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The use of phosphorus-free antiscalants in BWRO desalination plants and brine disposal pipelines

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ABSTRACT

Today, most RO desalination plants are using phosphorus-based antiscalants for preventing salt precipitation (scaling) and to achieve high membrane performance, as measured by reduced trans-membrane pressure, salt passage and increased permeate flow. However, phosphorus antiscalants in brine disposal can be an environmental issue that should be considered and studied when installing a desalination plant. The purpose of this research is to examine different types of phosphorus-free antiscalants and to find combinations of good membrane performance (varied recovery rates) and environmental antiscalants. Together, the Granot and Lahat BWRO desalination plants will produce approximately 30 Mm^3 in 2014. They are part of a large project: "The Aquifer Rehabilitation," which aims to protect the Israeli costal aquifer from saline infiltration. The concentrate from these inland BWRO desalination plants is sent along a unique 30-km-long brine disposal pipeline to the Mediterranean Sea ("Granot-Ashkelon" pipeline). Obviously, the preferred phosphorus-free antiscalant should prevent salt precipitation (scaling) in both the RO membranes and the lengthy brine disposal pipeline. The use of phosphorus-free antiscalant should achieve stable membrane performance. To date, five different antiscalants (four of them, phosphorus free) were tested at a pilot plant at the Granot site. This BWRO pilot plant contains two systems: (i) the desalination branch, which has similar alignment and pre-treatment as the Granot desalination plant, and (ii) a brine flow system that simulates true brine flow conditions. This system was used to validate the possibility of salt precipitation in the long brine pipeline. Experiment results carried out on four phosphorus-free antiscalants show that stable membrane performance did not occur. This research continues in pursuit of compounds that can satisfy the increasingly stringent environmental requirements in this field. According to the experiments schedule, additional phosphorus-free antiscalant will be tested in Granot BWRO pilot plant.

Keywords: Antiscalants; Phosphorous free; BWRO desalination plant; Reverse osmosis membranes

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1. Introduction

Granot and Lahat BWRO desalination plants, which were established in 2004 and 2011, respectively, are located in the southern part of Israel. In 2014, these plants will collectively produce approximately 30 Mm^3 of desalinated water annually; approximately, 41,600 m^3/d and 42,000 m^3/d for Granot and Lahat, respectively. Both plants are part of a larger project: "The Aquifer Rehabilitation Project," which aims to protect the Israeli coastal aquifer, one of Israel's main national groundwater sources, from saline infiltration. This is accomplished by pumping from a row of approximately 40 wells, which thereby act as a barrier (buffer zone) that prevents the penetration of saline water from the east, westwards into the coastal aquifer (quality of potable water). This saline flow (from east to west) is primarily caused by many years of over pumping from the coastal aquifer. Water extractions along the row of wells prevent the saline water from reaching the coastal aquifer. Instead, the saline water feeds the Granot and Lahat inland BWRO desalination plants, thereby providing additional potable water.

The brine disposal (concentrate) is transferred via a long underground pipeline (approx. 30 km), from the inland desalination facilities to the Mediterranean Sea, where it is discharged through the Ashkelon power station's outfall. This Mekorot-constructed "Garanot-Ashkelon" pipeline collects brine from three BWRO facilities: the Granot, Gat, and Lahat desalination facilities. Fig. 1 shows a schematic map indicating the facilities' locations, the row of wells, and the brine disposal pipeline [1,2]. Brine disposal via the brine pipeline has increased from approximately 3,000 m^3 a day in 2004 to approximately 10,000 m^3 a day in 2011 and will reach to about 13,000 m^3/d in 2014 [2]. Maximum capacity of the pipeline is 24,000 m^3/d. This Granot-Ashkelon brine disposal pipeline is unique in world that transports high concentrated brine solution across a distance of many kilometers. Enormous challenges are involved in the operation and maintenance of such an underground pipeline, including chemical and hydraulic control systems.

As is commonly known, most RO desalination plants use phosphorus-based antiscalants to control scaling and achieve high membrane performance, as measured by reduced trans-membrane pressure, salt passage, and increased permeate flow. However, phosphorus antiscalants in brine disposal can be an environmental issue that should be considered and studied when installing a desalination plant. Therefore, and in accordance with the Israeli Ministry of the Environmental Protection's requirements, phosphorus-free antiscalants were used in a pilot testing plant at the Granot desalination facility since 2009. The aim of the R&D research at this pilot plant is to examine different types of phosphorus-free antiscalants and to identify an effective replacement for phosphorus-based antiscalants in RO desalination facilities. Since phosphorus-free antiscalants would minimize environmental effects of the brine outflow, their usage would be advantageous [2].

To date, five different antiscalants (four of them, phosphorus free) were tested at the Granot pilot plant. Table 1 describes the chronological use of these phosphorus-free antiscalants in the Granot pilot plant, and their organic composition. Each of these antiscalants was examined in two separate experiments (two stages in the desalination process; Fig. 2). The first experiment examines the effect on RO membrane performance, in the *desalination branch*. It has a similar alignment and pre-treatment system as the Granot desalination facility. The second experiment examines the *brine recirculation simulation system* for identifying suitable brine flow conditions and salt precipitation potential within the brine pipeline. Together, the experiments with these two simulation systems are designed to identify environmental antiscalants that provide a combination of good membrane performance (varied recovery rates) without incurring salt precipitation (inorganic scaling) such as calcium carbonate ($CaCO_3$) along the lengthy brine disposal pipeline. Importantly, the experimental design of brine recirculation system is based on laboratory test results obtained at the Technion Institute, by Prof. Semiat's research teams [3].

2. Experimental methods

2.1. Granot pilot plant

The Granot pilot plant was established for optimal efficiency of the commercial plant and for testing the possibility of replacing commonly used polyphosphonate antiscalants with phosphorous-free antiscalants. Antiscalants are injected into the RO feed water to prevent scaling on the RO membranes. The disposed brine from the RO plants contains high concentrations of antiscalants.

The BWRO Granot pilot plant consists of two separate components, as illustrated in Fig. 2: an RO desalination component and a brine recirculation component. The RO desalination phase of the experiment was run first. If the RO desalination phase of the experiment was considered successful, the experiment was extended to the brine recirculation phase. Details of these two phases are as follows:

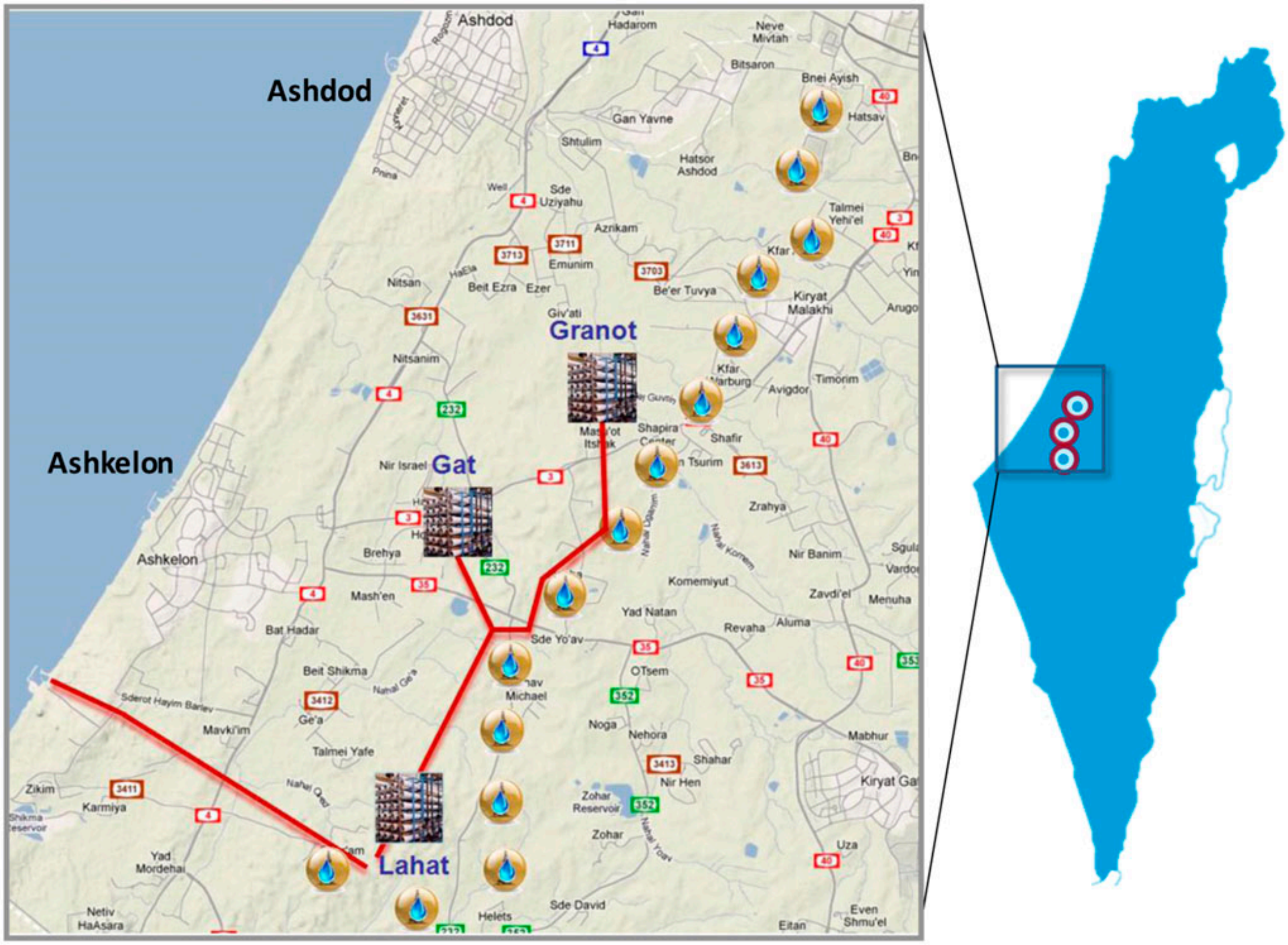

Fig. 1. A schematic map to demonstrate the locations of the coastal aquifer rehabilitation project: the row of wells along the "buffer zone", the inland Granot, Lahat and Gat Desalination Plants, and the brine disposal pipeline [2].

Table 1
Chemical composition of the phosphorus-free antiscalants that were used in the Granot BWRO pilot plant

Antiscalant type*	Organic material
X-Type	Phosphonate
A-Type	Copolymer of polyacrylate and polycarboxylic acid
B-Type	Dendrimer
C-Type	Polyacrylate
E-Type	maleic acid and polycarboxylic acid

*The antiscalants types represented using a letters since Mekorot Company obligate for manufactory confident.

(a) RO desalination phase

Overview of the RO desalination component of the pilot plant (upper section of Fig. 2): Pre-treatment of the raw well water includes acid addition to reduce the pH value to approximately pH 6.8, and is followed by coarse filtration (200 μm) and cartridge filters (5 μm). The final stage of the pre-treatment process involves addition of the antiscalant (phosphorus or phosphorus free).

This treated feed water is subsequently pumped at 20 m^3/h to the RO unit. Desalination involves two stages with two pressure vessels (PV) at the first stage and a single PV at the second stage. Each PV contains 7 commercial 8 inch diameter RO membranes.

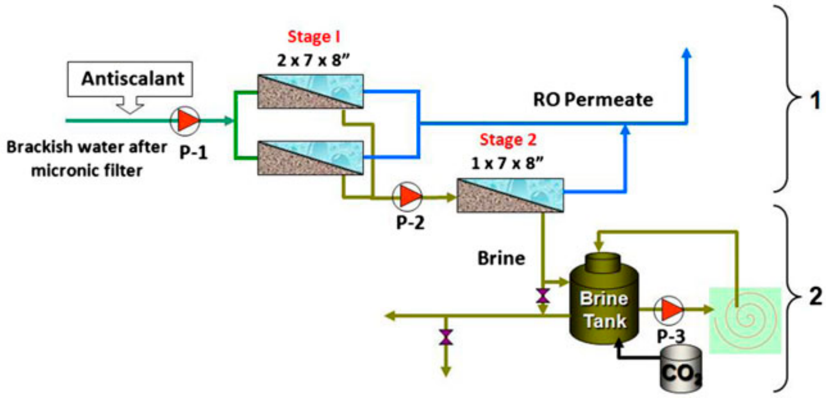

Fig. 2. A flow diagram of the Granot pilot plant consists of the two experiments (in each of the two components of the pilot system): (1) the upper RO desalination component and (2) the lower brine recirculation component.

Procedures for the RO desalination phase of the experiment: The targeted test period for each new antiscalant in the desalination component of the pilot plant is approximately three months, using a low recovery rate of 80%. During this period, membrane performance was monitored, including the pressure drop on the RO membranes, permeate flow, and salt passage through the membrane. Subsequently, an evaluation was made as to whether each antiscalants warranted further examination on the basis of the results from the membrane performance data. If the data were considered satisfactory (membrane performance was considered to have remained stable), the experiment was continued at a higher recovery rate. The experiment on a particular antiscalant did not continue beyond the initial 80% recovery level, if any of the membrane performance parameters rose by more than 10% over the three month period.

(b) Brine recirculation phase

Each of the antiscalants was tested in the brine recirculation phase, some of them with different recovery rates or with a mixture of two antiscalants (see Table 3).

Procedures for the brine recirculation phase of the experiment (lower section of Fig. 2): For each antiscalant type and specific recovery rate, the brine was tested in a follow-up experiment within the brine recirculation system. This experiment involved 200 l of brine that was circulated within the system for 100 h, thereby stimulating the flow of brine along the 30 km "Granot-Ashkelon" pipeline. Throughout this experiment, several field and laboratory parameters were monitored to measure the extent of precipitation occurrence within the system. The field parameters, such as pH, temperature, and turbidity, are clear indicators of salt precipitation (if it occurs). All additional laboratory-measured parameters, such as calcium, bicarbonate, silica, and total dissolved solids (TDS), can also specify the potential for precipitation during 100 h of brine recirculation. Moreover, in order to maintain comparable flow regime, as the real pipeline, CO_2 injection was added to stimulate full pipeline flow.

2.2. Feed water analysis

Table 2 provides the typical feed water analysis that was used to run all of the experiments at the Granot BWRO pilot plant. This analysis identifies

Table 2
Granot BWRO pilot plant feed water analysis

Parameter	Concentration [mg/l]
Ca	102
Mg	79
Na	300
K	6
Sr	2.1
Ba	0.18
NH_4	0.1
HCO_3	350
SO_4	80
Cl	580
NO_3	57
B	0.5–0.8
SiO_2	26–30
TDS	1,590

several challenges that require attention. The first one, as shown in Table 1 is the calcium carbonate precipitation potential, as indicated by Eqs. (1) and (2), which in the case of our feed water is relatively high:

$$2HCO_3^- \leftrightarrow CO_2^{2-} + CO_3^{2-} + H_2O \quad (1)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \quad (2)$$

Therefore, as a foremost priority, the desired antiscalant must prevent calcium carbonate precipitation on the RO membranes and along the Granot-Ashkelon brine disposal pipeline.

Two additional challenges that involve the raw water in these wells present challenges in the desalination process: boron and silica. The expected boron content in the raw water wells is between 0.5 and 0.8 mg/l, and the silica level in the raw water ranges from 26 to 30 mg/l (see Table 2). These components mainly affect three aspects of the desalination process: the selection of the ideal RO membrane type, the RO recovery ratio, and the chemical regime (i.e. the antiscalant type and dosage, as well as the acid usage). The Granot pilot plant operates at an RO recovery ratio of 80–84%. This recovery ratio is limited, primarily due to the silica content. Once the RO recovery ratio and the chemical regime are identified, it is then necessary to prevent salt precipitation in the long brine disposal pipeline [3,4].

3. Results and discussion

3.1. Experimental results—membrane performance at the RO desalination phase

Five different antiscalant types were tested in the Granot pilot plant. These antiscalants were distinguished on the basis of each of their differences in the respective unique active organic compounds, as shown in Table 1. Antiscalant type-X contains phosphorus, while the other four antiscalants do not contain phosphorous: type-A, type-B, type-C and type-D. To confirm the systems validation, the first experiment was done using the well-known phosphorus antiscalant, type-X, which is in use within full-scale commercial facilities, which was the first antiscalant to be used in the experiment. We used the type-X in order to validate the pilot plant, prior to all subsequent tests of the additional antiscalants.

As mentioned above, during about three month experimental treatment periods, membrane performance parameters, such as a pressure drop, permeate flow, and salt passage, are monitored daily and normalized to the system experimental conditions (such as temperature, conductivity, etc.). We identified the pressure drop parameter as being the most sensitive, and first indicator of the occurrence of precipitation on the RO membranes. Therefore, the following results are focused on the pressure drop parameter.

Fig. 3 illustrates the normalized pressure drop across the duration of each experiment, at the first RO stage of the desalination experiments. Results are shown for each of the five different antiscalants, all at a recovery ratio of 80%. As can be seen in Fig. 3, Type-X (the phosphorous-based) antiscalant generated constant pressure drop data which varied between approximately 1.32 and 1.38 bar. Fig. 3 also shows that the results obtained for all four of the phosphorus-free antiscalant types exhibited gradually increasing pressure drops during the first RO stage. The type-*A phosphorus-free antiscalant* is a copolymer of polyacrylate and polycarboxylic acid (see Table 1). The pressure drop during the first RO stage, using Type-*A* antiscalant, increases from about 1.25 to 1.86 bar (an increase in more than 30%) during the 4 month test period. A similar phenomenon was observed using antiscalant Type-*B* (dendrimer; non-phosphorous), where the pressure drop at the first RO stage increased from 1.63 to 1.91 bar (~15%) over a 1.5 month period. The pressure drop at the first RO stage, using Type *C* antiscalant (based on polyacrylate) demonstrates similar results, with an increase from 1.77 to 3.26 bar (~45%) in 2 months.

The most recent phosphorus-free antiscalant to be tested was Type-*E*, a relatively high biodegradable compound that is based on maleic acid and polycarboxylic acid that showed similar increasing pressure drop data over time.

The increasing pressure drop data were expected to reflect a proportional amount of biofouling on the first stage RO membranes. This expectation was proven by lab analysis of the RO membranes (autopsy), and the microbiological tests on the feed water. Probably, the addition of antiscalant to the feed water causes an increase in two orders of magnitude in bacterial densities within the feed water. This is a significant additional challenge in attaining water quality requirements. To eliminate the biofouling, a chemical cleaning (base) was used, which temporarily reduced the pressure drop changes by approximately 30% after approximately1,500 h of operation (Fig. 3). However, as can be seen in Fig. 3, the improvement in pressure drop was only temporary (increasing pressure drop data were again observed at the latter stage of the test period).

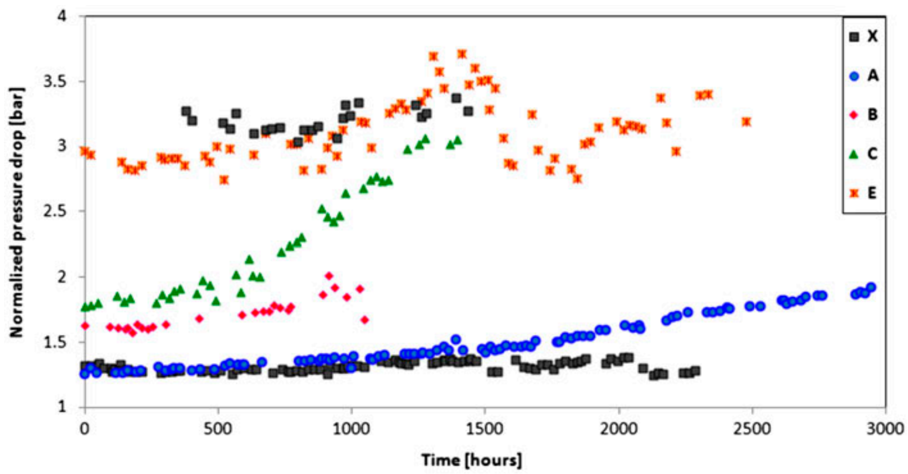

Fig. 3. Normalized RO pressure drop in the first RO stage of the Granot pilot plant using five different types of antiscalants, all at an 80% recovery rate. The Type *X* antiscalant was tested at the onset and at the end of the experimental period, yielding different normalized pressure drop data.

The Type-*E* test indicated that the organic basis of the phosphorous-free antiscalants provides nutrients that enhance biofouling and potential bacterial proliferation. Consequently, the antiscalants were apparently substantially enhancing membrane biofouling; a significant logistic problem [5–7]. Biofouling is the accumulation and growth of micro-organisms on membrane surfaces which creates severe operational problems in RO desalination processes. Biofouling affects RO membrane performance parameters, causing declines in membrane water flux, increases salt passage to the process water, and increases pressure-drops and energy requirements.

Evidence that the increasing pressure drops were caused by biofouling was obtained by a comparison between the pressure drop data after the first RO desalination stage in our pilot study experiment and at the commercial Granot desalination facility. The pilot and commercial plants were fed by the same feed water and followed the same pre-treatment procedures. However, in the commercial plant, a phosphorous antiscalant type-*X* was used and in the pilot plant, type-C was used. Fig. 4 indicates the normalized pressure drop measured on parallel dates after the first RO stage of the commercial and experimental desalination plants, using type-*X* and type-*C*, respectively, utilized in 80% recovery rate. It is explicitly seen that the commercial Granot plant exhibited a stable pressure drop, which was in the range between 3.2 and 3.5 bar. In contrast, over the same time period and feed water, a rapid rate of increase in the pressure drop data was observed at the pilot plant (approximately 45%). Since the RO system at the pilot plant has similar alignment to that of the commercial plant, the pressure drop is believed to have been caused by the phosphorous-free antiscalant. Moreover, autopsy measurements on the commercial and experimental membranes was carried out by Dr Moshe Herzberg, from Ben-Gurion University, Israel, and confirmed the presence of biofouling, as expected [7].

Fig. 3 show that Type-*X* (phosphorus- based) antiscalant clearly generated the best results (lowest rate of change in pressure drop). The worst performance was shown by the non-phosphorus antiscalants, Type-*C*.

It is important to emphasize that although the pressure drop increased rapidly at the first stage of the RO desalination experiment, for all four non-phosphorus antiscalants, the normalized pressure drops were stable during the second stage, as shown in Fig. 5. Moreover, the other two indicator parameters, such as normalized salt passage and permeate flow rate, were stable throughout the experimental period. The stable performance of the second RO stage indicates that salt scaling did not occur at this stage.

It is important to note that between each of the tested antiscalants, chemical cleaning (using a base and acid) was employed at both the pilot stages. Despite this standard procedure for cleaning the RO system, the pressure drop continually increased from the beginning to the end of the experimental period. The extent of this shift in the pressure drop data was quantified by repeating the initial test on Type *X*, at the onset of the experimental period (when the pressure drop was 1.2 bar; Fig. 3), and at the very end of the experimental period (when the pressure drop

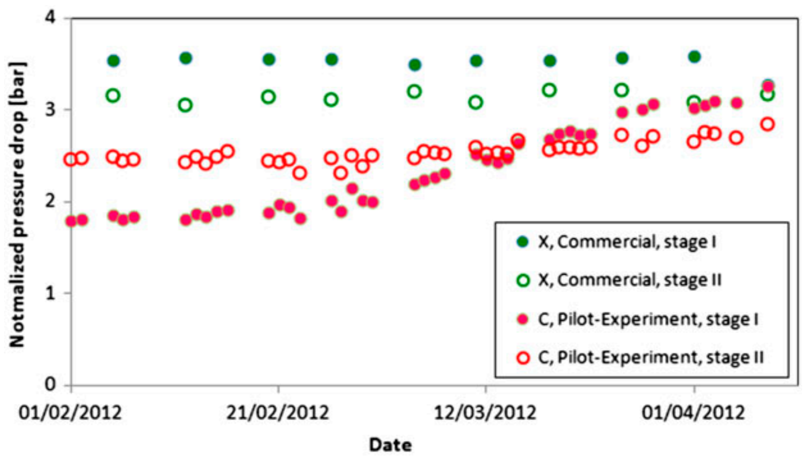

Fig. 4. Comparison in normalized pressure drops at a simultaneous time period, between the Granot pilot and Granot commercial plant operations. At the commercial plant, phosphorous antiscalant type-*X* was used and in the pilot plant, phosphorous antiscalant Type-*C* was used.

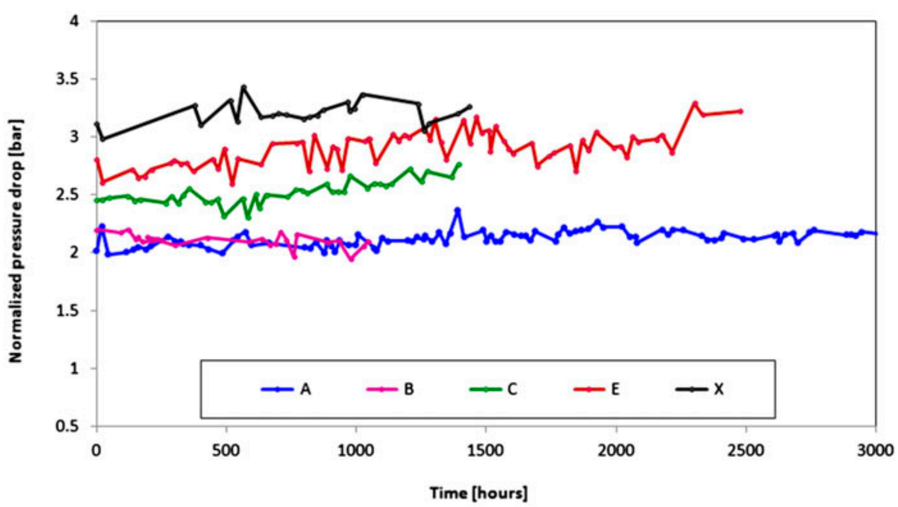

Fig. 5. Normalized RO pressure drop at the second RO stage of the Granot pilot plant using five types of antiscalants, all at an 80% recovery rate.

reached 3.3 bar). This shift in baseline pressure drop data indicates a progressive deterioration in the condition of the RO membranes over the experimental period, due to the phosphorus-free antiscalants. Test runs with the type-*X* antiscalant were intentionally conducted to quantify of the experimental system over time. The type-*X* data clearly indicate that the chemical cleaning (using acid–base cleaning) that was regularly employed across the duration of each experiment could not attain the initial pressure drop.

Despite this, the data appear to indicate that the best RO performance among all antiscalants types tested was achieved by the phosphorous-free antiscalant (Type *X*).

3.2. The brine recirculation system results

As described above, the second phase of the experiment for each antiscalant type was followed by the brine recirculation system. Some of the experiments were employed using different recovery rate ratios or using a blend concentrate of different antiscalants. Table 3 summarizes eight different brine recirculation experimental results using these five antiscalants, at 80 and 83% recovery rates. Table 3 shows that the dissolved calcium ion concentration remains almost constant after 100 h of recirculation and is not deposited in the form of calcium carbonate salt (according to Eqs. (1) and (2). Moreover, Table 3 indicates that all

Table 3
Results from brine recirculation experiments on each of the five antiscalant types: operational recovery rates, calcium concentrations (initial and final), LSI, and turbidity

	Initial		After 100 recirculation hours		
Antiscalant	Recovery [%]	$Ca_{(0)}$ [mg/l]	$Ca_{(100\,h)}$ [mg/l]	LSI	Turbidity [NTU]
A	80	478	478	1.41	0.3
A	80	586	604	1.38	0.2
B	80	523	523	1.41	0.22
C	80	520	518	1.53	0.19
E	80	515	500	1.66	0.16
X	83	610	600	1.57	0.18
A + *X*	80	460	468	1.5	0.21
B + *X*	80	460	468	1.55	0.21

experiments obtained Langelier saturation index (LSI) values that are less than 1.8 (LSI < 1.8); the saturation limit for ensuring that salt precipitation does not occur on the brine pipeline. Moreover, low turbidity (<1 NTU) that was acquired during the experiments also ensured the elimination of precipitation events. The combination of these three results led to a conclusion that no precipitation occurs on the simulated brine recirculation pipeline in all eight experiments (represented in Table 3).

4. Summary and continued research

Experimental results that were carried out on four different phosphorus-free antiscalants (Types *A*, *B*, *C*, and *E*) show that stable membrane performance did not occur, although the brine recirculation system indicated that there would be no occurrence of precipitation along the pipe transport system. The increase in pressure drop that occurred in the first stage of the RO desalination phase among all of the phosphorus-free antiscalants indicates the possibility of microbiological fouling (biofouling) growth due to the presence of the phosphorus-free antiscalants themselves in the feed water. This high rate of increase was not observed while using a phosphorous-based antiscalant (Type-*X*). It leads to the conclusion that some or all phosphorous-free antiscalants may enhance biofouling growth.

This research continues in pursuit of compounds that can satisfy the increasingly stringent environmental requirements regarding the composition of brine from desalination facilities. As such, additional phosphorus-free antiscalants will continue to be tested at the Granot BWRO pilot plant.

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