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ROIFA-5 Model for Predicting Total Hardness Fouling Flux and Saturation Factors on the RO Membrane

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Abstract: Based on the earlier dehydration model, the reverse osmosis inorganic fouling assessment model (ROIFA-5) and spreadsheet has been developed for predicting the inorganic fouling flux on the RO-membrane surface used for desalination and wastewater treatment at any desired recovery rate. Several important outputs could be obtained from the application of this spreadsheet, among them; the probable dissolved salt combination, total hardness fouling flux (THFF), silica fouling potential, molar ratios, total brine fouling load, wt/wt% of different hardness molecules, chemical composition of the resulted brine and saturation factor (SF%) for calcite and gypsum. In addition, some other useful information is obtained like: brine osmotic pressure, mechanical pressure, brine ionic strength, brine ion product (IP) of calcite and gypsum. Both SF and IP output have been estimated according to the saturation model based on the obtained upper solubility level of calcite and gypsum under variable chloride natural waters, and not on their solubility in pure water as considered in thermodynamics. It has been found that the solubility of carbonate and sulfate mineral salts are relatively increasing with the increase of chloride content (or probably NaCl) and follows natural tight rules. It is proved that the inorganic fouling potential is proportional to the brine total hardness fouling flux (THFF) and not its gross salinity. In many investigated cases the lower salinity water may acquire higher hardness fouling potential than the higher salinity water that may contain less dissolving hardness, like ocean water. The ROIFA program had been subjected to many laboratory tests and field investigations and was found satisfactory. This software is free for all and available upon request.

Keywords: ROIFA-5 Model, ROIFA-5 Spreadsheet, Dehydration Model, Inorganic Fouling, RO-membrane, Desalination, Wastewater Treatment.

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1 Introduction

During the last twenty years the present author was involved deeply in the laboratory chemical study and field investigation of many troubled RO-membrane desalination and treatment plants due to the formation of inorganic scales on the RO-membrane surface after short time of operation. All of the investigated cases (more than 80) were designed according to the widely used thermal indices such as LSI [1], RSI [2] and S and DSI [3] those failed in prediction of inorganic fouling potential as well as their chemical type. These thermal indices had been developed since 1936 for the empirical estimation of minerals supersaturation at elevated temperature in heat boilers and exchangers. This was a long time ago before the invention and the commercial uses of membranes at the late sixties of the last century. The basic difference between the two processes are that thermal distillation is a water evaporation process operating under high temperature and low pressure, while the RO-membrane desalting is a membrane separation process driving under high pressure and low temperature. Therefore, the prediction of inorganic fouling potential should be different in these different processes.

Between the year 2000 and 2020, a series of research papers were published [4-13] describing and discussing the chemical relationships between feed-water chemistry, concentrated brine solution left after desalting and the inorganic fouling/scaling potential. In brief, several important points were indicated:

a) Inorganic fouling potential increases with the increase of permeate recovery rate (i.e. increasing dehydration rate),

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b) The solubility of carbonate and sulfate mineral salts is generally increasing with the increase of the dissolved chloride ion concentration (probably NaCl),

c) The SO_4/Alk. molar ratio is highly indicative for carbonate and sulfate minerals fouling then scaling. At low Cl concentration the carbonate fouling is highly invited, while at higher Cl content the sulfate fouling is highly expected. It was possible to conclude a general guideline [8] for such delicate natural relationship.

d) The Dehydration model indicated that the magnitude of dehydration of hydrated molecules is directly proportional to the concentration of molecules, applied pressure and defusing rate of pure water through a given membrane type. It is assumed that all hydrated molecules could be subjected to dehydration, and only a fraction of low-solubility hard molecules (ex. $CaSO_4$ and $CaCO_3$) will foul and exit the aqueous system as solid micro particles, while other highly soluble molecules (ex. NaCl, Na_2SO_4 and $MgCl_2$) will re-dissolve again, i.e. re-gain their water shells or part of it. This depends on their relative solubility at a given chloride concentration and the available time necessary for re-dissolution.

e) The chemical material balance between the RO feed-water and the brine solution is always disturbed, that is because of the separation of some hardness species from the aqueous system as solid particulate, which cannot be determined by the standard water analytical methods and need strong acid digestion prior analysis.

f) The laboratory experiments on the closed recycling RO-setup indicated gradual and continuous change in chemical composition of the circulating solution as recycling progress. The acid-leach of the micron filter-cartridge proved that considerable amount of hardness suspended solids retained and accumulated on the filter surface during closed circulation. This must be greatly considered when such experiments are performed. These important field and laboratory observations support the idea of solid particulate formation due to reverse osmosis dehydration.

g) It was observed that there is a considerable difference between the analytical molar ratio ($CaSO_4$**:**$CaCO_3$) of the brine solutions and the deposited scales. This phenomenon is common for all investigated cases but with different magnitude. This means that not all of the dissolved hardness molecules are readily to precipitate upon dehydration. It is called readily precipitated hardness molecules as the fouling fraction (F_f).

h) The total hardness fouling flux is independent of salinity. In other words, it is not necessarily that the higher salinity water should have higher hardness molecules ready for fouling then scaling. It is clear that each water type acquire specific chemistry during its hydrologic cycle regardless its gross salinity.

ROIFA-4 (RO Inorganic Fouling Assessment) model and spreadsheet was published by the present author et.al [9] as a mathematical model that was used for prediction of total hardness fouling flux on the RO-membrane surface running under highly pressurized dehydration conditions, either in salty water desalination or in wastewater desalting.

The aim of the present paper is to introduce the fifth version of ROIFA-5 model and spreadsheet that was furtherly developed than the last edition considering all feedback from all colleagues. In addition, a new output sheet that is added in order to cover the saturation model that is based on pure chemistry calculations and not on thermodynamics bases. The ROIFA-5 spreadsheet is free for all and available upon request.

2 Total Hardness Fouling Flux Model

The proposed ROIFA (RO Inorganic Fouling Assessment) mathematical model was first published in 2005 as ROIFA-4 model and spreadsheet [9], based on the earlier dehydration statistical model [7] and many other trend-line equations obtained from statistical analysis of more than 1500 natural waters chemical analyses. These trend-line equations were used to estimate the brine fouling fraction (F_f) of dissolved carbonate and sulfate of Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+} expected to foul at a given chloride concentration level and at given permeate recovery.

In order to fulfill the requirement for this model it must convert the brine ion analysis into the corresponding brine salt type molecules, which could be estimated by using the “Probable Salt Combination Method” that depends on stoichiometric calculations for distributing brine-anions on brine-cations according to the regular method currently used in chemical laboratories. The accuracy of this stoichiometric ionic distribution is generally better than 97% depending on the accuracy of water chemical analysis.

It is possible to abstract the elements of estimating the total brine hardness fouling flux (as molecules/0.1cc.sec) in the following steps:

i) Convert feed-water ion concentration from (mg/l) to (mg/kg.w), dividing by the water density, which could be estimated from the TDS (mg/l) by using the following developed formula:

$$\text{Brine Density } (d_{brine}) = 0.000759\,[\text{TDS}] + 996.977739 \tag{1}$$

ii) Convert feed water (ion-mg/kgw) to (ion-mM/kgw or mM), dividing by molecular weight.

iii) Estimate the brine-ion concentration, multiplying by the concentration factor (C_F):

$$C_F = 1 \div (1 - R) \tag{2}$$

where R is the recovery decimal (e.g. 0.3, 0.5, 0.7, … etc.).

iv) Distribute brine-anions on the corresponding brine-cations dissoled in the brine solution, in order to obtain the brine probable salt combination -as salt molecule, mM/kg.w- and as described in detail in ROIFA-4 paper [9].

v) The total hardness load (F_{TL}) is the sum of the individual hardness loads in mM:

$$F_{TL},\text{ mM} = F_{L\text{-}CO3} + F_{L\text{-}SO4} + F_{L\text{-}SiO3} + F_{L\text{-}PO4} + F_{L\text{-}FeO3} + F_{L\text{-}MnO2} \tag{3}$$

where (F_{TL}) is the brine total hardness load in mM, ($F_{L\text{-}CO3}$) is the Ca+, Mg+, Ba+, Sr^{2+} carbonate-salts load, ($F_{L\text{-}SO4}$) is the Ca+, Mg+, Ba+, Sr^{2+} sulfate-salts load, ($F_{L\text{-}SiO3}$) is the silicate-salts load, ($F_{L\text{-}PO4}$) is the phosphate-salts load, ($F_{L\text{-}FeO3}$) is the non-soluble iron oxide load, and ($F_{x\text{-}MnO2}$) is the non-soluble manganese oxide load, all in mM.

From the total hardness load it is possible to calculate the individual percentage of each hardness salt, which reflects its relative abundance to other species. It was found that these values actually determined the dominating chemical type of the expected fouling/scaling materials.

vi) Calculate the individual brine fouling fraction ($F_{f\text{-mineral}}$, mM) and the brine fouling load ($F_{L\text{-mineral}}$, mM) of the estimated brine salt molecules (mM/kg.w or mM) at the given chloride concentration [Cl] by selecting the suitable equations:

a) Cl^{1-} range in brine: 0 – 10 mM/kgw:

$$F_{f\text{-}MCO3} = 0.0791\,[Cl] + 0.2945 \tag{4}$$

$$F_{f\text{-}MSO4} = 0.0645\,[Cl] + 0.0470 \tag{5}$$

b) Cl^{1-} range in brine: 10 – 200 mM/kgw:

$$F_{f\text{-}MCO3} = 0.0046\,[Cl] + 0.9168 \tag{6}$$

$$F_{f\text{-}MSO4} = 0.0013\,[Cl] + 0.6126 \tag{7}$$

c) Cl^{1-} range in brine: 200 – 800 mM/kgw:

$$F_{f\text{-}MCO3} = 0.00009\,[Cl] + 0.0946 \tag{8}$$

$$F_{f\text{-}MSO4} = 0.00019\,[Cl] + 0.8407 \tag{9}$$

d) Cl^{1-} range in brine: > 800 mM/kgw:

$$F_{f\text{-}MCO3} = 0.00 \tag{10}$$

$$F_{f\text{-}MSO4} = 1.00 \tag{11}$$

e) Carbonate Fouling load ($F_{L\text{-}MCO3}$), mM = $[MCO_3] \times F_{f\text{-}MCO3}$ (12)

f) Sulfate Fouling load ($F_{L\text{-}MSO4}$), mM = $[MSO_4] \times F_{f\text{-}MSO4}$ (13)

Because of possible mathematical extrapolation, it should be noted that the brine F_f value should be between zero and 1 (i.e. from 0% to 100% of foulant load), any results higher than 1 is to be considered as 1. In addition, there is no direct mathematical relationship between $F_{f\text{-}MCO3}$ and $F_{f\text{-}MSO4}$, this means that it is not necessary that summation of both is equal to 1, they are independent of each other.

The individual hardness fouling flux (F_x) is estimated from its concentration in brine that flows in a layer of 1 mm thickness spreading over 1 cm^2 of RO-membrane surface per time, which is normally around one second:

$$F_x = F_L \times F_f \times 10^{-3} \times A_C \tag{14}$$

Where (F_x) is the individual hardness molecule flux found in a layer of 0.1 cm^3 of brine solution flowing on the RO-membrane surface per one second, (F_L) is the sum of hardness-salt load, in mM/0.1 cm^3, (F_f) is the estimated specific fouling fraction for the specific hardness salt at a given chloride concentration, (A_C) is the Avogadro Constant ($6.02214199 \times 10^{23}$) [14].

For silicates, phosphate and iron oxide hardness salt the fouling fraction was considered as 1, this because we no mathematical relationship could be detected between their concentration in brine solution and in the precipitated scales.

The brine total hardness fouling flux (THFF, F_{tx}) is the sum of the individual hardness fouling flux dissolved in a layer of 0.1 cm^3 of brine solution following on the RO-membrane surface per one second:

$$F_{tx} = F_{x\text{-}CO3} + F_{x\text{-}SO4} + F_{x\text{-}SiO3} + F_{x\text{-}PO4} + F_{x\text{-}FeO3} + F_{x\text{-}MnO2} \qquad (15)$$

Where (F_{tx}) is the total hardness fouling flux (THFF) molecule/0.1 cc.sec, ($F_{x\text{-}CO3}$) is the Ca+, Mg+, Ba+, Sr carbonate-salts molecule flux, ($F_{x\text{-}SO4}$) is the Ca+,Mg+, Ba+, Sr^{2+} sulfate-salts molecule flux, ($F_{x\text{-}SiO3}$) is the silicate-salts molecule flux, ($F_{x\text{-}PO4}$) is the phosphate-salts molecule flux, ($F_{x\text{-}FeO3}$) is the non-soluble iron oxide molecule flux, and ($F_{x\text{-}MnO2}$) is the non-soluble manganese oxide molecule flux.

By using ROIFA-5 spreadsheet all these calculations are executed automatically to obtain the total brine hardness fouling flux, as molecule/0.1cc.sec, at the given chloride range. In addition, some other useful information such as: brine chemical composition at the given permeate recovery rate, probable salt composition in mM/kg.w and mg/kg.w, total brine fouling load and the relative percentage of the major foulants, and the different molar ratios of dissolved by ion. Those are very useful to identify the dominating chemical nature of the investigated water type.

The obtained total hardness fouling flux (THFF) is independent on the change in water temperature, as it is a molar concentration depending on the density. On the other hand, hardness fouling potential and tendency are affected by temperature change. However, in case of elevation of feed-water temperature from 25˚C to 35˚C the solubility of both calcite and gypsum is generally lowered, and as a result the fouling potential will increase slightly. On lowering temperature to less than 25˚C the solubility of calcite will increase, therefore no problem is expected. For gypsum, its solubility is almost steady along the temperature range from 15 to 30˚C, and then it goes down slightly towards 5˚C. Therefore, under normal conditions (20 – 35˚C) the obtained hardness fouling expectation will not differ significantly.

The ROIFA model and spreadsheet are sensitive to the accuracy of feed-water ion analysis. In the "output 1" sheet you will find the "Ion Difference %" between cations and anions, normally, this value is within 1% or lower. But if this value exceeds 1% up to 3% you may add some Na or Cl to bring down this value to be lower than 1%, the addition of Na or Cl will not affect the amount of hardness molecules. The negative sign means that anions are less than cations, while the positive difference means that cations are less than anions.

3 Carbonate-Sulphate Saturation Model

The present carbonate-sulfate saturation mathematical model is a new addition to the last ROIFA-4 version [9]. A new output-sheet was added to ROIFA-5 in order to cover this carbonate-sulfate saturation model based on pure chemistry calculations and not on thermodynamics bases.

Starting with the carbonate equilibrium in solution, there are two different routes for formation of calcite mineral salt. When dissolved carbonate ion (CO_3^{2-}) is available, equivalent calcite-1 ($CaCO_3$) will be formed according to equation (16), and its ion product ($IP_{calcite\text{-}1}$) could be calculated by equation (17). This reaction type is mostly limited in nature because most of equilibrated natural waters are shortly replace their carbonate with the steady bicarbonate ion (HCO_3^-) under the influence of the atmospheric acidic CO_2 gas.

$$Ca^{2+} + CO_3^{2-} + nH_2O \Leftrightarrow CaCO_3 \downarrow + nH_2O \qquad (16)$$

$$IP_{calcite-1} = \frac{[CaCO_3]}{[Ca^{2+}][CO_3^{2-}]} \qquad (17)$$

For the second reaction type, a fraction of dissolved bicarbonate ion (HCO_3^-) reacts with equivalent calcium in presence of water to form calcite-2 and CO_2 as shown in equation (18), then calculating its ion product ($IP_{calcite\text{-}2}$) is calculated from equation (19).

$$Ca^{2+} + 2HCO_3^{1-} + nH_2O \Leftrightarrow CaCO_3 \downarrow + CO_2 \uparrow + (n+1)H_2O \qquad (18)$$

$$IP_{calcite-2} = \frac{[CaCO_3][CO_2]}{[Ca^{2+}][HCO_3^{1-}]^2} \qquad (19)$$

On the other hand, the formation of gypsum mineral ($CaSO_4.2H_2O$) could be described by equation (20), where a fraction of dissolved sulfate (SO_4^{2-}) reacts with equivalent calcium in the presence of enough water. The reaction ion product ($IP_{sulfate}$) could be calculated from equation (21).

$$Ca^{2+} + SO_4{}^{2-} + nH_2O \Leftrightarrow CaSO_4.2H_2O \downarrow + (n-2)H_2O \tag{20}$$

$$IP_{Gypsum} = \frac{[CaSO_4][H_2O]^2}{[Ca^{2+}][SO_4{}^{2-}]} \tag{21}$$

In thermodynamics sense, it is considered that all analytical amounts of the reactants are involved in a single reaction, for example, all amount of the analytically measured sulfate reacts with all analytically measured calcium, and this is not correct. Calcium could be found in water as carbonate, bicarbonate, sulfate, chloride and phosphate molecules, while sulfate could be distributed between calcium, magnesium, barium, strontium, sodium, potassium, iron and manganese. This approximation is misleading indeed.

Another source of error in thermodynamics modeling is estimating saturation index for a mineral depending upon the solubility of pure mineral in pure water, and this also is wrong, why? It is clear now that the solubility of mineral salts are increase with the increase of chloride ion in water. In other words, the degree of saturation of an amount of dissolving mineral salt could vary widely depending on the dissolved chloride ion content, i.e. a high concentration of bicarbonate in a highly NaCl water, like seawater, could be under-saturation. This is true; the dissolved carbonate/bicarbonate in ocean water is under saturation and found almost constant and steady from long time under normal physiochemical conditions. Many researches proved that carbonate precipitation is mostly biologically and not chemically [15-19].

In the present work, in order to overcome these thermodynamics the estimated molecular composition of the possible salt combination has been estimated instead of the free ions concentration, as well as the relative solubility of dissolved mineral salts against the chloride concentration. Both ROIFA-4 and ROIFA-5 can calculate it automatically as mentioned before.

In such a way it is possible to quantify, with a reasonable degree of accuracy, the individual concentration (mg/kgw & mM/kgw) of the dissolving inorganic species like $CaCO_3$, $Ca(HCO_3)_2$, $CaCl_2$, $CaSO_4$, $Ca_3(PO_4)_2$ and so on for other components. As a result, it becomes easier to calculate all associated parameters of the desired mineral species correctly.

For example, when solving equations (16 to19) for Ocean water that contains: Ca^{2+}=412, CO_3^{2-}=32, HCO_3^-=142 mg/l, ROIFA-5 calculates $CaCO_3$=0.0299 mM and $Ca(HCO_3)_2$ =0.0978 mM depending on the available amount of calcium for these two species only, but not for all. Now, as the $CaCO_3$ is known (0.0299 mM), the concentration of reactants (Ca^{2+} and CO_3^{2-}) will be half (0.01495 mM) for each, and so on. For other multiple species, it must consider the number of reactants and their equivalent number as usual in chemistry calculations.

For mineral salt saturation factor the symbol ($S_{min}\%$) was introduced currently in order to differentiate between this new saturation term and the "Saturation Index (SI)" that is currently used in aqueous thermodynamics.

This new saturation factor ($S_{min}\%$) is the ratio percentage of the estimated mineral salt solubility to the estimated mineral salt upper saturation limit ($L_{mineral}$) at the given dissolved chloride content, equation (22).

$$S_{min}\% = 100x \frac{[C_{mineral}]}{L_{mineral}} x \frac{P_m}{T_f} \tag{22}$$

where, $T_f = exp(5.6*(65/(273+T)-2.3/89))$ (23)

where: $S_{min}\%$: saturation factor, $C_{mineral}$: mineral (calcite or gypsum salt) concentration in µMol/kgw, $L_{mineral}$: mineral salt upper saturation level in µM at the given chloride content, P_m: applied mechanical pressure in bar (= Osmotic Pressure x 2), and T_f: temperature correction factor. Equation (23) was specifically developed for this purpose. Osmotic pressure was estimated according to the following equation [16]:

$$P_{osm} = 1.19(T+273) * \sum(mi) \tag{24}$$

where P_{osm} = osmotic pressure (in psi), T is the temperature (in °C), and $\Sigma(mi)$ is the sum of molar concentration (M/L) of all ions in a solution.

In order to estimate the mineral salt upper saturation level ($L_{mineral}$, µM) eight equations were specially developed from earlier work [15] to suit the four chloride ranges (mM) forming the main framework of ROIFA-5 excel spreadsheet, as given below:

a) Cl^{1-} range in brine: 0 – 10 mM/kgw:

$$L_{calcite} = 1.7114*[Cl]+399.28 \quad (25)$$

$$L_{gypsum} = 1.8968*[Cl]+7658.9 \quad (26)$$

b) Cl^{1-} range in brine: 10 – 200 mM/kgw:

$$L_{calcite} = -5E\text{-}07*[Cl]\text{^}2+0.0588*[Cl]+18838 \quad (27)$$

$$L_{gypsum} = 0.0411*[Cl]+26784 \quad (28)$$

c) Cl^{1-} range in brine: 200 – 800 mM/kgw:

$$L_{calcite} = 3E\text{-}08*[Cl]\text{^}2-0.045*[Cl]+18212 \quad (29)$$

$$L_{gypsum} = 0.0214*[Cl]+30808 \quad (30)$$

d) Cl^{1-} range in brine: > 800 mM/kgw:

$$L_{calcite} = -0.001*[Cl]+4100 \quad (31)$$

$$L_{gypsum} = -0.0089*[Cl\}+54884 \quad (32)$$

Where the chloride ranges are in mM, and both $L_{mineral}$ and [Cl] expressed in µM.

4 Interpretation of the Obtained ROIFA-5 Results

A number of five water cases are selected, depending on its salinity trend, in order to discuss the capability of ROIFA-5 model. Their input chemical composition is given in Table 1. Four of these cases are actually local running RO-plants where the ROIFA model and spreadsheet were already used for correcting their troubled operation. More cases and discussion were also presented in published paper [9].

Table 1: ROIFA-5 input chemical composition of some selected natural waters.

Ion, mg/l	GW-1	GW-2	GW-3	Ocean[17]	Red Sea
Na^{1+}	712	1718	4926	10768	14114
K^{1+}	28	22	143	399	421
Ca^{2+}	334	408	578	412	494
Mg^{2+}	116	197	527	1292	1276
Ba^{2+}	0.17	3.27	2.61	0.01	0.28
Sr^{2+}	0.00	0.06	3.84	7.93	9.66
Cl^{1-}	1367	2592	8175	19353	23933
HCO_3^{1-}	278	119	197	142	175
CO_3^{2-}	0	0	0	0	0
OH^{1-}	0	0	0	0	0
SO_4^{2-}	677	1745	2675	2712	3647
SiO_3^{2-}	15.08	9.48	21.73	4.28	2.12
Fe^{3+}	0.12	0.43	0.63	0.002	0.02
Mn^{4+}	0.00	0.07	0.04	0.0002	0
PO_4^{3-}	10.13	5.03	11.83	0.42	1.27
TDS, mg/l	3538	6819	17262	35091	44073
pH-value	7.6	7.5	7.1	8.3	8.1

The first three investigated water cases are local groundwater (GW) of salinity 3538, 6819 and 17262 mg/l, located at different places, used as feed-water for BWRO plants of capacity less than 1000 m^3/day. The fourth “Ocean” case of salinity 35091 is mentioned here for comparison and discussion only. The last fifth water case is a surface Red Sea water of salinity 44073 mg/l at Sharm El-Sheikh city, south of Sinai, feeding a 5000 m^3/day SWRO desalination plant.

Except the Ocean water chemical analysis [20,21], the other four water chemical analyses were obtained from the archives of Geochemical Laboratories in Cairo. All selected water cases are representing wide spectrum of the natural water chemical types [8] normally found in nature.

Table 2 presents some highlighted ROIFA-5 outputs (output 1 & 2 in the spreadsheet) describing the inorganic fouling potential, as well as short notes on the chemical characteristics, of the resulted higher concentrated brine due to the effect of RO-membrane separation process.

The main features could be summarized in the following points:

a) In the first water case (GW-1, TDS=3538 mg/l) the ROIFA-5 output estimated the Total Hardness Fouling Flux (THFF) at recovery 55% is 8.04E+17 molecule/0.1cc.sec., which is very close to the safe guideline limit (8.00E+17) as given in Table 3. At the design recovery rate (70%) the inorganic fouling had been initiated clearly (THFF = 1.32E+18), where the carbonate hardness (46.86%) dominated over other types (phosphates 21.40%, silicates 15.91% and sulfates 15.42%). The choice was clear; by means of acidification it was possible to reduce the concentration of carbonate salts to be lower than the guideline limit. In addition, the cheaper sulfuric acid (H_2SO_4) used in this case as the amount of the formed sulfate salt will be lower than the estimated limit. The need for an expensive antiscalant was totally excluded.

Table 2: Some selected ROIFA-5 output-data of the investigated waters.

A) Water Type	GW-1	GW-2	GW-3	Ocean	Red Sea
B) TDS, mg/l	3538	6819	17262	35091	44073
C) Recovery (%)	Total Hardness Fouling Flux, THFF (molecule/0.1cc.sec.)				
30	4.80E+17	5.46E+17	6.70E+17	5.67E+17	6.12E+17
35	5.22E+17	5.97E+17	7.24E+17	6.11E+17	6.57E+17
40	5.73E+17	6.57E+17	7.87E+17	6.59E+17	7.08E+17
45	6.34E+17	7.30E+17	8.63E+17	7.17E+17	7.69E+17
50	7.09E+17	8.21E+17	9.54E+17	7.85E+17	8.41E+17
55	8.04E+17	9.36E+17	1.07E+18	8.67E+17	9.28E+17
60	9.26E+17	1.09E+18	1.21E+18	9.68E+17	1.04E+18
65	1.09E+18	1.12E+18	1.40E+18	1.10E+18	1.17E+18
70	1.32E+18	1.31E+18	1.65E+18	1.26E+18	1.35E+18
D) Brine Hardness Fouling Load %:					
Carbonates (%)	46.86	21.66	16.90	24.15	23.05
Sulfates (%)	15.42	42.94	31.01	62.34	64.94
Silicates (%)	15.91	16.07	23.88	11.28	5.39
Phosphates (%)	21.40	17.08	26.04	2.22	6.46
Iron Oxide (%)	0.41	2.24	2.17	0.02	0.16
E) Molar Ratios:					
SO_4/Alk	1.55	9.31	8.62	12.13	13.24
Cl/(Ca+Mg)	2.94	4.00	6.39	8.61	10.41
Na/(Ca+Mg)	2.42	4.12	6.04	7.54	9.64
Cl/(SO_4+Alk)	3.32	3.63	7.42	17.86	16.53

Table 3: Guidelines for Inorganic Fouling Flux on the RO-membrane surface.

Inorganic Fouling Flux Range (Molecules / 0.1cc.sec)		Fouling Potential Guidelines	Remarks
From	To		
0.00E+00	8.00E+17	No Fouling	No treatment is required
8.00E+17	9.00E+17	Low Fouling	Short flushing is essential
9.00E+17	1.00E+18	Medium Fouling	Antiscalant + Chemical Cleaning.
1.00E+18	1.50E+18	High Fouling	Antiscalant + Short Chemical Cleaning.
1.50E+18	2.00E+18	Very High Fouling	Antiscalant action is questionable.
>2.00E+18	-----	Excessive Fouling	Scale Blockage is a must

b) The second case (GW-2, TDS=6819 mg/l) was a bit complicated. The estimated THFF by ROIFA-5 was 9.36E+17 molecule/0.1cc.sec. At 55% recovery rate, this is higher than the guideline limit considerably. In addition, the sulfates are relatively high (42.94%) and the molar ratio (SO_4/Alk) is exceptionally higher than the average of such salinity water; this means that it is a sulfate-carbonate water type. Such high sulfate water type limits greatly the H_2SO_4 acidification. The expensive hydrochloric acid was necessary in this case for lowering carbonate hardness and leaving sulfate as it is. It was possible to raise recovery rate to around 63%, without addition of sulfate-antiscalant, economically under these conditions.

c) The third case (GW-3, TDS= 17262 mg/l) was further complicated where the estimated THFF was 1.07E+18 molecule/0.1cc.sec. At 55% recovery rate is much higher as compared with the safe guideline limit (8.00E+17). The three dominating potentially-high fouling salts are sulfates 31.01%, phosphates 26.04% then silicates 23.88%, while carbonates share with only 16.90%. This combination of hardness salts is very challenging even for the best antiscalant available in market. Under this condition the safe operation was estimated at recovery around 39% which will not be economic for such medium salinity water. The reasonable choice in this case was limited in to the use of nanofiltration membrane after slight acidification to pH~6.8 in order to remove most of sulfates, phosphates, silicates and carbonates molecules. It was possible to run the SWRO plant under this arrangement at recovery around 72%, however, the economics was still marginal due to its limited capacity (2000 m^3/d).

d) The "ocean, 35091 mg/l" water case is very interesting indeed. The chemistry of open Oceans is almost steady for long time as described by Nordstrom et al [21]. On applying ROIFA-5 program on the mean Ocean water analysis the following results were obtained:
- THFF at recovery rate 50% = 7.85E+17 molecule/0.1 cc.sec.
- (SO4/Alk) molar ratio = 12.13, see guidelines in Table 4 and Figure 1.
- (Cl/(SO4/Alk) molar ratio = 17.86.
- Carbonates percentage from THFF = 24.15%.
- Sulfates percentage from THFF = 62.34%.
- Silicates percentage from THFF = 11.28%, see guidelines in Table 5.
- Carbonates Saturation Factor at 50% recovery = 0%, see guidelines in Table 6.
- Sulfates Saturation Factor at 50% recovery = 99.95%, see guidelines in Table 6.

These important indicators are highly indicative for the typical Ocean water membrane desalination, which gives the highest product recovery rate (~50%) in a single stage without any need for antiscalant dosing.

From long experience, the deviation from these sensitive parameters, higher or lower, may lead to unexpected fouling problems in the SWRO desalination of other semi-closed seawaters. For example, when the East Mediterranean Sea water (TDS ~40500 mg/l) was analyzed with ROIFA-5 the following results were obtained:
- At R=40% THFF=8.56E+17 molecule/0.1cc.sec.
- (SO_4/Alk) molar ratio = 13.24
- (Cl/(SO_4/Alk) = 16.53

In this case ROIFA-5 spreadsheet indicates that the safe RO desalination could be achieved at only 30% recovery rate for a single stage. The difference between the Ocean and the Mediterranean waters seems to be small, but in fact most of the east Mediterranean SWRO plants are operating under 40% recovery rate and with the aid of qualified antiscalants. Over recovery rate 40% the inorganic fouling, especially sulfates, is highly invited even in the presence of antiscalants.

Table 4: Guidelines for Molar Ratio (SO_4/Alk) vs. Scaling Potential [10].

Water Type	Proposed Name	TDS Range* (mg/kgw)	Chloride Range (mMol/ kgw)	Molar Ratio (SO_4/ Alk**)	Carbonate Fouling Potential	Sulfate Fouling Potential
Type - 14	Brine Water	> 60000	> 800	> 15	Rare	Extremely High
Type - 13	Sub-Brine Water	50000 - 60000	700 - 800	12 - 15	Very Low	Very High
Type - 12	High Salty Seawater	40000 - 50000	600 - 700	11 - 14	Low	High
Type - 11	Sea Water	30000 - 40000	500 - 600	10 - 13	Medium	Medium
Type - 10	High Salty Water	15000 - 30000	200 - 500	9 - 11	High	Medium
Type - 09	Medium Salty Water	10000 - 15000	100 - 200	8 - 10	Very High	Medium
Type - 08	Low Salty Water	7000 - 10000	50 - 100	7 - 9	Very High	Medium
Type - 07	High Brackish Water	4000 - 7000	25 - 50	5 - 8	Very High	Medium
Type - 06	Medium Brackish Water	2000 - 4000	10 - 25	2.5 - 5	Very High	Low

Type - 05	Low Brackish Water	1500 - 2000	3 - 10	1.5 - 4	High	Low
Type - 04	High Fresh Water	1000 - 1500	1.5 - 3.0	1 - 3	High	Very Low
Type - 03	Medium Fresh Water	600 - 1000	1.0 – 1.5	0.5 - 1.5	High	Very Low
Type - 02	Low Fresh Water	300 - 600	0.5 - 1.0	0.25 - 1	Medium	Rare
Type - 01	Very Low Fresh Water	< 300	< 0.5	< 0.25	Low	Rare

*Total Dissolved Solids (TDS in mg/kgw) is approximated for guidance purpose.

**Alk.: sum of alkalinity ions (= $OH+CO_3+HCO_3$, in mM/kgw).

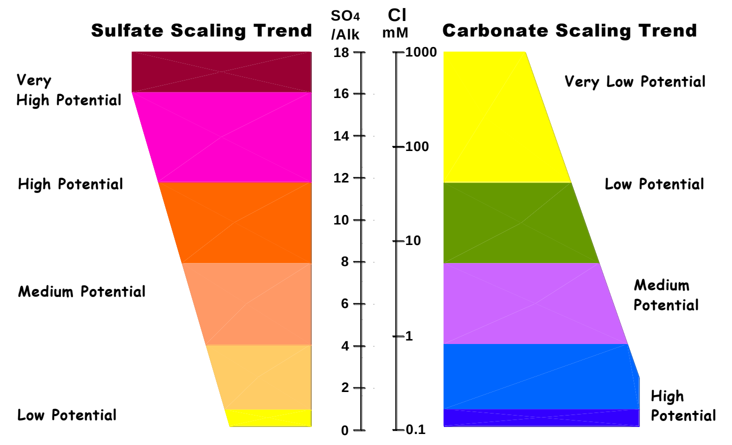

Fig.-1: The Relationship between (SO_4/Alk), Chloride & Relative Scaling Potential.

Table 5: Guidelines for Silicates Fouling on the RO-membrane Surface.

Silicate Fouling (%) of Total Fouling Load		Fouling Potential Guidelines	Remarks
From	To		
0	10	No Silicate Fouling	No treatment is required
10	20	Low Silicate Fouling	Short flushing is essential
20	30	Medium Silicate Fouling	Antiscalant + Chemical Cleaning.
30	40	High Silicate Fouling	Antisc. + Short Chemical Cleaning.
40	50	Very High Silicate Fouling	Antiscalant action is questionable.
> 50	-----	Excessive Silicate Fouling	Scale Blockage is a must

Table 6: Guidelines for the Carbonate & Sulfate Saturation Factor (%).

Saturation Factor (%)		Fouling Potential Guidelines	Remarks
From	To		
0%	100%	No Fouling	No treatment is required
100%	125%	Low Fouling	Short flushing is essential
125%	150%	Medium Fouling	Antiscalant + Chemical Cleaning
150%	200%	High Fouling	Antiscalant action is questionable
>200%	-----	Excessive Fouling	Scale Blockage is a must

e) Although the Red Sea surface water has a higher salinity 44073 mg/l than that of the Mediterranean Sea, its chemical combination permits a higher product recovery (THFF=7.69E+17 at recovery rate 45%) as safe operating conditions. Field investigation showed that several SWRO desalination plants located at Hurghada and Sharm El-Sheikh are running at recovery rate between 43% and 46% for years without any need for antiscalants, depending mainly on a shorter cleaning period.

5 Discussions

Based on laboratory study and long field correlation, the chemical guidelines are proposed and given in the fifth spreadsheet of ROIFA-5 model. These guidelines will help in safe designing of the RO-system considering the actual chemical brine fouling potential and its chemical type as well. For example, in Table 3 when the obtained THFF is about or lower than 8.00E+17 molecules/0.1cc.sec at recovery rate 45% the RO-system will run all right without need of antiscalant.

Field investigation shows that the initial inorganic fouling could happen at brine THFF value ranging between 8.00E+17 and 8.50E+17 hardness-molecules/01cc.sec. This may be attributed to the difference in membranes surface roughness as well as other local operational conditions. Therefore, the guideline limit 8.00E+17 had been considered for safety.

The use of a properly selected antiscalant -that meets the chemical nature of the brine fouling matters and as described in Table 4 can delay effectively fouling and scale formation at a higher recovery rate. However, at fouling flux higher than 1.50E+18 the action of the best antiscalant is generally very limited and the heavy scaling on the RO-membrane surface cannot be avoided.

The proposed calcite-gypsum saturation factor (S_{min}%) guidelines in Table 6 are somehow qualitative. It had been found in many cases that their relative saturation factors are reflecting their abundance in the formed scale.

When the brine THFF is higher than the proposed guideline, there are four available alternatives in order to solve this problem.

1) Using an appropriate antiscalant that meet the chemical type of the concentrated brine, which is not an easy job. Generally, the available antiscalants in the market could be interfering and contradictory, for example, the alkaline one for silica could react with the acidic one for carbonate. Unfortunately, there are no specifically designed antiscalant for each water-type cases. Therefore, the qualified laboratory investigation is essential for this purpose.
2) Lowering permeate recovery rate by using of ROIFA-5 in order to estimate the optimum rate that meets safe THFF guideline (8.00E+17). This is much safer but could be uneconomic depending on the case conditions and fresh water demand.
3) Change of feeding water source could be the best economic solution on the long run. However, in some other cases it is a very sensitive point technically and economically. From long experience it is believed that the best friend for the RO-membrane separation is the pure NaCl solution, while its worst enemy is the high dissolving hardness species. The low-salinity water could have higher dissolved hardness than the high-salinity water that may acquire lower hardness, as that found in the ocean water. In some other cases the surface water chemistry may seasonally change widely along the year due to the action of wet and dry seasons, such as the case of Tampa Bay Desalination Plant in Florida. Tampa Bay is semi-closed shallow carbonate estuary water body receiving big amount of flooded sediments during the summer rainy season causing lower salinity water (16000-26000 mg/l) that contains exceptional higher amount of hardness salts such as carbonates, sulfates, silicates, phosphates and heavy metals oxides. This dissolving hardness wave is of serious fouling potential that may block the RO-membrane in short time. Searching for another water source, either deep groundwater or open Ocean, of higher NaCl and lower hardness water will be the practical solution. ROIFA-5 program is able to explain this example easily.
4) Lowering of hardness content by means of softening can provide a reasonable solution as a last escape. There are four types of softening technologies namely: classical chemical softening, acidification, NanoFilteration softening and Alkalization. The first three techniques are regularly used economically for the pretreatment of the lower-salinity brackish feed water prior to the RO-membrane. For the higher salty water, the alkalization method (by using of NaOH to pH 10.5) could be more feasible than the NF due to higher reverse effect of osmotic pressure. The required amount of caustic soda for alkalization is easily prepared in site through the electrolysis techniques, either via the diaphragm cell or the bipolar membrane electrodialysis. The alkalization method described in detail by El-Manharawy and Hafez, 2002 [15]. The ROIFA-5 program is useful for lowering of hardness molecules in feed-water to an acceptable level economically, and no need to remove all.

6 Conclusions

The ROIFA-5 model and spreadsheet had been developed for predicting the inorganic fouling potential on the RO-membrane, either used for desalination or wastewater treatment**.** This software is based on the earlier dehydration model and depends on about 30 developed statistical equations obtained from laboratory study, field investigation and statistical survey on a big number of natural water cases. Simply, by estimating the probable dissolving salt combination and their relative fouling fractions at the given chloride ion concentration it becomes easy to estimate the inorganic fouling load. It has been found that the solubility of carbonate and sulfate mineral salts are relatively increase with the increase of chloride content (or probably NaCl) and follows natural tight rules. It is proved that the inorganic fouling potential is proportional to the brine total hardness fouling flux (THFF) and not gross salinity. In many investigated cases the lower salinity water may acquire higher hardness fouling potential than the higher-salinity water that may contain less dissolving hardness (like Ocean water). Upon the light of this important information many technical problems in the RO-desalination industry could be explained and find the way to be solved. The economic importance of ROIFA-5 lies in saving cost of total removal of hardness from feed water by just lowering a THFF to be around 8.00E+17 molecule/0.1 cc.sec. This guideline limit was tested for long time and considered satisfactory for either BWRO or SWRO safe design and smooth operation. This software is free for all and available upon request.

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