigated at laminar Re numbers extending from 700 to 1600.

The logarithmic plot of the CaCO\textsubscript{3} deposition data (Fig. 9), measured with the high solution concentration, shows again a straight line relationship. The power exponent of 0.39 is very close to the value of 0.4 measured in the pilot system (Fig. 8) with the lower solution concentration. Confrontation of the experimental data...
4.3. Modeling the kinetics of CaCO$_3$ precipitation

Electrochemical studies in laminar flow through annuli show that experimental mass transfer coefficients at the entry region conform to the Leveque solution [14]:

$$\frac{k_D \cdot d_h}{D_v} = 1.76 \cdot \left( \frac{Re \cdot Sc \cdot d_h}{L} \right)^{\frac{1}{3}}$$ (14)

where $k_D$ is the mass transfer coefficient, $d_h$ the hydraulic diameter, $D_v$ the diffusion coefficient, $Re$ the Reynolds number, $Sc$ the Schmidt number and $L$ the electrode length.

The experimental Reynolds number exponent of 0.4 observed in Figs. 8 and 9 is close to the theoretical value of 0.33 anticipated for a mass transfer controlled process. The proposed CaCO$_3$ deposition model was therefore based on mass transfer kinetics.

Evaluation of mass transfer coefficients took into account the fact that the entrance region of the pilot electrolytic cell had flow disturbances arising from the introduction of the feed at right angles to the cylindrical cell. Such flow disturbances are expected to increase the mass transfer coefficient. Eq. (14) was therefore modified to take into account the flow disturbances by introducing an empirical geometrical factor $\psi$:

$$\frac{k_D \cdot d_h}{D_v} = 1.76 \cdot \psi \cdot \left( \frac{Re \cdot Sc \cdot d_h}{L} \right)^{\frac{1}{3}}$$ (15)

Theoretical prediction of the CaCO$_3$ cathodic deposition rate was carried out by applying the following mass transfer kinetic expressions. Transport from the solution bulk to the cathodic deposition surface of each of the species involved in CaCO$_3$ reaction was expressed by the flowing flux equations:

$$J_i = k_D \left( [C_i]_{\text{bulk}} - [C_i]_{\text{interface}} \right)$$ (16)

where $J_i$ is the flux of species $i$ (Ca$^{2+}$, CO$_2$, HCO$_3^-$, CO$_3^{2-}$, H$^+$ and OH$^-$) from the solution bulk to the cathodic deposition interface, $C_{i,\text{bulk}}$ is the bulk concentration of species $i$ and $C_{i,\text{interface}}$ is the interface concentration of species $i$. Mass transfer coefficients $k_D$ were calculated from Eq. (15) using a value for $\psi$ fitting the experimental data. Hydroxyl ion concentration on the cathodic surface was evaluated from Faraday’s law:

$$J_{\text{OH}^-} = \frac{i}{F}$$ (17)

where $i$ is the current density and $F$ is the Faraday constant.

The equilibrium condition prevailing on the deposition surface is given by:

$$[\text{Ca}]_{\text{interface}} \cdot [\text{CO}_3]_{\text{interface}} = K'_sp$$ (18)

where $K'_sp$ is the solubility product of calcite, corrected for ionic strength effects.

Figs. 10 and 11 compare experimental data with calculated results, using a value for $\psi = 5$ for the low concentration runs and a value of $\psi = 4.5$ for the high concentration runs. It is seen that both series of experiments yield good support to the validity of the model.

4.3. Electrolytic precipitation in the presence of anti-scalants

Electrolytic precipitation of CaCO$_3$ in the presence of an anti-scalant is of interest for efforts aiming to improve the economics of brackish water desalination by techniques enabling higher water recoveries than currently achievable. The potential benefits of an increased
water recovery are both economic and environmental. Increased recovery augments the desalinated water production and acts to lower costs. More important, increased water recovery reduces the concentrate volume, thus alleviating the environmentally problematical difficulty of concentrate discharge.

The maximum possible water recovery is constrained by the supersaturation level that can be maintained in the presence of the anti-scalant dosed to the raw water so as to prevent early scale precipitation. Water recoveries could be significantly increased by recycling part of the brine concentrate to the feed, after precipitating and separating the scaling salts held in the concentrate solution by the anti-scalant. The major obstacle to overcome is the stabilizing effect of the anti-scalant which hinders the precipitation process.

One of the possibilities for precipitating CaCO$_3$ in the presence of an antiscalant is by an electrolytic process. Electrolytic CaCO$_3$ precipitation occurs in the high pH environment prevailing near the cathode exceeding a pH of 10. It is expected that the extreme CaCO$_3$ supersaturation levels created at such high pH conditions would act to destabilize the solution and enable effective CaCO$_3$ precipitation. Fig. 12 illustrates a scheme for an enhanced water recovery process based on this effect.

The hypothesis that effective electrolytic CaCO$_3$ precipitation can be achieved on a concentrate solution stabilized by an anti-scalant was tested in an experiment carried out in the pilot system with a solution having the initial composition of Table 2.

The solution, held in a feed vessel of 170 L, was recirculated through the electrolytic device of the pilot system. The following parameters were maintained constant: electric current of 1.5 A, voltage of 2.65 to 2.75 V, solution temperature of 28–30°C and flow rate through the electrolytic cell of 0.9 to 1.1 L/min. The pH was held constant at 7.1 by pH controlled CO$_2$ injection. Periodic analyses were carried out to determine changes in the hardness parameters (Ca, Mg, $T_{alk}$) and in the solution turbidity.

Fig. 13 shows the changes in solution composition with time. It is seen that Mg$^{2+}$ removal was insignificant and that only Ca$^{2+}$ was removed. The

Table 2
Initial composition of anti-scalant solution tested in the pilot system

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$, m-mol/L</td>
<td>134.4</td>
</tr>
<tr>
<td>Mg$^{2+}$, m-mol/L</td>
<td>17.3</td>
</tr>
<tr>
<td>Ca$^{2+}$, m-mol/L</td>
<td>17.0</td>
</tr>
<tr>
<td>Cl$^-$, m-mol/L</td>
<td>147.6</td>
</tr>
<tr>
<td>SiO$_2^{2-}$, m-mol/L</td>
<td>3.9</td>
</tr>
<tr>
<td>HCO$_3^-$, m-mol/L</td>
<td>47.4</td>
</tr>
<tr>
<td>Anti-scalant: Acumer 5000, ppm</td>
<td>50</td>
</tr>
</tbody>
</table>
Fig. 12. Enhanced water recovery process based on electrolytic precipitation.

Fig. 13. Changes in solution composition with time by electrolytic scale removal in the presence of an anti-scalant.

decrease in Ca\(^{2+}\) and T\(_{\text{alk}}\) reduced the CaCO\(_3\) scaling potential LSI at a substantially linear rate (Fig. 14).

The drop in both Ca\(^{2+}\) and T\(_{\text{alk}}\) also was substantially linear at a rate of about 4.7 mg CaCO\(_3\)/L per hour for Ca\(^{2+}\) and a rate of 3.7 mg CaCO\(_3\)/L per hour for T\(_{\text{alk}}\). Adopting the average value of 4.2 mg CaCO\(_3\)/L per hour, the rate of scale removal by the electrolytic cell was:

\[ W = \frac{0.0042 \text{ g/Lh} \times 170 \text{L}}{0.1389 \text{ m}^2} = 5.1 \frac{\text{g}}{\text{m}^2 \text{h}} \]  

(19)

This compares with values of the order of 15 to 30 g CaCO\(_3\)/m\(^2\)-hr estimated from previous kinetic studies of CaCO\(_3\) scale deposition on heat exchanger tubes in the absence of an anti-scalant [18].
4.4. Electrode area and energy requirements for electrolytic CaCO\textsubscript{3} removal

A series of experiments was carried out in order to obtain design data for an electrolytic cell treating a typical carbonate concentrate recycle solution containing a high anti-scalant concentration. The experiments were carried out with the more accurate bench size equipment (Fig. 2). The anti-scalant used was Calgon (SHMP). The effect of current intensity on the specific area requirement and the specific energy consumption was determined from runs conducted with various currents in the range of 0.08–2.5 A obtained by DC supply of 2.5 V at the lowest current and 8.4 V at the highest current.

The initial solution composition was as follows: Ca\textsuperscript{2+} = 11.8 m-mole/L, T\textsubscript{alk} = 1900 ppm as CaCO\textsubscript{3}, Na\textsuperscript{+} = 105.2 m-mole/L, Cl\textsuperscript{-} = 92.0 mmole/L, LSI = 1.4, SHMP = 30 ppm. The solution was kept at a pH of 7.6 throughout the test by pH controlled CO\textsubscript{2} sparging. The flow rate of the solution recycling through the annular passage of the cell was 2.3 L/min corresponding to a Reynolds number of 700.

The scale precipitation rate was evaluated from measurements of the decay of the Ca\textsuperscript{2+} concentration in the recycle vessel. The data in Fig. 15 show that decay of the Ca\textsuperscript{2+} concentration with time was substantially linear, enabling accurate assessment of the CaCO\textsubscript{3} precipitation rate.

Fig. 15. Effect of the current intensity on Ca\textsuperscript{2+} removal.

Important design information is given in Fig. 16 which relates current density with both the specific cathodic area requirement (\(E_L\) m\textsuperscript{2} per kg CaCO\textsubscript{3}/hr) and with the specific energy consumption (\(E\) kWh per kg CaCO\textsubscript{3} precipitated). As anticipated, increase of the current density augments energy requirement but reduces the equipment size.

Fig. 16. Effect of current density on the required electrode area and on the energy consumption.

5. Conclusions

Despite the widespread occurrence of the scaling difficulty in numerous industrial applications, viable scale control techniques are quite limited in number. The hitherto little studied electrochemical scale removal technique holds promise to find cost benefit applications in various industrial processes, notably desalination. This study was mainly concerned with CaCO\textsubscript{3} electro-precipitation. Current ongoing research indicates the possibility of successful electro-precipitation of other scaling species such as CaSO\textsubscript{4} and process modifications for overcoming the objectionable release of chlorine in the electrolytic removal of CaCO\textsubscript{3}.
6. Symbols

- $A$ — Electrode surface area, cm$^2$
- $C_i$ — Concentration of ionic species $i$, mol/L
- $d_h$ — Hydraulic diameter, cm
- $D_v$ — Molecular diffusivity, cm$^2$/s
- $E$ — Specific energy consumption, kWh/kg precipitated CaCO$_3$
- $E_L$ — Specific electrode area, m$^2$ hr/g CaCO$_3$
- $E_D$ — Decomposition potential, V
- $F$ — Faraday constant, 96,500 coulomb/equiv
- $i$ — Current density, A/cm$^2$
- $I$ — Electrical current, A
- $J$ — Ionic flux, mole/s cm$^2$
- $k$ — Solution conductivity, 1/ohm-cm or S/cm
- $k_D$ — Mass transfer coefficient, cm/s
- $K_{sp}$ — CaCO$_3$ solubility product, mol$^2$/L$^2$
- $L$ — Electrode length, cm
- $LSI$ — Langelier saturation index, pH units
- $Q$ — Flow rate, L/min
- $r_0$ — Radius of anode, cm
- $r_1$ — Internal radius of bare cathode, cm
- $r_2$ — Internal radius of scale covered cathode, cm
- $R$ — Electrical resistance, ohm
- $R_g$ — Cell geometrical factor, 1/cm
- $Re$ — Reynolds number
- $Sc$ — Schmidt number
- $t$ — Time, h
- $V$ — Voltage
- $W$ — Scale deposition rate, g/m$^2$ h
- $\Delta x$ — Scale layer thickness, cm

Greek

- $\varepsilon_s$ — Scale porosity fraction
- $\eta_A$ — Anodic overvoltage, V
- $\eta_C$ — Cathodic overvoltage, V
- $\tau$ — Tortuosity factor
- $\psi$ — Geometrical factor

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