

# Reverse osmosis of concentrated calcium sulphate solutions in the presence of iron (III) ions using composite membranes

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## Abstract

We investigated separation characteristics of composite membranes in the process of reverse osmosis of calcium sulphate acid solutions containing Fe (III), and the impact under these conditions of an additive of acidic polyelectrolyte, sodium carboxymethylcellulose Na-CMC. It is shown that in the absence of Na-CMC the separation properties of the membranes deteriorate owing to the formation of a deposit on them. Fe(III) ions are mainly responsible for deposition. Upon the introduction to the solution filtered of the Na-CMC additive one can observe a delay and change in the nature of deposition. In this case, substantial influence of Na-CMC concentration on the deposit filtering properties was detected. We obtained data indicating stabilizing action of Na-CMC on the calcium sulphate solution containing Fe (III) ions in the acidic medium.

*Keywords:* Reverse osmosis; Composite membranes; Scaling; Fouling; Polymer additive; Inhibiting effect

## 1. Introduction

Barely soluble salts, in particular calcium sulphate and iron, belong to the most abundant mineral impurities in natural waters causing deposition on membranes. Membrane scaling with  $\text{CaSO}_4$  occurs when the product of activities of its ions in the solution exceeds the product of solubility, i.e. the water filtered turns out to be oversaturated with this compound [1,2].

The presence in the water of Fe (III) may lead to the formation of the  $\text{Fe}(\text{OH})_3$  colloid deposit on membranes. In both cases the pH value of the solution plays a major role. The most intensive membrane fouling with  $\text{Fe}(\text{OH})_3$  occurs in the strongly acidic or alkaline medium [3].

The pH value also affects the calcium sulphate solubility. Barely soluble sulphates precipitate from strongly acid solutions with a lower rate than from neutral or alkaline solutions since their solubility may increase as a result of

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bonding  $\text{SO}_4^{2-}$  ions with  $\text{H}^+$  ions resulting in the formation of  $\text{HSO}_4^-$  [4]. In addition, the process of membrane filtration normally is accompanied with the change of the pH of the solution filtered as a result of preferable transport of  $\text{H}^+$  or  $\text{OH}^-$  ions. This, in its turn, also influences calcium sulphate solubility. Obviously, simultaneous presence in the solution filtered of calcium sulphate and Fe(III) substantially aggravates the precipitation picture.

Earlier [5], we showed that in reverse osmosis of neutral concentrated solutions of calcium sulphate the characteristics of cellulose acetate and composite polyamide membranes deteriorate due to scaling. Scaling during filtration of concentrated solutions and even solutions oversaturated with calcium sulphate may be prevented by the introduction to the solution filtered of acid poyelectrolyte sodiumcarboxymethyl cellulose (Na-CMC) [6]. Acting as an inhibitor, Na-CMC prevents the growth of calcium sulphate crystals and is conducive to maintaining stable characteristics of the membranes. The high positive effect of Na-CMC is achieved both on cellulose acetate and composite membranes [6].

In the present paper we have investigated the joint impact of  $\text{CaSO}_4$  and Fe(III) on the characteristics of composite membranes during reverse osmosis of solutions of these components in unfavourable conditions for the deposition, the low pH of the solution filtered, and studied the inhibiting effect of Na-CMC under these conditions.

## 2. Experimental

Reverse osmosis was conducted using three reverse osmosis composite membranes 'Akvapor' ('Polimersintez', Russia) of OFM-K (No. 1) and OFAM-K types (No. 2), and a test sample of new type 'wet membrane' (No. 3). The latter is distinguished from the first two types by increased salt rejection and much lower water

flux. A commercial product of Na-CMC of 75/400 type was used as an inhibiting additive.

The experiments were carried out in the laboratory unit described earlier [7]. The initial characteristics of the membranes were determined on a 5 g/l solution of NaCl. The reverse osmosis constant parameters were as follows:  $P = 30$  atm.,  $v = 1.3$  m/s,  $t = 22 \pm 1^\circ\text{C}$ . During reverse osmosis we controlled the water flux and salt rejection at the interval of 10 to 60 min. In order to control the change of calcium sulphate and iron ions to an insoluble form, every 1–3 h we determined the contents of calcium and Fe(III) ions in the circulating solution. All experiments were conducted on solutions of calcium sulphate close to saturation, with the constant concentration of 0.027 mol/l. The feed calcium sulphate solutions were prepared by mixing equivalent quantities of  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$  solutions and, therefore, contained  $\text{Na}^+$  and  $\text{Cl}^-$  ions. The Na-CMC additive was introduced into the feed solutions as a 0.2% solution. A dosing solution of iron containing 0.1 g/l Fe(III) was prepared from  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ . The experiments with solutions of different composition were conducted on the same pieces of the membranes. After the experiment on the working solution was over, right away without the rinsing of the membranes we determined the water flux and  $\text{Na}^+$  rejection on the solution of 5 g/l NaCl. Then, the membranes were rinsed with distilled water, and after that we again determined the flux and  $\text{Na}^+$  rejection on the NaCl solution.

## 3. Results and discussion

Fig. 1 shows the changes in the flux and rejection characteristics of the membranes over time during reverse osmosis of calcium sulphate solutions containing Fe(III) without introduction of Na-CMC to the solution filtered. It can be seen that the characteristics of the membranes deteriorate with time during filtration. The most

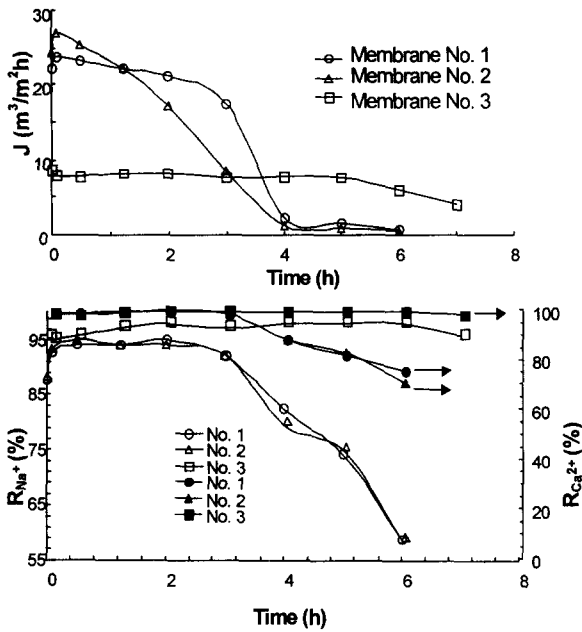


Fig. 1. Flux and cation rejection vs. time in RO filtration of the salt solution containing 0.027 M  $\text{CaSO}_4$  and 2.15 mg/l Fe(III), pH 3.05.

fast decrease of the flux and rejection could be observed for the membranes No. 1 and No. 2. The characteristics of the membrane No. 3 only slightly declined after 5 h of filtration.

The control of concentration of  $\text{Ca}^{2+}$  ions in the circulating solution during the time of the experiment showed its small fall by 4% that indicates a rather low rate of crystallization of calcium sulphate in the volume of the solution separated. At the same time, in the neutral solution of calcium sulphate having a concentration of 0.02 mol/l, in the absence of Fe(III), we registered more marked drop of  $\text{Ca}^{2+}$  (9%) in the circulating solution [6]. Relative small intensity of calcium sulphate crystallization under the conditions of the experiment is associated, perhaps, with the formation, in a strongly-acid medium, of  $\text{HSO}_4^-$  ions and, as a result, with some increase of the salt solubility.

Under the same conditions the concentration of Fe(III) ions in the circulating solution during filtration time decreased more than twice (from 2.15 to 1.00 mg/l). As follows from [8], with the pH value used in the experiment and with the accepted initial concentration of Fe(III), the latter is mainly in the form of  $\text{Fe}(\text{OH})^{2+}$  ions and, possibly, polyions of  $[\text{Fe}(\text{OH})^{2+}]_n$ . However, as a result of the Fe(III) concentration increase in the near-membrane region due to concentration polarization, a partial change of iron to a non-soluble form of  $\text{Fe}(\text{OH})_3$  is possible. The presence in the solution of polymer products generated by the hydrolysis of Fe(III) ions, which may be used as polymer bridges between the  $\text{Fe}(\text{OH})_3$  particles, can be conducive to the formation of flocs.

Therefore, the deterioration of membrane characteristics may be explained, most likely, by the formation on their surface of a deposit of colloid particles and flocs of Fe(III). This deposit creates additional resistance, decreases the flux and causes a reduction of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  rejection.

From the results of filtering a 5 g/l NaCl solution through the fouled membranes and through the rinsed membranes one may assume that the deposit formed possesses weak affinity to the membrane surface since it is easily rinsed by the tangential flow of the NaCl solution or distilled water.

One may assume that the composition of deposits on the three used membranes is not identical, since one may observe substantial difference in deposition rate and its impact on the ions rejection. On membrane No. 3 having the lower flux, compared with that of membranes No. 1 and No. 2, owing to smaller concentration polarization, conditions for the formation of colloid particles of  $\text{Fe}(\text{OH})_3$  are less favorable, and the deposit, perhaps, is formed mainly from hydrophilic polyions of  $[\text{Fe}(\text{OH})^{2+}]_n$ . And so, the water flux and rejection of this membrane do not practically change. The deposit on membranes No. 1 and No. 2 probably contains mainly

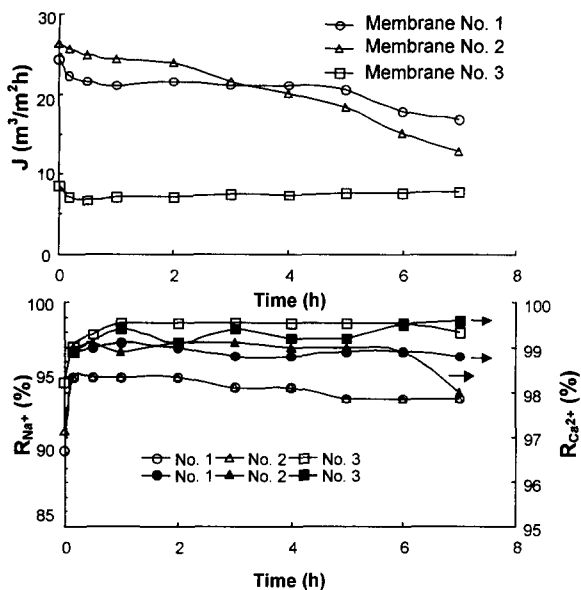


Fig. 2. Flux and cation rejection vs. time in RO filtration of salt solution containing 0.027 M  $\text{CaSO}_4$ , 2.15 mg/l  $\text{Fe(III)}$  and 16 mg/l Na-CMC; pH 3.05.

colloid particles of  $\text{Fe(OH)}_3$ , and this deposit substantially deteriorates the performance of the membranes. Based on the data cited one may suppose that during reverse osmosis of the acidic solution of calcium sulphate containing  $\text{Fe(III)}$ , namely  $\text{Fe(III)}$  ions rather than calcium sulphate are responsible for the deposition.

The nature of deposit formation on membranes changes in the presence of a Na-CMC additive in the solution filtered. Fig. 2 shows the change of water flux and rejection of the membranes over time, when filtering the calcium sulphate solution containing 2.15 mg/l of  $\text{Fe(III)}$  and the additive of 16 mg/l Na-CMC.

When comparing the data of Figs. 1 and 2, one can see that in the presence of Na-CMC the deposition process slows down. In this case the  $\text{Ca}^{2+}$  concentration in the volume of the circulating solution during the filtration time of 7 h remained unchanged. The concentration of  $\text{Ca}^{2+}$  ions did not change during subsequent

storage of this solution at the static conditions for 6 days. That indicates the Na-CMC stabilizing action with regards to  $\text{CaSO}_4$  in the acidic solution.

In the presence of the Na-CMC additive the  $\text{Fe(III)}$  concentration in the circulating solution during the time of experiment decreased only by 11.6% compared with 54.5% without the addition of Na-CMC. From this one may draw a conclusion that Na-CMC, on the one hand, inhibits  $\text{CaSO}_4$  crystallization and, on the other hand, prevents the formation of an insoluble deposit of  $\text{Fe(OH)}_3$ . Under these conditions the complexes of Na-CMC with adsorbed ions of calcium and hydrolysed iron can be formed. The stepwise increase of rejection and the decrease of flux for all membranes in the initial period of reverse osmosis filtration (Fig. 2) makes it possible to believe, in accordance with the data of [8], that Na-CMC partially blocks the pore mouths of the membranes ( $\text{Ca}^{2+}$  rejection may also increase due to the adsorption of  $\text{Ca}^{2+}$  ions on Na-CMC).

Further deposition on the surface of the membrane No. 3 practically is absent, while on the membranes No. 1 and No. 2 it is substantially delayed. This is indicated by the lower, compared with the data of Fig. 1, flux reduction (Fig. 2). As the deposit grows on membranes No. 1 and No. 2 some decrease of rejection occurs, however, in contrast to the reverse osmosis without introduction of Na-CMC (Fig. 1), the ions rejection of these membranes remains quite high. In the course of further filtration of 5 g/l NaCl solution through the fouled membranes, the deposits are rapidly washed off and the initial characteristics of the membranes are practically restored. Hence, the additive of 16 mg/l Na-CMC to the feed solution makes it possible to conduct the reverse osmosis without deposition or with substantial delaying deposition on the membranes investigated.

The inhibiting effect of Na-CMC in the acidic solution of calcium sulphate and delaying the

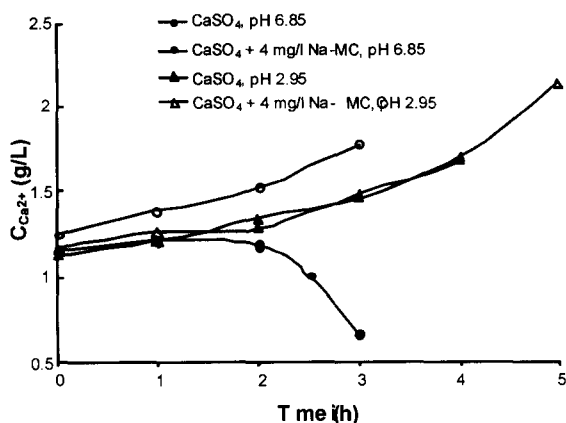


Fig. 3. Concentration of  $\text{Ca}^{2+}$  in the feed solution vs. time in dead-end ultrafiltration; UAM-100 membrane;  $P=0.4$  MPa.

salt crystallization in the acid medium have been additionally confirmed by the results of the dead-end ultrafiltration of  $\text{CaSO}_4$  solutions.

Fig. 3 demonstrates that the ultrafiltration of the neutral solution of calcium sulphate without a Na-CMC additive is accompanied by fast decrease of  $\text{Ca}^{2+}$  concentration in the solution volume and formation on the membrane of the dense crystalline deposit of  $\text{CaSO}_4$  (in this case  $J \rightarrow 0$ ). At the same time, in the ultrafiltration of the acid solution the  $\text{Ca}^{2+}$  content in the solution volume does not decrease, and even concentrating  $\text{Ca}^{2+}$  ions becomes possible. In this case the deposit on the membrane is small. The addition of 4 mg/l Na-CMC provides an explicit inhibiting effect in the ultrafiltration of both the acidous and neutral solution of calcium sulphate and makes it possible to concentrate the solutions.

Fig. 4 shows the reverse osmosis results for the solutions with the increased concentration of Na-CMC additive (32 mg/l). Our investigations under static conditions showed that increasing the Na-CMC concentration from 16 to 32 mg/l in the calcium sulphate solution containing Fe(III) enhanced the polymer stabilizing effect (the solution remained stable, respectively, for 7 and 9 days). At the same time, as seen from Fig. 4, the

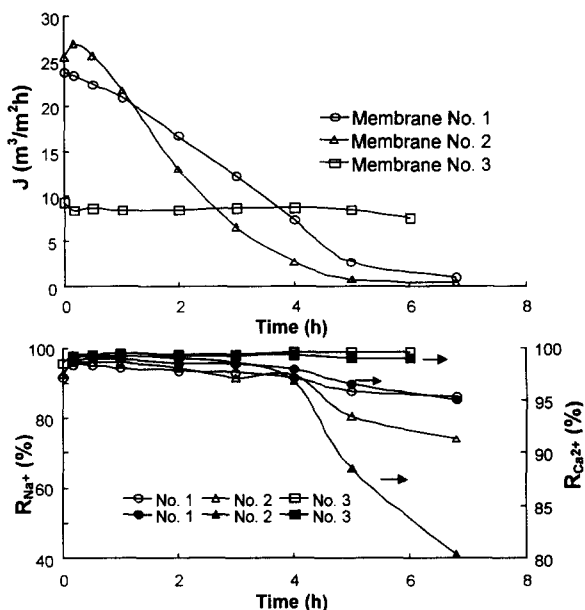


Fig. 4. Flux and cation rejection vs. time in RO filtration of the salt solution containing 0.027 M  $\text{CaSO}_4$ , 2.25 mg/l Fe(III) and 32 mg/l a-CMC; pH 3.05.

increase of Na-CMC concentration does not affect the flux and rejection characteristics of low-capacity membrane No.3 compared with the lower Na-CMC concentration. The content of ions of calcium and iron (III) in the circulating solution, as with the lower Na-CMC concentration remains the same. However, for membranes No.1 and No.2 having the higher water permeabilities the separation characteristics dramatically went down, as the Na-CMC concentration increased. For 7 h of filtration, the flux of both the membranes dropped practically to zero with a substantial decrease in salt rejection. One may assume that intensification of deposition on the membranes No. 1 and No. 2 at the increased Na-CMC concentration is caused by the presence in the solution filtered of free Na-CMC, not bound either with calcium or iron, and with its possible adsorption on these membranes.

As is known from [9], the Na-CMC additive (in concentrations up to 100 mg/l) in reverse

osmosis of NaCl or Na<sub>2</sub>SO<sub>4</sub> solutions produces the positive modifying effect on the membranes and increases the salt rejection owing to the packing of the membrane discriminating layer. However, in the acid medium the Na-CMC molecules are in the state of balls and the polymer loses its efficiency as a rejection enhancing agent. Therefore, an excess of free Na-CMC under the conditions of the experiment (pH 3.05), most likely, contributes to the additional deposition on the external membrane surface and to the change of the deposit composition. Thus, one may believe that in reverse osmosis of solutions, containing calcium sulphate and iron (III) ions, the effective Na-CMC concentration as an inhibitor at a low pH should not exceed concentration, equivalent to the formation of complexes of Na-CMC with deposit-forming components of the solution. It is important to note that under all conditions of experiments, both without a Na-CMC additive and with the Na-CMC additive of 16 or 32 mg/l, the initial characteristics of the membranes are restored quickly by rinsing with water. It means that all the deposits formed both in the absence and in the presence of the Na-CMC in the solution are mainly located on the external surface of the membranes and possess weak affinity to the membrane surfaces.

#### 4. Conclusions

1. Reverse osmosis of calcium sulphate acid solutions containing iron (III) ions using composite membranes results in fast deterioration of the flux and rejection characteristics of the membranes due to the deposit formation. Iron (III) ions are mainly responsible for the deposition.
2. Improvement of the membrane performance in reverse osmosis of these solutions can be attained by addition to the feed solution of sodium carboxymethylcellulose (Na-CMC), as an inhibitor. It is believed that the concentration of the Na-CMC additive in case of low solution pH should not exceed its concentration, equivalent to the formation of complexes of Na-CMC with the deposit-forming components of the solution.
3. It can be supposed that the composition of deposits formed on the membranes are different for the membranes with the low and high water permeability both in the presence and in the absence of Na-CMC in the solution filtered.

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