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SCALE FORMATION AND MITIGATION OF MIXED SALTS IN HORIZONTAL TUBE FALLING FILM EVAPORATORS FOR SEAWATER DESALINATION

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ABSTRACT

Scale formation on heat transfer surfaces is one of the most severe problems in the design and operation of multiple-effect distillers for seawater desalination. Because of the complexity of crystallization fouling, research has mainly been restricted to single-salt precipitation and not much attention has been given to the co-precipitation of calcium- and magnesium-containing salts from falling seawater films on horizontal tubes.

A horizontal tube falling film evaporator in pilot plant scale was used to study crystallization fouling under conditions close to those prevailing in industrial multipleeffect distillers. Experiments were performed with artificial seawater and model solutions based on artificial seawater under various process conditions.

In experiments with artificial seawater, the surface of CuNi 90/10 tubes was covered with a two-layer scale comprising a thin, flaky magnesium-rich and calcium-free base layer underneath a thick layer of calcium carbonate crystals in the form of aragonite. Analyses indicated $Mg(OH)_2$ (brucite) and iowaite in the thin base layer. The magnesium-rich scale layer was formed even at a low evaporation temperature of 50°C which promotes the assumption of locally high pH values at the metal-solution interface. A shift of pH to high values in the thin seawater film due to CO₂ release and, additionally, cathodic reactions resulting in a locally enhanced OH⁻ concentration may promote a high degree of supersaturation of Mg(OH)₂ to drive its rapid precipitation on the tube surface. Once the tube surface is completely covered with the thin Mg-rich scale layer, it seems that the growth of the Mg-rich layer ceases and aragonite crystals start to precipitate.

A decrease in the Mg^{2+} ion concentration in the solution results in an increase in the mass of calcium carbonate as aragonite in the scale layer. Results suggest that Mg^{2+} ions retard the calcium carbonate crystallization.

INTRODUCTION

Scale formation on heat transfer surfaces has a highly deleterious effect on specific energy consumption and production capacity in multiple-effect distillers for seawater desalination. Over-sizing the heat transfer surface area, scale mitigation measures, cleaning methods as well as production losses during plant shutdown for cleaning create considerable capital, operating, and maintenance costs. Therefore, achieving effective scale prevention by suitable anti-scalants is a major concern of the desalination industry especially when striving towards higher top brine temperatures.

In multiple-effect distillation (MED) plants with horizontal tube falling film evaporators, scale is formed on the outside of the tubes what prevents the use of mechanical cleaning methods such as ball cleaning systems. Brine flows as a thin film over the outside of the tubes and partly evaporates and, thus, the salinity rises from the top tube row to the bottom tube row up to a maximum of 70 g/kg. The maximum top brine temperature currently used in industrial MED distillers is 70°C. In MED distillers, carbon dioxide is released from the evaporating brine on the outside of the tubes. The release of CO₂ and the resulting pH value and the HCO₃⁻, CO₃²⁻ and CO₂ concentrations along the flow path of brine were investigated by Glade and Al-Rawajfeh (2008) and Al-Rawajfeh et al. (2004, 2005).

Since seawater is a multi-component electrolyte solution, scale formation is caused by co-precipitation of different calcium- and magnesium-containing salts. The solubility data and rate constants obtained for single-salt systems are not applicable to complex systems such as seawater with co-precipitating salts. The effects of process parameters, fluid properties as well as fluid dynamics on elementary scaling processes, e.g., crystal growth, on scale characteristics, e.g., composition and structure, and how anti-scalants interfere with these processes have scarcely been investigated.

Crystallization of pure salts, such as calcium carbonate, has been extensively studied for binary or simple systems, whereas not much attention has been given to the crystallization of magnesium-containing salts such as magnesium hydroxide (Mg(OH)₂), magnesite (MgCO₃), nesquehonite (MgCO₃*3H₂O) and hydromagnesite (4MgCO₃Mg(OH)₂*4H₂O) in multi-component systems. The complexity of the magnesium-carbonate system, with numerous different forms of basic and hydrated Mgcarbonates, is certainly one reason for the lack of a complete understanding of all the issues involved in the formation of Mg-carbonates.

The effects of process parameters on the predominance of one of the above-mentioned magnesium salts are poorly understood and controversially discussed. Furthermore, some of the magnesium salts have a similar appearance, e.g., hydromagnesite and magnesium hydroxide, which makes the identification difficult.

Even though calcium-containing scales are the main part of the deposit, the magnesium-containing base layer is important since it is the initial scale and upon this further crystal growth takes place (Neville and Morizot, 2002). A better knowledge of the type of the precipitating salt, depending on the process conditions, and the growth mechanisms of the initial magnesium-containing scale layer would facilitate the further improvement of scale control techniques and, thus, the efficiency of thermal desalination plants, particularly when striving towards higher top brine temperatures. Therefore, focus turns to co-precipitation of calcium and magnesium salts in complex multi-component systems. Fundamental investigations as well as further experimental studies in this area are required.

The objective of this study is to contribute to the understanding of formation of mixed salts in MED distillers for seawater desalination. In the following, an overview of literature dealing with calcium- and magnesium-containing scale is given. The experimental set-up is presented and the results of the experimental study are discussed.

CALCIUM- AND MAGNESIUM-CONTAINING SCALE IN MULTI-COMPONENT SYSTEMS

The deposit formed on the heat transfer surfaces in desalination systems is mainly composed of calciumcontaining and magnesium-containing salts. Depending on the scaling conditions, calcium carbonate may precipitate in three different anhydrous crystalline forms: vaterite, aragonite, and calcite. The three polymorphs have markedly different crystallographic characteristics, crystal growth habits, and solubilities. The formation of calcium carbonate polymorphs in aqueous supersaturated solutions is strongly influenced by the presence of dissolved cationic and anionic species. Kitano (1962) found that the presence of dissolved Mg²⁺ in magnesium-rich aqueous solutions strongly favors the precipitation of CaCO₃ as aragonite, rather than the more stable calcite. Experimental studies suggest that at a molar $Mg^{2+}:Ca^{2+}$ ratio higher than 3 aragonite is predominating whereas at a ratio less than 1 calcite is the dominant form (Berner, 1975). In seawater, the concentration of magnesium is sufficient to explain the precipitation and persistence of aragonite (Bischoff, 1968). Besides Mg²⁺ ions the presence of other salts/species affects precipitation in mixed salt solutions, e.g. the presence of NaCl (Sheikholeslami, 2003), strontium ions or sulfate ions (Akin and Lagerwerff, 1965; Bischoff, 1968; Bischoff and Fyfe, 1968). However, first and foremost magnesium is considered to be the strongest calcite reaction rate inhibitor.

Most of the above mentioned experimental studies were performed at low and constant temperatures. Thus, the $Mg^{2+}:Ca^{2+}$ ratio was identified as the main factor controlling

the predominance of either calcite or aragonite. More recent studies show the strong influence of temperature on calcite reaction rate in seawater and brines (Burton and Walter, 1987; Gledhill and Morse, 2006; Lopez et al., 2009; Morse et al., 1997). Morse et al. (1997) found that the CaCO₃ polymorph that forms from seawater-based solutions varies with temperature and Mg²⁺:Ca²⁺ ratio. Their studies indicate that calcite can directly precipitate from normal seawater with a Mg²⁺:Ca²⁺ ratio of 5:1 below about 6°C, and the critical Mg²⁺:Ca²⁺ ratio at which the change to aragonite precipitation occurs decreases sharply with increasing temperature.

In hydrogencarbonate-carbonate solutions, the following reaction mechanisms occur in parallel (Danckwerts, 1970; Kern, 1960; Stumm and Morgan, 1981):

Reaction mechanism I:

Step 1: $CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$ (1)

Step 2: $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ (2)

Reaction mechanism II:

Step 1: $CO_2 + OH^- \leftrightarrow HCO_3^-$ (3)

Step 2:
$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O.$$
 (4)

Depending on the temperature and the pH value, the acidic or the alkaline reaction mechanism predominates (Glade, 2001). The carbonate ions formed in the reactions may combine with calcium ions to calcium carbonate. The hydroxyl ions may combine with magnesium ions to form magnesium hydroxide or with magnesium and carbonate ions to form hydromagnesite or another Mg-carbonate.

Magnesium hydroxide $(Mg(OH)_2)$ in the modification brucite has a fine, plate-like crystalline structure (Klein and Hurlbut, 1985; Nesse, 2004; Phillips et al., 1977). Hydromagnesite is a magnesium hydroxyl carbonate also with a flaky appearance. Li et al. (2003) described the morphology of hydromagnesite crystals synthesized by a hydrothermal method as a rosette-like microstructure. Scanning electron microscope images of hydromagnesite crystals are similar to images showing brucite structures.

Harris et al. (1974) studied scale formation in boiling aqueous solutions containing magnesium and hydrogencarbonate ions or calcium/magnesium and hydrogencarbonate ions. They proposed that scale formation occurs via the decomposition of the hydrogencarbonate ion to carbonate ion and hydroxyl ion and that hydromagnesite precipitates in preference to calcium carbonate. They found that hydromagnesite then undergoes a solid state chemical change to magnesium hydroxide. Harris et al. (1974) proposed that anti-scalants, to be effective against magnesium scales, have to be capable of distorting the hydromagnesite structure.

Botha und Strydom (2001) performed experiments with magnesium-containing solutions and sparging CO_2 at various pH values and temperatures. They investigated the influence of pH at a constant temperature of 20°C and found that at a pH higher than 9 the formation of brucite predominates and at lower pH values magnesium hydroxyl carbonates are the dominant forms.

Mažuranić et al. (1982) reported about studies on the precipitation of brucite in the system MgCl₂-NaOH-H₂O. They found that at a high pH brucite preferentially occurs whereas at lower pH values the formation of Mg₃(OH)₅Cl*4H₂O and Mg₂(OH)₃Cl*4H₂O predominates.

Höfling (2004) carried out experiments with MgCl₂containing solutions. He showed that the formation of magnesium carbonate trihydrate (MgCO₃*3H₂O) occurs at temperatures below 42°C. At a temperature between 60°C and 90°C hydromagnesite is formed (Botha and Strydom, 2001; Hänchen et al., 2008; Cheng et al., 2009).

Königsberger et al. (1999) presented a low-temperature thermodynamic model for the geochemically important Na₂CO₃-MgCO₃-CaCO₃-H₂O system. Hänchen (2007) and Hänchen et al. (2008) examined the precipitation of magnesium salts in magnesium-carbonate systems in theoretical and experimental studies. The MgO-CO₂-H₂O system was investigated at various temperatures and partial pressures of CO₂. Depending on the temperature, the partial pressure of CO₂ and the kinetic inhibition, a large number of compounds is possible: brucite (Mg(OH)₂), magnesite (MgCO₃), nesquehonite (MgCO₃*3H₂O), lansfordite (MgCO₃*5H₂O), artinite (MgCO₃Mg(OH)₂*3H₂O) and hydromagnesite (4MgCO₃Mg(OH)₂*4H₂O).

Block and Watson (1976) presented results from experiments on seawater evaporation in the presence of typical distillation corrosion products. The formation of CaCO₃ was suppressed by the reduction of the total alkalinity. They found that the formation of brucite occurs at higher temperatures about 120°C and low CO2 residuals in the brine and iowaite at lower temperatures about 100°C and higher CO_2 residuals in the brine. Layered double hydroxides, also known as hydrotalcite-like compounds, such as iowaite, are lamellar hydroxides with two kinds of metallic cations in the main layers and interlayer domains containing anionic species (de Roy et al., 2001). The structure is made of brucite-type octahedral layers, in which mainly trivalent metal cations (Al, Mn, Fe, Co, Ni, Cr, Ga) partially substitute for divalent metal cations (Mg, Mn, Fe, Co, Ni, Cu, Zn) (de Roy et al., 2001; Bellotto et al., 1996). The positive charge of the octahedral layers resulting from this substitution is balanced by anions arranged in layers alternating with the octahedral ones. These interlayers are built from anions (inorganic or organic) and water molecules to fill up available sites (Bellotto et al., 1996). The crystal chemistry is complicated by the extreme compositional variability exhibited by layered double hydroxides (Bellotto et al., 1996). Braithwaite et al. (1994) re-examined iowaite and suggested the formula $Mg_6Fe_2(OH)_{16}Cl_2*4H_2O$ which is in compliance with the formula for iowaite given in the Handbook of Mineralogy by Anthony et al. (2001-2005). The formation of iowaite is limited by the concentration of iron which is a typical corrosion product of steels and copper-nickel alloys (Block and Watson, 1976). Block and Watson (1976) could not prove that the formation of brucite occurs via the intermediate phase hydromagnesite.

A possible explanation for the deposition of a base layer on the tube surface consisting of magnesium-

containing scales, such as Mg(OH)₂, is electrodeposition (e.g., Akamine and Kashiki, 2003; Hodgkiess and Najm-Mohammed, 2003; Lee et al., 2009; Nair and Misra, 1978; Neville and Morizot, 2002). Typical corrosion processes observed in thermal desalination plants may cause small local anodic and cathodic surface areas which lead to electrodeposition (Nair and Misra, 1978). Because of the cathodic reactions, the oxygen reduction

$$O_2 + 2 H_2O + 2 e^- \rightarrow H_2O_2 + 2 OH^-$$
 (5)

$$\mathrm{H}_{2}\mathrm{O}_{2} + 2 \,\mathrm{e}^{-} \rightarrow 2 \,\mathrm{OH}^{-} \tag{6}$$

and the hydrogen ion reduction

$$2 \operatorname{H}_{2}\mathrm{O} + 2 \operatorname{e}^{-} \to \operatorname{H}_{2} + 2 \operatorname{OH}^{-}, \qquad (7)$$

the interfacial pH at the metal-solution interface increases (Deslouis et al., 2000) and $Mg(OH)_2$ can precipitate.

Nair and Misra (1978) examined this electrolytic scale formation. They performed experiments with electrolytic cells under various conditions. Magnesium-containing scales in the form of brucite were predominant even at low temperatures of about 30°C. At a temperature of 90°C even 96% of the scaling constituents were Mg(OH)₂.

Neville and Morizot (2002) presented results from experimental and theoretical studies on calcareous scales formed by cathodic protection. Rotating disk electrodes were used in the studies at various rotational speeds, a constant potential and a constant temperature of 25°C for test periods up to 3 days. Test solutions were artificial seawater and magnesium- or calcium-free model solutions. With magnesium-containing solutions the metal surface was covered with a thin magnesium-rich and calcium-free base layer within minutes. These deposits were identified as magnesium-containing carbonate species and not only brucite which can be explained with the pH of saturation for these magnesium-containing compounds. On this initial base layer isolated calcium- and magnesium-containing crystals grew within the first hour. After 3 days a thick and dense layer of mainly aragonite crystals could be found.

Hodgkiess and Najm-Mohammed (2003) investigated the interrelationships between the performance of a cathodic protection system and the deposition of calcareous scale compounds in a steel pipe fed by seawater flowing to a thermal desalination plant. They identified a two-layer scale deposit comprising a thin compact $Mg(OH)_2$ (brucite) layer with an overlying columnar array of aragonite crystals over a range of applied potentials, flow rates and temperatures in a range between 25°C and 35°C. The precipitation of low-solubility compounds, e.g., calcium carbonate and magnesium hydroxide, was explained by the locally enhanced pH generated by the cathodic reactions. They concluded that the brucite layer forms in the early stages of cathodic protection application when the currents yield a sufficiently high OH⁻ concentration on the surface to promote a degree of supersaturation of Mg(OH)₂ large enough to drive its rapid precipitation. As the current diminishes due to the growth of the brucite layer, its growth ceases and CaCO₃ starts to precipitate.

EXPERIMENTAL

Test Rig

The experimental studies were performed in a horizontal tube falling film evaporator in pilot plant scale. Figure 1 shows a schematic diagram of the test rig.



Fig. 1. Schematic diagram of the test rig

The main part of the test rig is an evaporator fitted with a bank of 6 horizontal tubes, as depicted in Figure 2.



Fig. 2. Drawing of the horizontal tube falling film evaporator

Saturated steam is provided by an electrical steam generator. The steam is introduced into the tubes and condensed under vacuum conditions. The condensation temperature/pressure of the steam inside the tubes can be varied between 45°C/0.1 bar and 97°C/0.9 bar. The condensate flows back to the steam generator for reuse. The test solution is evenly distributed onto the first tube by means of a toothed overflow weir and trickles down by gravity forming a thin film flow over the horizontal tubes. Inspection glasses on both sides of the evaporator shell allow for a visual observation of the wetting behavior during the experiments. The enthalpy of condensation allows the feed water to be preheated to the boiling point on the upper tube and then part of it to be evaporated on the lower tubes. The evaporation temperature/pressure of the solution can be varied between 40°C/0.074 bar and 90°C/0.7 bar. The generated vapour is condensed in a plate heat exchanger. After leaving the evaporator, the concentrated test solution flows into a collecting tank. The condensate is mixed with the concentrated solution and the test solution is recirculated by a pump.

 CO_2 released from the evaporating test solution and ambient air potentially penetrated into the evaporator are extracted by means of a vacuum pump which maintains the saturation pressure in the evaporator shell. The pilot plant provides conditions for CO2 release from seawater very similar to those in industrial multiple-effect distillers. CO₂ release shifts the pH value of the seawater to higher values and influences the carbonate system.

Measurement instrumentation and automation of the test rig allow systematic studies by varying the process parameters and simulating process conditions in different stages of industrial MED plants. A detailed description of the test rig is given in previous work (Glade et al., 2005; Glade et al., 2008).

Test Procedure

The tubes can be removed from the tube sheets in order to renew the tubes, to test different tube materials and to analyze the adherent scale. In the experiments, tubes made of copper-nickel 90/10 (CuNi10Fe1Mn) were used (outer diameter $d_0 = 25$ mm, effective length L = 453 mm). Copper-nickel 90/10 is an established evaporator tubing material and was used with a typical roughness $(R_a = 0.5 \ \mu m).$

Test series were performed at a low evaporation temperature t_{EV} of 50°C and at a high evaporation temperature of 75°C exceeding the top brine temperatures currently used in industrial MED distillers. The difference between the condensation temperature t_{CO} inside the tubes and the evaporation temperature t_{EV} outside was t_{CO} - t_{EV} = 5°C. A typical wetting rate which is the mass flow rate of the solution \dot{m} per unit tube length L, $\Gamma = \dot{m}$ (8)

of $\Gamma = 0.1 \text{ kg/(s m)}$ or 0.09 kg/(s m), respectively, was chosen. Experiments were conducted with 240 or 300 liters of artificial seawater or model solutions based on artificial seawater and for a test period of 50 or 90 hours. In previous experiments, different volumes of test solution and time periods were tested. Experiments with 240 or 300 liters of test solution and time periods of 50 and 90 hours were found to be favorable because time periods are long enough to find differences in scale formation and supersaturation levels are still high enough.

After each test run the inside of the evaporator was cleaned manually with deionized water and with diluted acetic acid solution. The collecting tank for the seawater was cleaned with water jets. The whole circuit was cleaned by flushing with deionized water for several days. After a couple of tests the whole test rig was cleaned with methanesulfonic acid. For each test run, new tubes were used for the third, forth and fifth tube from the top of the tube bank because scale layers on these tubes were analyzed (see Section "Chemical and Structural Characterization of the Scales"). The tubes installed on the first, second and sixth position were used twice and then renewed. They were removed from the tube sheets and thoroughly cleaned after the first usage.

Test Solutions

In the horizontal tube falling film evaporator, artificial seawater and model solutions based on salt mole fractions for standard artificial seawater as suggested in the formulation by Kester et al. (1967) were used. The composition of artificial seawater is within 1 mg/kg of natural seawater for all the major constituents (Kester et al., 1967). After mixing the salts and stirring the solution, the model solutions were aerated. The aeration tended to equilibrate the solution with atmospheric gases and removed the excess CO_2 resulting from the conversion of HCO_3^{-2} .

The salinity of ocean surface waters throughout the world is fairly uniform about 35 g/kg. In areas with a high level of rainfall or river runoff, the salinity is less. In areas with higher rates of evaporation, the salinity is higher, e.g. in the Persian Gulf. In seawater, the relative proportion of the major ions compared to the salinity remains constant (Millero, 2006). Therefore, the artificial seawater used in the experiments is representative for natural seawater. Experiments were performed with artificial seawater having a salinity of 45 g/kg simulating, for example, the seawater in the Persian Gulf or having a salinity of 65 g/kg simulating the concentrated seawater on the bottom tubes in industrial MED plants taking into account a typical concentration factor between 1.3 and 1.6. Furthermore, experiments were conducted with model solutions having different calcium or magnesium concentrations at the same ionic strength

$$I = \frac{1}{2} \sum m_i \ z_i^2 \tag{9}$$

where m_i is the molality of ion i and z_i is the charge number of that ion.

The CaCl₂ or MgCl₂ was substituted by NaCl at a constant ionic strength of $I_{S=45g/kg} = 0.94$ mol/kg or $I_{S=65g/kg} = 1.39$ mol/kg, respectively. Table 1 gives an overview of the model solutions. For comparison, average seawater having a salinity of 35 g/kg has an ionic strength of 0.72 mol/kg. The pH of most surface waters in equilibrium with the atmosphere is 8.2 ± 0.1. The molar ratio of Mg²⁺ ions to Ca²⁺ ions in seawater is 5.1:1 (Millero, 2006). Seawater with a salinity of 45 g/kg, e.g. in the Persian Gulf, has an ionic strength of 0.94 mol/kg. The molar ratio of Mg²⁺ to Ca²⁺ ions is the same as for standard seawater, i.e. 5.1:1.

Table 1. Artificial seawater and seawater-based model solutions used in the horizontal tube falling film evaporator

Model solution	Ionic	pН	Mg ²⁺	Ca ²⁺
	strength		molality	molality
	mol/kg		mol/kg _{solvent}	mol/kg _{solvent}
Artificial seawater	0.94	8.3-8.4	0.072	0.014
Calcium-depleted	0.94	8.4	0.072	0.0046
Calcium-free	0.94	8.3-8.4	0.072	0
Magnesium-depleted	0.94	8.3	0.014	0.014
Magnesium-free	0.94	8.3	0	0.014
Artificial seawater	1.39	8.4	0.106	0.021
Calcium-free	1.39	8.5	0.106	0

Chemical and Structural Characterization of the Scales

The scale layers formed outside the tubes of the falling film evaporator were analyzed by various methods to obtain chemical, structural, and quantitative information. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDXS) and wide angle Xray diffraction (XRD) were used to provide qualitative information on structural and chemical characteristics of the scale, especially about composition, crystal structure, crystal size and orientation. The amounts of calcium and magnesium in the scale were detected by atomic absorption spectroscopy (AAS). Additionally, the thickness of the scale layer formed outside the horizontal tubes was measured with a gauge (MiniTest 2100, ElektroPhysik, Germany) designed for non-destructive and precise coating thickness measurement. The scale thickness was measured 10 times each at 4 different positions around the tube and at 9 different positions along the tube. The scale formed outside the tubes of the falling film evaporator was analyzed as follows: Scale thickness was determined on the third tube from the top of the tube bank. The scale of the fourth tube was dissolved in a hot solution of acetic acid and the concentrations of Ca^{2+} and Mg^{2+} ions in the solution were measured using AAS. Furthermore, the fifth tube was analyzed using SEM, EDXS, and XRD.

RESULTS AND DISCUSSION

In the following, the effects of temperature, test period and composition of the model solution as well as of a polymeric anti-scalant on scale formation are presented and discussed.

Effect of Temperature on the Formation of Magnesium Scale

The SEM images in Figure 3 show the scale formed on the tube surface in an experiment performed in the horizontal tube falling film evaporator with artificial seawater at a low evaporation temperature of 50° C, a salinity of 45 g/kg, and a wetting rate of 0.1 kg/(s m) for a test period of 50 hours. The tube surface was covered with thin and thick rod-shaped CaCO₃ crystals. The XRD analysis confirmed that mainly aragonite crystals had formed, but calcite was also indicated. The results of the AAS analyses suggest that there is a magnesium-containing base layer underneath the CaCO₃ crystals (see Figure 8).



Fig. 3. SEM images of the scale, artificial seawater, $\tau = 50$ h, $t_{EV} = 50^{\circ}$ C, $t_{CO} = 55^{\circ}$ C, S = 45 g/kg, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 1- CaCO₃ (aragonite).

With the calcium-free model solution under the same process conditions, a thin base layer comprising Mg/O/Cl-containing crystals with traces of C and Fe grew on the tube surface, as shown in Figure 4. Furthermore Cu/Ni/O-, Cu/O- and Cu/O/Na-containing compounds were found. The XRD analysis suggest that the magnesium-containing compound iowaite formed.



Fig. 4. SEM images of the scale, calcium-free seawater, $\tau = 50$ h, $t_{EV} = 50$ °C, $t_{CO} = 55$ °C, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 2-Mg/O/Cl (traces of C, Fe), 5-Cu/Ni/O (traces of C/Na/Mg/Cl/Mn/Fe), 8-Cu/O (traces of C/Mg/Cl/Fe/Ni).

The SEM images in Figure 5 show the scale formed on the tube surface in an experiment performed with artificial seawater at a high evaporation temperature of 75°C, a salinity of 45 g/kg, and a wetting rate of 0.1 kg/(s m) for a test period of 50 hours. The tube surface was densely covered with a thin base layer with flaky crystals composed of Mg/O/Cl with traces of C and Ca. Rod-shaped CaCO₃ crystals (aragonite) grew above this magnesium-containing base layer. Furthermore, some single CaSO₄ crystals and Mg/O/Cl-containing flaky agglomerates (with traces of C, Ca and Na) grew on top of the aragonite crystals.



Fig. 5. SEM images of the scale, artificial seawater, $\tau = 50$ h, $t_{EV} = 75^{\circ}$ C, $t_{CO} = 80^{\circ}$ C, S = 45 g/kg, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 1- CaCO₃ (aragonite), 2- Mg/O/Cl (traces of C/Ca), 3- CaSO₄, 6- Mg/O/Cl (traces of C/Ca/Na).

The scale formed on the tube surface in an experiment performed with the calcium-depleted model solution under otherwise identical conditions is shown in Figure 6. The surface was covered with a thin and flaky base layer consisting of Mg/O-containing crystals (with traces of Mn and Cl). The XRD analysis suggest that the magnesium-rich component iowaite formed. Furthermore, flat Mg/O-containing crystals (with traces of Na and Cl) were found. Due to the reduction of the calcium concentration in the solution no rod-shaped aragonite crystals grew, but some Ca/C/O-containing particles with a diameter up to 5 μ m were deposited on the tube surface.



Fig. 6. SEM images of the scale, calcium-depleted seawater, $\tau = 50$ h, $t_{EV} = 75^{\circ}$ C, $t_{CO} = 80^{\circ}$ C, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 2- Mg/O (traces of Na/Cl), 6-Mg/O (traces of Na/Cl), 7-Mg/O (traces of Na/Cl), 8-Ca/C/O, 9-Mg/O/Na/Cl.

Figure 7 shows the scale formed on the tube surface with a calcium-free model solution at 75°C. The tube surface was densely covered with a thin and flaky base layer made of Mg and O with traces of Mn and Cl. The XRD analysis indicated brucite (Mg(OH)₂) and manganese magnesium oxide ((MgO)0.305(MnO)0.695).



Fig. 7. SEM images of the scale, calcium-free seawater, $\tau = 50$ h, $t_{EV} = 75^{\circ}$ C, $t_{CO} = 80^{\circ}$ C, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 2- Mg/O (traces of Mn/Cl).

Figure 8 shows the AAS results for the masses of calcium and magnesium per unit tube surface area for experiments performed with artificial seawater and seawater-based model solutions at different evaporation temperatures ($t_{EV} = 50^{\circ}$ C and $t_{EV} = 75^{\circ}$ C).

At 50°C, the calcium content in the scale formed in artificial seawater was 5.9 g/m² and the magnesium content was 0.22 g/m². At 75°C, a higher calcium content of 7.6 g/m² was found, as expected. However, the magnesium content was 0.20 g/m² and similar to the magnesium content formed at 50°C. Furthermore, the results suggest that the masses of the magnesium salts formed on the tube surface do not significantly change in calcium-depleted and calcium-free model solutions, i.e., there is no clear indication that the magnesium-containing base layer grows stronger in the absence of calcium in the solution or CaCO₃ crystals on the tube surface, respectively.

The pH value increases because of the CO_2 release from the evaporating brine. Test runs with the pilot plant have shown that pH values significantly increase during plant operation, e.g., from 8.2 to 8.9 (measured at 25°C) after 50 hours. According to simulation results for the CO_2 release and the carbonate system in multiple-effect distillers this pH range is also expected to prevail in industrial distillers (Al-Rawajfeh et al., 2004). It was found that in the temperature and pH range prevailing in MED plants the alkaline reaction mechanism with reaction steps (3) and (4), producing OH⁻ ions, predominates (Glade and Al-Rawajfeh, 2008). Additionally, locally enhanced pH values at the metal-solution interface may be generated by cathodic reactions. A high OH⁻ concentration at the tube surface may promote a high degree of supersaturation of magnesium salts such as Mg(OH)₂ to drive the rapid precipitation and surface coverage. As described above, iowaite, having a structure based on the brucite structure, may form in the presence of corrosion products.



Fig. 8. Effects of temperature on masses of calcium and magnesium in the scale per unit tube surface area.

Effect of Test Period on the Formation of Magnesium Scale

In order to study the effect of the test period on the Mgrich scale layer, experiments were performed for a longer test period of 90 hours with an increased volume of test solution. In the experiments performed with artificial seawater having a salinity of 45 g/kg at a high evaporation temperature of 75°C and a wetting rate of 0.1 kg/(s m), the tube surface was covered with a dense layer of rod-shaped CaCO₃ crystals in the aragonite form after 90 hours. On top of and in between these aragonite crystals Ca-containing compounds with traces of magnesium grew. The results of the XRD analysis suggest that magnesian calcite (Mg0.129Ca0.871)*CO₃ was deposited. With a calciumfree model solution and a test period of 90 hours, the tube surface was completely covered with a thin and flaky Mg/O-containing base layer. Some Cu/O particles were detected. XRD examination indicated that the magnesiumrich component was iowaite.

Figure 9 shows the masses of calcium and magnesium in the scale per unit surface area of the tubes and the average thickness of the scale layers formed with artificial seawater and calcium-free model solutions at different test periods. Experiments performed with artificial seawater at an extended test period resulted in an increased crystalline deposit. The mass of calcium in the scale layer strongly increased from 7.6 g/m² in a test period of 50 h to 13.8 g/m² in a test period of 90 h. Accordingly, the average scale thickness approximately doubled with increasing test period from 50 h to 90 h. With the calcium-free model solution, a small average scale thickness of 0.1 µm was measured because only a thin magnesium-containing scale layer formed on the tube surface.





The mass of magnesium in the scale per unit tube surface area did not notably change with the test period or in the experiments with the calcium-free model solution. This observation supports the notion that the Mg-rich base layer forms in the early stages because of a high pH value generated by CO_2 release and, additionally, by cathodic reactions. Once the surface is completely covered with a thin Mg-rich base layer, its growth ceases as the current diminishes and CaCO₃, whose solubility is exceeded at lower pH than is the case for magnesium salts, such as $Mg(OH)_2$, starts to precipitate.

Formation of Magnesium Scale at High Temperature and Salinity

In the experiments performed with artificial seawater having a high salinity of 65 g/kg at a high evaporation temperature of 75°C and a wetting rate of 0.09 kg/(s m), the tube surface was densely covered with CaCO₃ crystals primarily in the form of aragonite. Transmission electron microscope (TEM) analysis identified a Mg/Cl/Cu/Ni/Mncontaining deposit on top of and in between the aragonite crystals. XRD analysis suggested the formation of brucite (Mg(OH)₂).

In the experiments with the calcium-free model solution performed under otherwise identical conditions, the tube surface was completely covered with a thin predominantly Mg/O/Cu-containing scale layer. XRD analysis indicated the formation of iowaite.

The mass of calcium per unit tube surface area strongly increased with increasing salinity of the artificial seawater from 45 g/kg to 65 g/kg, whereas the magnesium mass did not significantly change, as shown in Figure 10. The magnesium mass only slightly increased with the calciumfree model solution at a high ionic strength. These findings support the assumption that the growth of the thin Mg-rich base layer ceases once the tube surface is completely covered.





The effects of a polymeric anti-scalant on the calciumand magnesium-containing scale were studied using artificial seawater. A modified polycarboxylate developed and manufactured by BASF SE under the trade name Sokalan PM 15 I was used. At a high evaporation temperature of 75°C and a high salinity of 65 g/kg, the use of only 0.5 ppm of the anti-scalant considerably reduced the calcium mass and the magnesium mass in the scale, as shown in Figure 10.

Effects of Magnesium Concentration on Scale Formation

In order to investigate the influence of the Mg^{2+} ion concentration in the solution on scale formation, the Mg^{2+} ion concentration was reduced, as shown in Table 1. With the magnesium-depleted solution at a high evaporation temperature of 75°C, the tube surface was densely covered with CaCO₃, as shown in Figure 11. CaCO₃ crystallized as aragonite because of the high temperature and other salts in the solution. Furthermore, no Mg-containing deposit was found on the tube surface. Instead, the base layer was made up of small, plate-like Ca-containing crystals. It is assumed that calcium hydroxide Ca(OH)₂ formed which belongs to the brucite group and has a similar layered-lattice structure.



Fig. 11: SEM images of the scale, magnesium-depleted seawater, $\tau = 50$ h, $t_{EV} = 75^{\circ}$ C, $t_{CO} = 80^{\circ}$ C, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 1- CaCO₃ (aragonite), 6- Ca/C/O.

Figure 12 shows SEM images of the scale formed in a model solution without Mg^{2+} ions. The metallic surface is completely covered with rod-shaped calcium carbonate crystals in the form of aragonite and a flaky Ca-containing deposit which is assumed to be Ca(OH)₂.



Fig. 12. SEM images of the scale, magnesium-free seawater, $\tau = 50$ h, $t_{EV} = 75^{\circ}$ C, $t_{CO} = 80^{\circ}$ C, I = 0.94 mol/kg, $\Gamma = 0.1$ kg/(s m): 1- CaCO₃ (aragonite), 6- Ca/Na/C/O, 7- Cu/O/Cl.

Figure 13 shows the masses of calcium and magnesium per unit tube surface area for experiments performed with seawater-based model solutions having different magnesium concentrations. The results from AAS analyses correspond to the SEM images shown in Figures 5, 11 and 12. Calcium is the main component of the scale in the experiments performed with artificial seawater, magnesiumdepleted, and magnesium-free model solutions. The mass of calcium in the scale significantly increases with decreasing Mg^{2+} concentration in the solution. The mass of calcium in the scale using a solution without Mg²⁺ ions increases by almost 50% compared to the mass of calcium obtained with seawater. The results show that Mg^{2+} ions retard the growth of calcium carbonate. Aragonite still predominates in the Ca-containing scale even with a magnesium-free solution because of the elevated temperature, the high ionic strength, and possibly other species present in seawater. As mentioned above, besides Mg^{2+} ions the presence of other salts/species affects precipitation in mixed salt solutions, e.g. the presence of NaCl (Sheikholeslami, 2003), strontium ions or sulfate ions (Akin and Lagerwerff, 1965; Bischoff, 1968; Bischoff and Fyfe, 1968).



Fig. 13. Effects of magnesium concentration on the masses of calcium and magnesium in the scale per unit surface area of the tubes.

Figure 14 shows the average scale thickness after a test period of 50 hours. Corresponding to the increase in calcium mass, the scale thickness increases with decreasing Mg^{2+} ion concentration in the test solution which supports the assumption that Mg^{2+} ions retard CaCO₃ crystallization.



Fig.14. Effects of magnesium concentration on scale thickness.

CONCLUSIONS

The formation of calcium- and magnesium-containing scales was studied in a horizontal tube falling film evaporator in pilot plant scale using artificial seawater and various model solutions at different process conditions.

In the experiments with artificial seawater, the surfaces of the CuNi 90/10 tubes were covered with a two-layer scale comprising a thin, flaky magnesium-rich and calciumfree base layer underneath a thick layer of calcium carbonate crystals in the form of aragonite. Elements like Cu, Ni, Fe, Mn were often detected in the magnesium-rich scale layer. XRD analyses mainly indicated $Mg(OH)_2$ (brucite) or iowaite.

The thin Mg-rich scale layer formed on the tube surface even at a low evaporation temperature of 50°C which promotes the assumption of locally high pH values at the metal-solution interface. A shift of pH to high values in the seawater film due to CO₂ release and, additionally, cathodic reactions resulting in a locally enhanced OH⁻ concentration may promote a high degree of supersaturation of Mg(OH)₂ to drive its rapid precipitation on the tube surface. Iowaite, having a structure based on the brucite structure, may also form in the presence of corrosion products. The quantity of the Mg-rich scale on the CuNi 90/10 tubes did not notably change with increasing test period, ionic strength or in the experiments with a calcium-depleted or calcium-free model solution. This observation supports the notion that the Mgrich base layer forms in the early stages and its growth ceases and aragonite crystals start to precipitate once the tube surface is completely covered with the Mg-rich scale layer.

A decrease in the Mg^{2+} ion concentration in the solution results in an increase in the mass of calcium carbonate as aragonite in the scale layer and in the scale thickness. Results suggest that Mg^{2+} ions retard the calcium carbonate crystallization. In the experiments with the magnesium-depleted and magnesium-free solutions, a Cacontaining flaky base layer was found on the tube surface. Further investigations will help to better understand the interactive effects of co-precipitating salts and to further improve anti-scalants for scale prevention in seawater distillers.

REFERENCES

Akamine, K., and Kashiki, I., 2003, Corrosion protection of steel by calcareous electrodeposition in seawater: Part 1 - Mechanism of electrodeposition – *IHI Engineering Review*, Vol. 36, pp. 141-147.

Akin, G.W., and Lagerwerff, J.V., 1965, Calcium carbonate equilibria in solutions open to the air. II. Enhanced solubility of CaCO₃ in the presence of Mg^{2+} and SO_4^{2-} , *Geochim. Cosmochim. Acta*, Vol. 29, pp. 353-360.

Al-Rawajfeh, A. E., Glade, H., Qiblawey, H. M., and Ulrich, J., 2004, Simulation of CO₂ release in multipleeffect distillers, *Desalination*, Vol. 166, pp. 41-52.

Al-Rawajfeh, A. E., Glade, H., and Ulrich, J., 2005, Scaling in multiple-effect distillers: The role of CO₂ release, *Desalination*, Vol. 182, pp. 209-219.

Anthony, J. W., Bideaux, R. A., Bladh, K. W., and Nichols, M. C., eds., 2001-2005, Iowaite, in *Handbook of Mineralogy*, Mineralogical Society of America, Chantilly, VA 20151-1110, USA, retrieved from http://www.handbookofmineralogy.org/ on 7.10.2013.

Bellotto, M., Rebours, B., Clause, O., Lynch, J., Bazin, D., and Elkaim, E., 1996, A reexamination of hydrotalcite crystal chemistry, *J. Phys. Chem.*, Vol. 100, pp. 8527-8534.

Berner, R. A., 1975, The role of magnesium in the crystal growth of calcite and aragonite from sea water, *Geochim. Cosmochim. Acta*, Vol. 39, pp. 489-504.

Bischoff, J. L., 1968, Catalysis, inhibition, and the calcite-aragonite problem – II. The vaterite-aragonite transformation, *Am. J. Sci.*, Vol. 266, pp. 80-90.

Bischoff, J. L., and Fyfe, W. S., 1968, Catalysis, inhibition, and the calcite-aragonite problem - I. The aragonite-calcite transformation, *Am. J. Sci.*, Vol. 266, pp. 65-79.

Block, J., and Watson, B. M., 1976, Magnesium scales from seawater distillation, *Desalination*, Vol. 19, pp. 359-368.

Botha, A., and Strydom, C.A., 2001, Preparation of a magnesium hydroxy carbonate from magnesium hydroxide, *Hydrometallurgy*, Vol. 62, pp. 175-183.

Braithwaite, R. S. W., Dunn, P. J., Pritchard, R. G., and Paar, W. H., 1994, Iowaite, a re-investigation, *Mineralogical Magazine*, Vol. 58, pp. 79-85.

Burton, E. A., and Walter, L. M., 1987, Relative precipitation of aragonite and Mg calcite from seawater: temperature or carbonate ion control? *Geology*, Vol. 15, pp. 111-114.

Cheng, W., Li, Z., and Demopoulos, G. P., 2009, Effects of temperature on the preparation of magnesium carbonate hydrates by reaction of MgCl₂ with Na₂CO₃, *Chin. J. Chem. Eng.*, Vol. 17, pp. 661-666.

Danckwerts, P.V., 1970, *Gas-liquid reactions*, McGraw-Hill, New York.

De Roy, A., Forano, C., and Besse, J. P., 2001, Layered double hydroxides: synthesis and post-synthesis modification, in *Layered Double Hydroxides: Present and Future*, ed. V. Rives, Nova Science Publishers, Inc., New York, pp. 1-39.

Deslouis, C., Festy, D., Gil, O., Maillot, V., Touzain, S., and Tribollet, B., 2000, Characterization of calcareous deposits in artificial sea water by impedances techniques: 2-deposit of Mg(OH)₂ without CaCO₃, *Electrochim. Acta*, Vol. 45, pp. 1837-1845.

Glade, H., 2001, Transport und Reaktion von Kohlendioxid in Entspannungsverdampfern zur Meerwasserentsalzung, Fortschritt-Berichte VDI, Series 3, No. 699, VDI-Verlag, Düsseldorf.

Glade, H., Wildebrand, C., Will, S., Essig, M., Rieger, J., Büchner, K.-H., and Brodt, G., 2005, Pilot plant investigations on scale formation and control in multiple-effect distillers, *Proc. IDA World Congress on Desalination and Water Reuse 2005*, Singapore.

Glade, H., and Al-Rawajfeh, A. E., 2008, Modeling of CO₂ release and the carbonate system in multiple-effect distillers, *Desalination*, Vol. 222, pp. 605-625.

Glade, H., Cetinkaya, S., Will, S., Nied, S., and Schürmann, G., 2008, Effects of the wetting rate on scale formation in multiple-effect distillers, *Proc. EuroMed 2008*, Dead Sea, Jordan.

Gledhill, D. K., and Morse, J. W., 2006, Calcite dissolution kinetics in Na-Cl-Mg-Cl brines, *Geochim. Cosmochim. Acta*, Vol. 70, pp. 5802-5813.

Hänchen, M., 2007, CO₂ storage by aqueous mineral carbonation: olivine dissolution and precipitation of Mg-carbonates, dissertation ETH Zürich, Zürich.

Hänchen, M., Prigiobbe, V., Baciocchi, R., and Mazzotti, M., 2008, Precipitation in the Mg-carbonate system - effects of temperature and CO₂ pressure, *Chem. Eng. Sci.*, Vol. 63, pp. 1012-1028.

Harris, A., Finan, M. A., and Elliot, M. N., 1974, A theory of the formation of magnesium scales in seawater distillation plants, and means for their prevention, *Desalination*, Vol. 14, pp. 325-340.

Hodgkiess, T., and Najm-Mohammed, N. A., 2003, Influence of the scale deposition on cathodic-protection performance in desalination plant conditions, *Proc. IWA* 2003, Cranfield University, UK.

Höfling, V., 2004, Kristallisationsfouling auf wärmeübertragenden Flächen durch Mehrkomponentensysteme, Cuvillier Verlag, Göttingen.

Kern, D. M., 1960, The hydration of carbon dioxide, *J. Chem. Educ.*, Vol. 37, pp. 14-23.

Kester, D. R., Duedall, I. W., Connors, D. N., and Pytkowicz, R. M., 1967, Preparation of artificial seawater, *Limnology and Oceanography*, Vol. 12, pp. 176-179.

Kitano, Y., 1962, The behavior of various inorganic ions in the separation of calcium carbonate from a bicarbonate solution, *Bull. Chem. Soc. Jpn.*, Vol. 35, pp. 1973-1980.

Klein, C., and Hurlbut, C.S., 1985, *Manual of mineralogy*, 20th ed., John Wiley & Sons, New York.

Li, Q., Ding, Y., Li, C., Li, F., and Qian, Y., 2003, Fabrication of light-emitting porous hydromagnesite with rosette-like architecture, *Solid State Communications*, Vol. 125, pp. 117-120.

Königsberger, E., Königsberger L.-C., and Gamsjäger, H., 1999, Low-temperature thermodynamic model for the system Na₂CO₃-MgCO₃-CaCO₃-H₂O, *Geochim. Cosmochim. Acta*, Vol. 63, pp. 3105-3119.

Lee, M.-H., Moon, K.-M., Kim, J.-D., Jun, K., and Kim, K. H., 2009, Environmentally friendly hybrid coating prepared by electro-deposition method at various seawater conditions, *Transactions of Nonferrous Metals Society of China*, Vol. 19, pp. 110-113.

Lopez, O., Zuddas, P., and Faivre, D., 2009, The influence of temperature and seawater composition on calcite crystal growth mechanisms and kinetics: Implications for Mg incorporation in calcite lattice, *Geochim. Cosmochim. Acta*, Vol. 73, pp. 337-347.

Mažuranić, C., Bilinski, H., and Matković, B., 1982, Reaction products in the system MgCl₂-NaOH-H₂O, *J. Am. Ceram. Soc.*, Vol. 65, pp. 523-526.

Millero, F. J., 2006, *Chemical Oceanography*, 3rd ed., CRC Press, Boca Raton.

Morse, J. W., Wang, Q., and Tsio, M. Y., 1997, Influences of temperature and Mg:Ca ratio on CaCO₃ precipitates from seawater, *Geology*, Vol. 25, pp. 85-87.

Nair, M. K. V., and Misra, B. M., 1978, Electrolytic scale formation in sea water distillation systems, *Desalination*, Vol. 25, pp. 263-268.

Nesse, W.D., 2004, *Introduction to optical mineralogy*, 3rd ed., Oxford University Press, New York.

Neville, A. and Morizot, A. P., 2002, Calcareous scales formed by cathodic protection – an assessment of characteristics and kinetics. *J. Cryst. Growth*, Vol. 243, pp. 490-502.

Phillips, V. A., Kolbe, J. L., and Opperhauser, H., 1977, Effect of pH on the growth of Mg(OH)₂ crystals in an aqueous environment at 60°C, *J. Cryst. Growth*, Vol. 41, pp. 228-234.

Sheikholeslami, R., 2003, Nucleation and kinetics of mixed salts in scaling, *AIChE J.*, Vol. 49, pp. 194-202.

Stumm, W., and Morgan, J.J., 1981, *Aquatic chemistry*. *An introduction emphasizing chemical equilibria in natural waters*, 2nd ed., John Wiley & Sons, New York.