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The development and evaluation of new biodegradable acrylic acid based antiscalants for reverse osmosis

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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: low phosphorus and biodegradable. In this study 8 samples of low phosphorus inhibitors based on co-polymers of acrylic and methacrylic acid was prepared and tested to prevent calcium carbonate precipitation in comparison with commonly used chemicals. The results shows that the best effect was achieved using rarely cross-linked co-polymer of methacrylic acid and sucrose allyl ether (RPAC-4), rarely cross-linked co-polymer of acrylic acid and sucrose allyl ether (CAAC) and co-polymer of methacrylic acid and maleic anhydride (MAAC). The inhibition efficiency of synthesized polymers was the same or better in comparison with oxyethylidenediphosphonic acid (OEDP), nitrilotrimethyl phosphonic acid (NTP) and inhibitor "Aminat-K" (based on phosphonic acids). At the same time high antiscalant efficiency is achieved at the lower dose (3 mg/L) for inhibitor MAAC.

Keywords: calcium carbonate, green antiscalants, methacrylic acid, reverse osmosis, scale inhibition, sucrose allyl ether

Introduction

The reverse osmosis plant concentrates containing antiscalants (based on phosphonic or phosphoric acid) discharged into surface reservoirs, posing serious environmental problems associated with eutrophication of water bodies. A number of studies on the synthesis of new polymers are focused on the development of a new generation of inhibitors that do not contain phosphates and other nutrients as well as biodegradable in natural environment – the so-called "green" inhibitors. For the successful implementation in water treatment new inhibitors should ensure effective prevention of calcium sulfate and calcium carbonate scales in reverse osmosis membrane modules coupled with high recoveries and low doses, which will favour the economic attractiveness of their application.

The main problems associated with the addition of antiscalants to control mineral salts precipitation are the high cost of chemicals and environmental impact associated with concentrate disposal. If the concentrate stream is subjected to a chemical treatment for extraction or crystallization of salts the presence of antiscalant can cause certain difficulties and prevents the precipitation of calcium from concentrate even at high saturation levels.

The potential environmental impact of seawater desalination plants have been well discussed in literature (Lattemann et al, 2008; Chang, 2015; Feiner et al, 2015). Generally, the concentration of scale inhibitors in the discharged concentrate is low and presents a low risk for the marine environment and aquatic organisms, but the evaluation of antiscalants toxic effect on aquatic organisms carried out in (Feiner et al, 2015) showed that the its impact on the aquatic environment is not clearly understood. The potential problems can occur when using polyphosphates as they are simply hydrolyzed into orthophosphate and lead to eutrophication. Carboxylic acid and phosphates are more stable to biodegradation. High phosphate content causes a known problem in municipal wastewater treatment as well (Gogina et al, 2014).

Nowadays a large number of antiscalants is produced all over the world. These chemicals can be classified into the following groups:

1. Polyphosphates (Sodium triphosphate, Sodium hexametaphosphate etc.);
2. Complexons including phosphonates (Ethylenediaminetetraacetic acid (EDTA), Oxyethylidenediphosphonic acid, Nitrilotrimethyl phosphonic acid, Polyethylenepolyamine-N-methylphosphonic acid, 2-Phosphonobutane 1,2,4-tricarboxylic acid, Methylene phosphonic acid based compounds etc.);
3. Polymers (Polyacrylic acid, Polymethacrylic acid, Polymaleic acid, Polymethyl methacrylate, Polyethyl methacrylate, Polyisobutyl methacryalte etc.);
4. Co-polymers.

Polymers and co-polymers are used to synthesis a green scale inhibitors. Husson et al. (2011) states that the most promising green antiscalants are currently based on polyaspartic acid. These inhibitors were developed in the early nineties and have wide application, including corrosion inhibition, sludge formation, water softening and as ecologically friendly chemicals in detergent formulations (Hasson et al, 2011; Ali et al, 2015; Shemer et al, 2014). Poly(aspartic acid) does not contain nitrogen and phosphorus and is sufficiently biodegradable (Thombre et al, 2005; Gao et al, 2009).

The study (Martinod et al, 2009) conducted using the imitate of North Sea water shows that polyaspartic acid dose of 4 mg/L provides a significant reduction in precipitation of calcium carbonate, leads to vaterite formation in preference to calcite seen in uninhibited solutions. Numerous studies carried out under various conditions also showed high efficiency of this antiscalant for calcium sulfate scale inhibition (Ali et al, 2015; Shemer et al, 2014; Quan et al, 2008; Chaussemier et al., 2015). The best results are shown for antiscalant with lower molecular weight (Ali et al, 2015).

To improve the performance of polyaspartic acid based antiscalants there are modified with attachment of open-chain polysuccinimide functional groups. For example, in (Chen et al, 2015) was reported about scale inhibition property of polyaspartic acid modified by inculcation of serine. Modified polyaspartic acid was tested with respect to calcium carbonate, sulfate and phosphate and demonstrates scale inhibition efficiency close to 100% at a dose of 4 mg/L for calcium carbonate.

Another green antiscalant developed in the nineties in the US is a polyepoxysuccinic acid (Sun et al, 2009; Zhou et al, 2011). As well as a polyaspartic acid it has the favorable characteristics: does not contain nitrogen and phosphorus and is readily biodegradable. The findings of this study (Zhou et al, 2011) showed that polyepoxysuccinic acid dose of 10 mg/L have average efficiency of the calcium carbonate scale inhibition above 90% (with different content of calcium – 40 mg/L, 100 mg/L and 200 mg/L). This inhibitor can be used for various water compositions. In (Liu et al, 2012) was indicated that polyepoxysuccinic acid gives the best effect with respect to $CaCO_3$ and $SrSO_4$ and polyaspartic acid – with respect to $CaSO_4 \cdot 2H_2O$ and $BaSO_4$. Nevertheless, wide industrial tests of polyepoxysuccinic acid based antiscalants have not yet conducted and the performance of these compounds requires further confirmation (Quan et al, 2008).

A third promising class of inhibitors is a biodegradable and non-toxic polysaccharide-based polycarboxylates which are obtained from inulin by chemical synthesis (e.g. carboxymethylinulin). These compounds have significant inhibition effect on calcium carbonate crystallisation thanks to the presence of carboxylic acid groups in its structure (Martinod et al, 2009; Chaussemier et al, 2015). Kirboga and Öner (Kirboga et al, 2012) concluded that the higher the number of negatively charged functional groups of carboxymethylinulin, the higher its effectiveness was with respect to calcium carbonate precipitation. The inhibitor effects on the morphology and polymorph of calcium carbonate crystals.

A number of studies (Wang et al, 2014; Amjad et al, 2014; Popuri et al, 2014) devoted to maleic acid based antiscalants. Thus, in (Amjad et al, 2014) the test results of 14 inhibitors based on acrylic and maleic acid are presented. Tests were conducted using supersaturated solutions of calcium sulphate and calcium carbonate (hydrocarbonate) at 66 °C. The highest inhibitory ability at low doses (about 2 mg/L) showed a low molecular weight (~ 2000 MW) compounds – polyacrylic acid, polymaleic acid and other polymers with free carboxyl groups. More complex compounds created on the maleic acid base exhibit better scale control properties – for example hydrolysed polymaleic anhydride and its mixtures with 1-hydroxyethane-1,1-diphosphonic acid and polyacrylic acid (Shen et al, 2012).

However, we should also consider more traditional antiscalant – polycarboxylates due to their high efficiency and environmental suitability, the most common are polyacrylates with a molecular weight in the range of 5000-6000 g/mol and polymers based on polyacrylates (Antonya et al, 2011). Polyacrylates are highly effective at the stage of nucleation and crystallization for scale-producing salts due to its adsorption on the growing seed crystals. Selection of an optimal dose of polyacrylate is very important, since at lower concentrations polyacrylates do not effectively inhibit the formation of a precipitate, whereas the high concentration is uneconomical, and may additionally have side effects such as gel-formation on the membrane surface (Yuchi et al, 2007).

In addition to these simple compounds, a number of studies devoted to the development of complex mixed polymeric antiscalants (co-polymers). Using a set of polymers with different properties to synthesize inhibitors enhances its effectiveness and application range (Wang et al, 2014; Popuri et al, 2014; Zhang et al, 2007). Popuri et al (2014) used synthesized green antiscalants – copolymers of maleic and citric acids to prevent precipitation of calcium phosphate and Ling et al (2012) tested a new non-phosphorus antiscalant – acrylic acid (AA)-allyloxy poly(ethylene glycol) polyglycerol carboxylate copolymer – to prevent precipitation of calcium carbonate, sulfate and phosphate in cooling systems.

Recent advances in the antiscalant development are in the field of synthesizing dendritic polymers with highly branched three-dimensional structure, some of which can be used as an environmentally friendly antiscalants (Demadis et al, 2005). Mavredaki et al (2007) reported about the development of new types of green antiscalants for silica inhibition –

polyaminoamide dendrimers and polyethyleneimine, in combination with carboxymethylinulin and polyacrylate polymers.

Several reports have been made on natural organic molecules as scale inhibitors that are environmentally acceptable compared with conventional inhibitors (Chaussemier et al, 2015). It is known that the hydrophobic organic acids – humic and fulvic acids at concentrations of 0.2 mg/L and higher can reduce growth of calcium carbonate crystals. At a concentration of 5 mg/L scale formation is almost completely inhibited (Hoch et al, 2000). A SEM study suggested that the surface growth sites of the crystals were blocked by adsorbing ligands (Hoch et al, 2000). The same results were obtained by Gauthier et al (2012) who studied the calcium carbonate scale ability of humic acid in synthetic water. Nevertheless, the humic substances are not used as antiscalants for industrial applications.

The natural carboxylic acids also seem to be a good antiscalants. Wada et al (2001) studied the influence of five natural carboxylic acids (malonic acid, maleic acid, succinic acid, tartaric acid and citric acid) on $CaCO_3$ crystallisation and concluded that the inhibitory capacity is depended on the number of carboxyl groups in the molecule.

It is reported about studies on the effect of citric acid, leucine, glutamic acid, cysteine-rich peptide, xanthan on calcite (calcium carbonate) growth rate (Chaussemier et al, 2015). Also promising natural inhibitors may be plant extracts: several authors studied the antiscalant performance of different leaf extracts from the fig trees, olive trees, coffee trees, *Punica granutum*, *Aloe Vera* and other plants. The inhibitory effect of natural compounds related to the presence of polyphenols and polysaccharides which have a hydroxyl and / or carboxyl functional groups that interact with the divalent ions Ca^{2+} and Mg^{2+} to form complex compounds (Belarbi et al, 2014).

Another way to obtain biodegradable and eco-friendly antiscalants is chemical modification of natural by-products from industrial process (Chaussemier et al, 2015). It can be modified collagens with rich carboxyl groups from collagen extracted by hydrolyzing chrome shavings from leather production industry or a polysaccharide sulfonated salt synthesized from a hetero-polysaccharide extracted from corn stalks.

Natural scale inhibitors are still at the stage of laboratory research and, in addition to environmental and other benefits, have a drawback – low concentration of active ingredients and as a result the high doses needed to effectively prevent scaling of slightly soluble salts.

The review of antiscalant market in Russia conducted by authors shows that nowadays the quality of most scale inhibitors produced in Russia is unstable and need the improvement, at the same time biodegradable antiscalants is not produced and do not present on Russia market. The largest Russian manufacturers produce wide scale of antiscalants based on well-known compounds: NTP, OEDP, DIFALON and DIFONAT (the main active ingredient is a mixture of phosphonic and aminoalkylphosphonic acids), IOMC-1 (an aqueous solution of sodium salts methyliminobis-(methylenephosphonic) acid, NTP and phosphorous acid), AMINAT series (based on phosphonic acids and on aqueous solutions of sodium and ammonium salts of NTP and methyliminobis-methylenephosphonic acid) and others chemicals, based on OEDP, NTP and phosphonates.

Based on literary review, the availability of raw materials in Russian for antiscalant production and existing experience in polymer synthesizing the selection has been made in favour of acrylic and methacrylic acid co-polymers with biodegradable fragments and low phosphorus antiscalants.

2. Experimental

2.1 Materials

In order to obtain different spatial structure of polymers that meet the required properties the polymerisation reactions of acrylic acid have been chosen using the following cross-linking agents: N,N'-methylene-bis-acrylamide; polyallyl ethers of pentaerythritol (the main component is a pentaerythritol triallyl ether) and polyallyl sucrose (the main component is hexa-polyallyl sucrose).

These cross-linking agents were chosen due to the peculiarities in formation of different spatial polymer structures. Since N,N'-methylene-bis-acrylamide has two reaction sites for the polymerization process and it is commonly used in the synthesis of polymeric hydrogels based on the acrylic acid. A higher branched structure (as for dendrimers synthesis) is achieved using polyallyl ethers of pentaerythritol, but the most extensive structure will be exhibited for polyallyl sucrose derivatives. The general advantage of the selected cross-linking agents is the presence of a central group which joints the polymer chains branches.

Several test samples of new polymers were synthesized:

- RPAC-1 (rarely cross-linked polymer based on acrylic acid and N, N'-methylene-bis-acrylamide as a cross-linking agent);
- RPAC-2 (rarely cross-linked polymer based on methacrylic acid and N, N'-methylene-bis-acrylamide as a cross-linking agent);
- RPAC-3 (rarely cross-linked co-polymer based on methacrylic acid and allyl ether of pentaerythritol as a cross-linking agent);
- RPAC-4 (rarely cross-linked co-polymer of methacrylic acid and allyl ether of sucrose as a cross-linking agent);
- FPA (phosphorus compound based on derivatives of polymethacrylic acid);
- MAAC (co-polymer of maleic anhydride and methacrylic acid);
- RPAC-5 (mixture of RPAC-2 and polyhexamethyleneguanidine based compound);
- RPAC-6 (mixture of RPAC-6 and polyhexamethyleneguanidine based compound);
- CAAC (rarely cross-linked copolymer of acrylic acid and allyl ether of sucrose as a cross-linking agent).

The reference antiscalants were: NTP, OEDP and Aminat-K (a mixture of sodium salts of nitrilotrimethyl-phosphonic and methyliminobis-methylenephosphonic acids).

All chemicals except Aminat-K, RPAC-5 and RPAC-6 were dry (powder or crystals) and were prepared for dosage as 10 or 20 mg/ml solutions using distilled water. Water solution of

RPAC-4, MAAC and CAAC were prepared by swelling in distilled water during 24 hours to obtain 1 or 2 mg/ml solutions.

All samples were synthesized and characterized (using the NMR and IR spectroscopy) by Russian company ZAO “EKOS-1”. Scaling experiments was conducted in the Water treatment laboratory of Department of Water Supply, National Research Moscow State University of Civil Engineering.

2.2 RO membrane scaling experiments

Membrane scaling tests were carried out using the commercial RO spiral wound membrane modules and a laboratory membrane unit shown on Fig. 1. 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 tests were conducted using RE 1812 element (CSM, South Korea), but through the low flux each test lasted about 5 hours. To speed up the experiments it was decided to choose a 4040 membrane element (model ERN-B-45-300, ZAO STC "Vladipor", Russia) manufactured using ESPA membranes with selectivity up to 98,5 % (0,15% NaCl).

All scaling tests are conducted in circulation mode whereby reject flow (concentrate) is returned to the feed water tank (1) and permeate is collected in separate tank (4). The transmembrane pressure is maintained at 7,0 ± 0,2 bar. The product flux, depending on tap water temperature, is varied from 100 to 150 liters per hour. The virtual selectivity on the tap water was 97,5…98,0 %. The volume of feed solution is 80 ± 2 liters. Concentrate flow is kept constant at 100 ± 10 l/h and recovery rate is 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 is 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 CaCO3), 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 mg/L, chlorides of 8…10 mg/L.

The samples are taken for initial feed solution – from tank (1), for circulated solution – from tank (1) (for various concentration ratios) and for permeate – from tank (4) (one sample characterized the averaged quality of product water).

In all samples are determined: temperature, TDS (conductivity), pH, total hardness, total alkalinity, calcium. Conductivity and temperature is 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 typical doses as indicated below: 0 mg/L (without antiscalant), 3 mg/L, 5 mg/L and 10 mg/L (0; 3; 5 и 10 ml/L respectively for liquid chemicals Aminat-K, RPAC-5 and RPAC-6). Most tests were repeated twice to improve the accuracy of the results.

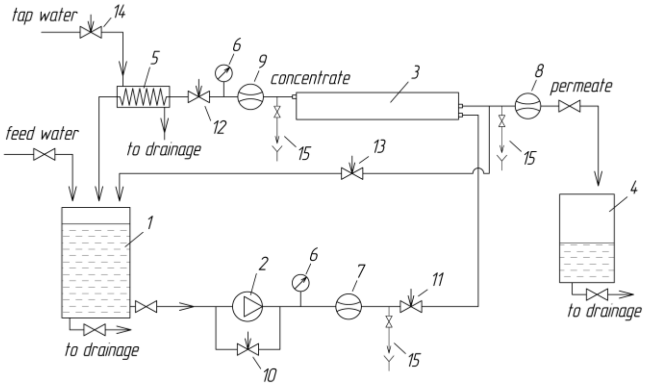


Figure 1. Schematic diagram of laboratory RO unit for membrane scaling tests: 1 – feed water tank; 2 – pump; 3 – spiral wound membrane module; 4 – permeate tank; 5 – heat exchanger; 6 – pressure-gauge; 7 – feed water rotameter; 8 – permeate rotameter; 9 – concentrate rotameter; 10 – by-pass adjusting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

The amount of scales of CaCO3 and CaSO4 (expressed as Ca2+ in meq or mg) accumulated in membrane module 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) (Pervov, 1991; 1999). This difference calculated for concentration ratio 2; 3 and 5. The total hardness and total alkalinity are determined to control the correctness of other parameters determination.

$$M_{Ca^{2+}} = V \cdot C_{Ca^{2+}} - (V_c^t \cdot C_{c\,Ca^{2+}}^t + V_p^t \cdot C_{p\,Ca^{2+}}), \qquad (1)$$

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;

$C_{c\,Ca^{2+}}^t$, $C_{p\,Ca^{2+}}$ – 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:

$$E(\%) = \frac{M_{CaCO_3}^{blank} - M_{CaCO_3}^{antiscalant}}{M_{CaCO_3}^{blank}} \cdot 100, \qquad (3)$$

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

3. Results and discussion

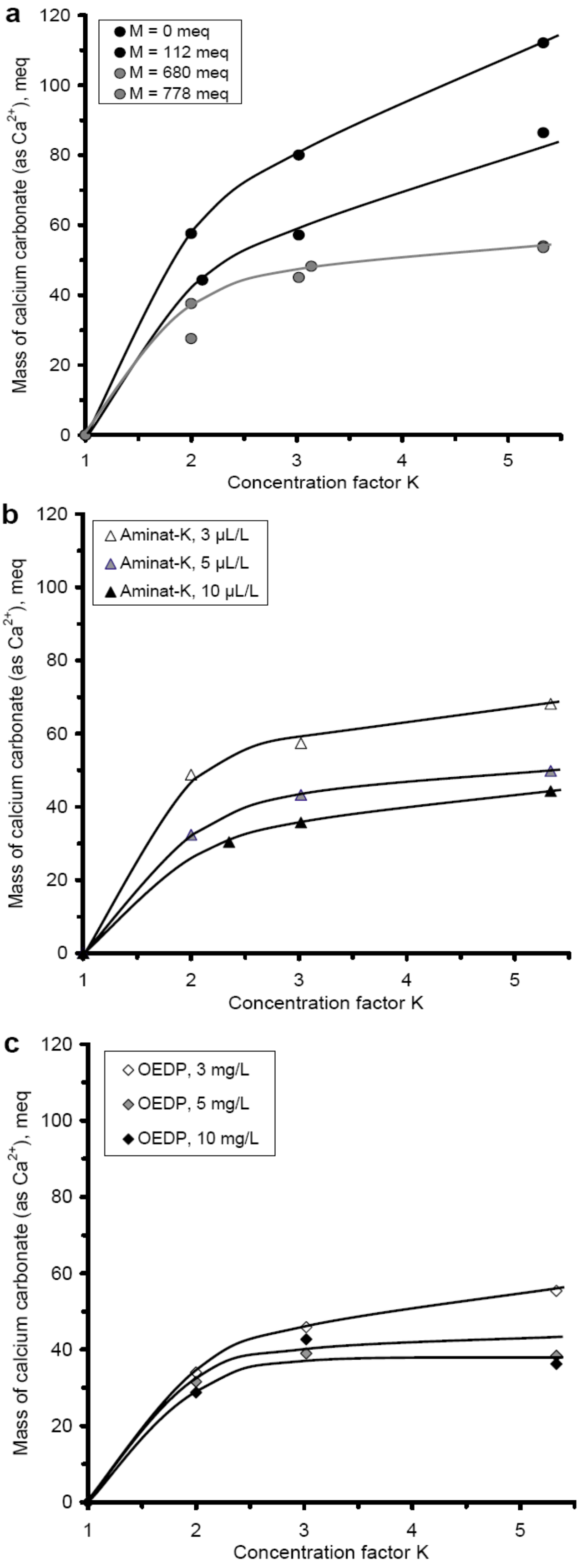
The relationships between the accumulated scale, antiscalant concentration and concentration ratio for selected antiscalants are shown in Fig. 2. The summary results of antiscalants efficiency are listed in the Table 1.

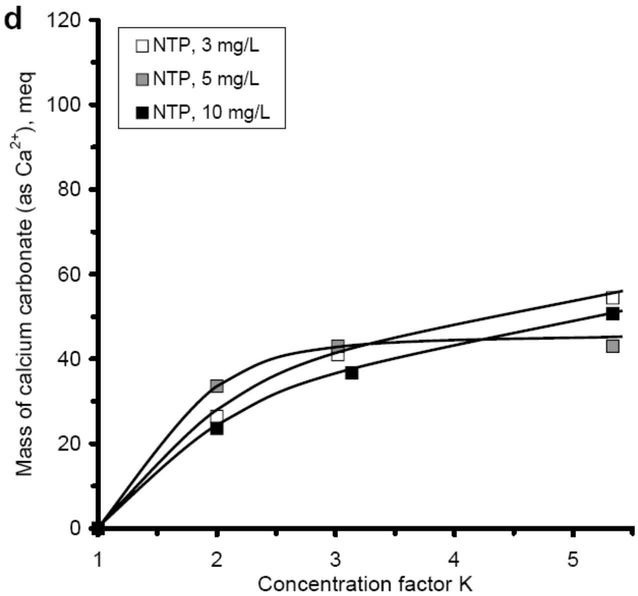
The results show that for a number of tested antiscalants the concentration of 3 mg/L is not sufficient to effectively inhibit calcium carbonate precipitation: OEDP, Aminat-K, FPA. The concentration of 10 mg/L has no significant impact on improving the inhibition efficiency compared with concentration of 5 mg/L so most of samples (CAAC and RPAC series) were tested at maximum concentration of 5 mg/L.

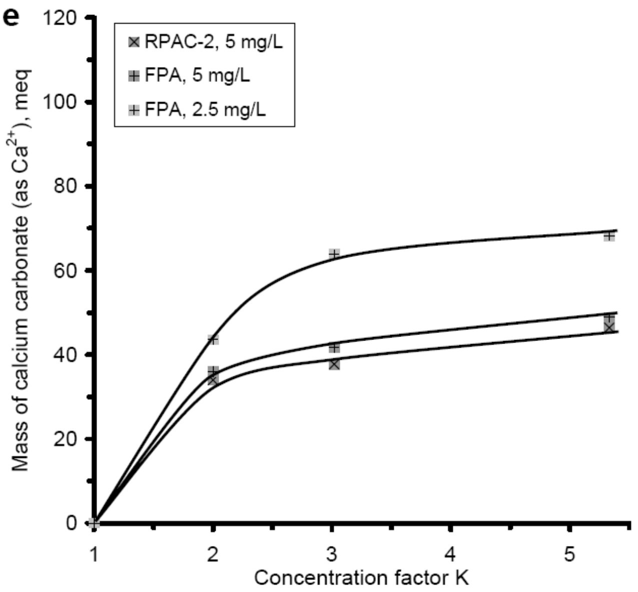
Table 1. The antiscalants efficiency in reverse osmosis tests (concentration factor 5.3)

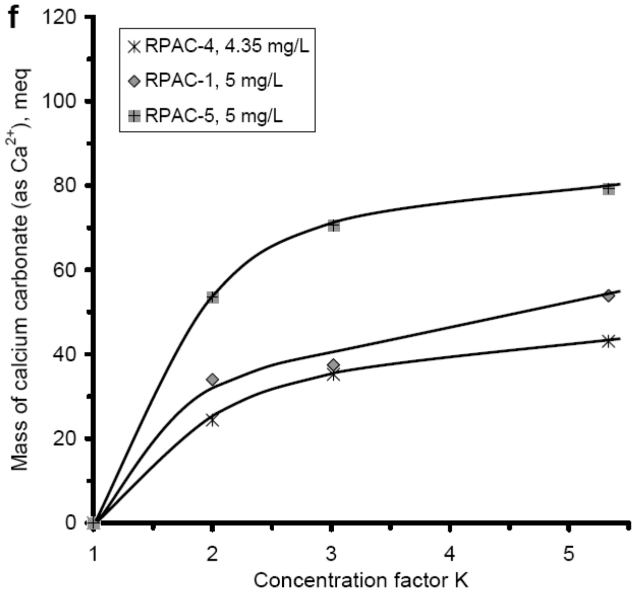
Antiscalant	Dose, mg/L (µL/L)	Inhibitor efficiency, %
Aminat-K	3	32±2
	5	50±3
	10	56±3
OEDP	3	45±3
	5	62±4
	10	64±4
NTP	3	46±3
	5	62±3
	10	49±3
RPAC-2	5	46±3
	5	54±4
FPA	2,5	32±2
	5	51±4
RPAC-4	4,35	57±4
MAAC	3	62±3
	5	75±3
	10	69±3
RPAC-1	5	47±3
RPAC-3	5	40±3
RPAC-5	5	47±2
RPAC-6	5	39±2
CAAC	5	56±3

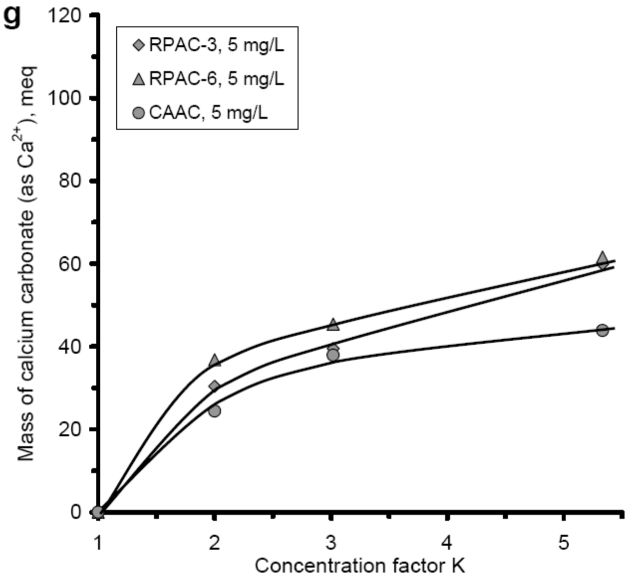
The highest efficiency was achieved for OEDP, RPAC-4, CAAC and MAAC. At the same time MAAC demonstrate the high efficiency at the lowest dose (3 mg/L).











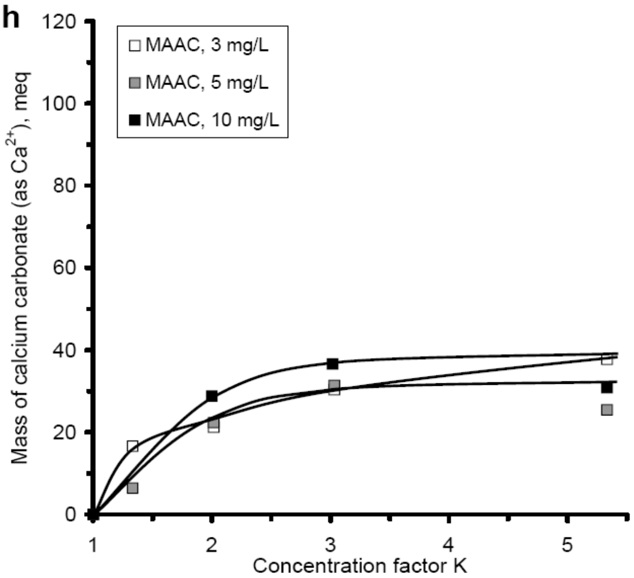
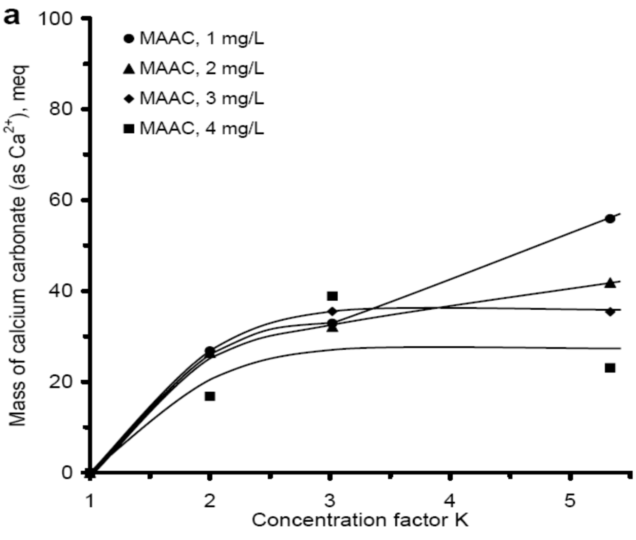


Fig. 2. The relationships between the accumulated scale, antiscalant concentration and concentration ratio



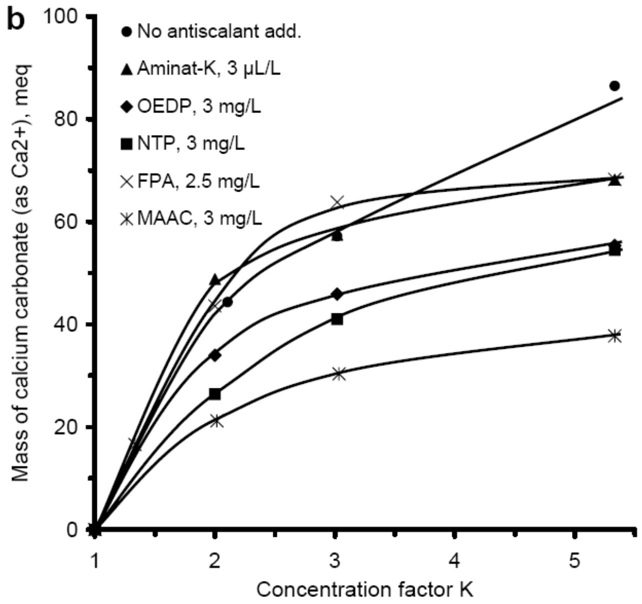


Fig. 3. The inhibition efficiency of MAAC for low concentrations (a) and in comparison with other antiscalants for concentration 3 mg/L (b)

For dose of 5 mg/L all investigated antiscalants can be arranged in the descending order of effectiveness: MAAC > OEDP > NTP ~ RPAC-2 ~ RPAC-4 ~ CAAC > FPA ~ Aminat-K > RPAC-5 ~ RPAC-1 > RPAC-3 ~ RPAC-6.
On the next step several tests were carried out for the best sample MAAC with lower concentrations – 1, 2, 3 and 4 mg/L (Fig. 3). For concentration of 1 and 2 mg/L the MAAC efficiency was low, but comparable to that of other tested samples in range of 5…10 mg/L. Best results were obtained with doses of 3 mg/L or more.
The shape of the relationships of accumulated scale on concentration ratio indicates that at relatively low water hardness (equal to 7…8 meq/L for concentration ratio up to 3) the performance of antiscalant at low concentrations is close to that for higher concentrations, but with further increase in the concentration ratio (and the hardness of circulating solution up to 12…14 meq/L) the mass of accumulated scale becomes inversely proportional to the antiscalant concentration. The further experimental study of these relationships allows us to determine the economically doses of MAAC antiscalant for various compositions of treated water.

4. Conclusions

The trend of the last decade is generation of environmentally friendly antiscalants: low phosphorus and biodegradable. The most promising compounds for synthesis of new inhibitors are polyaspartic acid, polyepoxysuccinic acid, polysaccharide-based polycarboxylates, polymaleic and maleic acid, methacrylic acid, etc. The recent advances in the antiscalant development are in the field of synthesizing dendritic polymers and complex mixed polymeric antiscalants (co-polymers). Finally, a lot of studies devoted to generation green inhibitors from plant extraction or by using natural organic molecules.
Eight samples of pilot low phosphorus inhibitors based on co-polymers of acrylic and methacrylic acid was prepared and tested to prevent calcium carbonate and calcium sulfate in comparison with three reference antiscalants: NTP, OEDP and “Aminat-K”. The best performance are shown by rarely cross-linked co-polymer of methacrylic acid and sucrose allyl ether (RPAC-4), rarely cross-linked co-polymer of acrylic acid and sucrose allyl ether (CAAC) and co-polymer of methacrylic acid and maleic anhydride (MAAC). The inhibition efficiency of these polymers was the same or better in comparison with OEDP, NTP and “Aminat-K”. At the lower doses (≤ 3 mg/L) MAAC showed the superior antiscaling efficiency.
Thus, several synthesized green inhibitors showed quite good inhibitory capacity and are quite competitive compared with traditional antiscalants, and in some cases (MAAK) surpass them. Nevertheless, to create more efficient and thus economically attractive antiscalants which are ready to commercialization the further studies on synthesis and scaling tests is required.
Moreover, the best samples of new antiscalants will be tested using model solutions with high hardness (from 10 to 20 meq/L) and high TDS (seawater) as well.

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