



Review

Mitigation of Biological Fouling and control of SHMP Antiscalant agent for Brackish Water Reverse Osmosis Plants

Mohammed Saleh Al. Ansari

Department of Chemical Engineering, College of Engineering, University of Bahrain, PO box 32038, Sukhair Campus, Kingdom of Bahrain Tel: +973-3944-1110
Email: malansari@uob.edu.bh

Accepted 30 October 2012

Sodium Hexametaphosphate (SHMP) is considered good antiscalant which is used to mitigate scaling in reverse osmosis membranes. The SHMP solution is made up in SHMP tank and dosed to the raw water via a point. It was found that the SHMP tanks were the major source of biological infection and the results of the TBC values in the SHMP tanks were TNTC within 2 -days of make-up. SHMP is a polyphosphate whose degenerate into orthophosphate, is affected by factors of concentration, temperature, known nutrient for biological organisms to grow and colonize, a study on free phosphate in SHMP was carried out. Due to the presence of H₂S in the raw feed water, chlorine is not used even in trace levels. Hence, sodium metabisulfite (SBS) was used for sterilization of SHMP tanks and dosing lines. Extensive laboratory studies were conducted to determine the optimum dose concentration of SBS into SHMP tanks required to sterilize the solution but minimize the version to free phosphate. This paper discuss the addition of SBS in the SHMP tanks, its application and results to confirm the effectiveness of SHMP with SBS related to Micron Guard Filter (MGF) condition and R.O performance.

Keywords: SBS, SHMP, Reverse Osmosis; SHMP (sodium hexametaphosphate); RO (reverse osmosis); antiscalant

INTRODUCTION

(Pandey,2012) studied the fouling of reverse osmosis (RO) plants and came up with the idea that is the most preferable process for water recovery because of its higher rejection of impurities with lower associated cost and higher quality of product. Fouling still is a major challenge during the water recovery due to higher contaminant loadings and high rejection capability of this membrane. (Winters, 1995) stated that the presence of suspended solids, colloidal and organic matters, and high level of biological activities further elevate fouling

potentiality. This review was performed to identify major foulants causing hindrance in sustainable application of reverse osmosis and to present available pre-treatment options for these foulants. There are four fouling types present in RO namely; bio-fouling, inorganic/scaling, organic, and particulate fouling. Among them; bio-fouling is less understood but dominant since the pre-treatment options are not well developed. Other fouling mechanisms have been overcome by well developed pre-treatments. The major foulants for RO are dissolved and

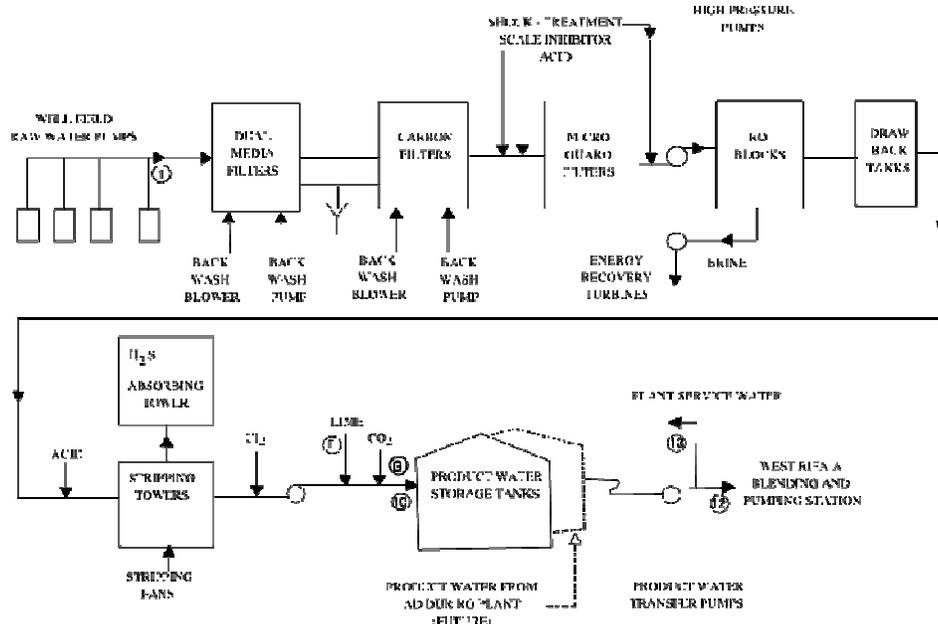


Figure 1. Typical Successful High Brackish Reverse Osmosis Plant (Working since 1984)

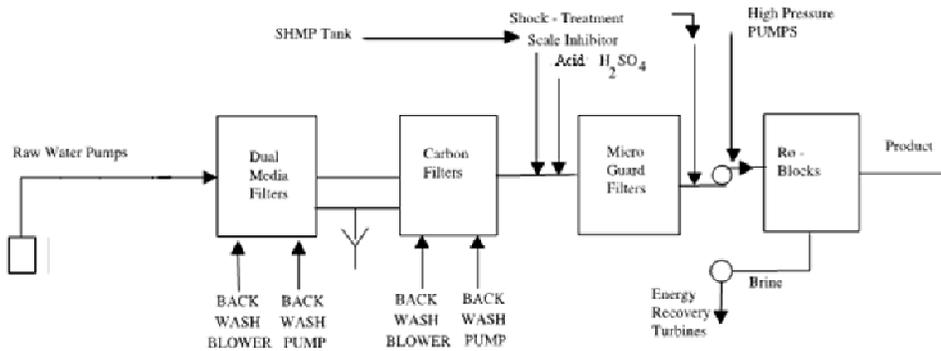


Figure 3. the layout of the current plant

macromolecular organic substances, sparingly soluble inorganic compounds, colloidal and suspended particles, and micro-organisms. Some of these potential fouling water quality parameters (PFWQPs) are interrelated with each others such as electrical conductivity is a surrogate measure of total dissolved solids with established stable relationship. Most of these PFWQPs such as total suspended solids, turbidity, chemical oxygen demand can be removed by conventional pre-treatment; some such as colloidal particles and micro-organisms by modern options and even others such as endocrine disrupting compounds, pharmaceutical and personal care products are still challenging for current pre-treatments. These foulants need to be identified properly to integrate appropriate pre-treatments for minimizing fouling potentiality to increase water recovery at minimal costs. In general, a decline in membrane performance can be corrected by cleaning the membrane. Cleaning can be

defined as “a process where material is relieved of a substance which is not an integral part of the material” (GuntrögÖrdh, 1989). Cleaning is done to restore membrane performance when it falls below the expected permeate yield by about 10 %. Although, there are a number of cleaning techniques such as physical or chemical or combination of both but the chemical cleaning methods are widely used by RO industries for membrane cleaning and regeneration (GuntrögÖrdh, 1989 ; Ebrahim, 1994). Membrane Manufactures recommend various chemical methods for cleaning and regeneration of their membranes. In all cases the cleaning process depends on the type of foulant deposited on the membrane surface, and for a successful cleaning of fouled membranes, identification of the type of foulant is essential which is done by extensive analysis of the foulants. A destructive autopsy which provides a scientific foundation on which to optimize the cleaning

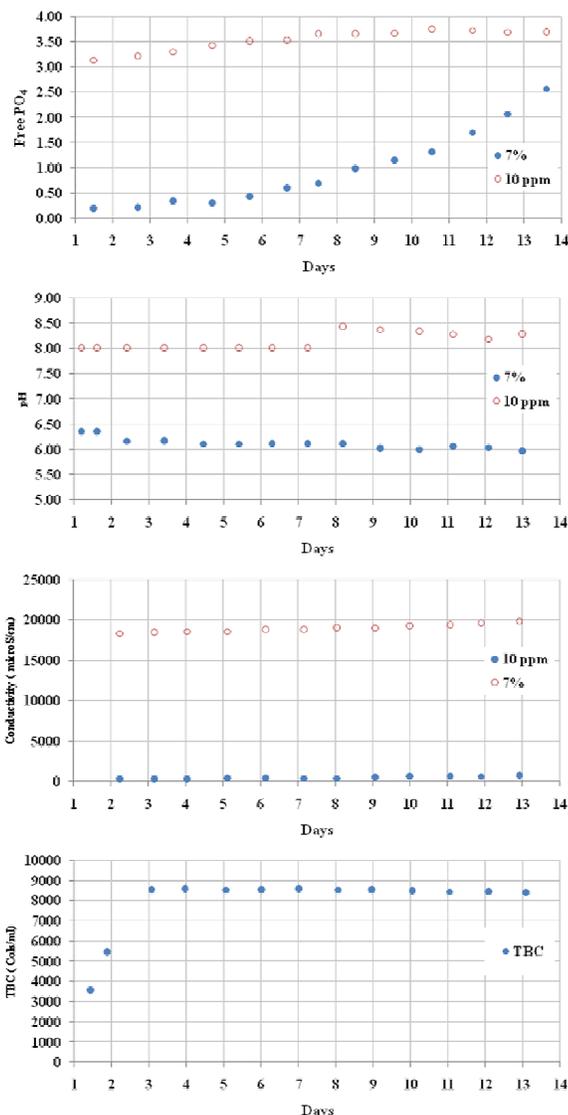


Figure 2. Behavior of SHMP in Raw Brackish Water

procedure is done as a last resort when cleaning fail to restore membrane performance (Ebrahim, 1994 ; Butt et al., 1995). This mainly involves cutting open the membrane, visual and microscopic examination of membrane surface, chemical and biological analyses of foulants, analyses of membranes surface and the membrane material.

Ahmed et al, 1989 studied the fouling problem in Ras Abu Jarjur RO plant, which uses deep ground water containing H_2S , has been in operation for the past four years without any serious problems. However, bio-fouling of the membranes has been gradually building up and appeared to start affecting the performance after 2 years of operation. Several investigations have been carried out to resolve this problem. It was found that the SHMP tanks were the major source of biological interaction and the results of the TBC values in the SHMP tanks were TNTC

within 2–3 days of make-up. SHMP is a polyphosphate whose reversion into orthophosphate is affected by factors of concentration, temperature, time and pH. Since free phosphate (orthophosphate) is a well known nutrient for biological organisms, a study on free phosphate to SHMP was carried out. Due to the presence of H_2S in the feed water, usage of chlorine is avoided even in trace levels. Hence, sodium metabisulfite (SBS) was considered for sterilization of SHMP tanks and dosing lines. Extensive laboratory studies were conducted to determine the optimum dose concentration of SBS into SHMP tanks required to sterilize the solution but minimize the reversion to free phosphate. Discuss gone on the basics of the addition of SBS in the SHMP tanks and its application results in detail to confirm the effectiveness of SHMP with SBS related to M.G. filter condition and RO performance.

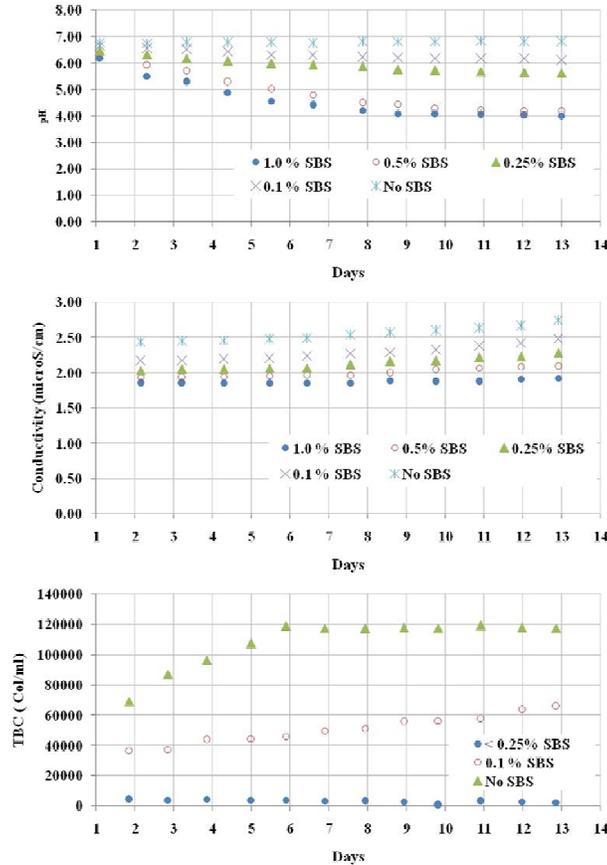


Figure 2. Effect of SBS in SHMP

Plant Design

The brackish R.O. Desalination plant receives its raw feed water is highly brackish ground water extracted from deep wells that contains high saline and contains approximately 2 – 5 ppm of dissolved sulfides. In view of these, no pre-chlorination is being done and a closed pressurized system is being maintained up to the gas stripping towers located in post treatment area in order to avoid air oxidation. Dissolved sulfides could be oxidized to elemental sulfur that could cause serious colloidal fouling in the R.O. membranes. The filtration as part of unit operation starts by Dual Media Filters. These filters are chlorinated off line periodically. The feed water passes through the Activated Carbon Filters. Although they were originally designed to remove hydrocarbons in the feed water, they are at present reducing the amount of suspended solids and adsorbing bacteria. Dosing of pretreatment chemicals is done after the carbon filters and sulfuric acid is dosed first followed by SHMP in the in-line mixer. These steps are taken for alkaline and perhaps non alkaline scaling control. This simple idea reflects the design and operation of typical high brackish RO plant that is similar to existed skid.

The last pretreatment of the feed water before entering the R.O. membranes is the Micron Guard Filtration.

Polypropylene filters of 1,5,10 micron pore size are exploited and sometimes less than that to avoid penetration of substances cause high level of fouling. The feed water coming out of this filtration system is considered completely compatible to the R.O. membranes. Feed water coming out of the micron guard filters is taken up by high pressure pumps and introduced into the R.O. blocks at pressures. The over-all recovery is between 72%. To further optimize cost, the third stage reject brine is passed through energy recovery turbines before dumping into the sea since the quality of the third stage brine outlet is lower in total dissolve solid of the normal seawater. Permeate water is forwarded to draw back tanks and then further acidified with sulfuric acid to pH 4.5. This is being done to release H₂S gas for subsequent removal in the gas stripping towers. The degasified water is then dosed with the post treatment chemicals Cl₂ in that order. The performance of RO Desalination is largely dependent on the quality of feed water and the service life of the permeators (Kah et al , 2011). Production decline follows a projected path but the rate of decline is directly affected by the effectiveness of pretreatment and method of operation and maintenance. Proper monitoring and cleaning procedures will bring the decline close to the projected trend. Most of the Corrective measures to improve R.O (Devin, 2012). Block

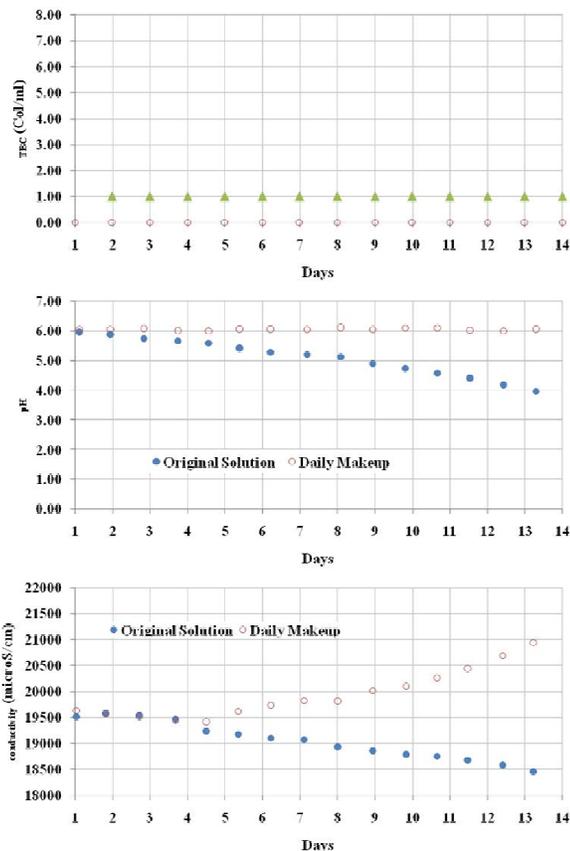


Figure 4. Simulation of SHMP in make-up condition

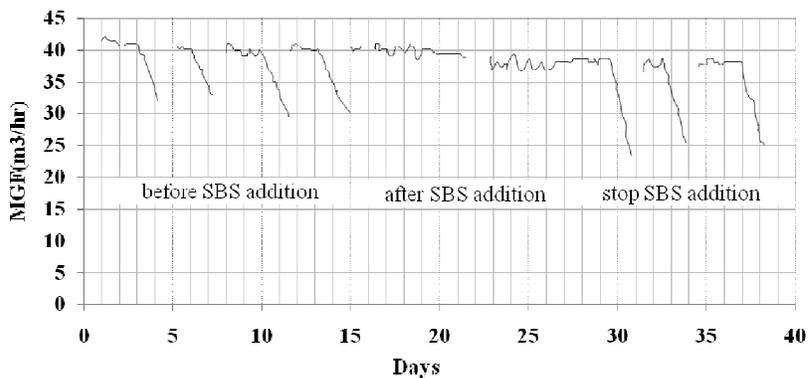


Figure 5. RO Micron Guard Filter Condition

performance are being incorporated in the pre- treatment system. However, the final adjustment is made in the RO Production section. The main polishing measure is the R.O Block cleaning program. The manufactures guidelines are extensively utilized along with actual experience.

As more data were gathered, it was observed that the manufacturer’s cleaning guidelines were not always effective. New cleaning programs were formulated using only recommended chemicals compatible with the R.O Membranes. It has been a practice that whenever there was a rapid production decline in any R.O. Block, a 5000

ppm SBS soaking was carried out for a period of 72 hours followed by flushing with high pH water.

Pre- Treatment System

The plant performance was relatively satisfactory and plant operation was smooth. One of the earliest problems indentified was the excessive bacterial growth in the dual media filters and activated carbon filters. This was followed by hydrogen sulfide smell and increasing trends of dissolved oxygen in the pretreatment system.

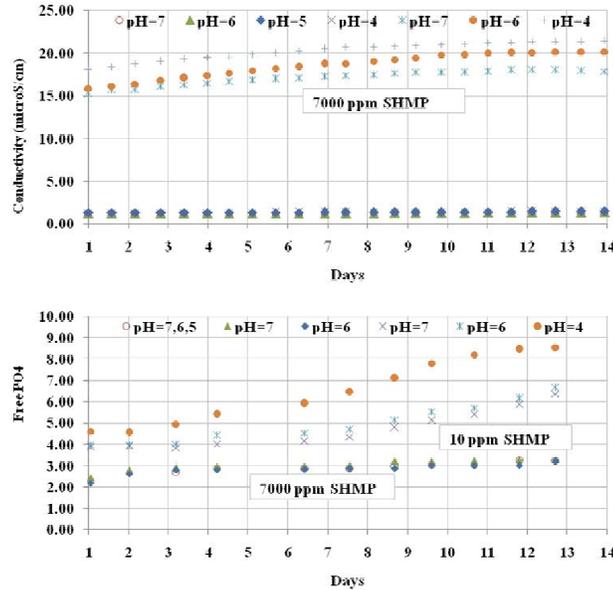


Figure 8. behavior of SHMP in different pH conditions

Investigations and studies were then made in order to find solutions to the problems. Findings resulted in the early modifications of the pre-treatment system which are still being applied to the plants. The increasing trend of dissolved oxygen in the pretreatment system was generated by the algal formation. The high DO content of the water suppressed anaerobic bacteria activity such as SRB. However, as the algal matter were physically removed or destroyed, and SRB activity was able to proceed producing one of their by-products, hydrogen sulfide. With the identification of the algal/bacteria problem, it was evident that sterility had to be maintained through each treatment stage. Painting only inhibited algal growth but additional measures had to be taken to control bacterial activity. The following techniques were then developed and implemented. Periodic sterilization of DM/F using 1000 ppm, Cl₂ dose to one DM/F every day followed by normal air scour and backwash and longer rinses period to ensure complete Cl₂ removal before placing the filter on line. Shorter filter element replacement of the MG/F (day cycle) in order to minimize bio-mass accumulation which could lead to bacterial infection in the R.O. Blocks. Addition of 0.25% SBS with 8% SHMP in the tanks. SHMP had been identified as a potential source of aerobic bacteria in its free phosphate form. If left unchecked, it could increase bacterial load on the RO Blocks when dosed as an anti-scalant. The addition of SBS, a well known bactericide, will keep the aerobic levels in check as well as eliminate time consuming offline Cl₂ sterilization of the SHMP tanks. Installation of cartridge guard filters in the R.O. shock treatment line. This does not directly control bacterial activity but it is a good safeguard from inorganic foulants coming from the SBS tanks. Chlorine sterilization

of the well collector pipes and MGF vessels during plant outages. Micron Guard Filter System (MGF's) system is the last on line filtration prior to treatment water entering the RO permeators.

When the condition the MGF cartridge elements started deteriorating with all the foulants, with decreased flow and high ΔP, a modification was designed to remove aerobic bacteria from HMP tanks entering the system. Addition of 0.25% in HMP tanks entering the system. Addition of 0.25% in HMP tanks was carried out on daily basis and this improved the quality of water, stabilized the flow rate and ΔP lower. MGF vessels were kept on line for a period of 16 weeks after the shutdown and improved considerably. The visual inspection of the elements also revealed, that they were quite clean for a period of 4 weeks with faint foul smell which could be due to the anaerobic bacteria present in the raw water and also due to the infection during installation of the elements. In order to eliminate the foul smell present at the bottom of the MGF vessel it was proposed to soak the vessel up to the outlet header with 5% H₂O₂ for a period of 4 hours prior to element installation which also helped in keeping the system clean. The cartridge elements used in the MGF vessel were previously disposed. Due to the high cost of the elements, various methods were tried to clean these elements. Finally these elements were soaked in 5000- 6000 ppm chlorine solution for a period of 24 hours followed by water jetting brought the condition of the elements to nearly new. When these were installed SDI, ΔP, and flow rates were measured which were quite acceptable. The reusing of elements upto 12 cycle saved considerable amount of money. On line tests using 10 Micron, 5 and 1 Micron cartridge elements in filter housings showed that the

Table 1. Chemical Analysis of High Brackish Reverse Osmosis Plant

Item	Raw Water	RO Brine	Final Product
Temp	30.1	33.0	29.2
PH	6.82	6.30	8.25
Conductivity	19243	45308	4.81
Turbidity	0.12	0.21	1.81
SDI	1.44	-	3.70
Dissolved O ₂	ppm 0.12	-	-
TS	ppm 3.12	-	<0.05
TBC	ppm 2	29	2
TDS	ppm 12674	34365	282
Total Hardness	ppm 2249	7608	82
HCO ₃	ppm 187	280	58
Ca	ppm 617	1718	21
PO ₄	ppm 0.35	22.00	-
Na	ppm 3170	9024	87
K	ppm 136	378	253
Mg	ppm 293	801	1.97
Sr	ppm 22	59	0.31
Ba	ppm 0.27	0.48	-
No ₄	ppm 0.08	0.22	0.08
Ma	ppm <0.03	0.05	<0.02
Cu	ppm 0.03	0.08	<0.02
Zn	ppm 0.07	0.08	<0.02
S ₂ O ₃	ppm 1193	3054	<0.17
Cl	ppm 6836	18722	95
SO ₄	ppm 610	1801	38
TOC	ppm 0.88	-	-
Oil	ppm <0.10	<0.10	-

debris accumulated in 1 Micron is higher than 5 Micron which higher than the 10 Micron filters, this, when actually performed in the plant conditions might necessitate the frequent replacement of MGF elements than the present, but high quality feed water would certainly assist in production stability as well as reduce membrane fouling. Moreover, the rigid specifications for SHMP and H₂SO₄ recently enforced on the chemical manufactures particularly low iron content helped in preventing the formation of Iron Sulfide. It is interesting, to note that when one shipment turned dark brown in colour and were put out of service within 10 days. Hence with the frequent cleaning of the MGF vessels with H₂O₂, low iron content in SHMP, and H₂SO₄, addition of SBS in SHMP tanks to prevent aerobic bacterial growth helped instable performance of MGF system.

Shock Treatment System using Sodium Meta Bisulfite (SBS) which is a known bactericide which is frequently used in the water treatment industry. This system is designed to shock treatment all the blocks for a brief period of half to one hour. Sodium Bisulfite is prepared every day in the shock treatment tank (Concentration 30000 ppm) and is dosed to each block either daily or alternate day. Cartridge filters are installed in the shock treatment system before the RO. Blocks as an additional safeguard against foulants. Filters 10 to 5 um and 1um is tried and used order to reduce foulants further.

Biological Fouling

The activated carbon filters used to absorb the H₂S gas for a limited period of time until saturation. It is recommended by many literatures to go on operation using the following protocols and methods:

- Periodical sterilization of Dual Media Filters.
- Periodical regeneration of Activated Carbon Filters.
- Periodical sterilization of Micron Guard Filters, and, Periodical sterilization of well collector pipes.
- Shock treatment with sodium metabisulfite for RO Membranes.
- Periodical sterilization of RO Membranes with SBS.
- Periodical sterilization of SHMP tanks.

However; the R.O. blocks by time shows signs of production decline, high differential pressure and high salt passage. The service period of the micron guard filter which used to be more than four weeks between cleanings had to be shortened due to low flow, high SDI, and high differential pressure.

Visual inspection of the micron guard filters were made and close monitoring was continued. Very foul smell was noted in the micron guard filters together with slime on the vessel sides and dark colored filter elements which all indicated biological fouling. This phenomenon were

Table 2. Averaged performance of MGFs

	Service Time (Days)	Flow Initial (m ³ /h)	Flow Final (m ³ /h)	SDI	Flushing Time (Hrs)
Without SBS	14	43	32	1.40	13.0
With SBS	14	43	40	0.70	3.0

experienced before and proper treatment done as per (Ahmed et al, 1989). The biological fouling can be attributed to the Sulfate reducing bacteria (SRB) and anaerobic bacteria from the wells, the unmemorable bacteria embedded in the permeators, Aerobic bacteria from SHMP tanks, and, Free PO₄ feeding the already embedded bacteria.

Laboratory Studies

Behavior of SHMP Solution

SHMP solution is well known to revert to orthophosphate although it depends upon the condition to which the solution is exposed. Various conditions have been prepared in the laboratory to confirm exact property/nature of SHMP in the existing plant condition. The SHMP was dissolved in the dechlorinated service water in different concentrations of 10ppm and 7%. The results are shown in Figure 2. SHMP is known to revert to orthophosphate within a few days and its tendency is higher at lower concentration. About 25% of original polyphosphate reverts to orthophosphate at 10 ppm.

Free phosphate has reverted in high concentration (7%) and no increase of three phosphate is observed during this limited time. pH and conductivity gradually increase with time but more changes are observed in low concentration. It should be noted that TBC increase is quite rapid in both concentrations (10 ppm and 7%). TBC increase does not appear to be dependent on the concentration of free phosphate. It could be said that environment for total bacterial growth is quite congenial in any SHMP concentration.

Effect of SBS in SHMP Solution

Laboratory studies were continued to confirm SBS effect to sterilize SHMP in different concentration and investigate any unknown side effect which might occur in SHMP tank. Various concentrations of SBS were added to 7% SHMP solution to simulate SHMP tank and analyzed for free phosphate, TBC, pH and EC. The results are shown in Figure 3 which indicates that low concentration that is less than 0.1% of SBS could not sterilize SHMP solution. Minimum 0.25% of SBS is found to be required to keep SHMP in sterilized condition. High concentration of SBS reduced pH within a few days and

reached to pH=4 within 5 to 6 days and conductivity is also found to increase rapidly in higher SBS concentration. From these test results optimum SBS concentration is found as 0.25% in which SHMP solution is not quite affected by adding SBS but still reached sterilized condition.

Simulation of SHMP Makeup Condition

During SHMP solution make up every day, about 25% remaining solution always remains behind in the tank. Thus old solution is topped up with daily fresh makeup solution. In order to simulate this condition in the laboratory, 0.25% solution in 7% SHMP was prepared in a beaker and tests such as pH, EC and TBC, were conducted on the sample. At the end of 24 hours, 75% of the solution was taken out from the beaker and fresh make up solution was taken out from the beaker and fresh make up solution was added. Same tests were conducted as above and repeated from the next 12 days.

The results showed that TBC in the simulated SHMP tank was kept steady at 0 even after daily makeup and the pH remained around 6.0 as initial makeup while the pH without daily makeup declines to 4.0 after 9 days. The conductivity also remained the same as initial makeup while the conductivity without daily makeup increased by time. From the above results, it is confirmed that addition of SBS at the concentration of 0.25% could keep TBC at 0 without interfering with SHMP in the simulated tank conditions.

TBC in SHMP Tank and MGF performance

Based on data obtained in the laboratory, 0.25% SBS was added into SHMP tanks in the daily makeup. Total bacterial count (TBC) level in the SHMP tank was monitored before and after SBS addition as shown in Figure 5. TBC trend quite clearly shows that aerobic bacteria are controlled at 0 in the SHMP tank. Performance of Micro Guard Filter (MGF) was checked and is shown in Table 2 and Figure. 6.

Due to the parallel operation of 7MGFs, differential pressure across the MGFs appears the same. However clogging of MGFs normally appears in the flow pattern clearly as shown in Figure 6. Within the same service time (14days), flow decline trend is quite different, i.e, the flow of MGF reached to 32 m³/hr with SBS addition. SDI,

although much lower than ordinary sea water. RO, indicates quite improved at the end of service time i.e 1.40 without SBS and 0.7.

Presence of Free Phosphate

Free Phosphate in the process is analyzed as a part of evaluation of the system. It is found that the level of the free phosphate is quite high in the membrane. Table 3 shows free phosphate in the membranes. This because Different concentration in each stage is due to concentration factor and free phosphate is more concentrated in the last stage. It should be noted that reversion is clearly happening in the first stage of membrane so that free phosphate in the feed water is less than one but 5ppm of phosphate is observed in the first stage brine. Increase in 2nd and 3rd stage bring is due to concentration factor but not due to reversion in these stages. Based on the above, it can be seen that SHMP still has the potential to be a nutrient for biological growth in the membranes even though addition of SBS has killed off the aerobic bacteria found to be present in the service tank and the dosing line.

CONCLUSION

This study evaluated alternatives to the traditional sulfuric acid/sodium hexametaphosphate (SHMP) chemical treatment program for use in reverse osmosis (RO) permeators. The aim was to find a simpler, safer, and more economical scale inhibition program. The study was conducted by using a working plant reverse osmosis skid. Membranes were used in each test were arranged in a 2:1:1 array, whereby the supply high saline brackish water was fed into the modules and the brine reject from these modules was combined and fed to a third module. The paper discusses in some detail the chemical analyses carried out. This series of experiments and trials in the plant have shown positive results such as improved Micron Guard Filter and also RO Membrane Performance by preventing aerobic contamination entering the feed water from the SHMP tanks and dosing lines. Optimum concentration of SBS to be added to the SHMP tanks is found to be 0.25% and this concentration is found to control bacteria and does not affect SHMP reversion to orthophosphate. The presence of free phosphate ions seems to have a potential to be a nutrient for biological growth, therefore it should be another consideration to remove phosphate compounds from the process, if possible. During the last annual shutdown of the plant, a new line was installed for the SHMP dosing system as a standby. After studying various conditions, it is also being considered to try 5 Micron Cartridge Filters

instead of the currently used 10 Micron Filters. In this trial, the biological fouling is a major factor of RO performance decline thus, the challenge to solve the problem will be continued until final success is achieved.

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