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Advanced Membrane Systems for Seawater Desalination. Kinetics of Salts Crystallization from RO Brines Promoted by Polymeric Membranes

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Abstract: The reliability of innovative membrane contactors technology (i.e. Gas/Liquid Membrane Contactors, Membrane Distillation/Crystallization) is today increasing for seawater desalination processes, where traditional pressure-driven membrane separation units are routinely operated. Furthermore, conventional membrane operations can be integrated with membrane contactors in order to promote possible improvements in process efficiency, operational stability, environmental impact, water quality and cost. Seawater is the most abundant aqueous solution on the earth: the amount of dissolved salts covers about 3% of its composition, and six elements (Na, Mg, Ca, K, Cl, S) account for more than 90% of ionic species. Recent investigations on Membrane Distillation-Crystallization have shown the possibility to achieve significant overall water recovery factors, to limit the brine disposal problem, and to recover valuable salts (i.e. calcium sulphate, sodium chloride, magnesium sulphate) by combining this technology with conventional RO trains. In this work, the kinetics of $CaSO_4 \cdot 2H_2O$, NaCl and $MgSO_4 \cdot 7H_2O$ crystallization is experimentally investigated in order to improve the design of the membrane-based crystallization unit.

Keywords: *membrane distillation crystallization, brine disposal, zero liquid discharge*

1. Introduction

Seawater represents a quite unlimited resource for the production of fresh water by desalination processes and for the extraction of dissolved salts present in large amount.

Recently, membrane distillation-crystallization (MDC) has increased in interest as an innovative process potentially able to recovery valuable salts dissolved in aqueous solutions [1] and to simultaneously increase the amount of desalted water. MDC combines the concept of membrane distillation (where microporous hydrophobic membranes are used to evaporate heated aqueous solutions [2]), and crystallization. The analysis of factors influencing the performance of this novel membrane operation under supersaturated conditions has encouraged some recent and interesting studies in literature [3-5].

The investigation of the crystallization sequence during membrane-aided evaporation of seawater requires the knowledge of solubility data; moreover, such kind of information is crucial in order to avoid scaling formation typically connected to the precipitation of calcium sulphate or calcium carbonates, or to separate salts from the products obtained during brine concentration.

The study of Balarew (1993) [6] considers the dissolved ions Na^+, K^+, Mg^{2+}, Cl^-, Ca^{2+} and SO_4^{2-} as the major components of seawater, determining their sol-

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ubility properties. During the progressive concentration of seawater, assuming that changes in composition are only due to a decrease of the amount of water present, the first precipitating salts are calcium carbonate with some amount of magnesium carbonates (8~10 mol%) [7]. At 25°C, calcium sulphate dehydrate (gypsum) starts to precipitate at solution density of 1.09, followed by sodium chloride at a density of 1.2185. A large amount of magnesium sulphate crystallizes together with NaCl at a solution density of 1.235.

According to the theoretical calculations of Cohen-Adad and colleagues (2002) [8], the second observed salt after NaCl formation at 25°C should be astrakanite (bloedite) $Na_2SO_4 \cdot MgSO_4 \cdot\cdot 4H_2O$ before co-precipitation with epsomite ($MgSO_4 \cdot 7H_2O$). However, the presence of a significant number of components in seawater, coupled to the fact that trace elements increase progressively their concentration during evaporation (so that they must be taken into account) make it difficult to obtain a well defined path through solubility diagram.

Along with equilibrium solubility, it was realised in recent years that the extent of supersaturation and kinetics of crystallization play a decisive role especially in high concentrated seawater system.

Gypsum scaling on NF-200 Filmtec membrane was investigated using the classical nucleation theory; however, the comparison of experimental and theoretical data showed that the predicted supersaturation values were generally lower than the measure ones [9]. The dependence of induction time on temperature, supersaturation, cation/anion molar ratios for calcium sulphate precipitation was the object of the study of Alimi and Gadri (2004) [10].

In this work, the kinetics of heterogeneous nucleation of calcium sulphate, sodium chloride and magnesium sulphate has been experimentally studied using dynamic light scattering (DLS) and ionic analysis. The role of the physical and chemical properties of the microporous polymeric membranes has been also investigated and discussed on the basis of thermodynamics of phase equilibria.

2. Materials and Methods

Solutions were prepared by dissolving $CaCl_2$, $MgSO_4$ and Na_2CO_3, all purchased by Sigma-Aldrich, in ultrapure water (Purelab, ELGA). Before experiments, solutions were filtered through 0.45 μm polysulfone porous membranes. Batch crystallization tests from supersaturated solutions were carried out at 25°C on microporous polypropilene (PP) hollow fiber membranes (Accurel), having a 0.20 μm pore size and external diameter of 1.8 mm.

Particle sizes and intensity correlation functions in undiluted suspensions were determined by DLS using a 90 Plus/Bi-Mas Particle Sizing Option (Brookhaven Instruments Corporation) with 15 nW diode laser operating at a wavelength of 678 nm.

Calcium concentration was measured by Idrimeter St kit (Carlo Erba Reagenti) with sensitivity of ±5 ppm. pH was evaluated by using expandable ion analyzer EA 920 pH-meter (Orion Research Inc.) with an error of ±0.01. Wettability degree of the membranes was evaluated by sessile drop method by CAM 200 contact angle meter (KSV instrument LTD, Helsinki, Finland). The morphology of the crystalline product was investigated by SEM (Stereoscan 360, Cambridge) operated at 20 kV.

3. Results and Discussion

3.1. Precipitation of Calcium Sulphate

Calcium sulphate occurs under six different polymorphic forms. Three of them, abundantly present in nature, are different because of their hydration degree: i) the calcium sulphate bi-hydrate ($CaSO_4 \cdot 2H_2O$, monoclinic) or gypsum, that is the most common form; ii) the calcium sulphate emi-hydrate ($CaSO_4 \cdot 1/2H_2O$, hexagonal); iii) the calcium sulphate anidrous ($CaSO_4$, orthorhombic). Compound i) and iii) precipitate at temperatures less than 100°C; the emi-hydrate form appears above 102°C. Fig. 1 shows the increase of the average length of gypsum particles in time, according to data

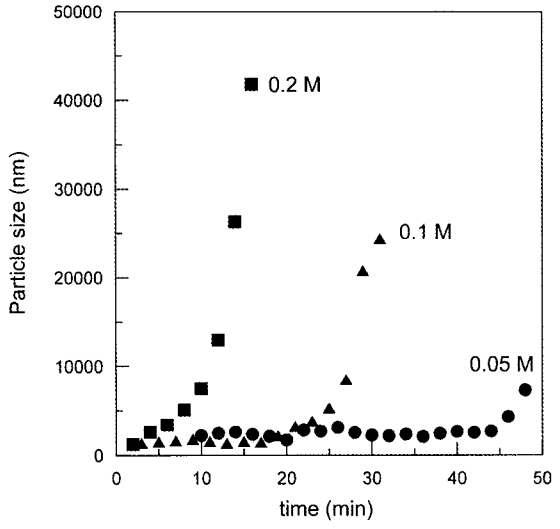

Fig. 1. Increase of the average length of particles of calcium sulphate in time at different supersaturation degree (solubility of calcium sulphate @ 25°C: 0.03 M).

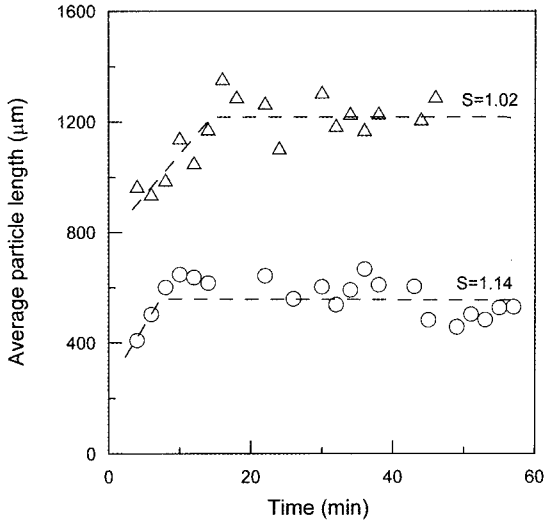

Fig. 2. Increase of NaCl particle size at different supersaturation degrees (S).

obtained by DLS.

Precipitated solids, formed in supersaturated solutions by equimolar mixing of $CaCl_2$ and $MgSO_4$, were analyzed by contacting 2 mL of mother solution with a PP fiber having a total area of 1 cm^2 (contact angle: 117 ± 3°).

For [Ca] = [SO_4^{2-}] = 0.1 M, corresponding to a supersaturation degree of about 3, the induction time - evaluated as the time corresponding to the detachment of the particle size curve from the abscissa axis - is of about 15 minutes. The effect of the membrane is evident when considering that, in case of homogeneous nucleation under a higher supersaturation degree (i.e. 4.5), the induction time is 10 minutes.

The comparison of experimental data with results present in literature shows that, for a supersaturation level lower than 5, the induction time is reduced by 2 ~3 times if precipitation is aided by the membrane [10].

3.2. Precipitation of Sodium Chloride

According to DLS analysis, crystals from NaCl solutions with supersaturation below 1.14 appeared only in presence of membrane, so confirming the ability of the polymeric support to enhance the nucleation rate even for concentrations close to metastability limit.

According to data reported in Fig. 2, the particle size increases sharply during the first 20 minutes; the subsequent steps are characterized by a kinetic deceleration up to the growth rate cessation. The increase of impurities in a crystallizing solution results in a reduction of the overall growth rate, with major evidence whenever diffusion phenomena represent the controlling step of a growth process.

At higher supersaturation, the enhanced nucleation rate increases the number of NaCl crystals formed, but reduces their size. After around one hour, crystals achieve an average dimension of 1.2 mm at S = 1.02, that is 120% higher than the average length at S = 1.14. In the latter case, however, the maximum crystal size (~ 0.55 mm) is achieved in about 9 minutes, while the time required at S = 1.02 is double.

The parameters of the crystallization kinetics have been quantitatively determined from growth rate experiments as abscissa and slope of the linear plot of the logarithm of growth rate (G) versus the logarithm of supersaturation. The regression gave a value of the overall growth rate constant k_g of 3.06×10^{-5} (G expressed in m/s).

In a previous study, for NaCl crystals grown from Nanofiltration retentate with a much higher Mg^{2+} con-

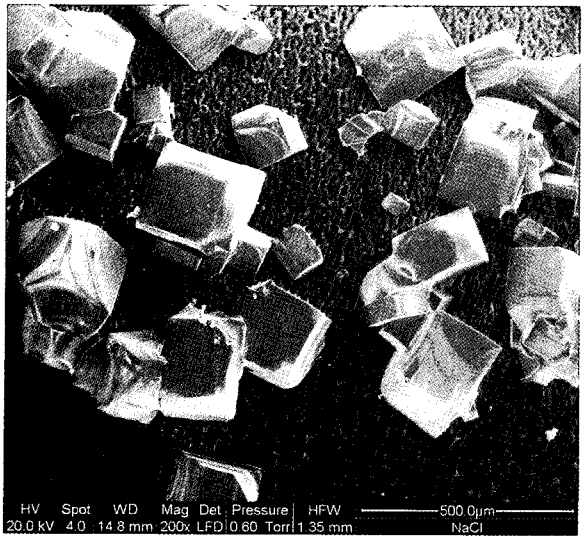

Fig. 3. Morphology of NaCl crystals grown on amicroporous PP membrane.

centration (4.3 g/mL), was k_g=1.9210^{-5} [7].

This work confirms that the presence of Mg^{2+} ions influences the growth rate of NaCl crystallization, and the overall growth rate constant k_g is comparable with the value reported by Al-Jibbouri and Ulrich [11] (k_g = 2.98 × 10^{-5} m/s) evaluated for impurity concentrations of $MgCl_2$ in the range of 0~250 ppm.

SEM micrographs of PP hollow fibers after crystallization tests at supersaturation of 1.14 show the NaCl crystals deposited on the microporous surface of the membrane (Fig. 3).

Although sodium chloride solids are characterized by the typical cubic shape, significant irregularities in the geometry of the crystalline habit that can be attributed to the impurities present in solution (and, in particular, to the significant amount of Mg^{2+}) have been observed.

3.3. Precipitation of Magnesium Sulphate

Magnesium is one of the most important product obtained from seawater, recovered commercially by precipitation as magnesium hydroxide with a dolomite slurry or with lime (Dow process [12]).

From and industrial point of view, $MgSO_4 \cdot 7H_2O$ is a commonly used fertilizer; this salt has also relevant applications in medical (treatment of eclampsia, hypertensive disorders, acute myocardial infarction etc.) and dosimetric measurement fields. Epsomite is stable in the β-form below 800°C and crystallizes from aqueous solutions within a orthorhombic cell.

DLS observations on the evolution of the average size distribution of epsomite crystals in a supersaturation range of 2.84~4.06, protracted for one hour in presence of microporous PP hollow fibers, have evidenced an increase of the growth rate at higher supersaturation.

In the interval of investigated crystallization conditions, the growth rate was of 4.2 ± 0.5 × 10^{-7} m/s, value that substantially agrees experimental results reported in [7] for epsomite crystallization from NF retentate. These data suggest a modest dependence of the $MgSO_4 \cdot 7H_2O$ growth rate on the supersaturation.

Kinetics data reported in literature, obtained for pure magnesium sulphate solutions in absence of other contaminants, are one order of magnitude smaller [13,14].

As previously observed for NaCl, the final average size of crystals is reduced at higher supersaturation: epsomite solids formed at S = 4.06 show - after about half an hour - a length of 900 μm, that increases to 1100 μm when S = 3.25.

Crystallization tests carried out at constant supersaturation demonstrated that crystals grown in presence of a polymeric membrane are smaller than those formed in a homogeneous environment.

For instance, at S = 3.25, epsomite crystals achieve an average length of 1600 μm in absenco of membrane.

Nucleation rate has been evaluated by counting the formed crystals in a given volume of solutions at various time intervals; data reported in Fig. 4 give evidence of the exponential increase of the number of the cluster formed at increasing supersaturation. The role of the membrane in epsomite crystallization is more evident than in the case of NaCl; in fact, in a homogeneous phase, nuclei are not detected within 30 minutes by DLS below a supersaturation degree of about 3.

Fig. 5 shows a SEM micrograph of epsomite crystals

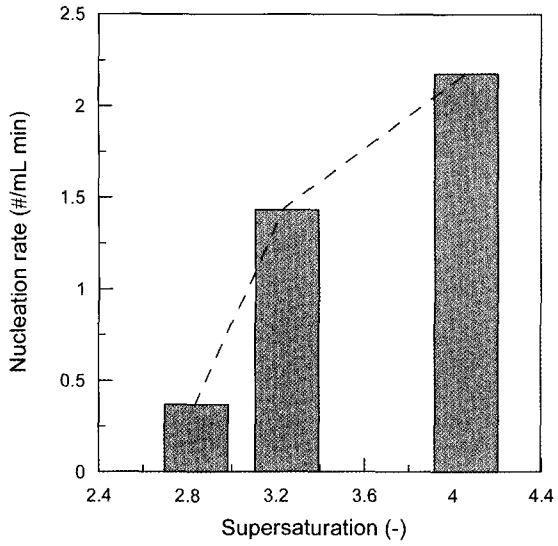

Fig. 4. Nucleation rate of epsomite crystals as a function of supersaturation.

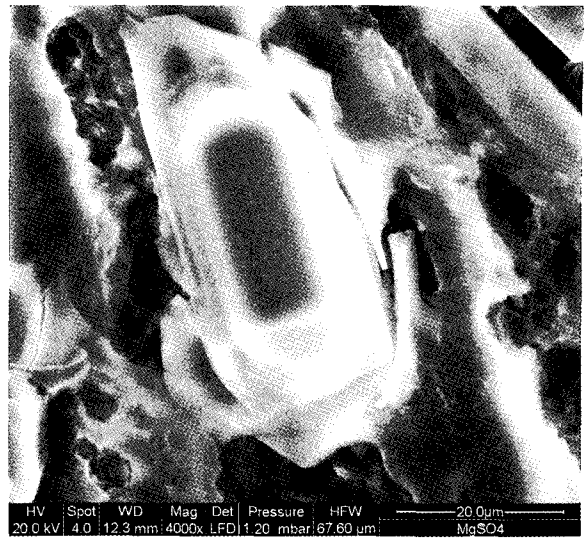

Fig. 5. Morphology of epsomite crystals grown on a microporous PP membrane.

grown on PP membrane for a supersaturation of 4.06. Although the particulate exhibits the characteristic orthorhombic habit, crystals tend to aggressively aggregate on a wide portion of membrane, so assuming a not well defined form.

For experiments carried out in absence of forced circulation, the crystal size distribution is characterized by a wide dispersion around its modal value; moreover, a significant number of crystals appear in acicular shape.

4. Conclusions

The reliability of the approach aiming to recover valuable salts dissolved in seawater process strictly depends on the control of thermodynamic and kinetic aspects of the crystallization from solution mediated by polymeric membranes. The choice of an opportune temperature-concentration pathway through the solubility diagram is mandatory in order to obtain the desired products and to limit the co-crystallization of species as impurities. In addition, the study of the heterogeneous nucleation and growth rates as a function of supersaturation is necessary for achieving the required product quality in terms of crystal size distribution and shape, and for preventing the accumulation of particulate on the membrane surface that causes the undesired decrease of the transmembrane flux.

In this work, the behaviour of the seawater system during the MDC process has been considered dynamic light scattering analysis has been used as a powerful tool for the investigation of the early stage of kinetic steps for $CaSO_4 \cdot 2H_2O$, NaCl and $MgSO_4 \cdot 2H_2O$, confirming that the presence of the membrane accelerate the formation of nuclei even at low supersaturation degree.

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