CALCIUM PHOSPHATE SCALE CONTROL IN WASTEWATER RE-USE RO SYSTEM

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Abstract:

The increasing number of municipal membrane systems (RO / NF) using wastewater as feed installed worldwide during the past decades, has triggered much attention to potential calcium phosphate scale formation on the membranes. Typical pretreated wastewater effluents would contain 5 – 15mg/l of phosphate in the RO feed stream. These higher amounts of phosphate in the RO feed, together with high amounts of calcium and fluoride, do easily trigger calcium phosphate scale formation especially at high recovery levels. The complex calcium phosphate scale formation mechanism has triggered laboratory development work on specific RO antiscalants to ensure smooth wastewater RO operation.

This paper investigates the antiscaling performance of 'SPE 0109POT', a new NSF Standard 60 approved specific calcium phosphate RO antiscalant developed by Thermphos's Dequest AG, through a pilot plant study carried out at Keppel Seghers Ulu Pandan NEWater site in Singapore. Factors affecting calcium phosphate scale formation and the minimum dosage level for effective antiscaling performance have been evaluated in this study. This field trial shows that proper selection of an optimized RO antiscalant technology, in accordance to specific feed water composition and quality is required in order to ensure smooth running of wastewater RO membrane systems and to reduce operating costs by minimizing the quantity of antiscalant used.

I. INTRODUCTION

Water resources are becoming increasingly scarce in many parts of the world, mainly due to rapid economic development and increased population resulting in an increased demand for fresh good quality water. During the past decades, wastewater recycle / re-use Reverse Osmosis (RO) technology has gained increasing popularity and attention as a complement to desalination and traditional water sources in order to meet higher fresh water demands. The rapid increasing number of wastewater re-use RO system worldwide is mainly driven by the lower operating energy required, as compared to conventional seawater desalination systems. Design and operating performance of wastewater re-use RO systems are closely dependent on the quality of waste effluent including the total dissolved & suspended solids, organic loading as well as mineral scale / fouling potential. Among all the mineral scales, calcium phosphate is typically the most predominant in waste water re-use RO systems. Calcium phosphate is one of the most complicated scaling systems, attributed to the chemical properties of phosphate species under different conditions, and the complicated co-existence of various calcium phosphate species at various RO feed / brine water pH’s. At present day, the most commonly applied calcium phosphate scale prevention techniques include pH adjustment (sulphuric acid), use of polymeric dispersants, threshold inhibitors or combinations thereof.

1.1 Singapore and NEWater

The island republic of Singapore obtains approximately 50% of its water supply from outside its nation border [1]. Since late 1990s, the Singapore government has actively pursued renewable water sources through the strategic “Four Tap Strategy” consisting of imported water from neighboring countries, water catchment, seawater desalination and wastewater re-use, which is better known as NEWater. Until today, Singapore has successfully installed and operated five NEwater factories including Bedok NEWater factory, Kranji NEWater factory, Seletar NEWater factory, Ulu Pandan NEWater factory and Changi NEWater factory. The new source of water, NEWater, is in fact cleaner than the other sources of Singapore’s water. The successful demonstration of NEWater has also greatly reduced the reliance of water supplied from the Johor state of Malaysia when compared to a decade ago. First successful commissioning of Bedok NEWater factory at the end of year 2002, has contributed an essential case study for the subsequent NEWater factories design and operation.

The calcium phosphate scale control case study mentioned in this paper, was carried out on a pilot plant situated at the Ulu Pandan NEwater factory. The objective of this study is to investigate the performance of the recommended phosphonate-based calcium phosphate scale inhibitor, in a complex waste effluent feed water prompting super-saturation of calcium phosphate.

~~I.~~II. PHOSPHONATES BASED ANTISCALANTS

Phosphonates, more correctly called, organophosphonates, are additives commonly used in industrial water treatment, as threshold mineral scale and corrosion inhibitors. Phosphonates based treatment programs have been widely accepted by the water treatment industry, since their first introduction in the mid 20th century in replacement of chromate-based inhibitors. Increasingly challenging water treatment conditions the industry has been faced with since the 1970’s have triggered more research focus on the development of new phosphonates molecules having different functionality profiles. At present, phosphonates-based antiscalants have become the “workhorse” products in Reverse Osmosis applications because they are very effective mineral scale inhibitors. They do an excellent job as calcium carbonate (calcite), calcium sulfate (gypsum), barium sulfate, strontium sulfate, silica and even calcium phosphate family scale inhibitors.

Some distinguished characteristics of phosphonates that contribute to their membrane scale control performance, include:

- Highly negatively charged molecules enable the phosphonates-based scale inhibitors to interact with crystal surfaces to prevent further agglomeration of small crystals into massive scaling systems.
- Presence of multiple active sites on the phosphonate molecule provides excellent sequestration performance to effectively control membrane fouling problems from metal oxides.
- Excellent hydrolytic stability which helps to prevent degradation of the phosphonate molecule when used in complex water condition
- Strong carbon-phosphorus (C-P) bonding prevents the phosphonate based scale inhibitor from being directly utilized by bacteria and contributing to biofouling.

Careful selection and appropriate use of specific phosphonates based scale inhibitors can greatly improve the Reverse Osmosis performance, as well as to help achieve an optimized chemical cost.

~~II.~~III. PHOSPHATE AND CALCIUM PHOSPHATE

Inorganic phosphate, or orthophosphate, is a salt of phosphoric acid. In dilute aqueous solutions, phosphate exists in four forms, namely phosphate ions in strong basic solution (PO_4^{3-}), hydrogen phosphate ions in weakly basic solution (HPO_4^{2-}), dihydrogen phosphate ions in weakly acidic condition ($H_2PO_4^-$) and aqueous phosphoric acid in strong acidic condition (H_3PO_4). Figure 1 below explains the co-existence and formation ratio of various phosphate species ions under various pH conditions.

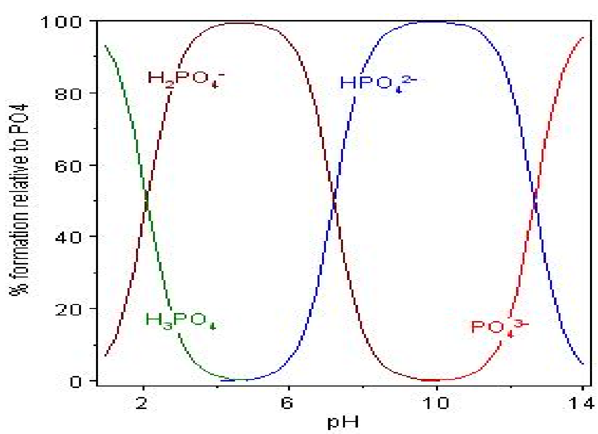


Figure 1: Phosphate speciation diagram

Based on Figure 1 and, under the typical operating pH's of wastewater re-use RO systems (pH = 6.0~8.0), co-existence of hydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$) in weakly acidic, neutral pH or weakly basic aqueous solution, is inevitable. The co-existence of these phosphate species, coupled with the presence of calcium in the feed water, is responsible for the potential threat of calcium phosphate scale formation on RO membrane surfaces. The calcium phosphate scaling potential can be estimated by using the rules of super-saturation, which is a ratio of the ionic activity product to the solubility product at standard condition. Activity coefficient would be required in order to justify the ionic interactions on scale formation as well:

$$S_{cp} = \alpha \frac{IAP}{K_{sp}^0} \quad (1)$$

Whereby, S_{cp} = Supersaturation ratio of calcium phosphate; IAP = Ion Activity Product; K_{sp}^0 = Solubility product under standard conditions; α = activity coefficient of $CaPO_4$ species under a specific water condition.

Calcium phosphate scaling on RO membrane constitutes a complex scaling chemistry whereby various solid species may be present at different stoichiometric levels.

The nucleation of calcium phosphate will be spontaneous at very high supersaturation level [7]. The nucleation process will be much slower at lower supersaturation and will only take place after a specific induction time depending on the level of supersaturation. Hydroxyapatite (HAP) is known as the least soluble and most thermodynamically stable form of calcium phosphate in aqueous solutions at pH values above 4.2. However, the formation of HAP is also known to be more complicated in neutral and/or slightly acidic condition. It is generally perceived that there are some precursors which could ultimately lead to HAP formation. Amorphous calcium phosphate (ACP) is usually formed when the pH is higher than 7 and become a template for formation of HAP. Under slightly acidic conditions Brushite (DCPD) and octacalcium phosphate (OCP) are predominantly formed and can again be converted into HAP. In a complex aqueous matrix, the hydroxyls group (OH^-) within HAP structure can often be substituted by chloride and/or fluoride, while calcium can be substituted by sodium, magnesium and/or strontium. Also the phosphate in HAP can be substituted by carbonate and/or sulfate. These substitutions play a complicating role in calcium phosphate scale formation, in particular the formation of fluoroapatite which has an even lower solubility than HAP.

~~III.~~IV. ULU PANDAN PILOT STUDY

A pilot study was carried out at the Keppel Seghers Ulu Pandan NEWater site, to investigate the calcium phosphate scale inhibition performance of the recommended phosphonate-based antiscalant developed by ThermPhos's Dequest AG. The configuration of pilot study is represented in Figure 2 below, while the design values of the pilot set-up are shown in Table 1:

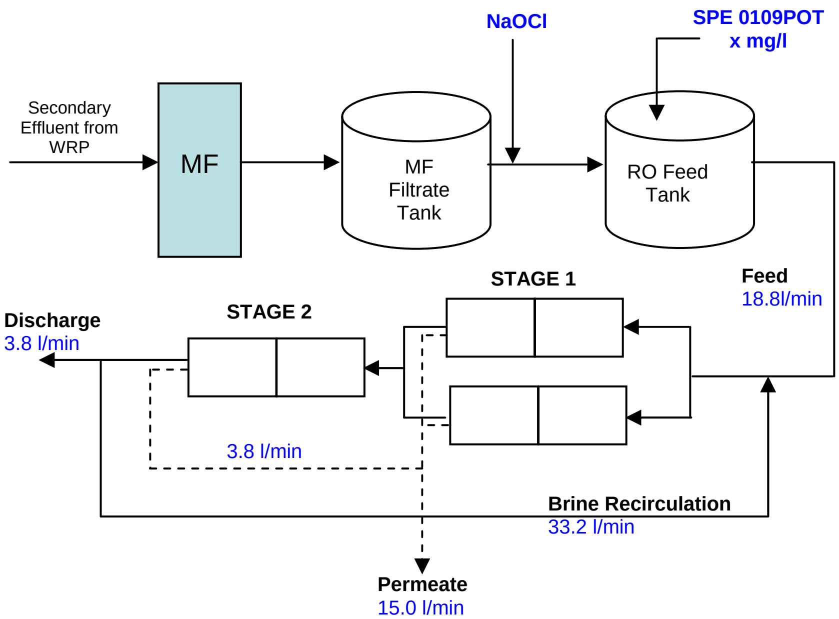


Figure 2: Configuration of pilot set-up at Keppel Seghers Ulu Pandan NEWater site

Parameters	Design Value(s)
a. Feed Flow	18.8 l/min
b. Permeate Flow	15.0 l/min
c. Brine (Recirculation)	33.2 l/min
d. Discharge	3.8 l/min
e. Flux	0.5 m^3/m^2/day
f. RO system recovery	28.85%
g. Overall recovery	80.00%
h. Feed Pressure	0.55 MPa
i. 1^{st} Stage reject pressure	0.51 MPa
j. 2^{nd} Stage reject pressure	0.43 MPa

Table 1: Design values of pilot set-up

The objective of the pilot study was to investigate the antiscalant performance under stressed conditions. The design of the pilot plant included a re-circulating brine stream from the second stage, in order to achieve minimum flux requirement of 0.5 m^3/m^2/day, as specified by the membrane manufacturer. Pilot study was carried out on 4" ESPA-2 membranes supplied by *Hydranautics*, with two elements loaded in each pressure vessel to achieve a two-stage configuration.

Sodium hypochlorite (NaOCl), was continuously dosed into the RO feed line to react with available ammonia in the effluent to yield monochloroamine being a membrane disinfectant for indirect potable water production. In case of insufficient availability of ammonia in the effluent, additional ammonium sulphate was dosed in order to achieve a minimum 5 mg/l of ammonia in the feed to react with NaOCl at all time.

Antiscalant was dosed directly into the RO feed tank by using a peristaltic pump manufactured by *Heidolph*. The antiscalant was mixed homogenously to ensure accurate dosing and homogenous distribution of scale inhibitor before entering RO unit. Feed water quality is depicted in Table 2 below.

Description	Unit	RO Feed	RO Feed (After mixing)
pH	pH unit	6.8	7.1
Aluminum	mg/l as Al	0.016	0.038
Barium	mg/l as Ba	0.0054	0.017
Calcium	mg/l as Ca	28.2	92.8
Potassium	mg/l as K	17.6	53.9
Total Iron	mg/l as Fe	0.036	0.14
Sodium	mg/l as Na	64.9	214
Bicarbonate	mg/l as HCO_3	63.1	194
Chloride	mg/l as Cl	82.4	249
Fluoride	mg/l as F	0.5	1.53
Nitrate	mg/l as NO_3	40.7	114
Phosphate	mg/l as PO_4	8.37	26.4
Sulfate	mg/l as SO_4	56.4	173
Total Silica	mg/l as SiO2	10.5	33.4

Table 2: Typical RO feed water quality

Based on the analysis of feed water samples collected during the pilot study the various relevant scaling indices were calculated in order to determine the scaling potential of the RO feed water. The calculations were made by using “CoRoLa-T”, a web-based scaling projection and product selection software developed by *ThermPhos’s Dequest AG*. The results of these calculations and the treatment limits of the recommended antiscalant on the respective scaling species commonly present in waste water re-use RO systems are represented in Table 3.

Type of Scale		Calculated Scaling indices	Treatment limit of SPE 0109POT
$CaCO_3$	LSI	0.51	2.5
$CaSO_4$	IP/Ksp	0.07	4.8
$BaSO_4$	IP/Ksp	1.26	150
SiO_2	SCR	1.23	2.0
$Ca_3(PO_4)_2$	IP/Ksp	1.28	4.5

Table 3: Calculated scaling indices vs. treatment limit of SPE 0109POT

~~IV.~~ V. RESULTS AND DISCUSSION

Flow and pressure data were collected throughout the entire 3 months period of the pilot plant study in order to monitor the operating performance of the pilot plant. The pressure and flow trends determined during the course of operation can be seen in figures 3, 4 and 5.

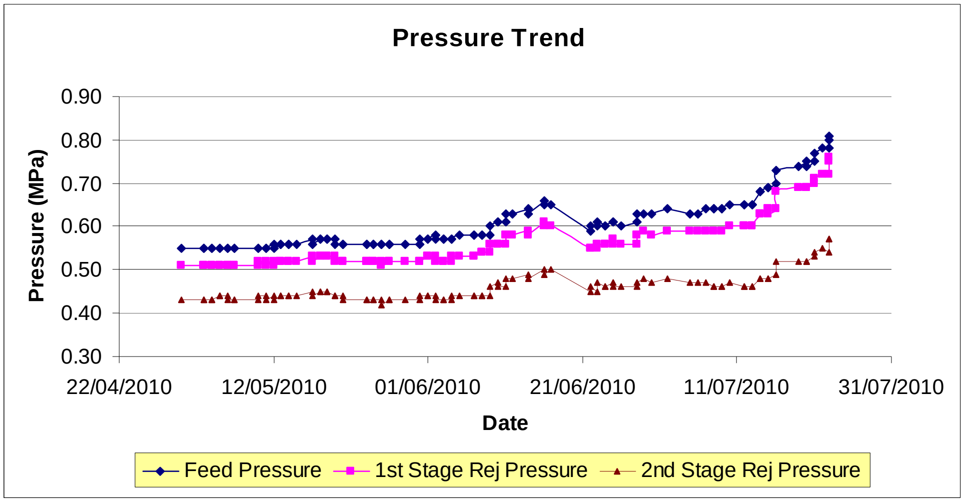


Figure 3: Pressure trending of pilot study (30 April 2010 ~ 23 July 2010)

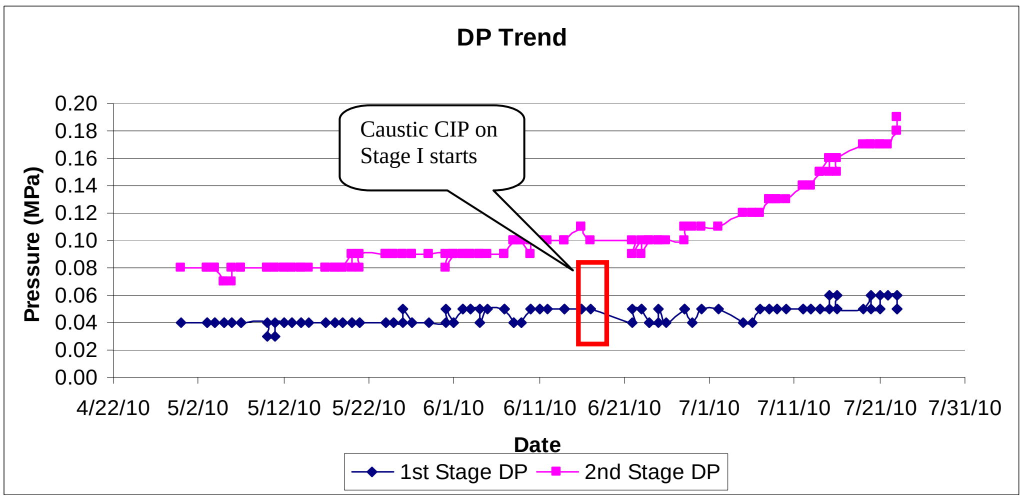


Figure 4: Differential pressure trending of pilot study (40 April 2010 ~ 23 July 2010)

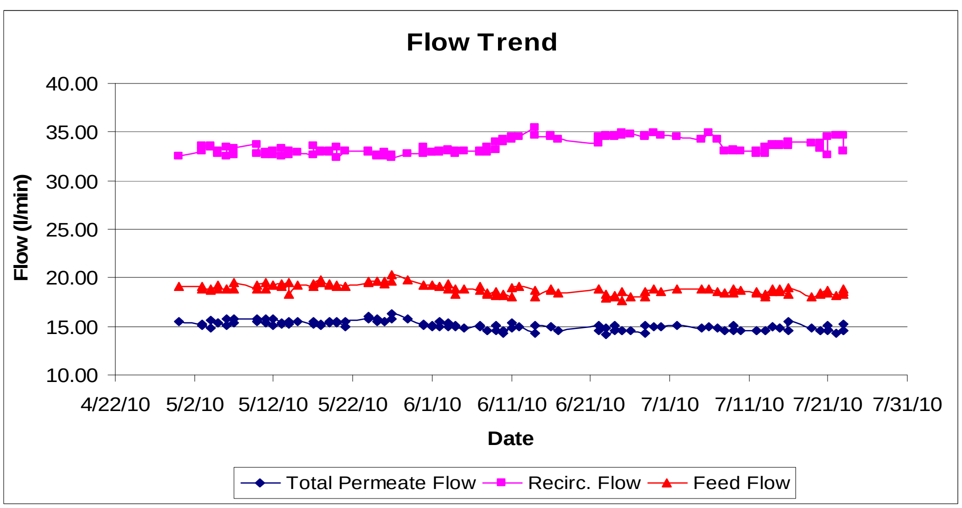


Figure 5: Flow trending of pilot study (40 April 2010 ~ 23 July 2010)

5.1 Observations

The key objectives of the pilot study were to assess:

- The performance of the recommended phosphonate-based antiscalant on calcium phosphate scale inhibition in a waste water re-use RO unit
- Feasibility of optimizing antiscalant dosage to improve cost-performance of the pretreatment chemicals used in the waste water re-use RO unit.

Throughout the three month observational period (30th April – 23rd July 2010), the dosage of the antiscalant was adjusted in order to determine its optimal dosage level. A summary of the series of events that took place during the course of the pilot study at the Ulu Pandan NEWater site is described in **Table 4.**

Event	Date	Remark(s)
Pilot plant start-up	30 April 2010	Initial dosage of SPE 0109POT @ **4.0mg/l**
Dosage Adjustment	21 May 2010	Antiscalant dosage reduced to **3.5mg/l**
Dosage Adjustment	11 June 2010	Antiscalant dosage further reduced to **3.0mg/l**
CIP cleaning	17 June 2010	Caustic cleaning on 1st stage membrane due to suspected biological fouling as a result of NaOCl dosing pump failure over the weekend
Dosage Adjustment	24 June 2010	Antiscalant dosage further reduced to **2.5mg/l**
Dosage Adjustment	5 July 2010	Antiscalant dosage further reduced to **2.0mg/l** (final)
Shutdown of pilot plant	23 July 2010	Pilot plant shut down for maintenance

Table 4: Summary of optimization events throughout the entire pilot study

5.2 Flow and Pressure Data

The flow and pressure data were collected to assess the degree of fouling and/or scaling in the RO system. According to the data collected, a significant initial onset of fouling was suspected into the 12th week of continuous running when feed pressure rapidly increased from 0.55MPa on 30th of April 2010 to 0.63MPa on 10th of June 2010. The feed pressure trending continued to increase thereafter and hit the 0.80 MPa feed pressure reading prior to a scheduled shut down for maintenance. Biological fouling on the membrane surfaces was suspected after an event of sodium hypochlorite dosing pump malfunction over a weekend in the first week of June 2010. The issue was rectified and the dosing pump was fixed three days after the event.

In view of the suspected biological fouling resulting from insufficient availability of monochloroamine in the feed water, an alkaline cleaning-in-place (CIP) was carried out solely on the first stage at pH 12.0 and at 28°C water temperature on 17th of June 2010 in order to remove the suspected biological fouling layer. No cleaning-in-place (CIP) was carried out on the Stage 2 membrane, in order to have a clear comparison with the cleaned Stage 1 membrane at the end of pilot study.

A plotted differential pressure trending has suggested the comparison of the degree of fouling in both Stage 1 and Stage 2 membrane elements. Without any cleaning-in-place performed on Stage 2 membrane elements, the Differential Pressure (DP) trending continues to increase exponentially, suggesting a higher water permeation barrier in the Stage 2 membrane elements due to suspected foulants building up on the membrane surface. The Stage 2 membrane elements were removed at the end of the pilot study and a membrane autopsy was performed to examine the fouling condition on membrane surface.

5.3 Dosage Optimization

A conservative initial dosage of 4.0 mg/l of scale inhibitor was suggested based on the calculated scaling potential depicted in Table 3. Gradual dosage reduction adjustments were carried out to examine the effectiveness of antiscalant at lower dosages, against calcium phosphate and other mineral scale inhibition. The final minimal dosage of antiscalant was achieved at 2.0 mg/l as of 23rd July 2010, at the end of three month pilot study period.

5.4 Membrane Autopsy Results

A full membrane autopsy has been performed on the used membrane elements to evaluate the nature of the foulants present on the membrane surfaces. The determined Fourier Transform Infrared (FTIR) spectrum illustrated in Figure 6 below matches the FTIR finger print of gram negative bacteria and confirms the biofilm nature of the deposit

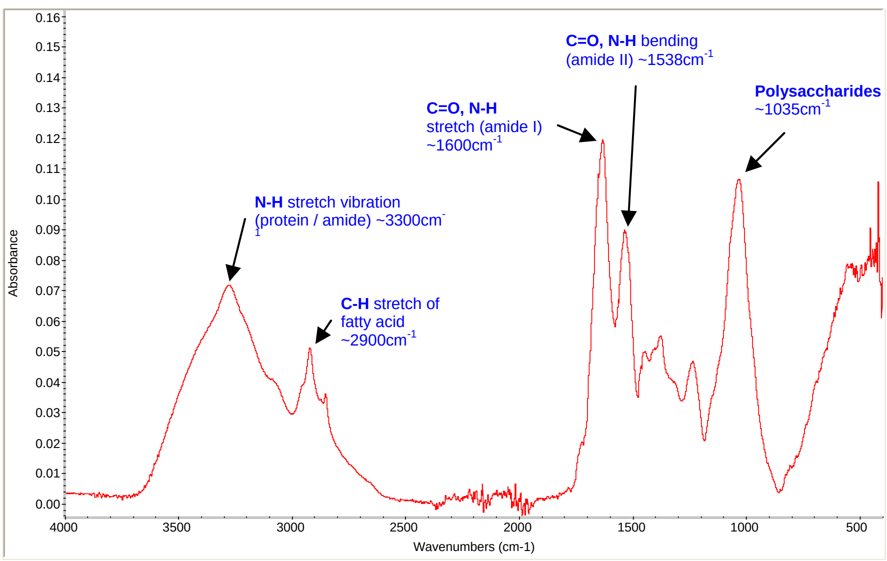


Figure 6: FTIR spectra on foulant found on membrane surface

Further SEM-EDX analysis (represented in Figure 7 below) has shown an excessive amount of carbon and oxygen elements in the foulant confirming again the biological nature of the deposit present on the membrane surfaces The membrane autopsy does not show any sign of mineral scaling on the membranes.

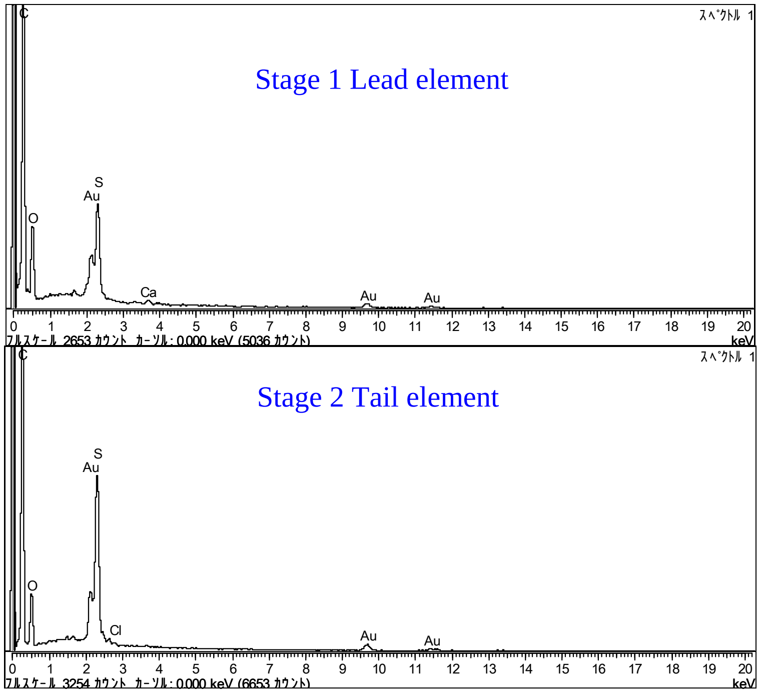
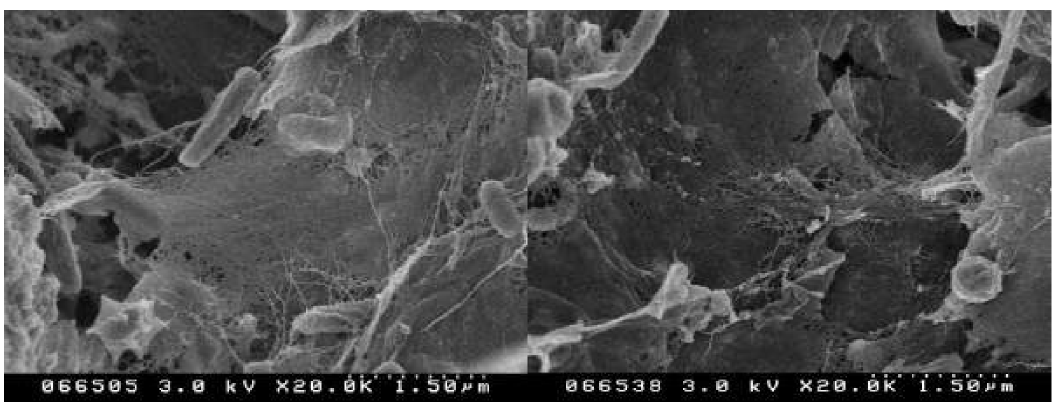


Figure 7: EDX results on stage 1 and stage 2 membrane elements



Stage 1 Lead Element (20,000x) Stage 2 Tail Element (20,000x)

Figure 8: Scanning electron (SEM) images on stage 1 and stage 2 membrane elements

~~V.~~VI. SUMMARY AND CONCLUSIONS

The pilot plant study carried out with thermPhos' Dequest AG "SPE 0109POT" at Keppel Seghers Ulu Pandan NEWater site in Singapore has successfully demonstrated its effectiveness as antiscalant for wastewater re-use RO systems. During the course of the field trial dosage level adjustments have been made in order to determine the optimal dosage of the antiscalant. In order to assess the antiscalant performance at various dosage levels relevant RO operating data have been collected continuously throughout the full period of the trial. Moreover a full membrane autopsy was performed at the end of the pilot study, to evaluate the chemical characteristics of the foulant present on the membrane surfaces.

Based on the findings from the pilot study and the results from the full membrane autopsies carried out at the end of the test period, we can conclude that,

- "SPE 0109POT" can effectively controlling calcium phosphate and other hardness scales at a low optimized dosage of 2.0 mg/l (which is about 20-25% lower versus traditional phosphonates based antiscalants) under operating conditions similar to the Keppel Seghers Ulu Pandan NEWater plant.
- Biological fouling has interfered with the antiscalant pilot plant test explaining the increased differential pressure (DP) on both stages of the RO system. The microbiological problems are fully attributed to an event of sodium hypochlorite dosing pump failure over a weekend..

In view of the severe biological interferences which occurred during the pilot study at Keppel Ulu Pandan NEWater site, a new pilot plant study is scheduled at the same site, to reconfirm the effectiveness of the recommended phosphonate-based antiscalant as a calcium phosphate scale inhibitor under more stringent biological control conditions.

~~VI.~~VII. ACKNOWLEDGEMENT

We would like to show our gratitude to Mr. Nozoe Munehiro of Nitto Denko (Singapore) Pte Ltd for all the supports and comments provided throughout the pilot study at Ulu Pandan NEWater site.

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