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A comparative study of some novel "green" and traditional antiscalants efficiency for the reverse osmotic Black Sea water desalination

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ABSTRACT

Desalination of seawater and brackish water by reverse osmosis to produce potable and process water has been widely used. But the precipitation of low soluble salts is one of the major problems in RO plants operation. Several well-known techniques are used to protect membranes and antiscalant dosing is one of the most widespread. A wide range of reliable and efficient inhibitors have been developed but the trend of the last decade is creation environmentally friendly ("green") chemicals: phosphorus-free and biodegradable. A relative ability of industrial samples of four phosphorus-free polymers (polyaspartate (PASP); polyepoxysuccinate (PESA); polyacrylic acid sodium salt (PAAS); copolymer of maleic and acrylic acid (MA/AA)) and of three phosphonates (aminotris (methylenephosphonic acid), ATMP; phosphonobutane-1,2,4-tricarboxylic acid, PBTC; and AMINAT) to inhibit carbonate membrane fouling in the simulated Black Sea water under reverse osmosis (RO) conditions for the dosages ranging from 1 to 25 ppm is tested. The following ranking ATMP > HEDP > PESA (400 ÷ 1500 Da) ~ PASP (1000 ÷ 5000 Da) > PAAS (3000–5000 Da) ~ MA-AA is found. A comparison of this ranking with that one performed following the NACE Standard TM0374-2007 under static conditions confirmed results provided by NACE Protocol.

Keywords: Reverse osmosis; Scale inhibition; "Green" antiscalants; Black Sea water

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1. Introduction

Scale formation in reverse osmosis (RO) desalination processes is a serious problem, causing a significant plugging of membranes, and increasing the production cost [1,2]. A widely used technique for controlling scale deposition is an application of chemical inhibitors [3]. For a long time the phosphonates were treated as the reagents of choice [4,5]. Among these, such reagents as aminotris (methylenephosphonic acid), ATMP; 1-hydroxyethane-1,1-bis (phosphonic acid), HEDP; 2-phosphonobutane 1,2,4-tricarboxylic acid (PBTC); ethylenediaminetetra (methylenephosphonic acid), EDTPH, are the most common. Recently these reagents are still dominating at the world market [6]. However, the broad phosphonate applications created a new environmental problem: a great number of RO facilities produce concentrate (retentate) streams that are discharged in surface reservoirs and pollute water resources [7–9]. Phosphorus discharges are therefore regulated now in many countries worldwide and permissible limits are constantly decreasing [10]. Increasing environmental concerns and discharge limitations have forced the scale-inhibitor chemistry to move toward "green antiscalants", which are readily biodegradable and have minimal environmental impact. Intensive efforts are applied recently to develop the "green" alternatives to organophosphonates and nonbiodegradable polyacrylates (PA) [10–12]. Among these novel inhibitors, such chemicals as polymaleates (PMA), polyaspartates (PASP),

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polyepoxysuccinates (PESA), as well as their various derivatives, including co-polymers with PA are worthwhile to mention [13–20].

It should be noted, that the new antiscalants should have acceptable levels of performance at cost-effective dose rates. This requirement generates a problem of reliable tests, which permit a correct efficiency comparison for the traditional and novel inhibitors. Unfortunately, most of the data published on calcium sulfate [21] and calcium carbonate [22] deposition are obtained under hardly comparable conditions, e.g. different supersaturation index, brine composition, temperature, measurement technique, etc. The known comparative performance ranking reports done by one and the same group are rare. At the same time such rankings reveal frequently rather conflicting results [21,22]. Meanwhile the recommended laboratory tests on the inhibitor efficacy evaluation [23] are shaped either for carbonate or for sulfate scales, while the sea water used in RO facilities has normally both carbonate and sulfate ions. In this respect a relative performance of some traditional antiscalants (phosphonates, polyacrylates) and of the novel environmentally friendly polymers (PASP, PESA) under comparable conditions at a RO facility operating with a particular sea water in comparison with static method proposed by a NACE protocol [23] becomes actual. In the present work, the effects of industrial samples of two novel phosphorus-free biodegradable polymers PASP and PESA, two non-biodegradable phosphorus-free polymers (polyacrylate, PAAS; polymaleate copolymer with polyacrylate, MA-AA) and of two traditional phosphonates (AMTP, PBTC) were tested with respect to their ability to inhibit membrane following during RO Black Sea water treatment.

Antiscalants are successfully used as pretreatment chemicals in majority of RO industrial applications to treat surface and well water. Along with treatment of well water antiscalants became demanded by seawater desalination facilities. This antiscalant market expansion was observed during last two decades. State of the art survey undertaken in 80–90-es showed that antiscalants were not widely used in seawater RO applications [32]. This can be explained by very high ionic strength value of seawater that increase solubility of calcium sulphate and calcium carbonate and operation of seawater desalination plants below supersaturation limits [32].

The main reason of growing interest to green antiscalants is World Health Organization (WHO) standards for boron content in drinking and desalinated water [24]. As it is well known, boron is poorly rejected by RO membranes under pH lower than 8. To ensure high and efficient boron rejection (no less than 90–95 %), feed water value should be increased to reach a value of 9–9,5. It is dangerous to add caustic or lime to the feed seawater as it could cause precipitation of calcium carbonate due to high calcium content. To treat seawater a double stage flow diagram was developed [24]. A flow diagram of seawater desalination is shown on Fig. 1. First stage product is treated by the second stage RO membranes. To increase rejection of the second stage membranes, caustic or lime are injected in the first stage product water. A potential hazard of calcium carbonate formation occurs in the second stage membrane units, as the first stage product water contains calcium and bicarbonate ions. The main problem of seawater desalination by modern thin film composite membranes is increased calcium ion transport through membrane. This is connected with seawater composition: the sum of concentration values of divalent calcium and magnesium ions are not balanced by concentration value of sulphate ions. Membrane rejection of divalent ions is usually higher, than of monovalent ions. As a result, sulphate ions are rejected by nearly 100% and calcium ions (excessive calcium concentration value) that are not connected with sulphate ions, penetrate into product water due to electrical neutrality.

Calcium penetration through membrane is also facilitated by the negative electrical charge of membrane.

Therefore, increase of pH values up to 9–9.5 provides increase of carbonate-ion concentration values and calcium carbonate supersaturation values.

Modern double-stage desalination units use nanofiltration membranes as a first stage, thus first stage product TDS reach 10000–120000 ppm. The use of nanofiltration membranes reduces power consumption and provides higher recovery values (up to 0.5). The use of low pressure equipment (tubing, pumps and vessels) also provides reduction of capital costs.

Addition of antiscalants to the first stage product water provides control of scaling in RO channels. Second stage recovery depends on the efficiency of antiscalants. Second stage concentrate is added to the sea feed water (Fig. 1). Therefore, overall desalination unit recovery value and operational costs are dependent on the second stage recovery. Also the increase of recovery provides the increase of boron concentration value in the second stage product water. To increase boron rejection, pH value of the first stage product water should be also increased. And recovery values depend on antiscalant efficiency. Thus, antiscalants used in seawater desalination facilities should conform to the following requirements:

1. Efficient performance under high pH conditions;
2. Efficient performance at high recoveries and high supersaturation values;
3. Low dosing and high efficiency;

Therefore the main objective of current study is to test the commercially available "traditional" and novel antiscalants in a particular reverse osmosis process operating with a modeled Black Sea water desalination. An additional objective is to compare the relative reagent efficiency found in reverse osmosis experiments with those provided by NACE protocol [23] static testament results [22].

Present article describes testing of antiscalants under different pH conditions after caustic addition. Investiga-

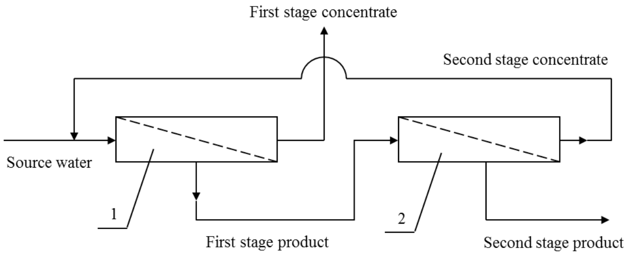


Fig. 1. Double-stage desalination process flow diagram: 1 – first stage membrane module; 2 – second stage membrane module.

tions were conducted using Black sea imitate and product water after treatment of imitate by low pressure RO and nanofiltration membranes. Experimental program was aimed at:

- selection of the most efficient antiscalant type for commercial use;
- comparison of technological and economical characteristics of different sea water desalination approaches: with caustic addition in the feed seawater; double stage seawater treatment with different membrane types at the first stage and caustic addition to the first stage product water;
- experimental determination of antiscalants efficiencies under high pH and supersaturation conditions;
- evaluation of operational costs of different seawater desalination techniques using new antiscalants and selection of optimum values of recovery, caustic and antiscalant doses.

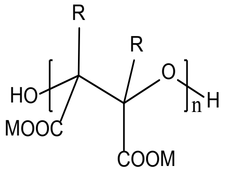
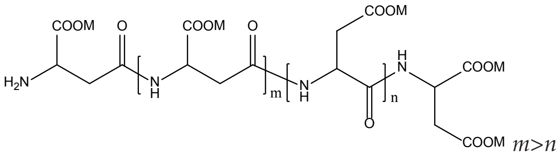
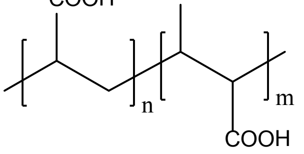
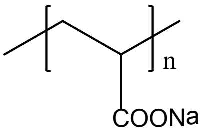
2. Experimental program: Materials and scaling tests

Polymer based industrial antiscalants polyaspartic acid sodium salt (PASA), copolymer of maleic and acrylic acid (MA/AA), polyepoxysuccinic acid (PESA) and sodium salt of polyacrylic acid (PAAS) have been kindly supplied by Shandong TaiHe Water Treatment Co. Ltd., and analyzed by NMR and dynamic light scattering technique (DLS). Polymer stock solutions were prepared on a dry weight basis. The desired concentrations of the polymers were obtained by dilution. Table 1 lists the properties of polymers tested.

Industrial solid phosphonates aminotris (methylenephosphonic acid), ATMP and 1-hydroxyethane-1,1-bis(-phosphonic acid), HEDP have been supplied by a manufacturer OAO "Khimprom", Novocheboksarsk, Russia, and liquid phosphonobutane-1,2,4-tricarboxylic acid (PBTS) was provided by Shandong TaiHe Water Treatment Co. Ltd. Commercially available liquid reagent Aminat-K (a blend of sodium salts of ATMP and methyliminobis(methylenephosphonic acid) was provided by a Russian company "Travers". All four reagents have been analyzed by NMR. ^{1}H, ^{31}P and ^{13}C NMR measurements of reagent aqueous solutions were recorded with Bruker AVANCE II 300 spectrometer at ambient temperature in the 5 mm diameter sample tubes. The external standard solutions of TMS (^{1}H, ^{13}C) or phosphoric acid (^{31}P) were placed in a 1 mm inner coaxial tube. Both solid samples are found to have nearly reagent grade purity and used without further purification. Phosphonate stock solutions were prepared on a dry weight basis. The desired concentrations of the polymers were obtained by dilution.

Some original phosphorous-free polymers have been developed by PJSC "Fine Chemicals R&D:

Table 1
Polymers studied as scale inhibitors in calcium carbonate supersaturated solutions

Reagent	Reagent formula	Appearance	Solid content, %	Molecular mass, Da	pH, 1% water solution
PESA	 M = Na, R = H	Amble transparent liquid	40.27	400÷1500	11.56
PASP		Umber liquid	40.94	1000÷5000	9.81
MA/AA	 free monomer as MA ≤ 9%	Brown transparent liquid	48.80	Not specified	2.17
PAAS	 free monomer as CH_2=CHCOOH ≤ 1%	White powder	92.49	3000÷5000	6.92

- PASP-FCC (polyaspartate, molecular mass 3000 Da);
- PA - FCC (polyacrylate, molecular mass 4500 Da).

Conventionally used industrial antiscalants were tested as reference samples.

The reference antiscalant was commercially available liquid reagent Aminat-K (a blend of sodium salts of ATMP and methyliminobis (methylenephosphonic acid) was provided by a Russian company "Travers".

All chemicals except Aminat-K were dry. Polymer stock solutions were prepared on a dry weight basis. The desired concentrations of the polymers were obtained by dilution.

All samples have been analyzed by NMR and IR spectroscopy at Russian company ZAO "EKOS-1". Scaling experiments were conducted in the Water treatment laboratory of Department of Water Supply, National Research Moscow State University of Civil Engineering.

RO and nanofiltration membranes were used for sea water desalination and scaling tests. To treat Black Sea water with 18000 ppm of TDS medium pressure RO membranes can be used. BE 4040 membrane element tailored with BE membranes supplied by CSM Co (Korea) was used for single-stage seawater desalination. Membrane working pressure was 16 and 32 Bars. For double stage desalination, nanofiltration membrane elements (model 4040 NE) tailored with 90 NE membranes and 4040 BLN elements were used.

For brine preparations the analytical grade chemicals were used. Stock solutions of calcium chloride, sodium carbonate, sodium chloride and magnesium sulfate were prepared from the respective crystalline solids (Aldrich; ECOS-1) using distilled water. Table 2 represents chemical imitates of the Black Sea water, product waters after different membrane treatment as well as Moscow tap water used in the present work. pH values of feed water was corrected by addition of 1N caustic solution.

Experimental program consisted of 4 experimental series:

Series 1: Preliminary antiscalant performance comparison tests conducted with Moscow tap water. Selection of the most efficient product.

Series 2: Determination of main technical characteristics of different sea water desalination flow diagrams: dependencies of membrane rejection and desalination efficiencies on membrane type, pressure and recovery;

Series 3: Comparative studies of antiscalant efficiencies in seawater desalination facilities with caustic addition to the feed water;

Series 4: Comparative studies of antiscalant performance in double-stage seawater desalination facilities with caustic addition to the first stage product water.

Membrane scaling tests were carried out using the commercial RO spiral wound membrane modules and a laboratory membrane unit shown in Fig. 2. The feed solution (tap water or model solution) is placed in the feed water tank (1) and delivered to membrane module via centrifugal multistage pump (2). The transmembrane pressure, cross-flow and recovery rate is adjusted by valves (10, 11 and 12) and controlled by pressure gauges (6) and rotameters (7 and 9).

First series tests were conducted using a 4040 membrane element (model ERN-B-45-300, ZAO STC "Vladipor", Russia) manufactured using ESPA membranes with rejection up to 98.5% (0.15% NaCl).

All scaling tests were conducted in circulation mode whereby reject flow (concentrate) was returned to the feed water tank (1) and permeate were collected in separate tank (4). The transmembrane pressure was maintained at 7.0 ± 0.2 bar. The product flux, depending on tap water temperature, was varied from 100 to 150 L/h. The virtual selectivity on the tap water was 97.5 … 98.0%. The volume of feed solution is 80 ± 2 L. Concentrate flow were kept constant at 100 ± 10 l/h and recovery rate were in the range of 50 and 60%. To extend scaling time and to escape flux changing due to increasing osmotic pressure of circulated solution a part of product water is returned to feed water tank in that way the product flow directed to the permeate tank were invariable all the time.

Experiments were carried out with Moscow tap water from April 2015 to May 2015. During this period the tap water had quite stable quality and TDS of 246 … 266 ppm, total hardness of 3.1 … 3.4 meq/L (155 … 170 ppm of $CaCO_3$), total alkalinity of 2.5 … 2.9 meq/L, calcium of 2.2 … 2.5 meq/L, pH of 7.75 … 8.2, sulphates of 10 … 13 ppm, chlorides of 8 … 10 ppm.

Feed water and retentate samples were withdrawn from tank (1), for circulated solution – from tank (1) (for various concentration ratios) and permeate samples were taken from tank (4) (one sample characterized the averaged quality of product water).

In all samples temperature, TDS (conductivity), pH, total hardness, total alkalinity, calcium were determined. Conductivity and temperature were controlled by a laboratory conductivity meter Cond 730 (WTW inoLab®); pH value – using laboratory pH meter HI 2215 (Hanna Instruments); total alkalinity – by titration with HCl; total hardness and calcium – by complexometric EDTA titration.

To restore membrane element performance and to remove accumulated scales every 10–15 tests chemical washing was conducted using citric acid or EDTA.

Scaling experiments were conducted by series for new antiscalants and selected reference scale inhibitors with typ-

Table 2
The Moscow tap water and feed water formulations used as imitates and product water chemical compositions

Feed water	Na^+, ppm	Ca^{2+}, ppm	Mg^{2+}, ppm	HCO_3^- ppm	SO_4^{2-} ppm	Cl^-, ppm	TDS, ppm
Moscow tap water	0.5	2.5	1.0	3.5	0.25	0.25	240–250
Black Sea imitate	261	10.0	50.0	1.0	20.0	300.0	17–500
First stage NF imitate	56.2	1.0	4.0	0.2	1.0	60	3,600
First stage BLN imitate	40.8	0.2	0.5	0.5	1.0	40	2,400

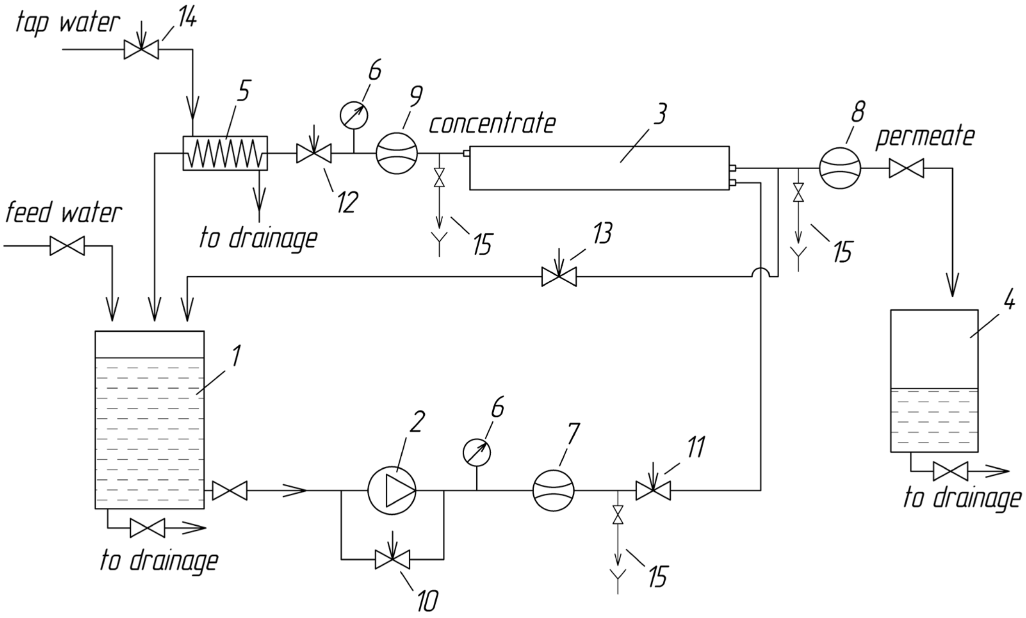


Fig. 2. Schematic diagram of laboratory RO unit for membrane scaling tests: 1 – feed water tank; 2 – pump; 3 – spiral wound membrane module; 4 – permeate tank; 5 – heat exchanger; 6 – pressure-gauge; 7 – feed water rotameter; 8 – permeate rotameter; 9 – concentrate rotameter; 10 – by-pass adjusting valve; 11 – feed water adjusting valve; 12 – concentrate adjusting valve; 13 – cooling water adjusting valve; 14 – sampler.

ical doses as indicated below: 0 mg/L (without antiscalant), 3 ppm, 5 ppm and 10 ppm (0; 3; 5 и 10 ml/L respectively for liquid chemical Aminat-K). Most tests were repeated twice to improve the accuracy of the results.

The amount of scales of $CaCO_3$ and $CaSO_4$ (expressed as Ca^{2+} in meq) accumulated in membrane module was calculated as difference between initial amount of calcium in feed solution and sum of amount of calcium in concentrate (circulating solution) and permeate (Eq. 1). This difference was calculated for concentration ratio values of 2; 3 and 5. The total hardness and total alkalinity are determined to control the correctness of other parameters determination.

The amount of precipitated calcium carbonate is calculated according to the following equation:

$$M_{ca^{2+}} = V \cdot C_{ca^{2+}} - \left(V_c^t \cdot C^t_{c\,ca^{2+}} + V_p^t \cdot C_{p\,ca^{2+}}\right), \qquad (1)$$

where: $M_{ca^{2+}}$ – amount of calcium accumulated in membrane module, meq; V – feed solution volume, l; $C_{ca^{2+}}$ – concentration of calcium in feed solution, meq/L; V_c^t, V_p^t – volume of circulating solution and total permeate respectively for time t, l; $C^t_{c\,ca^{2+}}, C_{p\,ca^{2+}}$ – concentration of calcium in circulating solution and total permeate respectively for time t, meq/L.

The amount of calcium can be converted to mass of calcium carbonate (mg):

$$M_{CaCO_3} = M_{ca^{2+}} \cdot 50 \qquad (2)$$

Antiscalant efficiency as a calcium carbonate inhibitor was calculated by using the following equation:

$$E(\%) = \frac{M^{blank}_{CaCO_3} - M^{antiscalant}_{CaCO_3}}{M^{blank}_{CaCO_3}} \bullet 100\,, \qquad (3)$$

where: $M^{blank}_{CaCO_3}$, $M^{antiscalant}_{CaCO_3}$ – mass of calcium carbonate accumulated in membrane module in the absence of antiscalant and with antiscalant dosing respectively, meq (mg).

Imitates of seawater and product water after seawater treatment by nanofiltration and low pressure reverse osmosis membranes were prepared according to Table 2 datasheet. For pH correction, caustic solution was added to the feed water. pH values varied from 7.7 to 9,1. Fig. 3 shows various antiscalants performance with doses 2, 5 and 10 ppm. Antiscalant efficiency is evaluated by dependencies of calcium carbonate amount accumulated on membranes versus concentration coefficient K values.

Lower amount of calcium carbonate scale is observed for conventional reference antiscalant Aminat-K and shows high efficiency of newly proposed PASP-FCC formulation. A special experimental series was devoted to investigation of antiscalants behavior at high pH values. Fig. 4 shows comparison of PASP- FCC, MA/AA and Aminat-K efficiencies with doses 5 and 10 ppm. As it was already discussed, sea water desalination requires high pH values in the feed water to efficiently reject boron. To increase pH, caustic solution was added to the feed water solution. Fig. 5 shows results of calcium carbonate scaling rates determination in the presence of Aminat-K and PASP-FCC under different pH conditions (pH = 7,7 and pH = 8,9) and antiscalant concentrations 5 ppm and 10 ppm. The raise of pH value also increases calcium carbonate scaling rate and requires increase of antiscalant concentration to better control scaling. At 10 ppm MA/AA antiscalant exhibits even better performance than Aminat-K.

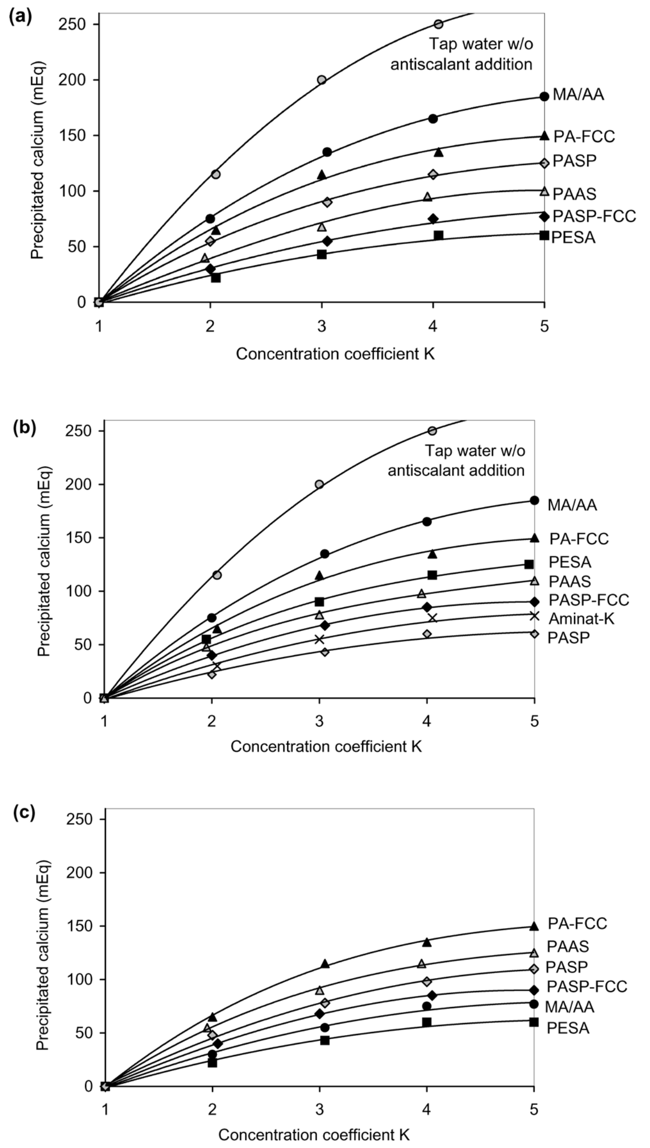


Fig. 3. Experimental results: mass of precipitated calcium carbonate in the presence of antiscalants versus K, influence of antiscalant dose (pressure is 16 bar, pH = 8.8): 1) antiscalant dose is 2 ppm; 2) antiscalant dose is 5 ppm; 3) antiscalant dose is 10 ppm.

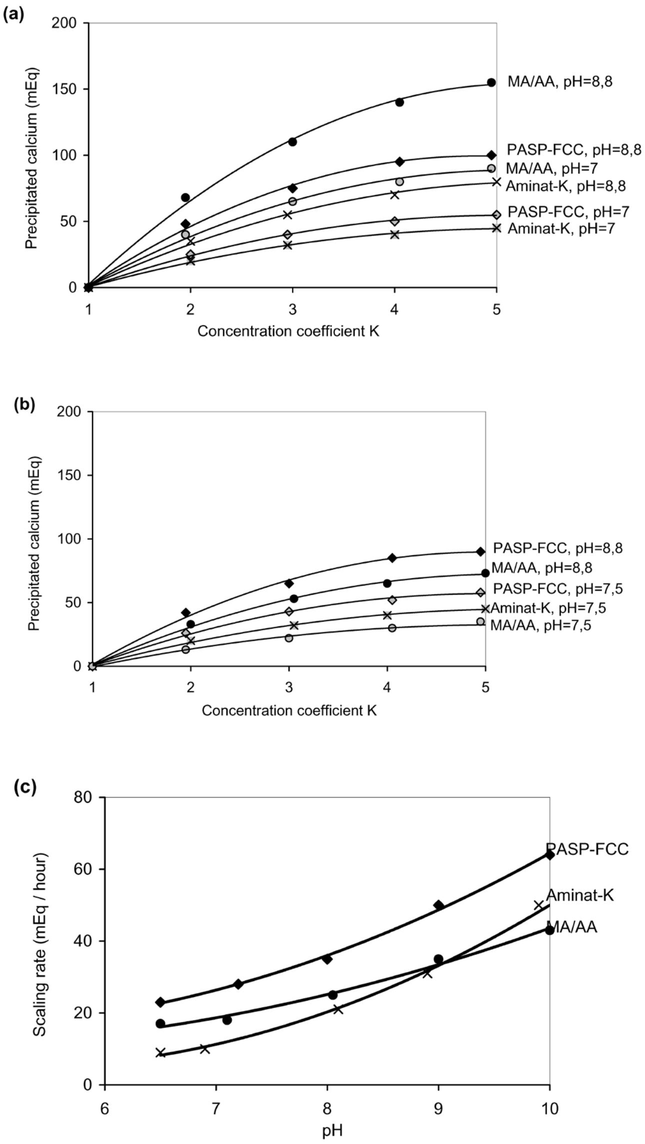


Fig. 4. Influence of pH and antiscalant dose values on efficiency of calcium carbonate growth reduction: a) antiscalant dose is 5 ppm; b) antiscalant dose is 10 ppm; c) antiscalant dose is 10 ppm; pressure is 16 bar.

3. Results and discussion: Industrial application of results

The relationships between the accumulated scale, antiscalant concentration and concentration ratio for selected antiscalants are shown in Fig. 3.

The results show that for a number of tested antiscalants the concentration of 3 mg/L is not sufficient to efficiently inhibit calcium carbonate precipitation. The concentration of 10 mg/L has no significant impact on improving the inhibition efficiency compared with concentration of 5 mg/L so most of samples (PESA, PA-FCC, PAAS) were tested at maximum concentration of 5 mg/L.

The highest efficiency was achieved for PASP, Aminat-K, PASP-FCC.

For dose of 5 ppm all tested antiscalants can be arranged in the descending order of efficiencies:

PASP > Aminat-K > PASP-FCC > PAAS > PESA > PA-FCC > MA/AA

And for 10 ppm dose the efficiency descending order looks different:

PASP > MA/AA > PASP-FCC > PESA > PAAS > PA - FCC

Fig. 4 shows results of calcium carbonate growth rates evaluation at high pH values (pH = 8.8) after sodium hydroxide was added to Moscow tap water. Antiscalant doses were 5 ppm (Fig. 4a) and 10 ppm (Fig. 4b). For these experiments PASP-FCC and MA/AA were selected as efficient and available chemicals to recommend for seawater desalination. Fig. 5 shows results of antiscalant testings for

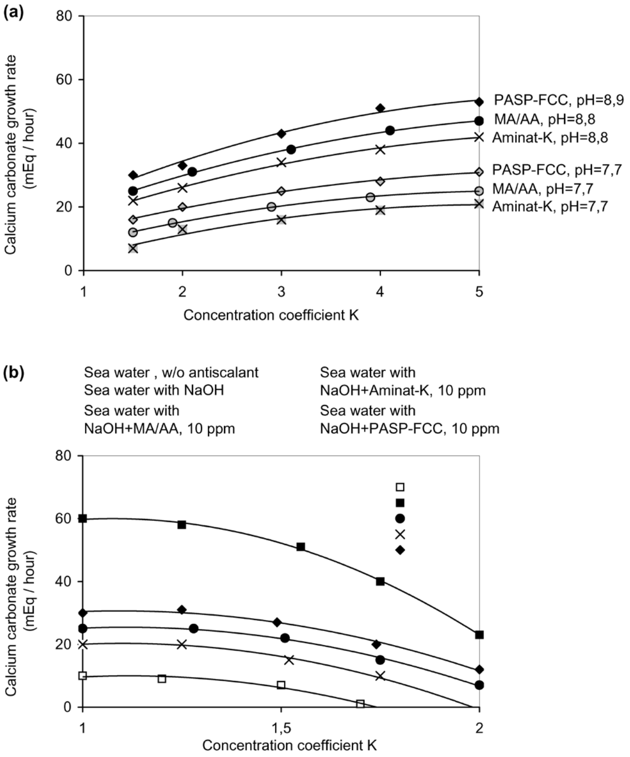


Fig. 5. Results of scaling rates determination during the Black Sea water treatment. Influence of pH values and antiscalant presence: a) scaling rates versus concentration coefficient K during treatment of the first stage product water with BLN membranes, antiscalant dose is 10 ppm; b) influence of pH on scaling rates in 4040 BLN modules during the Black Sea water treatment, BLN membranes.

double-stage seawater treatment. Scaling rates versus concentration coefficient K values were determined at different pH values for treatment of the first stage product water (Fig. 5a). Scaling rates vs. K values for treatment of seawater with BLN membranes for different pH conditions are demonstrated in Fig.5b. Antiscalant doses were 10 ppm.

The descending order for the first stage product water treatment at high pH values is shown below:

MA/AA > Aminat-K > PASP-FCC.

Treatment of the first stage product water (pH values 7.7 and 8.8) membranes provides the following descending order:

Aminat-K > MA/AA > PASP

To sum it up, we can conclude that MA/AA performs better than PASP and Aminat-K at high doses and high pH values. The obtained results for doses less than 5 ppm and for pH values below 8 confirm relative reagent efficiencies found in static testament [1] and those provided by NACE Protocol [22]:

ATMP > HEDP > PESA(400 ÷ 1500 Da) ~ PASP(1000 ÷ 5000 Da) > PAAS (3000–5000 Da) ~ MA-AA

To investigate influence of antiscalant on the structure and shape of growing crystals, SEM microphotos of formed crystals were made.

Scale crystals were flushed off membrane surface after each experiment conducted in circulation mode. Flushing was initiated by opening of pressure regulation valve 15 (Fig. 2) and flush water was collected in flushing tank. The collected flushing solution was filtered through the laboratory filter cell with 0.8 micron microfilter. Microfilters with sedimented sludge were rinsed by distilled water and dried in the oven under 50 degrees (Celsius). Filters were treated by scanning using SEM Quanta 250 FEI under 12.5 and 15 kW voltage in vacuum. Results of microfilters scanning are presented on Fig. 6. For all samples it is obvious that the presence of antiscalant influences growing crystals shapes. It was concluded, that for polymers with high inhibition efficiencies (MAAC, PASP) small size long rounded shape crystals are formed. Fig. 6 demonstrates SEM photos of scale crystals formed in the presence of antiscalants and without antiscalant addition.

For relatively low values of the feed water hardness (up to 8 meq/L) and small values of concentration coefficient K the dose of antiscalant (varied from 2 to 5 ppm) does not significantly influence scaling rates. For larger hardness values and higher recoveries antiscalant doses of 10 ppm become more efficient (Fig. 3c).

To select optimum conditions for seawater desalination (energy consumption, caustic and antiscalant dosing, recovery value), analysis and comparison of all operational costs (energy and chemical consumption, membrane replacement) is required. Rejection and product flow were determined throughout antiscalant testing. To calculate energy consumption of the double stage desalination scheme, energy consumption values of the first stage and of the second stage are summarized. Power consumption values were determined for different membrane types used on the first stage (BLN and 90-NE) and different concentration coefficient K values on the first stage: 1.3; 1.5; 1.5. Second stage recovery value determines overall recovery value of the double stage desalination unit and should have the highest possible value. Calculations were performed for three operational modes of the double stage desalination unit:

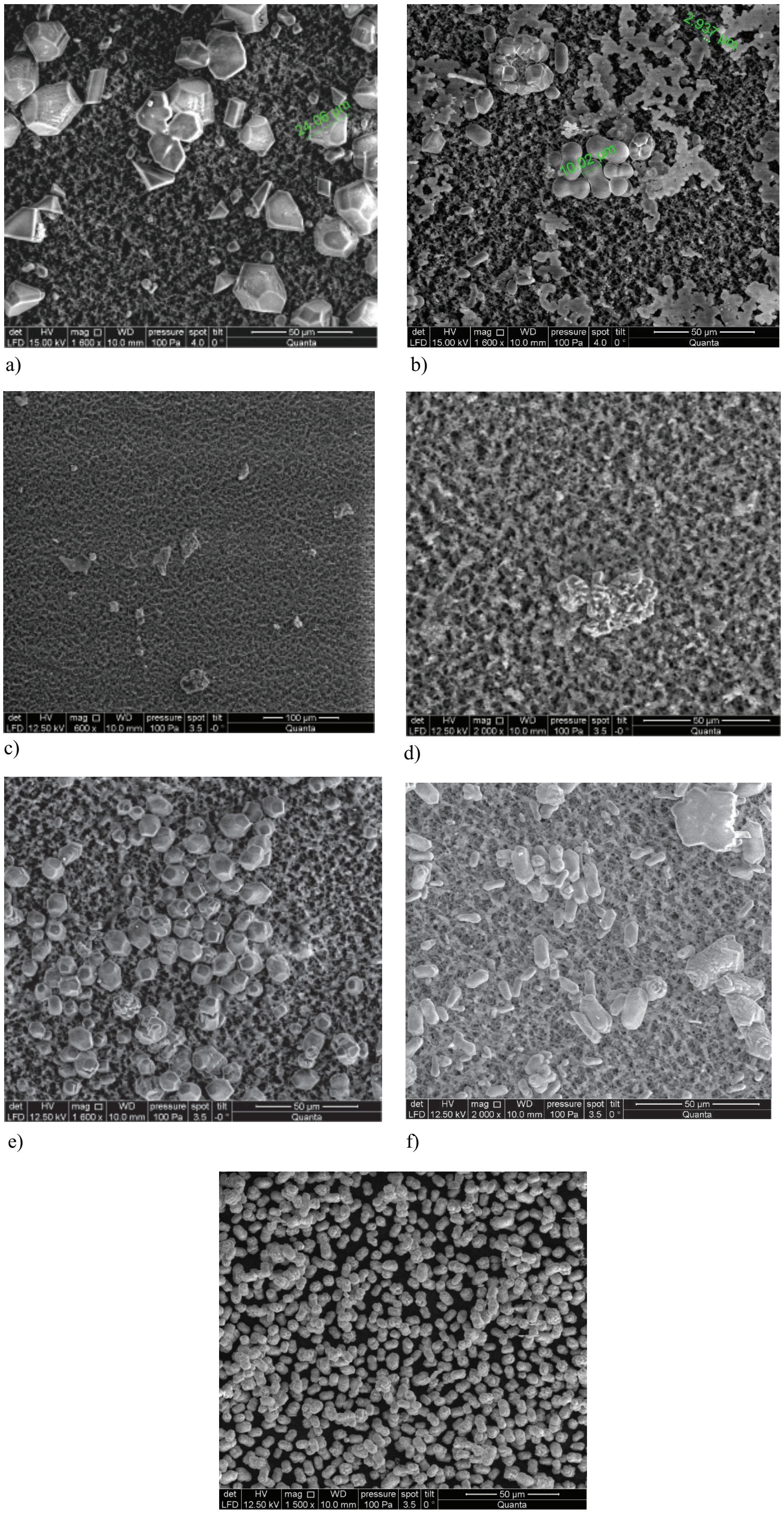
1. First stage K is 2 (90-NE membranes are used on the first stage). Second stage K is 2.5;
2. First stage K is 1.5 (BLN membranes are used on the first stage). Second stage K is 4;
3. First stage K is 1.3 (BLN membranes are used on the first stage). Second stage K is 5.

Operational costs are presented as a function of the double stage total coefficient K value.

Selection optimum recovery value is dependent on boron rejection. Fig. 7 shows dependencies of boron rejection on the feed water pH values [24]. Membrane rejection characteristics during one-stage sea water treatment are taken from our previous publications [1] and shown in Fig. 8a. Fig. 8b shows the dependence of boron rejection on the K value for the case when NE 90 product water is further treated by BLN membranes on the second stage.

The first stage product water is provided by 90 NE nanofiltration membranes.

Fig. 8c shows rejection characteristics of BLN membranes on the second stage when the first stage BLN membrane product water was treated. First stage product water pH value was corrected by caustic addition and had 7.0 ; 8.0 and 9.0 values. High product water quality at the highest



a) b) c) d) e) f) g)

Fig. 6. Microphotos of calcium carbonate crystals formed without antiscalant addition (a) and in the presence of MA/AA, 5ppm (b), PASP, 3 ppm (c), Aminat-K, 5 ppm (d), PAAS, 2 ppm (e), PESA, 10 ppm (f) and PASP-FCC, 2 ppm (g).

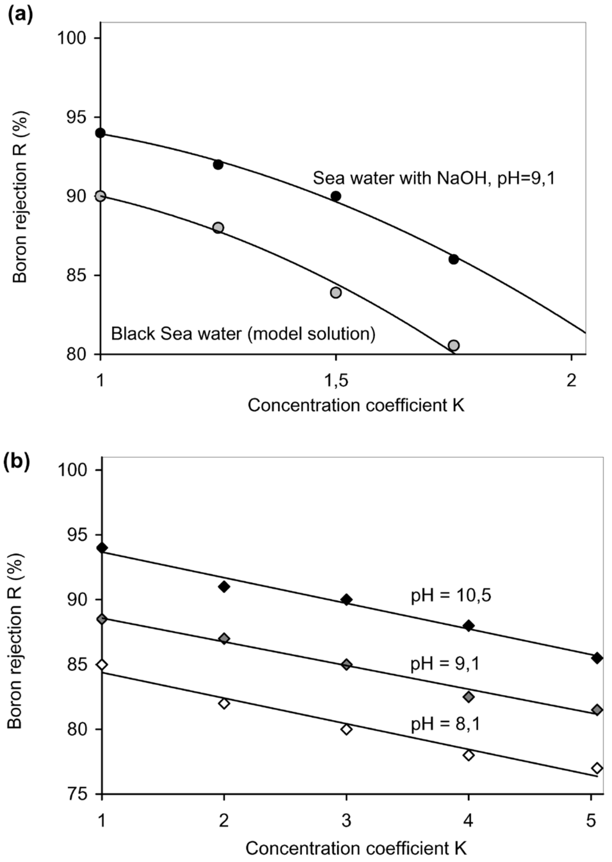


Fig. 7. Boron rejection (%) versus concentration coefficient (K) and pH values at different stages of seawater desalination: a) first stage, pressure 16 bar, medium pressure membranes BE (CSM), b) second stage, pressure 16 bar, low pressure membranes BLN (CSM).

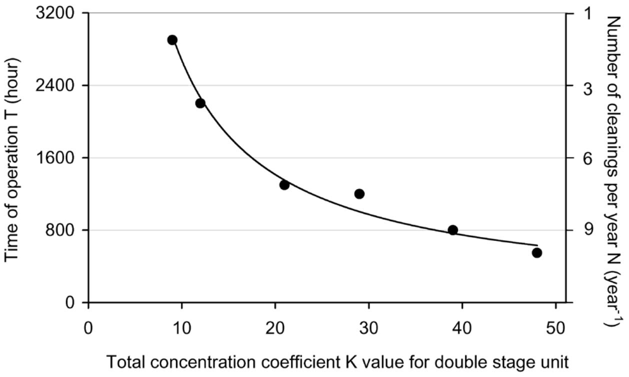


Fig. 8. Determination of operational time between cleanings and annual number of cleanings.

possible recovery value corresponds to the highest feed water pH value. The higher second stage recovery is, the lower are energy costs on the second stage and the double stage scheme at large.

Chemical costs constitute an important and largest part of annual operational costs. Time intervals between routine cleanings are determined basing on scaling rates data and antiscalant performance. Fig. 8 shows the plot that determines the operational time between cleanings versus calculated calcium carbonate scaling rate values (in meq/h/m^2) in industrial spiral wound modules obtained in previous research [1,25]. Cleaning costs for one 8040 type module were evaluated as $20. Scaling rates under certain conditions (antiscalant type, antiscalant dose, feed water pH, feed water chemical composition, recovery value etc.) are determined throughout experiment conduction. Fig. 9 shows antiscalant and cleaning chemicals annual costs per

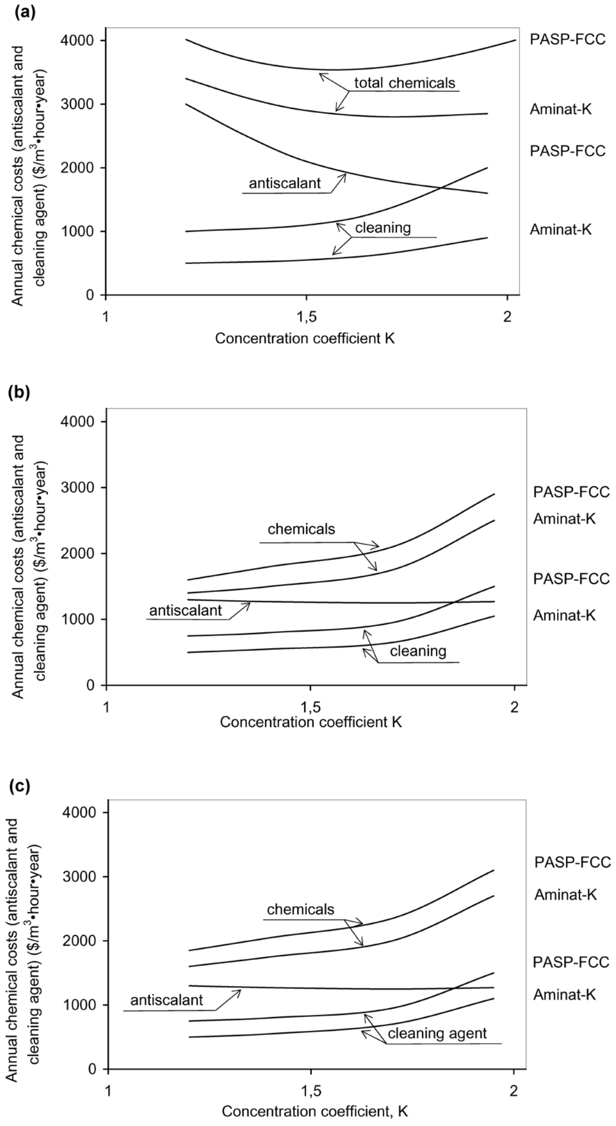


Fig. 9. Calculation of annual chemical costs (cleaning agents and antiscalant): a) single-stage scheme: cleaning agent consumption – 16 kilos per cleaning; antiscalant dose – 10 ppm; b) double-stage scheme, first stage: NE-90 membranes; second stage: BLN membranes: cleaning agent consumption – 4 kilos per one cleaning; antiscalant dose – 10 ppm; c) double-stage scheme, first stage: BLN membranes, second stage: BLN membranes: cleaning agent consumption – 7 kilos per cleaning; antiscalant dose – 10 ppm.

1 m^3/h desalination unit for one stage and second stage desalination schemes. The costs are presented as dependencies versus concentration coefficient values K on the first and the second stage. Chemical costs are determined for severe scaling conditions in the feed water assuming that pH value of the seawater (with one stage treatment) and of the first stage product water (with double-stage treatment) was 9. Antiscalant dose was 10 ppm. The cost of caustic addition is not accounted in these calculations as it could be considered negligible compared to antiscalant and cleaning agents pricing.

Fig. 10 shows an example of determination of optimum operational modes that correspond to minimum of operational costs and corresponding values of total concentration coefficient K. Optimum recoveries were determined for three different desalination flow diagrams, both for single-stage and double-stage desalination schemes. For Black Seawater desalination double stage with BLN membranes on the first and on the second stages demonstrated the lowest value of operational costs (Fig. 10c). This is explained by low TDS of the first stage product water and high recovery (and high K value) reached on the second stage with lowest energy consumption.

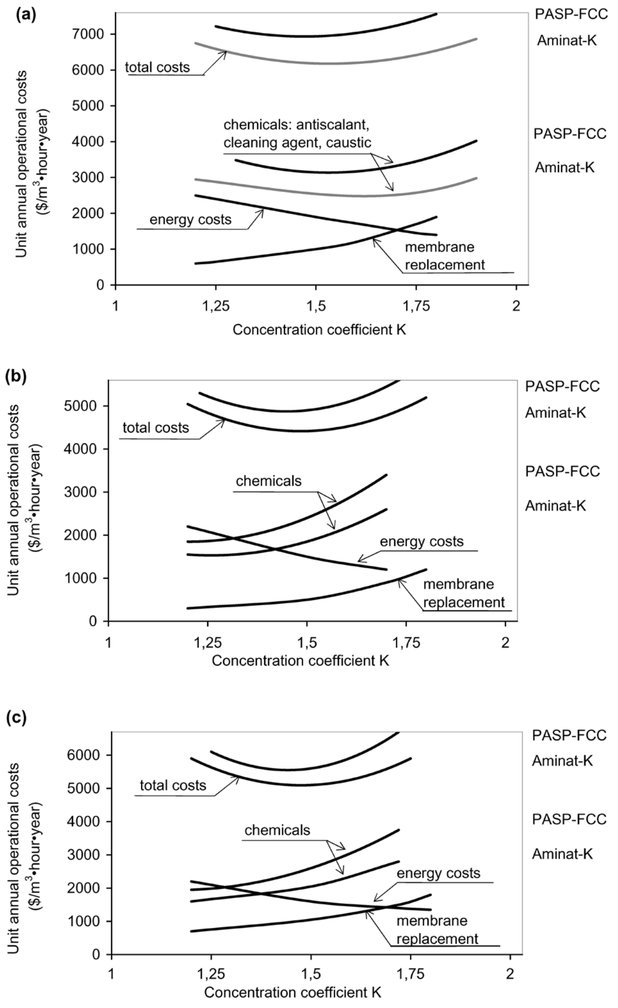


Fig. 10. Determination of optimum values of K for different desalination schemes.

The use of antiscalant plays very important role in implementation of this double-stage desalination due to necessity of pH increase and scaling control. The decrease of recovery causes the increase of energy consumption. The use of low efficient antiscalant (that is reflected by the increase of scaling rate in membrane modules on the second stage) requires increase of annual cleaning costs. Thus antiscalant efficiency becomes a decisive factor when sea water desalination techniques are developed.

To sum it up, main steps to determine operational costs are reviewed:

1. Select the desalination scheme: double-stage or single-stage. Depending on membrane type we determine recovery and K values and membrane costs.
2. Determine the required boron rejection value basing on feed water composition (Fig. 8);
3. Determine the necessary pH value in the feed water to efficiently reject BO_3^- ion. Evaluate required amount of caustic to increase pH value.
4. For selected antiscalant type, feed water required pH value and K value we determine scaling rate value (Fig. 5);
5. Scaling rate values give us a recommended operational time intervals between cleanings and cleaning costs (Fig. 8).

4. Conclusions

New phosphorous-free antiscalants were tested and their efficiencies were compared to performance of commercially available "conventional" phosphonic-based antiscalant Aminat-K. Antiscalants were tested under severe pH conditions of seawater desalination. The test procedure was aimed at determination of calcium carbonate scaling rates in commercial membrane modules during treatment of the Black Sea water imitates after pH adjustment. A newly developed product PASP-FCC (polyaspartate-based polymer) was selected as most promising and available chemical for sea water desalination.

Processing of experimentally obtained data provided scaling rate values for different recoveries of RO desalination facilities and pH values of the feed sea water.

The increase of recovery on both steps of sea water desalination provides energy savings and reduces chemical consumption. Analysis of main relationships describing sea water desalination with RO and NF membranes indicates that antiscalant efficiency plays a significant role in total operational costs formation. Along with economic advantages and cost savings new "green" antiscalants provide a substantial ecological effect.

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References

[1] A. Antonya, J.H. Low, S. Gray, A.E. Childressc, P. Le-Clecha, G. Leslie, Scale formation and control in high pressure membrane water treatment systems: A review, J. Membr. Sci., 383 (2011) 1–16.

[2] A.G. Pervov, Scale formation prognosis and cleaning procedure schedules in RO systems operation. Desalination, 83 (1991) 77–118.

[3] J. MacAdam, S.A. Parsons, Calcium carbonate scale formation and control, Rev. Environ. Sci. Biotechnol., 3 (2004) 159–169.

[4] M.M. Reddy, G.H. Nancollas, Calcite crystal growth inhibition by phosphonates, Desalination, 12 (1973) 61–73.

[5] T.A. Hoang, H.M. Ang, A.L. Rohl, Investigation into the effects of phosphonic inhibitors on the formation of calcium sulfate scales, Desal. Water Treat., 29 (2011) 294–301.

[6] Scale Inhibitor Market by Type and by Application – Global Trends & Forecast to 2019 /http://www.researchandmarkets.com/reports/2933881/scale-inhibitor-market-by-type-and-by-application#pos-0.

[7] S. Lattemann, T. Höpner, Environmental impact and impact assessment of seawater desalination, Desalination, 220 (2008) 1–15.

[8] J.-S. Chang, Understanding the role of ecological indicator use in assessing the effects of desalination plants, Desalination, 365 (2015) 416–433.

[9] M. Feiner, S. Beggel, N. Jaeger, J. Geist, Increased RO concentrate toxicity following application of antiscalants – acute toxicity tests with the amphipods Gammarus pulex and Gammarus roeseli, Environ. Pollut., 197 (2015) 309–312.

[10] D. Hasson, H. Shemer, A. Sher, State of the art of friendly “Green” scale inhibitors: A review article, Ind. Eng. Chem. Res., 50 (2011) 7601–7607.

[11] K.D. Demadis, E. Neofotistou, E. Mavredaki, M. Tsiknakis, E.-M. Sarigiannidou, S.D. Katarachia, Inorganic foulants in membrane systems: chemical control strategies and the contribution of green chemistry, Desalination, 179 (2005) 281–295.

[12] K.I. Popov, N.E. Kovaleva, G.Ya. Rudakova, S.P. Kombarova V.E. Larchenko, Recent state-of-the-art of biodegradable scale inhibitors for cooling water treatment applications (review), Thermal Eng., 63 (2016) 122–129.

[13] S.A. Ali, I.W. Kazi, F. Rahman, Synthesis and evaluation of phosphate-free antiscalants to control $CaSO_4·2H_2O$ scale formation in reverse osmosis desalination plants, Desalination, 357 (2015) 36–44.

[14] H. Wang, G. Liu, J. Huang, Y. Zhou, Q. Yao, S. Ma, K. Cao, Y. Liu, W. Wu, W. Sun, Z.Hu, Performance of an environmentally friendly antiscalant in $CaSO_4$ scale inhibition, Desal. Water Treat., 53 (2015) 8–14.

[15] J. Chen, L. Xu, J. Han, M. Su, Q. Wu, Synthesis of modified polyaspartic acid and evaluation of its scale inhibition and dispersion capacity, Desalination, 358 (2015) 42–48.

[16] Y.H. Sun, W.H. Xiang, Y. Wang, Study on polyepoxysuccinic acid reverse osmosis scale inhibitor, J. Environ. Sci., 21 (Supplement 1) (2009) S73–S75.

[17] Z. Amjad, P.G. Koutsoukos, Evaluation of maleic acid based polymers as scale inhibitors and dispersants for industrial water applications, Desalination, 335 (2014) 55–63.

[18] M. Chaussemier, E. Pourmohtasham, D. Gelus, N. Pécoul, H. Perrot, J. Lédion, H. Cheap-Charpentier, O. Horner, State of art of natural inhibitors of calcium carbonate scaling. A review article, Desalination, 356 (2015) 47–55.

[19] M.M. Jordan, E. Sorhaug, D. Marlow, Red vs. green scale inhibitors for extending squeeze life-a case study from the North Sea, Norwegian sector-part II, SPE Product. Oper., 27 (2012) 404–413.

[20] A. Benbaki, T. Bachir-Bey, Synthesis and characterization of maleic acid polymer for use as scale deposits inhibitors, J. Appl. Polym. Sci., 116 (2010) 3095–3102.

[21] K. Popov, G. Rudakova, V. Larchenko, M. Tusheva, E. Afanas’eva, S. Kombarova, N. Kovaleva, A comparative performance ranking of some phosphonates and environmentally friendly polymers on $CaCO_3$ scaling inhibition by NACE protocol, Desal. Water Treat., in press.

[22] K. Popov, G. Rudakova, V. Larchenko, M. Tusheva, S. Kamagurov, J. Dikarev, A comparative calcium sulfate scaling inhibition performance of some phosphonates and polymers characterized by NACE protocol, DLS, XRD and SEM, Desalination, in press.

[23] NACE Standard TM0374-2007 (formerly TM0374-2001). Item No. 21208. Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution (for Oil and Gas Production Systems), 2007.

[24] A.G. Pervov, A.P. Andrianov, A new solution for Caspian Sea desalination: low pressure membranes, Desalination, 157 (2003) 377–384.

[25] A.G. Pervov, Scale formation prognosis and cleaning procedure schedules in RO systems operation, Desalination, 83 (1991) 77–118.

[26] A.G. Pervov, A simplified RO process design based on understanding of fouling mechanisms, Desalination, 126 (1999) 227–247.