Investigation of scaling mechanism on reverse osmosis membranes using «fluorescent» antiscalant

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Abstract. Scaling of sparingly soluble salts could be recognized as a main factor that limits wide application of reverse osmosis (RO) membrane facilities in drinking water production and industrial water recycling. The report demonstrates a new approach to evaluate scaling rates and antiscalant behavior in commercial membrane spiral wound modules through the use of the fluorescence-tagged antiscalants and laser scanning confocal microscope (LSM) observations. Throughout the conducted study the "visualization" of scale inhibitors behavior appeared to be a very promising and universal tool for their activity understanding. Examination of membrane surface and calcite crystals in autopsied membrane modules demonstrated new unexpected results: antiscalant adsorbed either on membrane surface or on crystal surface. In the presence of calcium ions during ground water treatment antiscalant was adsorbed only on crystal surface and sorption on membrane was not detected. Fluorescence was more intensive on the surface and on the outer edges of crystal surface than inside crystal. To investigate antiscalant adsorption to membrane surface, experiments with distilled water containing antiscalant were performed. Intensive sorption of fluorescent inhibitor molecules to membrane was observed.

1. Introduction

Mechanisms of sparingly soluble salts scaling that occurs in membrane facilities during their operation are still not understood. A lot of research publications and scientific reviews reveal that different authors demonstrate rather contradictory conclusions and inconsistent results [1-3]. To develop efficient techniques to predict and prevent scaling, crystal formation and inhibition mechanism should be understood. Crystal inhibition using various antiscalant was widely investigated, but results of the majority of publications often do not correspond with practical experience of reverse osmosis water treatment facilities. Recommendations to use antiscalants in membrane applications often are based on results of laboratory tests [4-7] that do not provide supersaturation and nucleation conditions in membrane channels [8-10].

Supersaturation conditions as well as nucleation and crystal growth rates at membrane surface are still unknown. And product flow and rejection decrease due to scaling are still neither described nor predicted.

The majority of existing views on crystal formation mechanisms are based on assumption that nucleation is heterogeneous and takes place on membrane surface [8]. It is also assumed that "active sites" exist on membrane surface that act as the place where heterogeneous nucleation begins [8,9]. Mechanism of antiscalant behavior is explained by its adsorption on these "sites" and inhibition of their activities [10, 11]. Therefore, different experimental results can be explained by different views on scaling mechanisms and different experimental conditions to arrange nucleation and crystal growth [11-14].
It was always very difficult to describe conditions of crystal formation in membrane modules as well as to predict scale growth and its influence on membrane performance [15]. In [15, 16] scale formation in spiral wound reverse osmosis modules were investigated. It was reported, that nucleation takes place in the "dead areas" where supersaturation reaches very high values. Still it seems very difficult to detect formation of crystal sand calculate supersaturation values inside the "dead areas". It is obvious that to control scaling in reverse osmosis membrane facilities, antiscalants testings should be conducted in real industrial conditions that exist in commercial membrane modules. During last years a new generation of "green" antiscalants is being introduced into membrane desalination practice to decrease discharge of biogenic elements into natural water sources [13, 16, 17]. To compare new antiscalants with conventionally used in membrane water treatment practice and to confirm their efficiencies to inhibit scaling, the testing procedures should account for real supersaturation and scale formation conditions.

During long time all investigations to evaluate inhibiting efficiencies of commercial antiscalants were conducted using "seed crystals" techniques that consisted of addition of seed crystals into supersaturation solution and detecting their growth rates [16]. It was already presented [15] that values of recommended antiscalant dosed and values of crystal growth rates in the presence of antiscalants obtained during "seed" growth experiments do not correspond to results of industrial operation and real conditions of scaling process in membrane channels. Also many companies that sell commercial antiscalants recommend different doses of their products that depend on feed water hardness [3]. Meanwhile, antiscalant testings conducted with industrial spiral wound modules confirmed that antiscalant dose of 1 to 5 ppm does not influence antiscaling efficiencies at low calcium hardness values below 5 meq/liter [15]. This can be explained that nucleation occurs in membrane "dead areas" where calcium and bicarbonate as well as antiscalant concentrations reach high values that provides "severe" supersaturation conditions.

Main views on scaling mechanism in membrane facilities were developed and postulated basing on results of long observations and investigations [15]:
- nucleation in membrane modules is homogenous and occurs in the "dead areas" where concentrations of dissolved salts reach high values thus providing high supersaturation conditions for sparingly soluble salts like calcium sulphate and calcium carbonate;
- crystal are formed in "dead areas" , get out of these areas and sediment on membrane surface;

Present research demonstrates behavior of the newly developed antiscalants that use fluorescent fragments built in their polymer structure [19,20].

These developments provided new opportunities to observe and "visualize" antiscalants behavior and inhibiting process. The present study used fluorescent antiscalants to reveal their adsorption behavior in commercial membrane modules used for water treatment. The goal of the present article was to compare inhibiting efficiencies of different antiscalants, both conventional and fluorescent, to investigate their adsorption abilities and their influence on scaling suppression. The test procedure to evaluate scaling rates in commercial spiral wound modules was developed by the authors [15] and involved SEM observations of autopsied membranes.

2. Materials and Methods
Commercial product - phosphonic antiscalant "Aminat-K" produced by "Traverse Co"(Russia) was used in experiments. "Aminat-K" is a composition of nitriltri-methylene-phosphonic acid and imino-dimethylene-phosphonic acid.

In our experiments we tested a novel fluorescent-tagged polymeric "green" antiscalant that contained "fluoroform fragments" - PAA-F1 - a copolymer of N-allyl-4-metoxy-1,8-napftalimid and acrylic acid . This antiscalant belongs to a polyacrylate family.

The experiments were conducted in conformity with procedure developed by the authors [15, 16]. Also microscopic studies were performed to detect influence of antiscalant adsorption on calcite crystals structure. In all cases the visualization of antiscalants inhibitors appeared to be a very promising and universal tool for their inhibiting efficiency understanding. The microscopic studies
involved use of electron scanning microscope (SEM, Hitachi TM-3030) and a fluorescent laser scanning confocal microscope (laserscanning confocal microscope LSM-710-NLO, Carl Zeiss Microscopy, Germany).

Antisalant adsorption rates on growing crystal surface were evaluated and presented as a function of crystal growth rates. Also antisalant adsorption on membrane surface was tested as well as the influence of crystal surface on sorption efficiency. To reach this goal, along with determination of calcium carbonate scaling rates, rates of inhibitor adsorption on scale crystals during their formation was evaluated. The obtained results of further investigations of antisalant sorption on membrane surface and on the surface of already formed scale crystals enabled us to conclude that antisalant can adsorb either on membrane surface or crystal surface. Inhibitor sorption rate can characterize antisalant efficiency. Application of fluorescent-tagged antisalant provides determination and control of antisalant concentration values in test solution during scaling process. Also fluorescent properties of new antisalant enable us to "visualize" scaling and inhibiting process and to observe accumulation of antisalant both on membrane surface and on crystal surface.

Experimental program consisted of three experimental series:

Series 1: Evaluation of calcium carbonate scaling rates in spiral wound membrane industrial module in the presence of conventional "Aminat-K" antisalant with dosage values of 3, 5 and 7 ppm;
Series 2: Evaluation of calcium carbonate scaling rates in membrane module using newly developed fluorescent antisalant PAA-F1 with dosage values of 3, 5 and 7 ppm;
Series 3: Evaluation of antisalant adsorption rates to membrane surface in the absence of calcium carbonate scaling.

3. Results and Conclusions
All experiments were conducted using laboratory membrane test unit. A flow diagram of the test unit is shown on Figure 1. The test unit was operated in circulation mode whereby concentrate after membrane module was returned back to feed water tank. The feed water was added to feed water tank 1. The volume of tank 1 was 5 liters. Feed water from tank 1 was supplied by small gear pump 2 to membrane module 3. In all experiments industrial spiral wound modules of 1812 standard tailored with low pressure reverse osmosis membranes with 100 GPD capacities were used. The module used low pressure reverse osmosis membranes BLN type developed and manufactured by CSM Co (Korea). Membrane area in 1812 membrane element was 0,5 square meter. Pressure value and concentrate flow rate were regulated by pressure regulation valve 12. Concentrate stream after membrane module was returned back to feed water tank 1 and product water stream was collected in separate tank 4 or discharged in drain. Working pressure volume in membrane module was maintained at the level of 7 Bars. The volume of concentrate that circulated in feed water tank was determined using marks on transparent walls of the tank 1. Concentrate water samples were withdrawn from the tank 1 and product water samples were taken directly from product water tube.
Figure 1. Schematic diagram of laboratory RO unit for membrane scaling tests: 1- feed water tank; 2- pump; 3- spiral wound membrane module; 4 - permeate tank; 5 - heat exchanger; 6 - pressure gauge; 7- feed water flow meter; 8 - permeate flow meter; 9 - concentrate flow meter; 10 - by-pass adjusting valve; 11 - feed water adjusting valve; 12 - concentrate adjusting valve; 13 - cooling water adjusting valve; 14 - sampler.

During each test run samples were withdrawn and temperature, unit conductivity, pH as well as hardness, calcium, bicarbonate concentration values were determined. Conductivity and total dissolved solids values were controlled using laboratory conductivity meter Cond 730 (WTW inoLab), and \( \text{pH} \) values were determined using laboratory \( \text{pH} \)-meter HI 2215 (HannaInstruments). Bicarbonate, hardness and calcium concentration values were determined by titration.

To remove calcium carbonate deposits accumulated on membranes during test runs, we applied chemical cleanings of membranes between different experimental series conduction using 2% citric acid solution. To prepare cleaning solution tap water was used. Cleaning procedures were performed using the pump 2. Both the first and the second experimental series were conducted using the same membrane element BLN 1812. As it was presented and discussed earlier [15], all comparison studies of scaling rates and antiscalant efficiencies determination should be performed using one membrane element: different membrane elements have different amount of "dead" areas and therefore demonstrate different scaling propensities at equal operation conditions.

Concentration of "Aminat-K" antiscalant was controlled by determination of phosphate-ion concentration values in conformity with the method described in [16]. Concentration of new fluorescent antiscalant in concentrate was controlled by fluorescence determination. First and second experimental series were conducted using Moscow tap water as a feed. The volume of feed water in tank 1 in the beginning of each experiment was 5 liters. Product flow of membrane element BLN 1812 throughout each test run was 6-6.3 liters per hour and depended on temperature value. Moscow tap water TDS value was 240-260 ppm. Total hardness was 3.1 - 3.4 mill equivalents per liter, bicarbonate was 2.8-3.1 mill equivalents per liter, calcium concentration was 2.8 - 3.1 mill equivalents per liter. Chloride concentration was 28-30 ppm and sulphate was 10-13 ppm.

The amounts of calcium carbonate deposited on membrane surface during each test run were determined as a difference between calcium amount in tank 1 in the beginning of experiment and amount of calcium in the feed tank at the certain moment of the test run [15] that corresponded to concentration coefficient \( K \) value, which is a relation of the initial feed volume \( V_i \) to concentrate volume in feed tank \( V_k \) (\( K=V_i/V_k \)). Figure 2 shows experimental dependencies of calcium concentration values versus \( K \) value (Figure 2, a) and accumulated calcium carbonate amount versus \( K \) (Figure 2, b). Calcium carbonate growth rates were evaluated in conformity with our method described in [15] and were determined as tangents of the slope of curves that yield calcium carbonate
scale amount versus time (Figure 3, a). Results of calcium carbonate growth rate determination are presented on figure 3(b) as dependencies of scaling rates (expressed in mill equivalents per hour) on concentration coefficient K values. K is determined as the volume in tank 1 reduction ratio: the ratio of the volume in tank 1 in the beginning of experiment to the volume in the certain moment of experiment. The volume of concentration coefficient K is a function of membrane unit recovery value α (product flow to feed water flow ratio) expressed by equation: $K = \frac{1}{1 - \alpha}$.
Along with calcium carbonate growth rates evaluation also rates of antiscalant adsorption (or accumulation in membrane module) were determined. The amount of adsorbed antiscalant was calculated as a difference of antiscalant amount in the tank 1 in the beginning of experiment and the amount of antiscalant in tank 1 at the certain moment of experiment. Both "Aminat-K" and PAA-F1 were tested, and doses of each antiscalant were 3, 5 and 7 ppm. Additionally each series included three test runs to evaluate the influence of accumulated calcium carbonate on antiscalant adsorption rate to the surface of already formed crystals. Figure 3 shows results of determination of antiscalants adsorption rates versus K values. Adsorption rate values do not increase with the growth of deposited calcium carbonate: antiscalant was consumed only during crystal formation. Adsorption rates are presented as functions of calcium carbonate growth rates (Figure 4) and of K value for scaling rate of 10 meq./hour (Figure 5).

The third experimental series was devoted to investigation of antiscalant adsorption on membrane surface. Experiments were conducted with the aim to exclude influence of calcium carbonate crystals on antiscalant behavior in the feed water solution. Experiments were conducted using laboratory test unit shown on Figure 1 in full circulation mode. As a difference to Series 1 and 2, in Series 3 experiments not only concentrate flow, but also the product water flow were returned back to feed water tank 1. As it was claimed and discussed earlier [15, 16, 18], calcium carbonate is not deposited in a "closed" conditions even under high initial supersaturation values: deposition of even small amount of calcium carbonate is followed by a change of pH and carbonate ion concentration values. To initiate calcium carbonate deposition during experimental test run, a "driving force" should be applied to increase calcium and carbonate concentration values as well as pH value to provide adequate supersturation conditions. Therefore, operation of the test unit in circulation mode does not provide calcium carbonate deposition in membrane module and antiscalant can be adsorbed only on membrane surface. Figure 6 demonstrates results of adsorption rates evaluation. Adsorption rates rapidly decrease during the first minutes of feed water circulation. The detected small decrease of antiscalant concentration in the beginning of circulation cycle is attributed to deposition of a small calcium carbonate amount that occurs in the first minutes of tap water circulation. A new experimental test run was performed using distilled water as a feed. PAA-F1 antiscalant concentration value in distilled water was 10 ppm. Figure 7 shows amounts of antiscalant adsorbed on membrane surface. After we detected antiscalant adsorption on membrane surface, it was decided to treat tap water with reverse osmosis membrane without antiscalant addition to evaluate calcium carbonate scaling rates in the module treated by antiscalant. Results of experiment are shown on Figure 8, where values of antiscalant penetration rates from membrane layer into bulk solution (tap water) are presented as a function on K.
Figure 8. Calculated PAA-F1 penetration rates into tap water solution together with scale inhibiting process versus K.

1 - the observed rate of antiscalant Aminat-K penetration from membrane into concentrate versus K; 2 - rate of adsorption of Aminat-K, 7 ppm, on crystal surface, versus K; 3 - rate of adsorption of Aminat-K, 5 ppm, on crystal surface, versus K; 4 - rate of adsorption of Aminat-K, 3 ppm, on crystal surface, versus K; 1a , 1b, 1c - predicted rates of Aminat-K penetration from membrane surface into concentrate for different scaling rates

Figure 9. Fluorescent microscope photo of membrane (a) and crystals (b) from CSM 1812-100 GPD module after finishing of second series of experiments (after dosing PAA-F1 antiscalant, 7 ppm)
Figure 10. Fluorescent microscope photos of membrane (a) and calcite crystals (b) from CSM 1812-100 GPD module after finishing of 3-d experimental series: treatment of membrane with distilled water with PAA-F1 antiscalant (10 ppm) and further operation on tap water without antiscalant addition.

Experimental results presented on figures 7 and 8 confirm the assumption that antiscalant adsorbed on membrane surface after circulation of distilled water containing antiscalant. PAA-F1 antiscalant accumulated on membrane surface and later penetrated in the tap water and inhibited calcium carbonate growth (Figure 8). After the end of the second and the third experimental series membrane elements were withdrawn from their vessels and their autopsies were performed. Dependency of antiscalant penetration rate from membrane into concentrate on K value is shown on figure 8. The obtained values of antiscalant penetration from membrane surface into concentrate are obtained by summing of observed values of antiscalant growth rates in concentrate throughout the experiment and rates of antiscalant consumption by growing crystals obtained earlier (figures 3-5). Membrane fragments were dried and examined using laser scanning confocal microscope. Figures 9 and 10 demonstrate fluorescent antiscalant behavior using laser scanning confocal microscope. Photos of membrane surface and calcite crystals formed in membrane elements in the second series (Figure 9) and in the third series (Figure 10) are presented.

For the cases when tap water was treated by reverse osmosis and calcium carbonate scaling occurred, the adsorption of both PAA-F1 on calcite crystals was detected. Fluorescence was more intensive on the surface and on the outer edges of crystals than inside of crystal. During nucleation process "dark" area of crystals was formed and later was covered by antiscalant's adsorption layer that blocked crystal growth.

Experiments conducted with industrial membrane modules demonstrated that formation of crystal scale deposit occurs under conditions that often differs from conditions of laboratory tests. Thus one has a right to question the validity of beaker tests normally used for the "true" inhibitor selection for RO facilities. By all means an application of the fluorescent-tagged antiscalant may put light on many aspects of scale inhibitor applications. Visual observation of crystal formation and growth process opens new and unique perspectives in scaling mechanisms investigation and developing new ways to control scaling.

4. Conclusions

The higher the antiscalant dose is, the more intensive is its adsorption on crystal surface. Inhibiting efficiency of antiscalant can be attributed not only to its sorption properties, but mainly to its ability to block active sites of crystal growth on the surface of growing crystal. Rate of antiscalant adsorption to crystal surface increases with increasing of crystal growth rate. In natural water molecules of antiscalant are always chemically bonded with calcium ions and therefore do not adsorb on membrane
surface. In cases where calcium is not contained in water (such as distilled water) antiscalant can adsorb on membrane surface.

Nucleation (formation of nuclei crystals) phase occurs without involvement of antiscalant even if antiscalant is added. After nucleus is formed, further crystal growth is controlled by adsorption of inhibitor on the crystal surface.

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