

# A systematic approach to reduce operational cost for a medium-sized RO.

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## **AUTHORS**

Nagham Najeeb, Avista Technologies Lee Durham, Avista Technologies Ray Eaton, Avista Technologies Jessica Foster, Avista Technologies

## ABSTRACT

This paper will cover a systematic plan to optimize the performance of a medium-sized reverse osmosis (RO) system in Southern California. The RO system's operational costs significantly increased over the span of 10 years due to multiple factors including lack of maintenance, operator training and personnel turnover. The approach to improve the RO system's operations and reduce costs was set by a new management team with the help of their new chemical provider.

The most important goal was to reduce the membrane replacement rate. The 1st Pass RO membranes were being replaced once a year due to a loss in flow and high conductivity. The pretreatment was inspected, and a water analysis was performed. The findings identified that the feedwater quality had changed over time and now had higher concentrations of manganese and silica. The inspection of the greensand (GS) filters indicated that almost 100% of the metals were removed prior to the RO system; however, a cartridge filter analysis and membrane autopsy identified the cause of the fouling to be manganese. Additionally, the membrane autopsy showed oxidation damage.

A detailed audit of the original system design, pretreatment, water quality and membrane autopsy results are provided in this paper. The audit identified the source of membrane fouling and the pretreatment was optimized to prevent future fouling. This tactical planning approach can be applied to help other reverse osmosis treatment plants reduce their operational costs and increase membrane life.

# CASE STUDY OF A DRINKING WATER BOTTLING FACILITY

### BACKGROUND & PROCESS OVERVIEW

This case study is about a drinking water bottling facility in Southern California producing 115,200 gallons per day (GPD) of RO permeate. In addition to its product usage, the permeate water is used for maintenance of RO operations (cleans/ flushes), cleaning of equipment and other daily functions. The feed is well water that contains moderate amounts of manganese, iron and silica. The pretreatment consists of three GS filters continuously injected with potassium permanganate (KMnO<sub>4</sub>). The KMnO<sub>4</sub> is injected for the complete oxidation of iron and manganese present in the well water to assist in the removal of these metals by the GS filters. The filtrate is stored in a holding tank to ensure there is enough water for RO production at all times. The holding tank is followed by a 5-micron cartridge filter (CF). An antiscalant is injected at approximately 10 parts per million (ppm) prior to the high-pressure feed pump to control scaling. The RO system is a 2-Pass unit; the 1<sup>st</sup> Pass is composed of 2 Stages, with the concentrate from Stage 1 feeding Stage 2. Stage 1 of the 1<sup>st</sup> Pass consists of 3 pressure vessels which feed 2 pressure vessels in Stage 2. Each pressure vessel holds 4 elements, meaning 8 elements operate in series. The system recovery was initially set at 57%. The 2nd Pass RO is composed of 2 Stages. Stage 1 of the 2<sup>nd</sup> Pass consists of 2 pressure vessels which feed 1 pressure vessel in Stage 2. Each pressure vessel contains 4 8-inch membranes. The 2<sup>nd</sup> Pass RO recovery was set at 85%.

The water treatment plant is 10 years old and has been operated by multiple teams over the course of its lifetime. The operational cost gradually increased over the 10-year period, requiring attention from upper management. The membranes in the 1<sup>st</sup> Pass were replaced approximately once per year, due to irrecoverable performance and loss in membrane integrity, and the system was cleaned approximately once every other week. The CF lifespan varied from as little as two days to three weeks.

Plant management agreed to allow an outside company that specializes in membrane system diagnostics and specialty chemical solutions into the facility to offer improvements. The site suspected that insufficient removal of metals by their GS filters was leading to excessive fouling of the CFs and 1<sup>st</sup> pass of the RO.

Upon arrival, the company reviewed key information that would lead to improving system operation and efficiency. A walkthrough of the plant revealed black CFs, which had just been replaced after being online for only three days. Blackcolored foulant is most often associated with manganese, especially in well waters. One of the CFs was sent to an analytical laboratory to confirm if manganese was the primary foulant. This was evidence that the site's suspicion of metal fouling was correct. Additionally, a well water sample was sent for full ion analysis and a historical analysis was requested from management to determine if water quality had changed since system startup. As bypass from the GS filters was the suspected source of the rapid fouling, particle count, turbidity, iron and manganese profiles across the different pretreatment equipment were suggested as the easiest way to identify the source of the leak. Samples were taken from the feed to the GS filters, filtrate of each filter, post holding tank and after the CF.

#### SYSTEM PERFORMANCE DATA INTERPRETATION

The next investigative step for troubleshooting the system was to review system performance trends. There are many causes for poor RO system performance. However, regardless of the cause, symptoms fall into one or more of the following categories:

- Increases or decreases in permeate flow
- Decreases in salt rejection
- Increases in differential pressure (DP)

It is important to determine whether changes in system performance are due to variations in operating variables, such as temperature and pressure, which are not associated with degradation through fouling or damage to the membranes themselves. To make this assessment, normalized system performance data is essential. When the normalized performance data show unexplained changes in performance, troubleshooting measures should be employed to find the cause and furthermore the corrections needed to stabilize system performance. Different types of fouling have unique symptoms. The normalized data can give an indication on which foulant is the most probable cause for the decline in system performance.

The normalized permeate flow severely decreased while the Stage 1 DP increased over time. The Stage 2 DP increased as well, but not as acutely. As the system did not have flow meters on every stage, the normalized permeate flow data was the overall flow rate of the 1<sup>st</sup> Pass RO. The disadvantage of only looking at the total permeate flow is that it was not possible to tell whether Stage 2 performance had been compromised. The CIP efforts did not appear to help with restoring the permeate flow rate or the DP back to baseline and also did not provide sustainable performance over time.

The system performance further supported the site's suspicion that bypass from the GS filters was the cause of their issues as increased Stage 1 DP with decreased permeate flow coupled with more stable Stage 2 performance is consistent with colloidal fouling in Stage 1. In general, membrane autopsies show that colloidal and particulate fouling are the most frequent causes for Stage 1 RO element performance loss. Colloidal and particulate foulants include:

- Clays
- Colloidal silica
- Metal silicates
- Alum floc (aluminum hydroxide)
- Iron floc (ferric hydroxide)
- Macromolecules

Effective filtration can minimize but not eliminate this type of fouling. Unlike other types of fouling, colloidal and particulate fouling occur primarily in Stage 1. Optimization of pretreatment

and hydraulic parameters within the RO system can minimize this type of fouling.

#### **CARTRIDGE FILTER ANALYSIS**

The cartridge filter (Figure 1) was completely coated with a black-colored, granular material.

#### FIGURE 1. IMAGE OF THE CARTRIDGE FILTER

Foulant analysis including Energy Dispersive Spectroscopy (EDS) was performed on the CF. EDS is used to determine the relative concentration of elements present in a sample.

The foulant analysis confirmed manganese as the main inorganic constituent in the foulant material (Table 1). Small amounts of iron and a trace amount (<0.50% by weight) of calcium was also detected. The analysis identified the main foulant as manganese. Carbon and oxygen shown in the EDS analysis were attributed to the material of the CF. After confirming the material as primarily manganese, the next step was to determine how it was bypassing the GS filters and fouling the membranes.

#### TABLE 1. EDS ANALYSIS OF THE CF EXTERIOR AT 150X

Elements	Cartridge Filter (Weight %)
Carbon	82.61
Oxygen	13.16
Manganese	2.61
Iron	1.49
Calcium	0.13

#### WATER QUALITY ANALYSIS

The well water was analyzed and compared to a previous analysis from 2009. The feedwater quality changed slightly over time and now contained higher concentrations of manganese, iron and silica. The water analyses are provided in Table 2 below.

# TABLE 2. WATER ANALYSIS COMPARISON BETWEEN ANALYSES FROM 2009 AND 2019

Parameter	Raw 2009 As Ion (mg/L)	Raw 2019 As lon (mg/L)
Sodium (Na)	110	122.3
Potassium (K)	3.8	4.9
Calcium (Ca)	58	79.2
Magnesium (Mg)	23	26.5
Iron (Fe)	0.42	0.70
Manganese (Mn)	0.10	0.29
Barium (Ba)	0.0019	None Detected
Strontium (Sr)	0.13	0.16
Chloride (Cl)	180	202.5
Sulfate (SO <sub>4</sub> )	95	109.5
Bicarbonate (ppm)	170	200
Nitrate (NO <sub>3</sub> )	None Detected	3.99
Fluoride (F)	0.65	0.98
Silica (SiO <sub>2</sub> )	47	54.2
pН	7.60	7.71

Additionally, a profile of iron, manganese, particle count and turbidity removal throughout the system was performed to determine the source of the manganese bypass. Results are shown below in Table 3.

# TABLE 3. IRON, MANGANESE, PARTICLE COUNT AND TURBIDITY REMOVAL ACROSS THE SYSTEM

Sample ID	Iron	Manganese (mg/L)	Particle Count (#2-50µm/mL)	Turbidity (NTU)
Raw Well	0.70	0.29	1070	0.63
GS #1	0.09	0.09	39	0.10
GS #2	0.05	0.02	86	0.10
GS #3	0.04	0.01	77	0.14
Pre-CF	0.09	0.90	4610	1.03
Post-CF	0.03	0.24	315	0.13

Reviewing this information, the site was surprised to see that the GS filters were achieving efficient removal of iron, manganese and particulates. However, manganese levels increased above the raw well values before the cartridge filter. The primary explanations for this result include slugs of manganese coming into the system that were not observed at the time of sampling or issues within the holding tank. This finding prompted the operators to inspect the holding tank. Black sludge streamed from the tank doorway once opened. Photos of the inside of the tank were taken revealing the walls and the floor of the tank were heavily coated with a layer of manganese. An emergency tank cleaning was scheduled for next day. The tanks were cleaned with a specialty cleaner designed to remove metals. Figure 2 depicts the manway door after being partially cleaned.

#### **FIGURE 2. MANWAY DOOR**



It was later discovered that the tanks had not been inspected or cleaned since the startup of the system 10 years ago. The site believed that the manganese in the tank was likely a result of small bypasses throughout the years accumulating, which then sloughed off the tank periodically, fouling the cartridge filters and RO. This would explain the variable lifespan of the CFs.

After the tank was cleaned, it was believed that the cause of the system fouling was resolved. Thus, the RO system was also cleaned with a specialty cleaner targeting metals. The water production and DP were restored but the permeate conductivity was too high. The decision was made to replace the membranes in the first pass because they did not provide the needed quality. Loss in membrane integrity historically influenced the replacement of the first pass membranes; however, the site did not know the cause for the decrease in permeate quality. A lead and tail membrane were chosen for dissection and membrane autopsy to troubleshoot the loss in element rejection.

#### MEMBRANE AUTOPSY RESULTS

Single element wet testing is one of the most powerful troubleshooting tools in RO system performance evaluation. Many systems, such as this site, only monitor full system permeate flow, which does not provide information on the location of issues within the system. Having the permeate flow of each stage gives a much more detailed look at where issues arise but being able to test single elements provides a full profile of a system to pinpoint problems. Testing the lead element from the site revealed 141% of normal permeate flow, normal DP and significantly lower than normal rejection (57.3%) while the tail element produced too low of permeate flow to measure. Although the system had been cleaned and full element permeate flow appeared to be restored, Stage 2 was not, suggesting a different type of fouling than the colloidal fouling of Stage 1. The focus of the autopsy on the Stage 1, Lead element was troubleshooting rejection while the analysis of the Stage 2, Tail element was to identify the foulant material and adequate cleaning procedures.

#### **STAGE 1, LEAD POSITION**

Significant fouling of the membrane was not observed and foulant identification through SEM and EDS analysis confirmed the lack of foulant. These results indicated that the system clean was effective for the Stage 1 elements.

The full element and flat sheet samples produced significantly lower than normal salt rejection. Fujiwara testing for the presence of halogens (e.g. chlorine) in the membrane structure was negative. Dye testing was performed to determine the cause/extent of damage to the membrane surface. Flat sheet samples were exposed to dye in a cell test apparatus at 100 psi for 15 minutes. Physically and/or chemically damaged membranes will absorb the dye on the membrane surface. Dye penetration through the membrane backing indicates severe physical and/or chemical damage. Figure 3 shows the results of the dye test.

#### FIGURE 3. IMAGE OF THE DYE UPTAKE ON THE MEMBRANE SURFACE (LEFT) AND DYE PENETRATION TO THE MEMBRANE BACKING (RIGHT)



Significant dye uptake was observed on the membrane surface. Inspection of the membrane backing revealed dye penetration in a pattern consistent with the feed spacer voids. The results of dye testing are indicative of chemical damage to the membrane surface. Since Fujiwara testing was negative for halogen oxidation, it was determined that the most probabl cause of oxidation was non-halogen oxidation.

#### **STAGE 2, TAIL POSITION**

Dissection of the Stage 2, Tail element revealed a thin, even layer of fine-granular foulant. This is consistent with the Stage 2 normalized data from on-site which showed a stable DP across Stage 2.

SEM imaging displayed a distinct botryoidal morphology which is commonly associated with silica scale and EDS confirmed silicon as the dominant inorganic element of the foulant (Figure 4).

# FIGURE 4. SEM IMAGE AT 1500X (LEFT) AND EDS ANALYSIS AT 150X (RIGHT) OF THE MEMBRANE SURFACE



Elements	Membrane Surface (weight %)
Carbon	34.20
Oxygen	47.96
Sulfur	5.41
Silicon	12.43

Based on the foulant analysis it was determined that the foulant material on the membrane was primarily composed of silica scale. The autopsy results showed that the antiscalant used was not effective in inhibiting scale formation.

Additionally, after cleaning with a specialty silica-targeted cleaner, the flat sheet samples produced significantly higher than normal salt passage, which matched the salt passage of the first stage element. Fujiwara testing of the flat sheet was negative and dye testing displayed a consistent pattern with the Stage 1, Lead element. A symptom of chemical damage is damage across the full system. The system design was again reviewed for membrane incompatible chemistries including strong oxidizers. This revealed carryover of KMnO<sub>4</sub>, a strong oxidizer, as the most likely cause for the damage to the membrane.

#### KMnO<sub>4</sub> DOSE CALCULATION

GS filter applications include the removal of soluble iron, manganese, and hydrogen sulfide. However, the most important GS application is soluble manganese (Mn<sup>+2</sup>) removal, which is difficult to achieve by conventional precipitation methods at pH values of less than approximately 9. Operators generally regenerate GS filters with potassium permanganate. The two regeneration methods used are continuous permanganate addition and off-line regeneration. From an operational standpoint, continuous regeneration method is easiest. GS compensates for variations in manganese levels by adsorbing permanganate when manganese levels decrease then losing oxidative capacity when the levels increase. However, permanganate leakage into downstream RO systems can cause catastrophic membrane damage.

The operators did not know how much  $KMnO_4$  was being dosed and stated that the continuous injection was set by the previous staff and had not been checked since. The dose was back calculated using the following formula:

#### C1V1=C2V2

C1= Bulk KMnO<sub>4</sub> concentration (14,988 ppm) V1= KMnO<sub>4</sub> pump injection rate 25 ml/min (0.0066 gpm) C2= KMnO<sub>4</sub> ppm dose injected to feed stream (unknown) V2= Feed flow rate to the three GS filters (180 gpm) C2=0.55 ppm

The following equation can be used to calculate potassium permanganate demand (1):

KMnO4 demand, mg/l =  $(1 \times mg/l Fe^{+2}) + (2 \times mg/l Mn^{+2}) + (5 \times mg/l H_2S)$ 

#### Raw Water:

0.70 mg/l Fe<sup>+2</sup> x 1.0 = 0.7 mg/l KMnO<sub>4</sub> demand 0.29 mg/l Mn<sup>+2</sup> x 2.0 = 0.58 mg/l KMnO<sub>4</sub> demand 0.2 mg/l H<sub>2</sub>S x 0.0 = 1.28 mg/l KMnO<sub>4</sub> demand 1.28 mg KMnO<sub>4</sub> demand/liter raw water or 59 ml/min

Contrary to expectation, the calculation results showed that the  $KMnO_4$  was being underdosed which could explain the amount of manganese fouling found in the holding tanks and on the CF and membranes. The cause for the severe membrane damage remained a mystery until the pretreatment procedures were reviewed. The site kept records

of maintenance procedures performed on the GS filters and realized that the  $KMnO_4$  dose remained consistent regardless of how many of the GS filers were operational. At times, only one GS filter was running therefore  $KMnO_4$  was overdosed, causing membrane damage.

#### ADDING REDUCING AGENT

The plant was able to change the dosing procedures of KMnO<sub>4</sub> to account for the number of filters online by installing a flowpaced injection pump. But to be on the safe side the plant management decided to opt in to adding a reducing agent to neutralize any residual oxidizer.

The procedure for calculating reducing agent dosages for  $KMnO_4$  compounds is based upon redox half-reactions and milliequivalent (mEq) weights. Oxidation-reduction reactions involve a pair of chemical equations. One equation represents the oxidation portion of the reaction and the other, the reduction reaction.

In the case of  $KMnO_4$ , the oxidizing species is permanganate. Permanganate has a reduction half-reaction involving the transfer of five electrons per mole (1).

 $MnO_4 + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$ 

A common reducing agent is sodium metabisulfite (SMBS), which has the following oxidation half reaction involving the transfer of four electrons per mole (1):

 $Na_2S_2O_5 + 3H_2O \longrightarrow 2NaHSO_4 + 4H^+ + 4e^-$ 

Combining the permanganate and SMBS half reactions gives the overall balanced chemical equation:

 $(MnO_4 + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O) \times 4$  $(Na_2S_2O_5 + 3H_2O \longrightarrow 2NaHSO_4 + 4H^+ + 4e^-) \times 5$ 

4MnO<sub>4</sub> + 5Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>+ 12H+ → 10NaHSO<sub>4</sub> + 4 Mn<sup>+2</sup> + H<sub>2</sub>O

Note that it was necessary to multiply the half reaction of  $MnO_4$  and SMBS by 4 and 5, respectively to cancel electrons appearing on the reactant and product sides of the overall reaction. Using the half-reaction calculation method requires the calculation of mEq weights of both oxidizer and reducing agent. In redox reactions, mEq weight is the formula weight in mg of the reactant divided by the number of electrons either gained or lost. For KMnO<sub>4</sub>, the mEq weight is 158/5 = 31.6 mg/mEq. The mEq weight of SMBS is 190/4 = 47.5 mg/mEq.

Table 1 lists the mEq weights for chlorine compounds and ozone, which are of interest to water treatment personnel.

In a redox reaction, the required reducing agent dosage is equal to the oxidizer concentration times the mEq weight ratio of reducing agent to oxidizer:

DR = CD x mEq wtR/mEq wtD DR is reducing agent dosage, mg/l CD is disinfectant dosage, as mg/l Cl2 mEq wtR is the mEq weight of the reducing agent mEq wtD is the mEq weight of the disinfectant

To calculate the SMBS dosage needed to neutralize 1 mg/l of  $\rm KMnO_4$ :

D<sub>SMB</sub> = 1.0 x 47.5/31.6 = 1.50 mg/l

The management decided to dose 1.5 ppm of SMB at first to be on the safe. Permanganate test was also done to verify the complete removal of the oxidizer.

#### SYSTEM OPTIMIZATION

The autopsy results of the Stage 2 tail element identified the presence of silica scale. The antiscalant used at the plant prior to the audit was not a targeted formulation but a generic product used to disperse ions in solution. Based on the data collected from the full mineral analysis, it was apparent that using a specialized antiscalant that would target silica would offer better results. The new water analysis was entered into the chemical provider scaling prediction software to determine the maximum recovery in regard to the water chemistry. The software indicated the max recovery with the use of specialty antiscalant is approximately 82%. The software also showed that silica scale is the limiting factor. However, with current system design hydraulics limitations, the membrane design software indicated design warnings when exceeding the current recovery of 57%.

Further inspection of the RO unit revealed disconnected pressure vessels in both stages of the first pass. By reconfiguring the array of the system to be 6:3, the design software determined that the system recovery could be increased to 75% without any hydraulic issues. A target recovery of 75% was initiated in order to maintain a safe buffer against any variations in ion concentrations, pump inaccuracies, product dilution errors or other shortcomings. The plant experienced a cost savings based on the fact that a lesser volume of the specialized chemistry was needed

(greater efficacy of a targeted product) and a decreased amount of feed water was being rejected into the concentrate stream. The saturation indices for the maximum recovery of 75% are provided below in Figure 5.





#### **DISCUSSION & CONCLUSION**

The importance of an onsite audit of the system is highlighted. The site suspected that insufficient removal of metals by their GS filters was leading to excessive fouling resulting in CF and membrane replacement. Loss in membrane integrity historically influenced the replacement of the first pass membranes; however, the site did not know the cause for the decrease in permeate quality.

A foulant analysis of the discarded CFs led to the identification of manganese as the predominant foulant. Tests results of particle count, turbidity, iron and manganese showed that the GS filters were achieving efficient removal. However, manganese levels increased above the raw well values after the holding tank and before the cartridge filter. With this evidence it was possible to discover the source of this issue to be the feedwater holding tank.

Membrane autopsies of the lead and tail elements showed signs of membrane oxidation. Back calculating of the KMnO4 dose surprisingly showed that it was being underdosed. This finding could explain the amount of manganese fouling found in the holding tanks but not the membrane damage. After thorough review of historical maintenance records, it was discovered that the KMnO<sub>4</sub> dose remained consistent regardless of how many of the GS filers were operational. At times, only one GS filter was running therefore KMnO<sub>4</sub> was overdosed, causing membrane damage.

The tail element autopsy identified silica scale. The plant operators did not expect having problems with scaling because an antiscalant was being dosed. As the system did not have flow meters on every stage, the normalized permeate flow data was the overall flow rate of the 1<sup>st</sup> Pass RO. The disadvantage of only looking at the total permeate flow is that it was not possible to tell whether Stage 2 performance had been compromised. The autopsy results showed that the antiscalant used was not effective in inhibiting scale formation.

System optimization was achieved by cleaning the holding tank, implementing a proper dose of SMBS to offset potassium permanganate oxidation and changing the antiscalant to a silica-inhibiting antiscalant. Further system improvements were gained by optimizing the recovery of the system based on the new recoveries made possible by implementing a silica scale inhibitor at a lower dose rate than the previous scale inhibitor. These improvements resulted in an actual cost savings for the system overall operation. The CF replacement rate decreased from almost daily to quarterly. CIP is projected to be performed every 8 months rather than every week. And the membranes are expected to last for 3-5 years when they were replaced every year.

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#### HEADQUARTERS GERMANY NORTH, CENTRAL & SOUTH EAST EUROPE

Kurita Europe GmbH Theodor-Heuss-Anlage 2 68165 Mannheim ☎ +49 621 1218 3000

#### FRANCE, LUXEMBOURG & NORTH AFRICA

Kurita France SAS ZI du Bec d'Ambès F-33810 AMBES 🕿 +33 (5) 56 84 34 09

#### GREECE

Kurita Europe GmbH 11, Korinthou str. GR-144 51 Metamorfosi Athens 🕿 +30 210 28 37 559



www.kurita.eu info@kurita.eu

#### IBERICA

Kurita Iberica SL. Av. Alcalde Barnils, 64-68 Bloque B, Planta 2ª, Local 1-2 E-08174 Sant Cugat del Vallés Barcelona 2 +34 93 675 0345

#### UNITED KINGDOM

Kurita UK Ltd Avista I Centre of Excellence 13 Nasmyth Square, Houstoun Industrial Estate Livingston, EH54 5GG United Kingdom 20 +44 131 449 6677

#### ITALY

Kurita Italia srl Via Piero e Alberto Pirelli 6 I-20126 Milano 2 +39 02 295 164 53

# POLAND, ROMANIA, BALTICS, UKRAINE & BELARUS

Kurita Polska Sp.z.o.o. ul. Uniwersytecka 13 PL-40-007 Katowice 🕿 +48 32 700 25 65

#### SLOVAKIA

Kurita Polska Sp.z.o.o. Organizacná zložka Bajkalská 22 SK-821 09 Bratislava 🖀 +421 2 53 41 89 68

#### SWEDEN & SCANDINAVIA

Kurita Sverige AB Marieholmsgatan 56 SE-415 02 Göteborg ☎ +46 31 725 34 60

#### TURKEY

Kurita Turkey Kimya A.S. Tugayyolu cad. Ofisim Istanbul Plazalan No:20 B Blok Kat 4 Daire 23 TR-34846 Maltepe Istanbul 🖀 +90 216 450 08 62

#### MIDDLE EAST REGION

Kurita AquaChemie FZE PO Box 216800 Street S1100, Plot S40801 Jebel Ali South, Dubai United Arab Emirates ☎ +971 (0) 48 844 990

Kurita AquaChemie Saudi Arabia Company PO Box 7950 Street 16, 2nd Industrial Area, Dammam 31472 Kingdom of Saudi Arabia 2 966 13 8641172

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