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Seeded crystallization of calcite and aragonite in seawater as a pretreatment scale control process, a study of supersaturation limits

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ABSTRACT

The seeding crystallization of calcite and aragonite in seawater was evaluated theoretically and experimentally. The level of supersaturation with respect to calcium carbonate, which is the driving force for the crystal growth, was found to be influenced by the pH value of seawater, the temperature and the seed morphology. It was proven experimentally and theoretically that the level of supersaturation in seawater with respect to calcium carbonate is more sensitive to pH than to temperature. The growth process of calcite or aragonite cannot start if the pH value of seawater is not adjusted to be higher than 8.0 in the basic medium. An initial pH value of 8.2 is found to be enough to initiate the growth process of both calcite and aragonite seeds. Calcite seeds were found to be subjected to higher levels of supersaturation than aragonite.

Keywords: Seeding crystallization; Seawater; Calcium carbonate; Scale control; pH, Calcite; Aragonite

1. Introduction

One of the main obstacles which effectively contributes in increasing the costs and operational problems in thermal desalination units is the scaling of the heat exchange surfaces. Scaling control and inhibition is successfully achieved by using organic anti-scaling compounds. However, using such anti-scaling additives always goes in line with environmental impacts as well as increasing costs of the desalination.

An alternative investigated in this study is the application of seeding of seawater with selected seed crystals. level of supersaturation will lead to a decrease of the amount of scaling materials in seawater, thus decreasing the scaling potential of seawater. The seeding of seawater with selected crystals composed of the same elements of the scaling materials existing in seawater, e.g. calcite or aragonite can have the potential to reduce the concentration of calcium and carbonate ions. This ions cause more than 98% of the scaling layers at temperatures less than 90°C.

In the literature there are many old studies [1–22] of experimental investigations which tried to answer the question if a seeding technology can be practically applied for scale inhibition on an industrial scale or not. These studies gave positive and promising results concerning the possible scaling control via seeding processes.

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Results presented by Pfefferkorn et al. [8,9] showed a successful application of a seeding technology ($CaSO_4$ crystals) for scale inhibition through an experiment conducted in a pilot plant forced circulation evaporator with a 3800 m^3/d capacity. A control of the residence time of crystals to achieve the required growth rate was found to be a key factor of the successful of seeding process. This parameter was controlled by implementing a settling technique. A suspension density of 5 wt.% and a slurry flow rate of 1.8 m/s were found to be optimum to completely inhibit the gypsum scaling. Stickney and Fosberg [10] introduced the concept of using a seeding process in industrial waste water treatments which is now applied in evaporation equipments of a 50 m^3/h capacity. A vertical pipe falling film evaporator was used to concentrate waste water. The application of seeding technology was successful to inhibit the scaling of $CaSO_4$ and SiO_2.

The objective of this study is to find out the limits for the application of seeding crystallization as a pretreatment unit operation for scale control in thermal desalination industry. The factors influencing the supersaturation which is the driving force for the crystal growth were studied theoretically and experimentally. The effect of temperature, seed morphology and pH were evaluated.

2. Theoretical

The supersaturation is the driving force for calcium and carbonate ions to leave the seawater and then to integrate in the crystal lattice of seeds. However, the supersaturation with respect to calcium and carbonate ions in seawater is not a function of only one parameter (temperature or concentration) like in a conventional crystallization process. It is rather more complicated and several chemical equilibrium reactions are controlling the level of supersaturation for the growth of calcium carbonate crystals in seawater.

The driving force for seeds growth in seawater is the supersaturation (Ω) which can be defined as:

$$\Omega = \left[\frac{[\mathrm{Ca}^{2+}][\mathrm{CO}_3^{2-}]}{K_{sp}}\right] \tag{1}$$

K_{sp} in Eq. 1 is the solubility product of calcium carbonate in seawater which is defined as:

$$K_{sp} = \left[\mathrm{Ca}^{2+}\right]_{\mathrm{eq}}\left[\mathrm{CO}_3^{2-}\right]_{\mathrm{eq}} \tag{2}$$

where $[Ca^{2+}]_{eq}$ and $[CO_3^{2-}]_{eq}$ are the equilibrium concentrations of calcium and carbonate ions in seawater in mole/kg seawater. The seawater is supersaturated with respect to calcium carbonate only when the value of Ω is greater than one. Obviously, calcite possesses a higher supersaturation than aragonite at the same conditions due to its smaller values of K_{sp}.

In seawater the supersaturation of carbonate and calcium ions during the crystal growth of different polymorphic forms of calcium carbonate seeds is governed mainly by several reactions which take place during the crystal growth. These reactions form the so-called carbonate system in seawater, which are summarized schematically in Fig. 1.

As Fig. 1 shows the concentration of carbonate ions $[CO_3^{2-}]$ in seawater is determined from the liquid/solid, liquid/liquid and liquid/gas equilibrium reactions which occur simultaneously during the crystal growth of calcium carbonate in seawater. The concentration of carbonate ions $[CO_3^{2-}]$ in seawater can be determined from the knowledge of these equilibrium reactions and from the empirical relations in the literature [23–29]. Obviously the concentration of carbonate ions $[CO_3^{2-}]$ in seawater, which determines the level of supersaturation with respect to calcium carbonate, is affected directly by pH and temperature of seawater.

The role of temperature and pH in controlling the mole fractions of CO_2, HCO_3^- and CO_3^{2-} in seawater at constant salinity was investigated by Millero [30]. The calculations showed that at constant pH, the mole fraction of CO_3^{2-} increases with increasing temperature. Increasing the pH value to more than 7.5 will result in a decrease of HCO_3^- and an increase of CO_3^{2-}, and therefore the thermodynamic driving force for the crystal growth will be increased (see Eq. (1).

Rearrangement of Eq. (1) to include all the above-mentioned parameters by using the liquid/liquid equili-

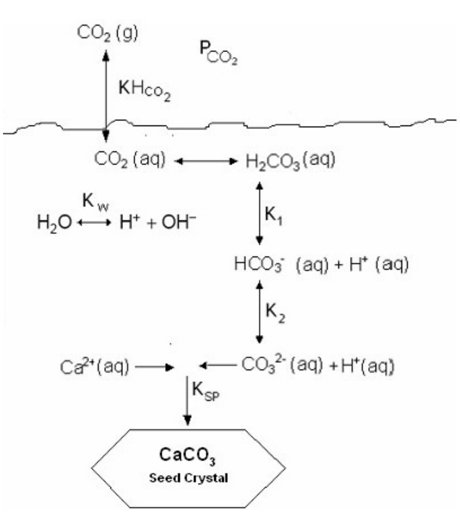

Fig. 1: Equilibrium reactions that take place in seawater during crystal growth of calcium carbonate seeds.

brium constants (see Fig. 1) will yield:

$$\Omega = \frac{[\mathrm{Ca}^{2+}].TA}{K_{sp}\left(2+[\mathrm{H}^{+}]/K_2\right)} \quad (3)$$

where TA is the total alkalinity of seawater in mol/kg. The total alkalinity in seawater is defined as its capacity to neutralize acidic solution. This is dependant on carbonate, bicarbonate and hydroxide ions in seawater. The total alkalinity results from these three components. Quantitatively the total alkalinity can be determined using the end point potetiometric titration (pH = 4.3) method.

The only parameter which depends on the solid/liquid equilibrium in Eq. (1) is the value of K_{sp} (the solubility product). It represents the equilibrium solubility of the crystals in seawater. The value of K_{sp} depends on the temperature, salinity of seawater and the crystal morphology of calcium carbonate (calcite or aragonite).

The parameters TA, K_2, and $[\mathrm{H}^+]$ are the most effective parameters which influence the supersaturation. These parameters determine the amount of carbonate ions in seawater, which is the key parameter and can be manipulated to increase the level of supersaturation. The values of these parameters are strongly dependent on the pH and the temperature of the seawater.

In a closed seeded batch crystallizer, $[\mathrm{CO}_3^{2-}]$ decreases due to the crystal growth of calcium carbonate seeds in the metastable seawater. This is accompanied by a pH-decay as can be obtained from the following equation which represents a combination of the liquid phase equilibrium reactions in Fig. 1:

$$[\mathrm{CO}_3^{2-}] = \frac{K_1 K_2 [\mathrm{H_2CO_3}]}{[\mathrm{H}^+]^2} \quad (4)$$

3. Results and discussion

3.1. Calculation of effect of temperature on supersaturation

Changing the temperature of seawater at constant salinity will result in changing the values of pH, K_{sp}, K_1, K_2, K_w and TA. Also the solubility of carbon dioxide in seawater or its partial pressure above the seawater (P_{CO2}) will be affected by temperature. This will be reflected finally on the concentration of carbonate ions, which is the most important component affecting the driving force for the crystal growth of calcium carbonate in seawater.

The calculated supersaturation with respect to calcite and aragonite as function of seawater temperature is shown in Fig. 2. The results presented in Fig. 2 indicate that increasing temperature to, e.g., 40 °C will increase the supersaturation (Ω) with respect to calcite to about 4 and with respect to aragonite to about 2.5. Referring to the results presented in Fig. 2, the growth rate at this level of supersaturation is still very low for both polymorphs and thus it will not be attractive for the industrial seeded crystallization process to operate the process at moderate temperature levels. This is due to the decrease in pH with temperature. It is, however, recommended to manipulate the pH to increase the supersaturation level at low temperatures.

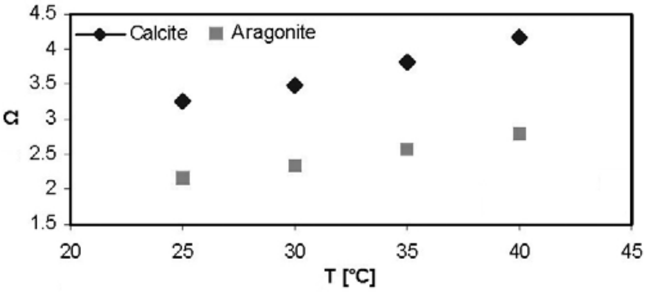

Fig. 2. Changing supersaturation with respect to calcite and aragonite with temperature at constant salinity of 35 g/kg.

3.2. Effect of variation of pH on level of supersaturation

Changing the value of pH at certain constant values of temperature and salinity can dramatically influence the carbonate system of seawater and hence the supersaturation. All the chemical equilibrium reactions can be shifted by the variation of the pH of seawater. The calculated influence of an increase of the pH value of seawater from 7.98 to 8.5 at a constant temperature of 25 °C and a constant salinity of 35 g/kg on the carbonate ions concentration and total alkalinity is shown in Figs. 3 and 4, respectively.

Figs. 3 and 4 display a strong increase in carbonate ion concentration and total alkalinity due to increasing pH. The increase of the pH value of seawater at constant temperature and salinity will have the following consequences which effects directly the supersaturation (Ω):

- TA will strongly increase, Ω will increase [see Eq. (3)];
- $[\mathrm{H}^+]$ will decrease, Ω will increase;
- K_2 and K_{sp} remain constant at constant temperature and salinity

The calculated supersaturation (Ω) with respect to calcium carbonate polymorphs (calcite and aragonite) at the different pH values is presented in Fig. 5. The results presented in Fig. 5 are of paramount importance for industrial seeding crystallization processes. Obviously, increasing the pH value from its normal level (~8) to a higher level, e.g. 8.2, will be sufficient to achieve the required supersaturation around Ω = 6, which is the minimum required level to obtain a fast enough growth rate for both calcite and aragonite at 25°C and 35°C to get sufficient crystal growth [19]. The results calculated in Fig. 5 represent a key information for the control of the seeding crystallization in seawater.

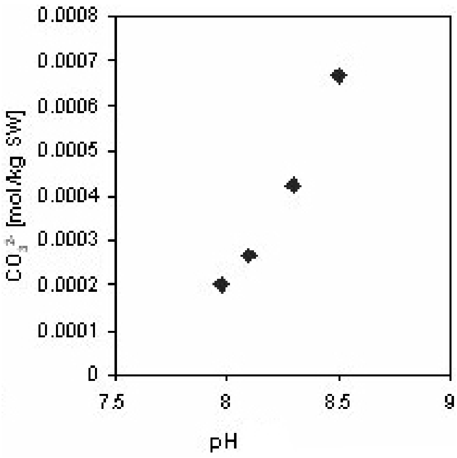

Fig. 3. Variation of carbonate ion concentration in seawater with pH at constant temperature of 25 °C and constant salinity of 35 g/kg .

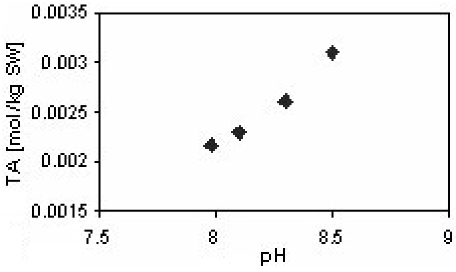

Fig. 4. Variation of the total alkalinity in seawater with pH at constant temperature of 25°C and constant salinity of 35 g/kg.

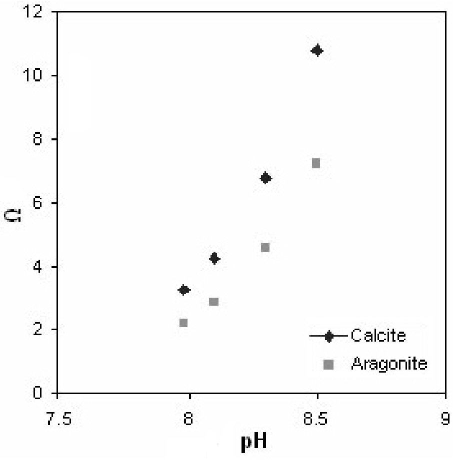

Fig. 5. Effect of pH on the supersaturation level in seawater with respect to calcite and aragonite seeds at constant temperature of 25°C and constant salinity of 35 g/kg.

4. Experimental investigations

In order to assess the key calculated results in Fig. 5 experimentally, seawater in a 500 mL stirred batch crystallizer was seeded by calcite and aragonite under the same conditions of salinity, temperature and seeding ratio. The measured rate of the pH decay for calcite is faster than that for the aragonite morphology (see Fig. 6). The faster pH decay for calcite seeds means that the crystal growth rate of calcite is faster than the crystal growth rate of aragonite according to Eq. (4). These experimental results indicate that the calcite seeds are subjected to higher supersaturation levels than aragonite seeds under the same conditions. This is in agreement with the calculated results of Fig. 5.

The role of pH in changing of the level of supersaturation was experimentally tested by seeding seawater with calcium carbonate (calcite) at different initial pH values. The measurements are conducted in an agitated batch crystallizer at constant temperature, salinity, stirrer speed and seeding ratio. In all seeded batch experiments which were conducted at different initial pH values, a decrease in the pH value of seawater with time is measured.

During the crystal growth of calcite seeds in seawater, the concentration of carbonate ions in seawater will

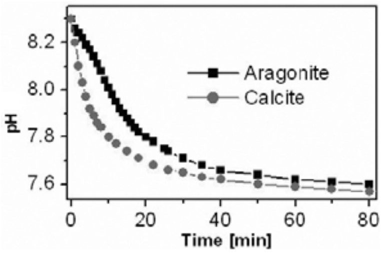

Fig. 6. Measured rate of pH decay of seawater with calcite and aragonite seeds. Stirrer speed (N) = 269 rpm, temperature (T) = 50°, initial pH = 8.3, seeding ratio (SR) = 1 g/L, salinity (S) = 45 g/kg.

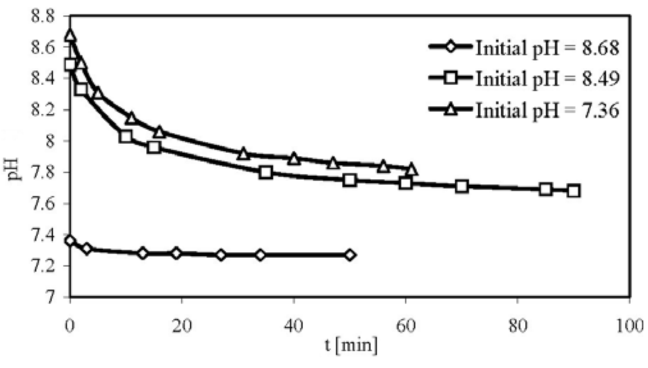

Fig. 7. Measured pH value with time during crystal growth of calcite in seawater. Salinity (S) = 35 g/kg, stirrer speed (N) = 269 rpm, seeding ratio (SR) = 1 g/L, temperature (T) = 50°C.

decrease. Consequently, more [H^+] ions will be generated according to Eq. (4); therefore, a pH decrease will be associated with the crystal growth of calcite in seawater (see Fig. 7). The measured faster rate of pH decay at higher initial pH values means faster initial growth rates and thus higher initial levels of supersaturation. These results agree with the calculated results in Fig. 5.

5. Conclusions

The results obtained in this study indicate that the growth process of calcium carbonate in seawater can be realized under certain conditions for possible application of seeding crystallization processes as a pretreatment unit operation. The key factor is to create the required amount of supersaturation to initiate crystal growth. The level of supersaturation can be manipulated by changing the pH and the temperature of seawater. Applying this method on industrial scale will be attractive for the desalination industry; however, engineering design and operation studies must be carried out to enhance the practical applicability of this type of process.

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References

[1] H.J. Bull, Treatment of liquids containing sulfate of lime, US-Patent No. 1,399,845, 1919.
[2] G.E. Coury and G. Weth, Seeding techniques for scale prevention in water treatment systems, Proc. Nat. Conf. on Water Ruse, AIChE, New York, 1973, pp. 116–124.
[3] J.E. Jones, Seeding of brackish water in a spray film evaporator, US-Army Mobility Equipment Research and Development Center USAMERDC, 1970.
[4] J. Weinberg and Y. Rostein, Operation of horizontal tube brine concentrator, Desalination, 40 (1982) 159–168.
[5] R.J. Sikora, Brine concentrator and seeded reverse osmosis, Chemeca ’85, 13th Austral. Chem. Eng. Conf., Perth, Australia, 1985, pp. 33–40.
[6] F.C. Standiford and J.R. Sinek, Stop scale in seawater evaporators, Chem. Eng. Prog., 571 (1961) 58–63.
[7] R.J. Gainey and C.A. Cadwallader, $CaSO_4$seeding prevents $CaSO_4$ scale, Ind. Eng. Chem., 55(3) (1963) 39–43.
[8] O. Pfefferkorn, W.H. Weber and T.H. Sikora, Calcium sulfate seed slurry process for scale prevention, Water Sewage Works, 9 (1973) 128–132.
[9] O. Pfefferkorn, The economics of the seed slurry process for scale control, Desalination, 19 (1976) 75–82.
[10] W.W. Stickney and T.M. Fosberg, Treating chemical wasted by evaporation, Chem. Eng. Proc., 4 (1976) 41–66.
[11] F. Bulda, K.R. Fröhner and H. Kolbe, The barium sulfate seeding process, Desalination, 21 (1977) 59–70.
[12] W. Wöhlk and G. Hofmamm, Verkrustungsprobleme — Verhinderungsmöglichkeiten, Chem.-Ing.-Tech., 52(11) (1980) 898–900.
[13] G. Hofmann, Behandlung von Waschlösungen aus Rauchgasreinigungsanlagen, Brennstof Wärme Kraft, 4 (1993) 116–123.
[14] C. Mostofizadeh, Verfahren zur Eindampfung von Abwasser aus Verbrennungsanlagen, Berichte Landesamt für Wasser u. Abwasser, NRW, 1986, pp. 169–219.
[15] R. Exner, P. Hinsen and P. Sporer, Pilotanlage für die Erprobung unterschiedlicher Eindampfverfahren von REA–Abwässern, Brennst. Wärme Kraft, 40 (1988) 17–19.
[16] R. Bond, S. Veerapaneni and E. Brandt, Reducing costs of inland desalination ZLD treatment, J. AWWA, (2005) 56–59.
[17] R. Rautenbach and J. Widua, Application of seeding to the horizontal tube film evaporators as scale prevention method, Proc. World Congress on Desalination and Water Sciences, Abu Dhabi, 1995, pp. 559–576.
[18] W. Omar, J. Chen, A. Al-Atia and J. Ulrich, Application of seeding Crystallization as a pre-treatment stage for the reduction of scaling tendency of seawater feed to thermal desalination units, Proc. 17th International Symposium of Industrial Crystallization –ISIC 17, P. Jansens, ed., Maastricht, The Netherlands, 2008.
[19] J. Chen, W. Omar, A. Al-Atia and J. Ulrich, Determination of the limits for the growth of calcite and aragonite in seawater, Proc. 17th International Symposium of Industrial Crystallization–ISIC17, P. Jansens, ed., Maastricht, The Netherlands, 2008.
[20] W. Omar and J. Ulrich, Fouling crystallization in seawater at heat exchangers—Study of the solid layer (incrustation) formation processes, Proc. BIWIC 2008, 15th International Workshop on Industrial Crystallization, H. Lorenz ,ed., Max Planck Institute for Dynamics of Complex Technical Systems Magdeburg, Germany, 2008.
[21] W. Omar, J. Chen and J. Ulrich, Application of seeded batch crystallization methods for reduction of the sca ling tendency of seawater—A study of growth kinetics of calcium carbonate in seawater, Cryst. Res. Technol., (2009) 1–8.
[22] W. Omar, J. Chen and J. Ulrich, Reduction of seawater scale forming potential using the fluidized bed crystallization technology, Submitted for publication.
[23] A. Mucci, The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure, Amer. J. Sci., 283 (1983) 780–799.
[24] R.A. Brener, Principles of Chemical Sedimentology, McGraw-Hill, New York, 1971.
[25] P.V. Danckwerts, Gas–Liquid Reactions, McGraw-Hill, New York, 1970.
[26] H. Glade, Transport und Reaktion von Kohlendioxid in Entspannungsverdampfern zur Meerwasserentsalzung, PhD Thesis, University of Bremen, VDI, Düsseldorf, 2001.
[27] L.N. Plummer and E. Busenberg, The solubility of calcites, aragonite and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. Geochim. Cosmochim. Act, 46 (1982) 1011–1040.
[28] F.J. Millero, Thermodynamics of the carbon dioxide system in the ocean. Geochim. Cosmochim. Acta, 59 (1995) 661–677.
[29] A.G. Dickson and J.P. Riley, The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. Mar. Chem., 7 (1979) 89–99.
[30] F.J. Millero, The carbonate system in marine environments, in: Chemical Processes in Marine Environments, A. Gianguzza, E. Pellizzetti and S. Sammartano, eds., Springer, Berlin, 2000, pp. 9–41.