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A new phosphorous-free antiscalant for membrane desalination

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ABSTRACT

Phosphorous containing antiscalants, which are commonly used in RO desalination process, have become an environmental concern for RO concentrate disposal. These chemicals are suspected of contributing to algal blooms in the water bodies where RO concentrate is discharged. Therefore, phosphorous-free antiscalants are increasingly being required for both brackish and seawater membrane desalination systems. Nalco recently developed a phosphorous-free antiscalant (PC-1611T) to address this environmental concern. In the laboratory testing, this product performed similar to ATMP (commonly used phosphonate based antiscalant) for $CaCO_3$ scale inhibition up to 3.0 LSI (Langelier Saturation Index). It also inhibited $CaCO_3$ scale in presence of up to 1 ppm Fe^{3+} and residual levels of poly(DADMAC) based pre-treatment coagulant. It also showed 2–5× lower bio-growth contribution potential than polycarboxylates and is compatible with polyamide RO membranes. Full-scale evaluation of this product is in progress and the results for first 4 weeks show stable RO performance, indicating successful scale-control.

Keywords: Antiscalants; Reverse osmosis; Phosphorous-free; Non-phosphorous; Desalination; Environmental; Sustainable; Nanofiltration

1. Introduction

Due to significant improvements in membrane performance, energy minimization/optimization and decrease in membrane cost over last few years, revere osmosis (RO) and nanofiltration (NF) membrane based desalination has now become a common practice for both brackish and seawater desalination. However, 15–25% of feed water is still discharged in the form of concentrate. This is because permeate recovery in brackish water RO desalination is limited due to scale formation from sparingly soluble salts whose solubility limits exceed as more water is recovered. Antiscalants successfully delay scale formation and allow higher water recovery. Most commercial antiscalants are based on organo-phosphonates, polyacrylates, acrylamide copolymers or their blends. However, phosphorous containing antiscalants have become an environmental concern for RO concentrate disposal [1] in many parts of the world, as these chemicals are suspected of contributing to algal blooms in the water bodies where RO concentrate is discharged. Polyacrylate based antiscalants, although phosphorous-free, are known to contribute to RO biofouling [2] and also do not function well in presence of Fe^{3+}. Therefore there is a need for developing phosphorous-free RO antiscalants, which also do not contribute to membrane biofouling. Objective of this study was to evaluate performance of recently developed phosphorous-free antiscalant in

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laboratory and full-scale RO systems for $CaCO_3$ (main scale) scale inhibition.

2. Experimental

2.1. Scale inhibition tests

Scale inhibition efficacy of a new antiscalant (PC-1611T) was determined in a jar by measuring solution turbidity and soluble Ca level during 2 h, both in presence and absence of antiscalant. The water chemistry used for these experiments was that of RO concentrate from one of the full-scale plants and is shown in Table 1. The pH was maintained at 8.1 during the 2 h of experiment, using 1 N HCl or 1 N NaOH.

The % scale inhibition efficiency (E) was calculated as:

$$E = \frac{[\mathrm{Ca}^{2+}]_1 - [\mathrm{Ca}^{2+}]_2}{[\mathrm{Ca}^{2+}]_0 - [\mathrm{Ca}^{2+}]_2} \quad (1)$$

where, $[Ca^{2+}]_0$, $[Ca^{2+}]_1$ and $[Ca^{2+}]_2$ are Ca concentrations (determined by EDTA titration) initially, in presence of antiscalant and in absence of antiscalant of respectively.

Scale inhibition efficacy of PC-1611T was also determined in presence of residual amount of (polydiallyldimethylammonium chloride), a commonly used pre-treatment chemical, to ensure that activity of negatively charged antiscalant is not adversely affected if the residual amount of positively charged coagulant does pass through pre-filters and enter the RO feed stream. This test was done with different water chemistry (not shown) than in Table 1. Different water chemistry was used to ensure that antiscalant is effective under different ionic compositions.

2.2. Microbial growth potential

Microbial growth potential was assessed from BPP (biomass production potential) studies with 2 and 50 ppm PC-1611T and another polycarboxylate-based antiscalant for comparison, at pH 8.1. This test uses a natural culture of bacteria and carbon source from the test product. Detailed procedure for this test is given by Vrouwenwelder et al. [2].

2.3. Membrane compatibility

Compatibility of PC-1611T with polyamide RO membrane (Dow BW30) was measured at 5 and 50 ppm in 2000 ppm NaCl in a cross-flow test cell (0.023 m^2 membrane area, 1 L/min cross-flow rate, 25°C). NaCl solution flux and rejection were compared before and after exposure of PC-1611T under dynamic (24 h pressurized circulation) as well as static (2 weeks soak) conditions.

2.4. Dilute solution stability studies

Many smaller RO systems use dilute antiscalant on-site due to smaller daily requirement and/or pump capacity. Therefore, the antiscalant solution should remain stable for few days until the next batch of fresh solution is made. Effect of dilution on PC-1611T stability was determined by measuring bacteria and yeast growth at 0, 5, 10 and 20× dilutions at 20 and 35°C for up to two weeks. All glassware was washed, rinsed with DI water and autoclaved before the experiment. Disposable sterile tips were used for dilution of the products. All experiments were performed in duplicate. 1 ml sample was taken from each bottle (containing 50 ml sample volume) after 24 h, 48 h, 7 d and 14 d and plated in the Nalco microbial analytical laboratory for total viable counts and differential microbial analysis (aerobic bacteria, SRB, mold and fungi).

2.5. Scale inhibition performance in a full-scale RO system

After confirming that PC-1611T controlled $CaCO_3$ scale in jar tests, was membrane compatible and showed lower BPP than polycarboxylates, it was decided to evaluate this product in full-scale or pilot scale RO systems. The first trial is being conducted in an industrial RO plant in Southern China. The RO system parameters and feed water chemistry are shown in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Scale inhibition tests

Scale inhibition efficacy of PC-1611T was measured from the change in solution turbidity and residual soluble

Table 1
Water chemistry for scale inhibition jar tests

Cations	ppm as ion	Anions	ppm as ion
Ca^{2+}	320	Cl^-	1454
Mg^{2+}	126	SO_4^{2-}	236
Fe^{3+}	0.8	CO_3^{2-}	3.6
Na^+	1835	HCO_3^{2-}	1367
pH	8.1	SiO_2	72
LSI	2.0		

Table 2
RO system parameters in a full-scale trial

Parameter	Value
Permeate flow, m^3/h	50–75 (Design 140)
Recovery, %	63–75
Current (baseline) antiscalant dosage in feed, ppm	3 ATMP (phosphonate based)
Trial antiscalant dosage in feed, ppm	3 PC-1611T*

* Dosage to be lowered after 3–4 weeks at 3 ppm

Table 3
RO feed water chemistry in a full-scale trial

Cations	ppm as ion	Anions	ppm as ion
Ca^{2+}	73	Cl^-	422
Mg^{2+}	50	SO_4^{2-}	135
K^+	7.3	O-PO_4^{3-}	1.9
Na^+	360		
Ba^{2+}	0.09	SiO_2	17
Sr^{2+}	5.1	pH	7.4
		Conductivity	2.2 mS/cm

Ca with time. Fig. 1 shows solution turbidity after 2 h at different PC-1611T dosages (on polymer actives basis) for concentrate water chemistry (Table 1). Note that these dosages are for concentrate (LSI = 2.0) and therefore feed dosages would be 4–5× lower than these dosages, depending on recovery.

As a comparison, dosages of ATMP (amino tris-methylene phosphonate), a commonly used phosphonate-based antiscalant, required for the same performance, are also shown. With an active dose of 1.5 ppm PC-1611T, turbidity was maintained below the desired value of 2 NTU for 2 h. In contrast, the control turbidity increased rapidly to 30 NTU within 24 min. The 2 h time limit was used to account for any scale formation in systems which are not flushed with feed or permeate water immediately after system shutdown, such that concentrate remains in the system for sometime until re-start or flushing. The ideal RO antiscalant should continue to delay the scale precipitation kinetics for some period, even in the absence of flow conditions.

It is also apparent from Fig. 1 that the PC-1611T dosage for the same performance was slightly lower (1.5 ppm vs. 1.7 ppm) than ATMP. This may be due to multifunctional nature of PC-1611T active components compared to ATMP. Due to presence of several surfaces such as spacers, pipes, particles and membranes in membrane systems, the actual dosage required for effective scale control in RO system may be slightly higher than that observed in jar testing (Fig. 1) where only glass surface of the jar is involved for adsorption (if any) of antiscalant. Therefore, optimization of dosage for a given feed water chemistry (and therefore scaling potential) is necessary in pilot/full-scale RO system. Furthermore, scale inhibition jar testing does not simulate the heterogeneous nucleation and crystallization that occurs in membrane systems due to concentration polarization at the membrane surface, but does simulate to some degree the bulk (homogeneous) nucleation and crystallization processes.

$CaCO_3$ scale inhibition, measured from residual soluble Ca level after 2 h, was in excess of 80% (data not shown), supporting the observed turbidity trends.

3.2. *Microbial growth potential*

One of the important criteria for success of phosphorous-free RO antiscalants is that they should not appreciably contribute to membrane biofouling. Microbiological growth potential of PC-1611T was measured using biomass production potential (BPP) method. BPP values (ng ATP/mg antiscalant) measured with 2 and 50 ppm (as product) PC-1611T were 1.0 and 2.9, respectively, whereas for polycarboxylate-based antiscalant, the corresponding values were 4.7 and 5.8. Thus, PC-1611T has 2–5× lower BPP than polycarboxylate, supporting a lower risk of

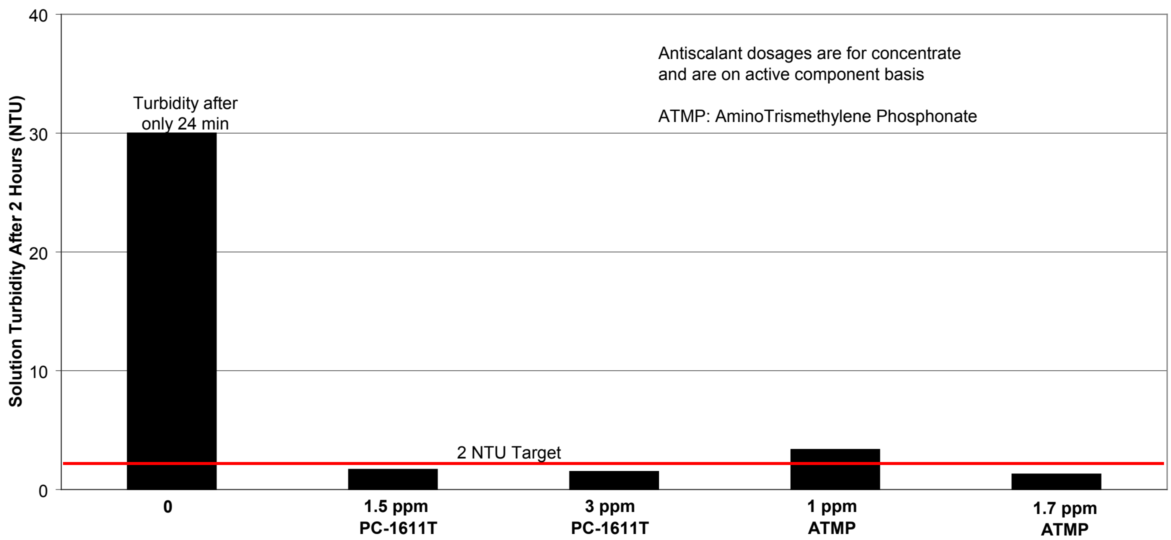

Fig. 1. Solution turbidity after 2 h as a function of antiscalant type and dosage.

membrane biofouling. As a comparison, Vrouwenvelder et al. [2] observed 0.1–7.4 BPP in their study with various antiscalants in biologically stable slow sand filtrate. This test does not simulate the surfaces and hydrodynamics of RO systems; nevertheless, it gives a relative indication of microbio growth potential of different products.

3.3. Membrane compatibility

A successful RO antiscalant should also be compatible with polyamide selective layer that is present in most commercial spiral wound RO membranes, at least at application dosages (in brine), if not higher and also under similar salinity conditions. Most antiscalants are charged molecules and salinity of RO feed water does affect the charge interactions of these molecules with membrane surfaces. Table 4 shows change in NaCl solution flux and salt rejection of RO membrane after exposure to PC-1611T under both, static (2 weeks soak) and dynamic (24 h pressurized circulation) conditions.

The two PC-1611T concentrations tested represent upper range of feed and concentrate concentrations, including at 90% recovery. It is apparent from Table 4 that under all conditions tested, change in flux and rejection is small enough to be acceptable for RO operation, concluding that PC-1611T is compatible with polyamide RO membrane.

3.4. Dilute solution stability

PC-1611T solutions made in sterile water at 5, 10 and 20× dilutions did not show any bacteria or yeast growth up to 7 d at both 20 and 35°C. These results (data not shown) indicated that it is safe to use diluted solution of PC-1611T for few days when made in clean water. This is important for relatively smaller RO systems with small daily antiscalant requirement.

3.5. Scale inhibition performance in full-scale RO system

Fig. 2 shows normalized data for permeate flow, differential pressure (DP) and salt passage (SP) for the 140 m^3/h (616 gpm) permeate flow system. The permeate flow and recovery during the trial period were 50 m^3/h and 63%, respectively. The period includes baseline data with phosphonate antiscalant (period I), shutdown period (period II) and PC-1611T treatment trial (period III), which was still ongoing at the time of submission of this paper.

This system is undergoing some pre-treatment optimization to address higher SDI (silt Density Index) issues for RO feed water; therefore it is being cleaned in approximately every 2 weeks, including during the trial period.

Period I (baseline):

It is apparent from Fig. 2 that during period I (baseline with phosphonate antiscalant), the normalized flow declined, salt passage remained almost constant, but first stage DP increased suggesting colloidal fouling in the first stage. If it was scaling, the second stage DP would have increased, which did not happen during this period, suggesting good scale control by phosphonate based antiscalant.

Period II (shutdown):

System was cleaned and PC-1611T feeding was started, but for maintenance and sorting out SDI issues, it was shut down for about a week.

Period III (PC-1611T evaluation):

During this period (June 22–July 6, 2010), normalized salt passage and differential pressure remained stable between 5–6% and 4–5 bar, respectively. The normalized permeate flow also remained stable for about 5 d but a decline to 15% limit was observed after 6th day, therefore system was cleaned. Due to ongoing SDI issues, it was difficult to identify the reason for this decline. If it was a scaling event, salt passage and DP should have increased substantially, which did not happen. After CIP, all major RO parameters became stable. Even though data is not shown here, these parameters (permeate flow, DP and SP) were stable for two more weeks, i.e. for total of four weeks and continuing. Last week of this 4-week period with PC-1611T also saw an increase in recovery from 63 to 75% (75 m^3/h permeate and 100 m^3/h feed flow) due to increased demand for permeate water for the plant, but PC-1611T dosage was still maintained at 3 ppm.

In summary, PC-1611T appears to be controlling $CaCO_3$ scale in full-scale RO system. This field evaluation will continue for several months, to also ensure that this product does not contribute to biofouling. This can be determined from any change in CIP frequency and membrane autopsy.

Table 4
PC-1611T compatibility with polyamide RO (Dow BW 30) membrane

Time	% flux change with time		% salt rejection	
PC-1611T concentration	5 ppm	50 ppm	5 ppm	50 ppm
0			98.4	98.1
24 h pressurized circulation	–6.0	–0.8	98.3	98
2 week static soak test	1.0	5.0	98	98.1

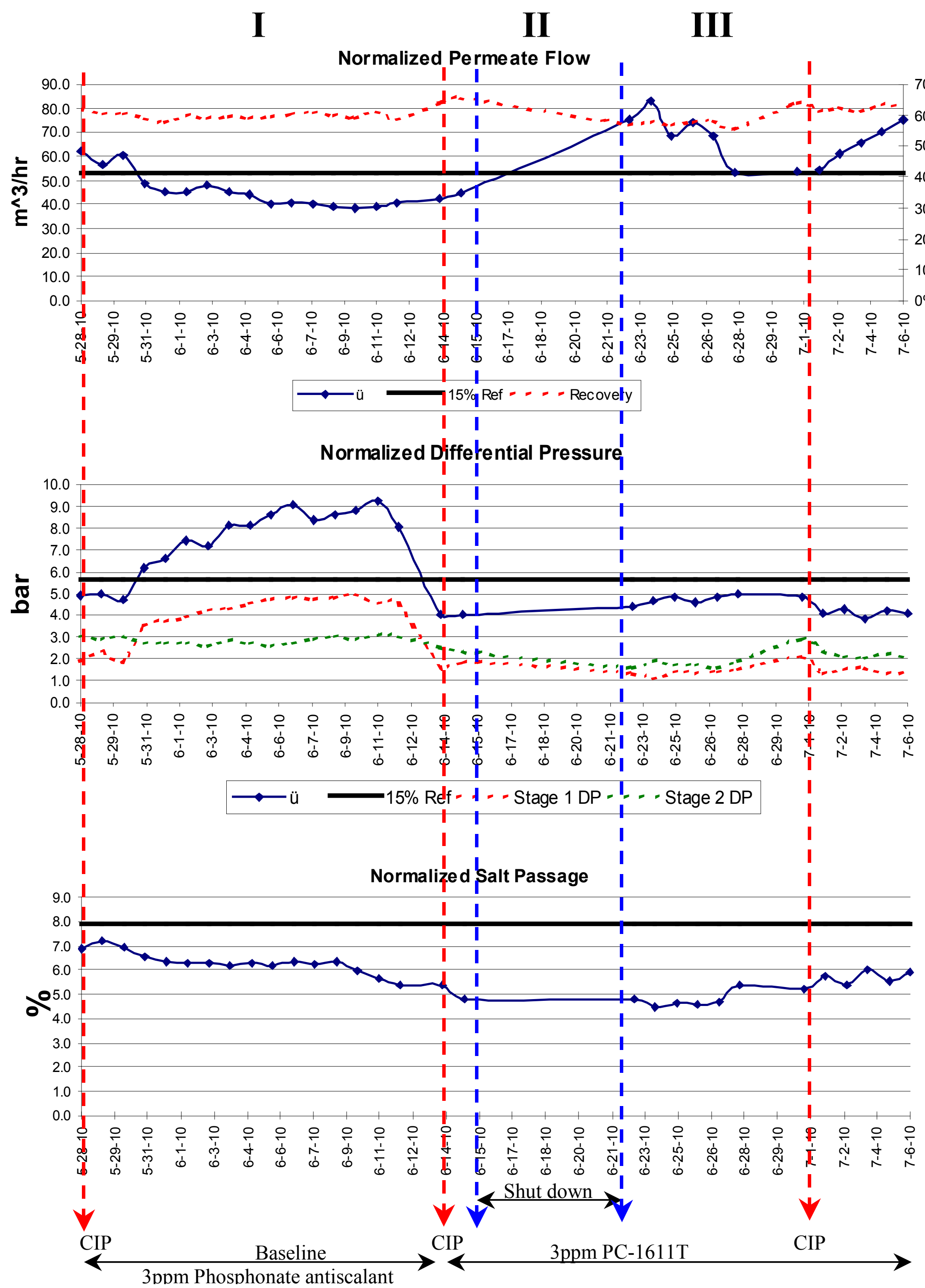

Fig. 2. Normalized data for permeate flow, differential pressure and salt passage for a full-scale trial of PC-1611T.

This product is being evaluated in several brackish water RO systems globally. Its efficacy for scale control in seawater RO (for first pass or high pH second pass) is also being studied.

4. Conclusions

Nalco recently developed a patent pending phosphorous-free RO antiscalant (PC-1611T) that:

- Controls $CaCO_3$ scale
  - At brine LSI of up to 3.0 (data shown here only up to 2.0 LSI)
  - In presence of up to 1 ppm Fe^{3+} in brine
  - In presence of 75 ppm silica in brine (higher silica is being studied)

- Is compatible with polyamide RO membrane
- Has 2–5× lower BPP (biomass production potential) than polycarboxylates, indicating possibly a lower risk of contribution to membrane biofouling
- Is effective in presence of residual levels of polyDADMAC-based pre-treatment coagulant.
- Does not contribute to bio growth under dilution conditions > dilute antiscalant solutions could be used for few days in smaller RO systems
- Its dosage can be monitored and controlled online using Nalco's 3D TRASAR® technology (data not shown)
- Has shown effective scale control in ongoing field trial in full-scale brackish water RO system in China
- Is being evaluated in several full-scale RO systems globally
- Is compliant with EU REACH program, is NSF certified and is being certified by Chinese Ministry of Health (MOH)

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