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Low electrode area electrochemical scale removal system

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ABSTRACT

Effective prevention of scale deposition is one of significant issues involved in desalination practice. The number of scale control techniques is rather limited. The most common scale control technique in desalination processes is based on dosage of inhibiting compounds which are able to suppress scale precipitation up to a certain degree. Electrochemical scale precipitation has long been used to reduce the hardness of water circulating in cooling tower systems. Despite its conspicuous advantages, the electrochemical scale removal technique has not been applied to-date in desalination processes because of two main limitations — high electrode area requirement and the existence of a limiting current density beyond which the precipitation rate remains unchanged. This paper presents a modified electrochemical system which overcomes the above limitations. The novel electrochemical seeds system enables drastic reduction of the electrode area requirement and has no limiting current restrictions. Data are presented showing that the specific electrode area can be reduced by a factor exceeding ten.

Keywords: Scale control; $CaCO_3$ removal; Electrochemical precipitation; Electrode area; Energy consumption

1. Introduction

The salts concentration effect accompanying the separation of pure water from a salt solution in both thermal and membrane desalination processes generates a potential for the precipitation of the sparingly soluble salts present in raw water feeds. The highly deleterious effects caused by scale deposition on heat-transfer and membranes surfaces make it essential to incorporate scale control measures in every desalting process. Currently, the most common technique for scale control in desalination processes is based on dosage of inhibiting compounds which are able to suppress scale precipitation up to a certain degree.

An interesting technique used to reduce the hardness of water circulating in cooling tower systems is based on electrochemical precipitation. Electrochemical scale removal offers many advantages: environmental compatibility, no need to handle and dose chemicals, accessibility to automation and convenient process control [1,2]. To-date, the electrochemical technique has not been applied in desalination practice because of technical limitations described below. The present paper describes a modified electrochemical seeds technique we have recently developed which overcomes limitations of the current technology and opens new scale control possibilities.

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2. Electrochemical water hardness abatement

2.1. Physical principle

Electrochemical scale precipitation is based on the creation of a strongly basic environment near the cathodic surface by the following reduction reactions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

The high alkaline environment acts to convert the HCO_3^- ion into the CO_3^{2-} form. The ensuing increase of the ionic product $[Ca^{2+}][CO_3^{2-}]$ promotes $CaCO_3$ precipitation:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{3}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{4}$$

The rate of hydroxyl ion generation (R_{OH} mole/s) with a current of i ampere is given by Faraday's law:

$$R_{OH} = \frac{i}{F}\eta \tag{5}$$

where F is Faraday constant (96,485 Coulomb/mole) and η is the current efficiency expressed by the ratio of moles $CaCO_3$ precipitated to theoretical moles OH^- generated by a current of i ampere. The high pH conditions also promote precipitation of magnesium hydroxide:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \tag{6}$$

The main anodic reactions are oxygen and chlorine generation:

$$2H_2O \longrightarrow 4H^+ + O_2 + 2e^- \tag{7}$$

$$2Cl^- \longrightarrow Cl_2 + 2e^- \tag{8}$$

The techniques for removing the deposit precipitating on the cathode are rather cumbersome and include polarity reversal, periodic mechanical scrapping and ultrasonic cleaning [3–5]. Polarity reversal is the most widely technique. Its drawback is that it restricts the allowable current density so as to prevent damage to the anodic DSA electrode by a high negative polarity [6].

2.2. Performance data

The major parameters characterizing the performance of electrochemical scale removal are the required electrode area and the energy consumption. The electrode area requirement is related to the specific scale precipitation rate (W g $CaCO_3$/h m^2) and the energy requirement, to the specific energy consumption (E kWh/kg $CaCO_3$).

There are virtually no published data on the magnitude of the performance parameters W and E of commercial equipment. Data measured in laboratory studies [7–11] are summarized in Table 1 and plotted in Fig. 1. It is seen that at current densities up to 10 A/m^2 the highest measured value of W was 30 g $CaCO_3$/h m^2 and at higher current densities reaching 108 A/m^2, the value of W approached 90 g $CaCO_3$/h m^2.

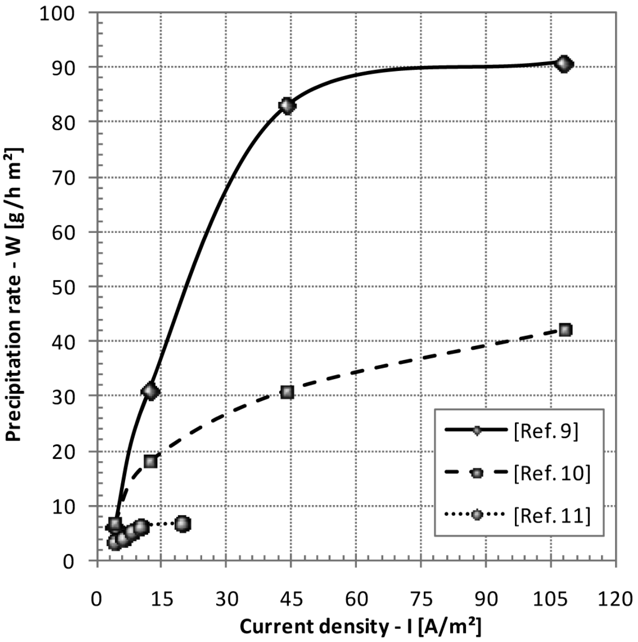

Fig. 1. Effect of current density on precipitation rate in conventional systems.

Electrochemical $CaCO_3$ precipitation is a complex process which depends on electrical, chemical and hydrodynamic parameters. Increase of the current density is found to augment the precipitation rate up to a certain limit after which the rate reaches an asymptotic level. The data of various studies plotted in Fig. 1 clearly indicate that the precipitation rate tends to an asymptotic limit at a current density in the range of 10–45 A/m^2. Gabrielli et al. [11] observed a limiting current density of 10 A/m^2 and suggested that limitations in the mass transfer rate of Ca^{2+} and HCO_3^- from the solution bulk to the reaction zone is responsible for the asymptotic precipitation tendency.

As may be anticipated, the $CaCO_3$ precipitation rate increases as the hardness level of the solution is augmented. The presence of species inhibiting $CaCO_3$ precipitation, notably Mg ions and anti-scalants (A.S.), acts to retards the electrochemical precipitation rate. An important finding of the study of Hasson et al. [10] was that the precipitation rate is mass transfer controlled. Increase of the Reynolds number increases the precipitation rate and reduces the specific energy consumption.

The above laboratory performance data indicate that electrochemical scale control can be of interest for desalination applications only if much higher precipitation rates can be achieved. This can be illustrated by considering the Gat brackish desalination plant in Israel

Table 1
Performance data of $CaCO_3$ electrochemical precipitation

T. Alk ppm as $CaCO_3$	Ca ppm as $CaCO_3$	Mg ppm as $CaCO_3$	A.S ppm	Cond mS	T °C	pH	Re	i A	I A/m²	V V	W g/h m²	E kWh/kg $CaCO_3$	η %	Ref
150	165	140	0	1.0	—	7.3–7.4	130–650	1.5	10.9	3.8	2.5–5.0	8–16	13–25	[7]
150	155	140	0	1.0	32	7.3	259	1–3	7.5–22	3–5	3.2–5.5	7–19	13–25	
150	160–610	140	0	1.0	32	7.3	259	1.5	10.9	2.8–3.3	3–14	2–9	20–71	
2370	1700	1730	50	—	28–30	7.1	—	1.5	10.9	2.7	5.1	5.8	13	
97	119	135	0	1.1	26–27	7.2–7.4	—	1.5	—	5.1–5.2	2.5	21	8	[8]
300	300	123	0	1.1	26–27	6–6.6	—	1.5	—	4.8–5	7.0–8.7	5.5–6.9	19–23	
120–300	300	0	0	1.6	26–27	6.3–6.6	—	1.5	—	5.0–5.1	4.1–5.9	9–12	10–16	
1840	1180	0	10–30	—	—	7.6	—	2.5	78	—	39	—	—	[9]
1950	2360	0	30	—	—	7.7	—	0.1–3.5	4–108	—	6–91	1.2–3.8	23–72	
1850	1180	0	30	—	—	7.6	—	0.1–3.5	4–108	—	7–42	4–108	11–49	[10]
—	222	18	0	—	24	—	—	0.2–1.1	4–20	—	3.4–6.9	—	—	[11]

which has a yearly output of 1.4 MCM and operates at a water recovery of 88%. It generates a concentrate stream having a calcium content of 1700 ppm as $CaCO_3$. In order to reduce the calcium content by one half so as to extract additional permeate, it is necessary to precipitate about 18 kg/h $CaCO_3$. Assuming a $CaCO_3$ removal rate of 40 g $CaCO_3$/h/m^2, the required electrode area is as high as 450 m^2. Thus, application of an electrochemical technique for improving scale control in desalination practice awaits development of systems based on considerably reduced electrode area requirements.

3. Seeded electrochemical system

In the conventional equipment currently used for hardness reduction in cooling tower systems, the water is in contact with both the cathode and the anode electrodes. The cathode performs two functions: it generates alkalinity and serves as a scale deposition surface. The precipitation reaction occurs only in the water film adjacent to the cathodic surface where hydroxyl ions are generated while the bulk of the water substantially retains the feed pH level.

The novel process we have developed adopts the scheme used in industrial production of NaOH. The anode and cathode are placed in disconnected compartments separated by a cationic ion exchange membrane (Fig. 2). In this case a high alkaline environment is generated throughout the whole volume of the cathodic compartment and not only in the boundary layer adjacent to the cathode. In the anodic compartment, the gas generation reactions (7) and (8) occur leading to transfer of cations to the cathodic compartment.

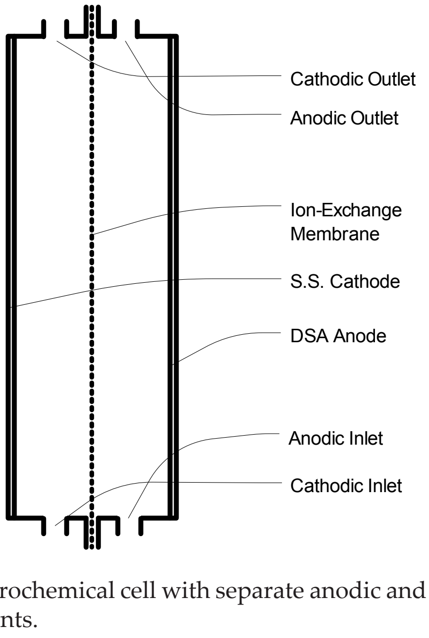

Fig. 2. Electrochemical cell with separate anodic and cathodic compartments.

Significant enhancement of the $CaCO_3$ rate of precipitation is achieved by transferring the alkaline solution emanating from the cathodic compartment into to a separate reaction vessel containing a suspension of calcium carbonate seeds. The seeds offer an extensive precipitation area, in contrast to the restricted area available in a system relying on the cathode to provide a crystallization surface. Moreover, transfer of the deposition function from the cathode to the seeds overcomes the difficulty of disposal of scale adhering to the cathode.

The rate of $CaCO_3$ precipitation in a seeds crystallizer can be modeled by the widely used kinetic expression proposed by Nancollas and Reddy [12]:

$$\frac{[\mathrm{Ca}]_i - [\mathrm{Ca}]_o}{\tau} = k_{RS} \cdot S_{\mathrm{CaCO_3}} \cdot \left\{[\mathrm{Ca}^{2+}]\cdot[\mathrm{CO}_3^{2-}] - K'_{SP}\right\} \tag{9}$$

where the bracketed terms denote concentrations, k_{RS} is the temperature dependent kinetic coefficient, S_{CaCO_3} is the precipitation area, K'_{sp} is the $CaCO_3$ solubility product corrected for ionic strength, τ is the retention time in the crystallizer and superscripts *i* and *o* denote inlet and outlet conditions respectively.

4. Experimental

Electrochemical precipitation of $CaCO_3$ was studied in the continuous flow once-through system shown in Fig. 3. Two electrochemical cells were constructed. The initial cell had a total volume of 900 mL and was separated into two compartments by a cationic ion-exchange membrane (Nafion N-966 of DuPont). The solution leaving the cathodic compartment with an augmented pH flowed into a 1 L stirred vessel in which the main crystallization process took place. The anode consisted of a 100×100 mm DSA plate while the cathode consisted of stainless steel plate of the same dimensions. The 900 mL cell enabled operation at current densities in the range of 40–120 A/m^2.

The second electrochemical cell was designed to provide higher current densities. The cell had a total volume of 50 mL and was similarly constructed with an ion-exchange membrane separating the cationic and anionic compartments. The anode consisted of a 100×25 mm DSA plate while the cathode consisted of a stainless steel plate of the same dimensions. The 50 mL cell enabled operation at current densities of up to 600 A/m^2.

The experimental systems enabled feed flow rates through the cathodic compartment in the range of 50–150 mL/min. Flow in the cells was laminar at Reynolds numbers below 50. Test solutions fed to the cathodic compartment were prepared by dissolving technical grade $CaCl_2$, NaCl and $NaHCO_3$ in distilled water. To prevent water permeation through the membrane, a solution of NaCl in distilled water having an osmotic pressure similar to that in the cathodic compartment, was recycled through the anodic compartment.

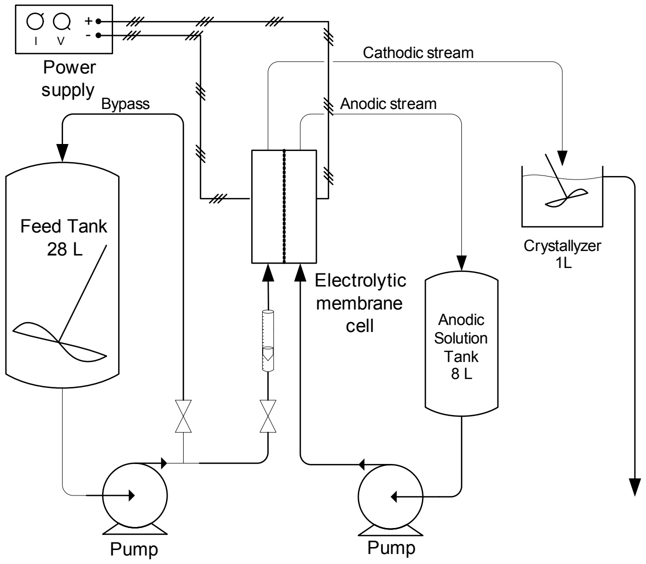

Fig. 3. Flowsheet of the electrochemical seeds precipitation system.

The calcium removal rate was evaluated from the difference in calcium concentration between the feed and the solution leaving the crystallizer. Calcium concentrations were determined by EDTA titrations. Repeat experiments were carried out so as ascertain the accuracy of the results.

5. Results

5.1. Effect of current density on the precipitation rate

Fig. 4 displays data showing the effect of current density on the precipitation rate. The data at the low current densities below 120 A/m² were measured with the 900 mL electrolyzer using solutions having a calcium content of 400–800 ppm as $CaCO_3$ and an alkalinity of 300–480 ppm as $CaCO_3$. The data at the high current densities of 400 and 600 A/m² were measured with the 50 mL electrolyzer using solutions having a calcium content of 1500 ppm as $CaCO_3$ and an alkalinity of 480 ppm as $CaCO_3$.

A striking result observed in Fig. 4 is the very high specific precipitation rate obtained with the seeds system. A $CaCO_3$ removal rate as high as 1.2 kg/h per 1 m² electrode area can be achieved, compared to less than 0.1 kg/h per 1 m² electrode area in conventional systems. Another striking observation is that increase in current density in the seeds system elevates the precipitation rate, in contrast to the asymptotic limit present in conventional systems (Fig. 1).

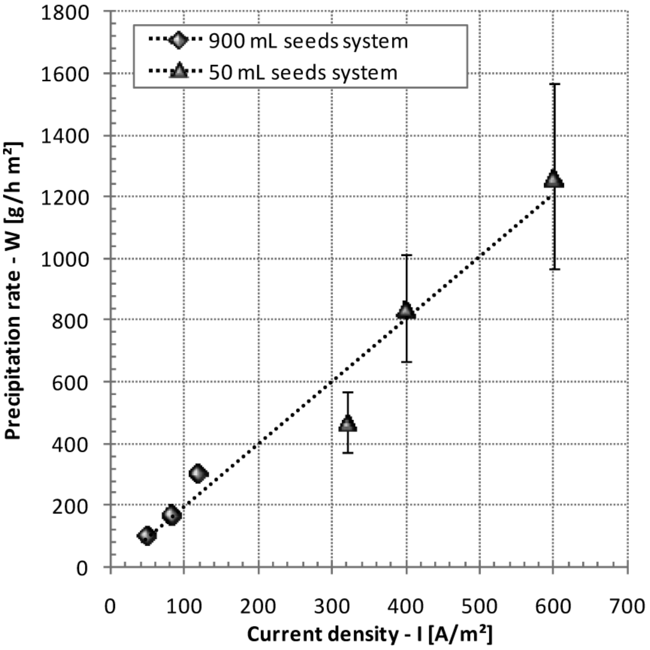

Fig. 4. Effect of current density on the precipitation rate in seeds electrochemical systems.

5.2. Effect of pH of feed solution on precipitation rate

The effect of feed pH on the precipitation rate was studied in the 50 mL electrolyzer at a current density of 600 A/m² and a feed flow rate of 70 mL/min (Re = 50). The feed solution had a calcium content of 1500 ppm as $CaCO_3$ and a total alkalinity of 480 ppm as $CaCO_3$. The data plotted in Fig. 5 show that the feed pH exerts pronounced effect on the $CaCO_3$ precipitation rate. Increase of the feed pH from 6.2 to 6.5 augments the precipitation rate per unit electrode area by as much as 50%.

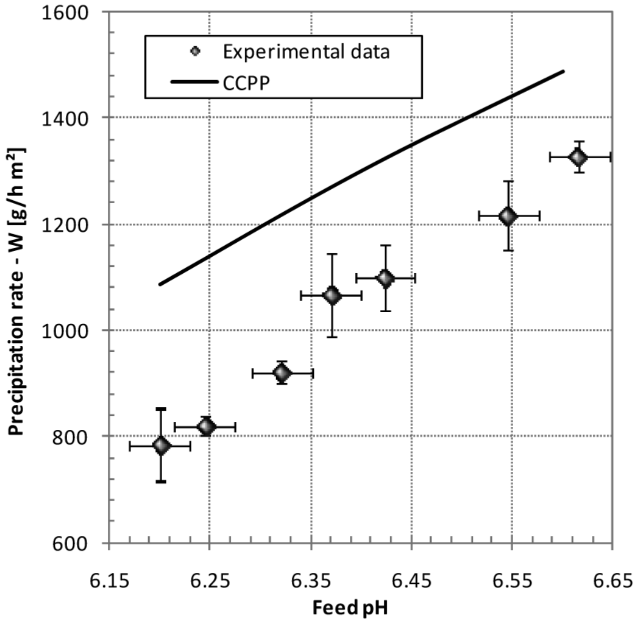

Fig. 5. Effect of feed pH on the precipitation rate.

The reason for this result lies in the effect of the pH on the calcium carbonate precipitation potential (CCPP). A CCPP value indicates the maximum amount of $CaCO_3$ precipitated when a given solution reaches equilibrium. CCPP values plotted in Fig. 5 were evaluated using the equivalent NaOH amount produced at the current density of 600 A/m². It is seen that increase of the pH has a strong effect on CCPP values of the studied solution, comparable to the experimentally observed effect.

5.3. Effect of Ca^{2+} concentration on the precipitation rate and energy consumption

The effect of calcium concentration on the specific precipitation rate and the specific energy consumption was studied in the 50 mL electrolyzer at a constant current density of 600 A/m² and a constant feed flow rate of 70 mL/min (Re = 50). The feed solution was maintained at the pH of 6.4 and the molar ratio of Ca to alkalinity was held at 1.6. Since the current density and feed flow rates were maintained constant the feed solution in the cathodic compartment was essentially exposed to a constant dosage of electrochemically generated NaOH. Because the molar feed ratio of calcium to bicarbonate was held constant, increase of the calcium feed concentration should result in augmented carbonate content and increased $CaCO_3$ precipitation potential. The theoretical CCPP curve plotted in Fig. 6 together with the experimental data confirms the observation that $CaCO_3$ precipitation rate increases with calcium content.

Fig. 7 shows the specific energy consumption and the current efficiency as functions of calcium concentration. The decrease in energy consumption with the concomitant rise in current efficiency are due to the increase in $CaCO_3$ precipitation rate.

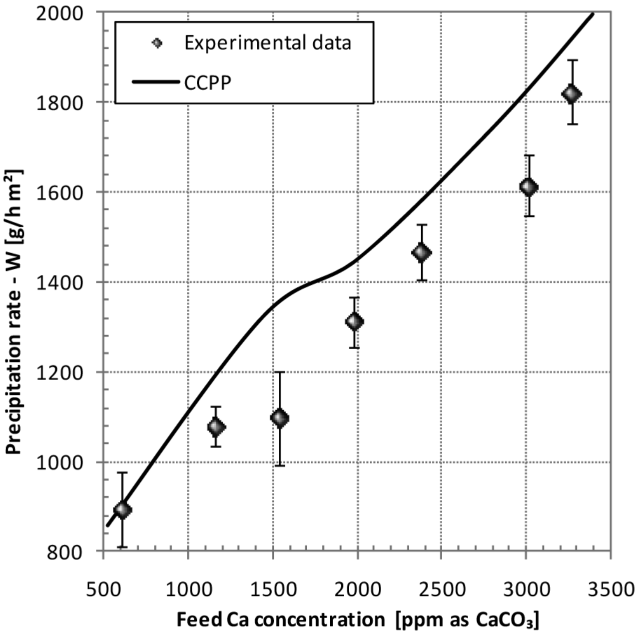

Fig. 6. Effect of feed calcium concentration on the precipitation rate.

6. Concluding remarks

The novel seeds precipitation system presented in this paper enables drastic reduction in the electrode area of conventional electrochemical scale removal equipment and opens the possibility for viable scale control applications in desalination processes. Experimental data and theoretical considerations indicate that high electrochemical precipitation rates leading to low electrode area requirement are achieved at high current densities, high solution concentrations and a high feed pH level. The highest specific precipitation rate measured in this study by the novel seeds system was 1800 g/h per m² electrode area (Fig. 6) which is 10–20 times higher than that reported for conventional electrochemical precipitation systems.

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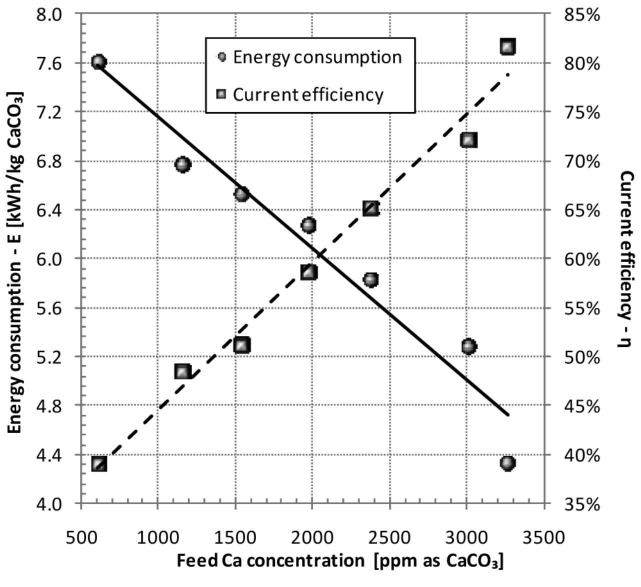

Fig. 7. Effect of feed calcium concentration on the energy consumption and the current efficiency.

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