

An Application for New Reliable Approach to Predict the Onset of Barite, Celestite and Gypsum Scaling during Reverse Osmosis Treatment for Produced Water

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Abstract— Reverse osmosis (RO) desalination is considered a promising solution for Produced Water treatment and reuse in the oil and gas industry. However, scaling problem is one of the main challenges that face Produced Water RO desalination. In this paper, the use of new completely theoretical approach for assessing fouling propensity along a full scale reverse osmosis process is introduced to predict the onset of barite, celestite and gypsum scaling, as major scaling salts facing the RO desalination of Produced Water. Thus, the scaling propensity of barite, celestite and gypsum have been assessed and discussed. Moreover, the effect of applied pressure, initial cross flow velocity, feed salinity and feed temperature on scaling propensity of barite, celestite and gypsum have been examined and discussed. This procedure could be considered as a very important guideline, for any attempt to use RO in Produced Water treatment. It could provide help on the specific design of RO process as well as in simulation of the operating variables for optimization of RO system.

Index Terms—Barite, celestite, produced water desalination, reverse osmosis, scaling, scaling propensity.

I. INTRODUCTION

Produced Water is the wastewater produced during hydrocarbon (such as oil, gas and tar sand) processing. Desalination of Produced Water is attractive for the oil and gas industry for four reasons: Firstly, the substantial amount of globally Produced Water is estimated at around 250 million barrels/day compared with around 80 million barrels/day of oil [1]. The amount of Produced Water makes it the largest waste stream by volume associated with the oil and gas industry and makes the disposal of it a grave problem and burdens the operations of oil and gas industry. Secondly, the high overall cost of the Produced Water disposal as a result of increasing regulatory constraints for environmental concerns makes the economics unpalatable. Thirdly, the fresh water shortage especially in the arid regions like gulf region, where most oil and gas produced countries are located, makes the desalination of Produced Water beneficial, which could potentially help to reduce the problem of fresh water scarcity. Finally, the results of recent research studies by BP [2] show that injection of desalted water to the oil well

has a significant positive impact on the oil recovery.

Scale formation seems to be a limiting factor in the desalination of Produced Water. Scaling limits the economic viability of Produced Water desalination by increasing the energy consumption and decreasing the efficiency of the process. Therefore, scaling mitigation is crucial for viably applying the desalination technology to the Produced Water. The first step on scaling mitigation is the prediction of the scaling propensity for specific feed water within the RO unit. As detailed elsewhere [3] the current practices for assessing the scaling propensity are based on empirical relationships that are not suitable for membrane processes; the empirical indices used for assessment the potential of precipitation fouling which is commonly referred to as scaling have been discussed in detail elsewhere [4]. In fact the complex characteristics of Produced Water exacerbate the problem of scaling because of the high probability of scaling when salts such as CaCO_3 , CaSO_4 , BaSO_4 and SrSO_4 co-exist. Since, the mechanism of fouling is expected to be different for different salts as it was demonstrated [5] for CaCO_3 and CaSO_4 . Sheikholeslami [6] and her research group show that the co-existence of precipitating salt affects the mechanism of fouling, the thermodynamic, and kinetic behavior of each salt; hence, the single salt data is not applicable to the situation where salts co-exist. Thus, the application of the current industrial practice for assessing scaling propensity in desalination plant is limited and may only be able to crudely approximate the scaling propensity for simple feed water at the entrance to the RO desalination unit. Any effort for scaling propensity prediction must consider the substantial change on system variables and parameters throughout full scale RO desalination process and module. Indeed, the current practices make their prediction unrealistic for describing full-scale RO process by assuming homogeneity along the membrane channel, where system variable and parameters change substantially along the long channel [7].

Therefore, In this paper, the application of a newly developed reliable approach [8] is introduced for assisting and predicting the onset of scaling propensity during full scale RO treatment of Produced Water. This new approach is discussed in detail elsewhere [8] and is based on combining Sheikholeslami's Scaling Potential Index (SPI) [4] with a simulation for the behavior of salts' concentration and process parameters within a long membrane filtration channel. This reliable approach has been used to study the effect of operation variables, such as applied pressure and feed salinity, on onset of scaling propensity for the major scaling salts that could be faced during Produced Water

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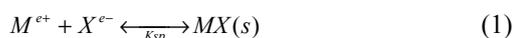
desalination. The results of this paper could be used as a guideline in the process design and operation of a full scale RO for Produced Water treatment.

II. APPROACH DEVELOPMENT

To accurately predict the onset of scaling along a membrane channel there is a need to understand and include the thermodynamics of precipitation, which signify the effect of temperature, pressure, co-precipitation, high ionic strength and salinity on the solubility product. Then combining this solubility product with a simulation for the behavior of ions concentration along the membrane channel, which could be reached through using the principles of membrane transport and mass conservation used by [8], [9] to predict the variations of parameters in a long membrane channel. Thus, using this fundamental principle; the effect of operating parameters such as feed flow rate and the applied pressure on the onset of scaling propensity could be examined and verified.

A. Thermodynamic Analyses

Barite, celestite and gypsum are the common forms of barium sulphate, strontium sulphate and calcium sulphate that could be formed in Produced Water desalination. Equations (1)-(4) represent a general precipitation reaction for (*MX*) salt and the precipitation reactions of barium sulphate, calcium sulphate and strontium sulphate, respectively. Scaling potential of any salt could be assessed using the Scaling Potential Index (*SPI*) as described in (5)-(8). *SPI* was suggested and tested by Sheikholeslami [3],[4]; in fact, Sheikholeslami with introducing the *SPI* has opened the way for a completely theoretical assessment of the scaling propensity of any precipitation salt, through a fundamental and unified approach and by hypothesizing [10],[11],[12] the effect of product structure on Gibbs Free Energy of precipitation reaction and hence the thermodynamic solubility product (*Ksp*) not being a constant and by incorporating the principles of thermodynamics including Gibbs free energies as described below in (9)-(12) and the ion activities.



$$SPI = \log \left(\frac{IAP}{K_{sp}} \right) \quad (5)$$

$$SPI_{barite} = \log \left(\frac{\{Ca^{2+}\} \cdot \{SO_4^{2-}\}}{K_{sp_{barite}}} \right) \quad (6)$$

$$SPI_{gypsum} = \log \left(\frac{\{Ca^{2+}\} \cdot \{SO_4^{2-}\}}{K_{sp_{gypsum}}} \right) \quad (7)$$

$$SPI_{celestite} = \log \left(\frac{\{Sr^{2+}\} \cdot \{SO_4^{2-}\}}{K_{sp_{celestite}}} \right) \quad (8)$$

As seen in (5)-(8), *SPI* calculation for a targeted scaling salt required the calculation of Ion Activity Product (*IAP*) as well as the thermodynamic solubility constant (*Ksp*) for that salt as discussed before based on Sheikholeslami's approach using Gibbs Free Energies of reaction as described below in (9)-(12); where $\Delta_r G$ is Gibbs free energy of reaction, *a* is the activity, *T* is the absolute temperature (*K*) and *R* is the universal gas constant.

$$\Delta_r G = \Delta_r G^\phi + RT \ln \left(\frac{a_{M^{e+}} \cdot a_{X^{e-}}}{a_{MX}} \right) \quad (9)$$

At equilibrium, the Gibbs free energy of reaction ($\Delta_r G$) is zero. Thus,

$$-RT \ln \left(\frac{a_{M^{e+}}^{equ} \cdot a_{X^{e-}}^{equ}}{a_{MX}^{equ}} \right) = \Delta_r G^\phi \quad (10)$$

$$\text{By definition} \left(\frac{a_{M^{e+}}^{equ} \cdot a_{X^{e-}}^{equ}}{a_{MX}^{equ}} \right) = K_{sp} \quad (11)$$

For pure *MX* precipitation, the activity of *MX* (a_{MX}^{equ}) is by convention unity and the standard Gibbs Free Energy of reaction ($\Delta_r G^\phi$) is the difference between the total standard Gibbs free energy of formation of products and the reactants [4] and a function of precipitate structure [10],[11],[12].

$$\Delta_r G^\phi = (\Delta_f G^\phi)_{products} - (\Delta_f G^\phi)_{reactants} \quad (12)$$

For accurate calculation of the *SPI* along RO filtration channel, the effect of temperature and high ionic strength and salinity should be considered and also combined with a simulation for the change on concentrations and operational variables along the filtration channel.

1) Effect of temperature:

Effect of temperature is incorporated as discussed elsewhere [4] through the following equation for RO processes.

$$-RT \ln(K_{sp}) = \Delta_r G^T = \frac{T}{298.15} \Delta_r G^{298} + \Delta_r H^{298} \left(1 - \frac{T}{298.15} \right) \quad (13)$$

where *R* is the gas constant (1.987×10^{-3} kcal/mol.K), and *T* is the temperature (*K*); standard Gibbs free energies are at 298K, ($\Delta_r H$) is the enthalpy of reaction.

2) Effect of high ionic strengths and salinity:

As the second author originally introduced for RO desalination and discussed elsewhere [3],[4],[13] Pitzer model [14] was used to incorporate the high ionic strengths and salinity effects through the effects of ionic strength as well as the electrostatic effects and short and long range ion interaction forces. The *IAP* is calculated by using (14) and the activity coefficients (γ) are calculated by using (15).

$$IAP = a_{M^{e+}} \cdot a_{X^{e-}} = \gamma_{M^{e+}} [M^{e+}] \gamma_{X^{e-}} [X^{e-}] \quad (14)$$

$$\gamma = f(\text{salinity and concentration of species}) \quad (15)$$

B. Modeling for Variation of Concentration Along Membrane Channel.

The variation of ions concentrations and the operational variables in full scale RO is simulated by using finite differences for solution of differential equations of transport and continuity along the module. The details of the mathematical model are discussed elsewhere [8],[9].

In order to simulate the effect of operating parameters on onset of scaling propensity inside practical RO systems; the effects of temperature, pressure, high ionic strength and salinity on *SPI* were examined. The parameter values used in these simulations were either chosen from the manufacturers' specifications or from practical operating conditions as also used by others [9], [7],[15]. This simulation is capable to predict the effects of the variations of operational parameters along membrane channel on the onset of scaling tendency. Our procedure could be used as a very important guideline, for assessment of RO scaling in Produced Water treatment. It could guide on the specific design of RO process as well as in simulation of the operating variables for optimization of RO system.

III. SIMULATIONS FOR THE ONSET OF SCALING

Numerical simulations have been conducted to investigate the effect of operating parameters on onset of scaling propensity prediction along a full-scale RO process. The confidence of the simulation has been discussed and shown elsewhere [8]. Unless otherwise specified, Table 1 shows the values of the parameters that have been used in these simulations - these values were also used by others [9]. The simulation parameters can be adapted to specific operating conditions and manufacture's design to suit any full scale RO process.

TABLE I: PARAMETER VALUES FOR MODEL SIMULATIONS

Length of RO system, L (m)	6
Channel height, H (m)	7×10^{-4}
Applied (pump) pressure, p_0 (Pa)	5.516×10^6
Feed Salinity (mg/l)	30000
Cross flow velocity at entrance (m/s)	0.1
Membrane intrinsic resistance, (Pa.s/m)	1.8×10^{11}
Number of elements along RO system	400
Temperature, °C	25
pH	7.1
Friction coefficient due to spacers	5
Initial Ca^{2+} concentration, ppm	1500
Initial SO_4^{2-} , ppm	2000
Initial Ba^{2+} , ppm	0.02
Initial Sr^{2+} , ppm	30

A. Scaling Propensity of BaSO_4 , SrSO_4 and CaSO_4 along 6 m Membrane Modules.

The *SPI* gives a conservative estimate for assessing scaling potential; when *SPI* is negative, certainly no scale will form; when zero the system is at equilibrium; when the *SPI* is positive, the salt has a "potential" to form scales [4]. Fig. 1 shows the onset of scaling propensity for barite, celestite and gypsum in terms of *SPI*. The figure shows that at these

particular simulation conditions the *SPI* for barite, celestite and gypsum were negative for the first meter of the module and this means that onset of scale formation will not be in the first meter. However, due to permeation and concentration factor, scaling propensities of barite, gypsum, and celestite increases afterwards and *SPI* becomes positive after about 1.5m and increases further along the channel.

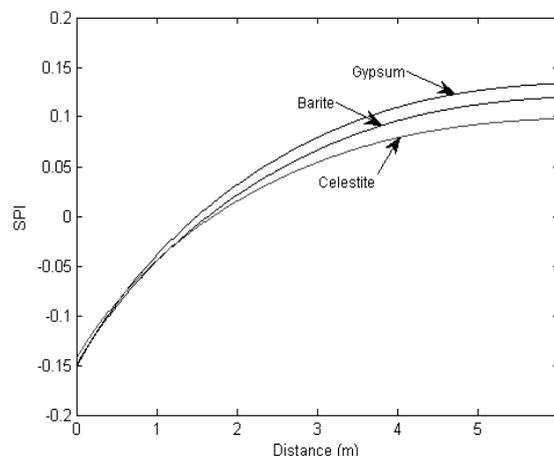


Fig.1. Onset of scaling propensity of Barite, Celestite and Gypsum along 6m membrane channel.

These observations demonstrate that scaling is expected to take place after 1.5m of the membrane channel.

B. Effect of Initial Cross Flow Velocity on Onset of Scaling Propensity for Barite, Celestite and Gypsum.

Fig. 2 shows the effect of various initial cross flow velocities on local *SPI* values for celestite along 6m RO permeation channel. It is shown that cross flow velocity has very important impact on localized scaling propensity. The same trends are observed for the barite, celestite and gypsum scales, confirming that the lowest cross flow velocity results in the highest scaling propensity. Thus, cross flow velocity should be optimized to reduce scaling propensity for all scaling salts. An optimum cross flow velocity can be obtained from our proposed approach. As seen in Fig. 3, under our simulation conditions, operating the RO at 0.2 m/s cross flow velocity will help to minimize barite, celestite and gypsum scaling. This observation could be used as a reference to set the best possible operational limit.

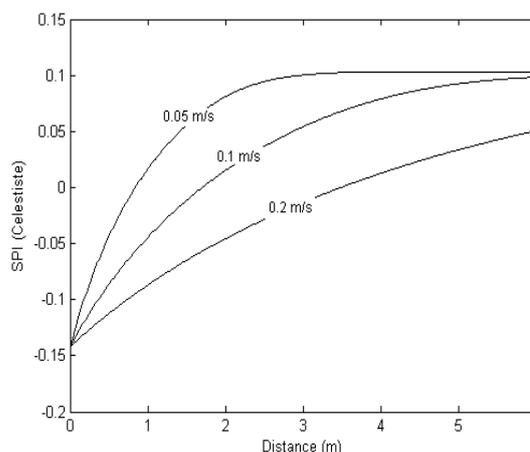


Fig.2. Effect of initial cross flow velocity on onset of scaling propensity for Celestite.

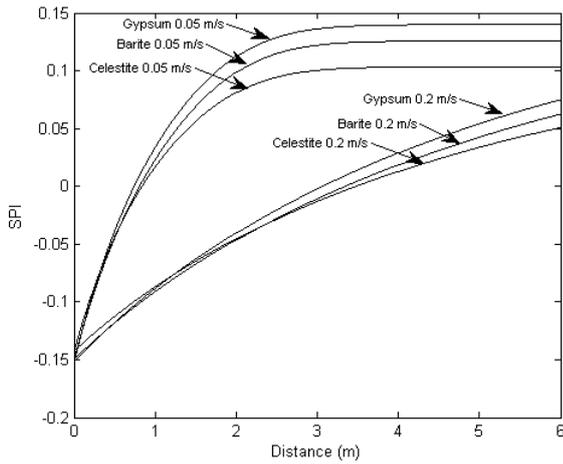


Fig.3. Effect of initial cross flow velocity on onset of scaling propensity for Gypsum, Barite and Celestite.

C. Effect of Applied Pump Pressure on Onset of Scaling Propensity for Barite, Celestite and Gypsum

The applied pressure is one of the operating variables that affect the onset of scaling propensity as shown for gypsum in Fig. 4 for different values of applied pressure. It is shown that increasing applied pressure increases the potential for onset of scaling propensity. At the highest applied pressure, the membrane is most prone to scale formation under otherwise identical feed Produced Water conditions. Thus, theoretical assessment of the scaling potential enables one to operate within the safe operational limit. For example Fig. 5 shows operating the RO at 45 bar will certainly minimize the potential barite, celestite and gypsum scaling.

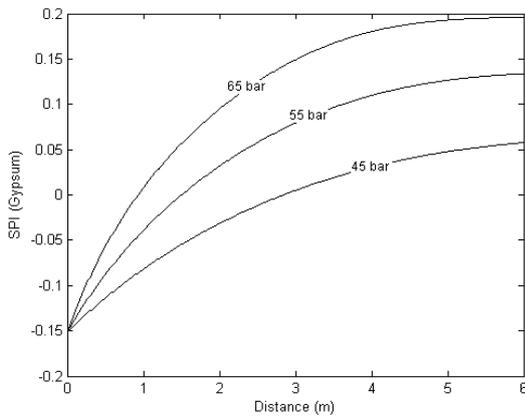


Fig. 4. Effect initial applied pump pressure on onset of scaling propensity for Gypsum.

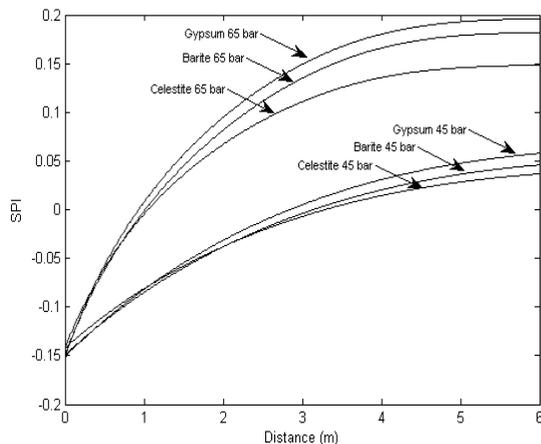


Fig. 5. Effect initial applied pump pressure on onset of scaling propensity for Gypsum, Barite and Celestite.

D. Effect of Initial Feed Water Salinity on Onset of Scaling Propensity for Barite, Celestite and Gypsum.

Salinity of feed water to RO process varies from location to location and may also vary with time at a given location. Therefore, Fig. 6 has been plotted to show the effect of salinity variation on scaling propensity of barite in term of SPI. It shows that at higher feed water salinities, with other parameters constant, the lower would be onset of barite scaling propensity along the membrane channel. Fig. 7 shows that at salinity of 40000 ppm no scales form along the channel, since the SPI curves for these three salts (barite, celestite and gypsum) are negative along the whole channel. The decrease in the potential for onset of scaling propensity along the permeation channel, as the feed water salinity increases is due to the salinity effects on the permeation driving force as well on the ion activity. As the salinity increases the net driving force decreases and the permeate flux will decrease leading to decrease in concentration factor and potential for scaling. Another reason for the decrease in scaling propensity as a result of an increase in feed salinity is the increase in solubility limit, due to the increase of non-scaling salt (NaCl) concentration [3],[4], [11], [13].

It should be noted that in Fig. 6 and Fig. 7 the only variable between the curves are the concentration on “non-scaling” species; the concentration of scaling species and other parameters are the same in all the curves on the figures.

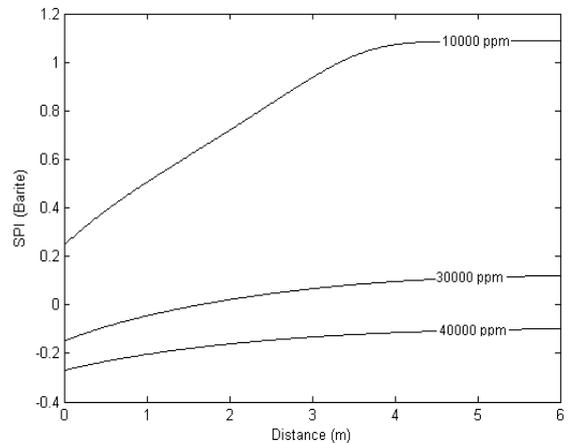


Fig.6. Effect of feed salinity on onset of scaling propensity for Barite.

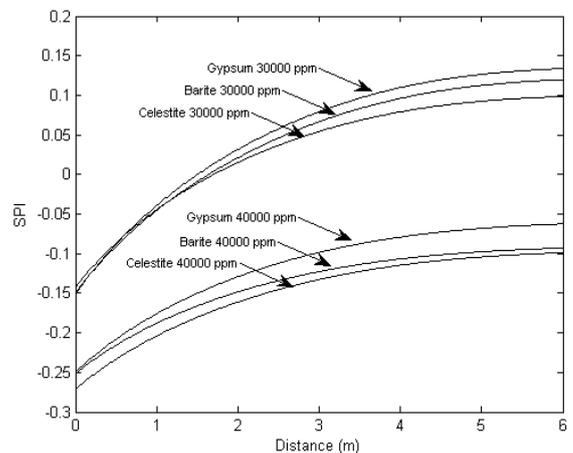


Fig.7. Effect of feed salinity on onset of scaling propensity for Barite, Celestite and Gypsum.

E. Effect of Feed Water Temperature on Onset of Scaling Propensity for Barite, Celestite and Gypsum

Figs. 8-10 show the scaling propensity (*SPI*) for barite, celestite and gypsum along a 6m permeation channel at different feed water temperatures. The thermodynamic solubility constant (*K_{sp}*) was calculated by using (13) at the simulated temperatures; the effect of temperature on density and viscosity was also taken into account. As seen in Fig. 8, increasing temperature from 15°C to 70°C appears to reduce the possibility of barite scale formation. By operating at 40°C, barite scaling can be avoided. Fig. 9 shows that increasing the temperature will increase the probability of celestite precipitation, as seen in Fig. 9 at 70°C the *SPI* curve of celestite will be positive along the whole 6 m filtration channel. As seen in Fig. 10, increasing temperature did not appreciably effect the scaling propensity of gypsum though gypsum is an inverse solubility salt. The effect of temperature on membrane properties should be considered and further attention should be given for the effect of high temperatures on the membrane structure and performance as it could be one of the main drawbacks of operating at high temperatures.

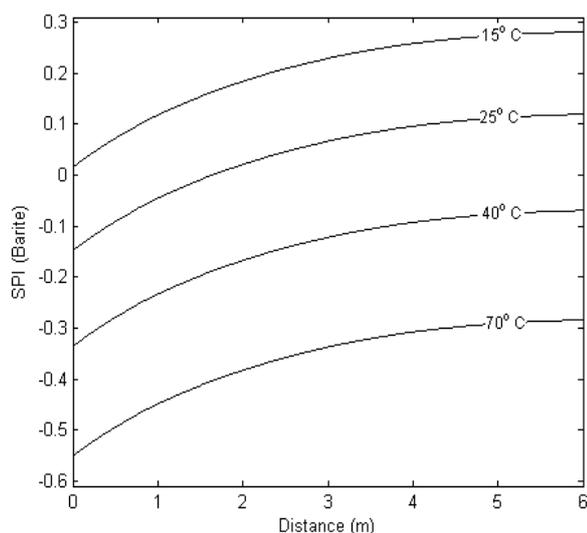


Fig. 8. Effect of feed temperature on onset of scaling propensity for Barite.

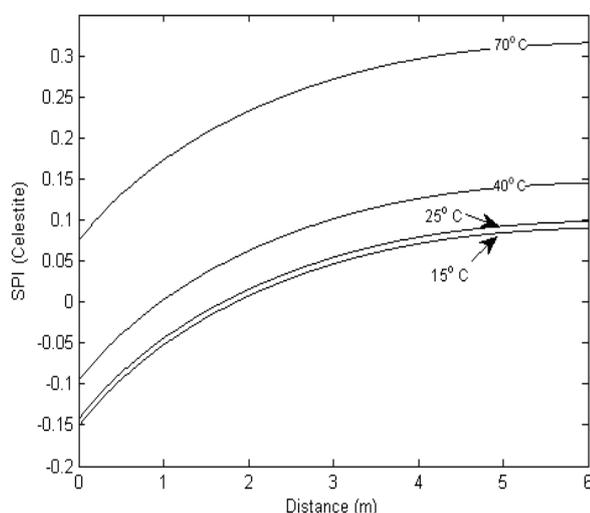


Fig. 9. Effect of feed temperature on onset of scaling propensity for Celestite.

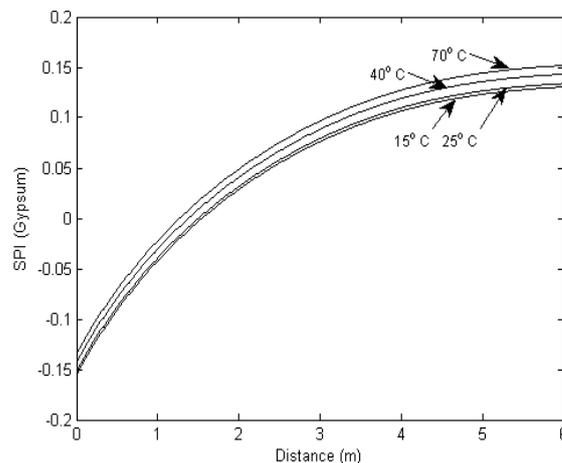


Fig. 10. Effect of feed temperature on onset of scaling propensity for Gypsum.

IV. CONCLUSION

In this paper fundamental relationships were used to reliably simulate and assess scaling propensity of barite, celestite and gypsum, along full-scale RO membrane. This reliable simulation has been reached through incorporation of the localized parameters along the membrane filtration channel in a fundamental and unified approach for assessing the scaling potential. This approach allows studying the effect of hydrodynamic and interactive effects on scaling potential from the fundamental principles. The effects of initial applied pressure, initial cross flow velocity, initial feed water salinity and feed water temperature on scaling propensity development of barite, celestite and gypsum were investigated. The ability to simulate the operational conditions and performance is important for process design and for operating the RO unit within the most suitable operational limit to avoid scaling.

V. NOMENCLATURE

- G* standard Gibbs free energy
- IAP* ion activity products
- K_{sp}* thermodynamic solubility product
- R* the universal gas constant
- SPI* scaling potential index
- T* temperature (K)

Greek letters

- α activity
- Δ denote the difference between two values
- $\Delta_r G^\ominus$ standard Gibbs free energy of formation
- $\Delta_r G^\ominus$ standard molar Gibbs free energy of reaction
- $\Delta_r H$ enthalpy of reaction
- γ activity coefficient

Subscripts

- equ.* equilibrium
- f* formation
- r* reaction

Superscripts

- 0 reference value
- Φ reference temperature value

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