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# AN EMPIRICAL MODEL FOR BUILD-UP OF SODIUM AND CALCIUM IONS IN SMALL SCALE REVERSE OSMOSIS

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### Abstract

A simple models for predicting build-up of solute on membrane surface were formulated in this paper. The experiments were conducted with secondary effluent, groundwater and simulated feed water in small-scale of RO with capacity of 2000 L/d. Feed water used in the experiments contained varying concentrations of sodium, calcium, combined sodium and calcium. In order to study the effect of sodium and calcium ions on membrane performance, experiments with ground water and secondary effluent wastewater were also performed. Build-up of salts on the membrane surface was calculated by measuring concentrations of sodium and calcium ions in feed water permeate and reject streams using Atomic Absorption Spectrophotometer (AAS). Multiple linear regression of natural logarithmic transformation was used to develop the model based on four main parameters that affect the build-up of solute in a small scale of RO namely applied pressure, permeate flux, membrane resistance, and feed concentration. Experimental data obtained in a small scale RO unit were used to develop the empirical model. The predicted values of theoretical build-up of sodium and calcium on membrane surface were found in agreement with experimental data. The deviation in the prediction of build-up of sodium and calcium were found to be 1.4 to 10.47 % and 1.12 to 4.46%, respectively.

Keywords: build-up, membrane, model, osmosis, water

#### 1. Introduction

Fouling and scaling is a major problem in the membrane desalination processes. It is evident when undesirable solids and biomass deposit on the membrane surfaces after prolonged of operation. The major ions that cause fouling and scaling problems on the membrane of RO include calcium, magnesium, bicarbonate, sulfate, silica, iron and barium [1,2]. Sodium, a dominant ion in feed water such as seawater and brackish water encountered in the form of NaCl also considered in fouling problems during RO operation. Calcium ions in the form of CaCO<sub>3</sub> and calcium sulphate are known as sparingly soluble solute in feed water which causes scaling during membrane operation.

Even though the membrane can reject sodium and calcium ions easily, a small portion of these compounds will remain on the membrane surface and block the pores after prolonged operation. It is essential to reduce the concentration of foulants in feedwater as RO membranes are prone to fouling and scaling. Indeed, the pretreatment processes would have an important role in the successful operation of RO. Additionally, reducing or eliminating materials that cause fouling and scaling is preventive endeavor to extend the membrane lifetime. Hence, fouling and or scaling can be diminished using appropriate pretreatment processes. Fouling rate and or quantity also depend on the particle size of foulants which is can be classified as settleable solids (>100  $\mu$ m), supra-colloidal solid (1  $\mu$ m to 100  $\mu$ m), colloidal solid (0.001  $\mu$ m to 1  $\mu$ m) and dissolved solids (<0.001  $\mu$ m) [3]. Colloid and dissolve solids cannot be avoided in membrane separation due to the characteristic of particles and hydrodynamics of flow regime in most of RO operation.

Increasing of applied pressures may reduce the effect of fouling or scaling by those particles. However, the specific energy consumption for water production using RO will increase significantly with increases in operating pressure. Other technique can be employed to reduce the fouling and scaling effects is alteration the bulk solution flow regime from laminar to turbulence using promoter and spacer in membrane module configuration. The presence of promoter and spacer in membrane configuration is expected to reduce the concentration polarization effects and minimized the fouling and scaling.

Despite fouling and scaling being a complicated phenomenon in membrane separations, there are three

factors that can be considered as promising including feed characteristics, build-up of sparsely soluble solute, and by products of growth of microorganism [4]. However, Badger and Carnahan [5] suggested that fouling can occurs in RO membrane in several ways including: i) deposition of colloidal particles in the feed water on the membrane surface, ii) precipitation of slightly soluble organic and inorganic near the membrane surface, iii) accumulation of biological growth in the system and/or its attachment to the membrane, iv) physical or chemical reaction of some feed water component with membrane itself, and v) flocculation of organics and inorganic constituents to form large, insoluble polymer that will deposit on the membrane.

The mechanism of deposition of particles which can restrict the flow in membrane operation is still not fully understood for most of fouling case. Thus, the fouling mechanism will be different for different combinations of particles and membranes. In addition, due to complexity of fouling phenomenon it seems extremely difficult to develop the mathematical model for fouling [4].

In this work, an empirical model for predicted the fouling and scaling based on two ions namely sodium and calcium has been proposed. For this purpose, two important aspects were considered namely, i) formation of build-up on the membrane surface and ii) characteristic of the membrane.

#### 2. Methods

In order to predict the solute build-up on the membrane surface, the two individual ions namely sodium and calcium were considered as predominant ions which promote fouling and scaling in the RO system. Several of the following assumptions are taken into account for developing the build-up of solute model includes:

- 1) In a small-scale of RO build-up of solute mainly affected by applied pressure and concentration of salt in feed samples.
- 2) Build-up of solute can be predicted by concentration polarization and cake formation theory.
- 3) Effect of temperature on build-up of solute was negligible as temperature kept constant in all experiments.
- 4) Flow regime in the bulk phase was considered to be turbulent.

The important information about the RO system include feed characteristic, operating condition and membrane itself can be employed to develop the empirical model for predicting the solute deposit on the membrane surface. Table 1 shows the important parameters for solute build-up prediction.

Model to determined the fouling of membrane base on cake formation are proposed by a numerous authors [6-8].

Fable 1. Parameter (	Considered for	<b>Empirical Model</b>
----------------------	----------------	------------------------

	Parameter
Feed	Concentration, Viscosity, pH,
	TDS, Electrical conductivity,
	Osmotic pressure, Solute particle
	diameter, Temperature
Operating condition	Applied pressure, Feed pressure,
	Time
Membrane	Length, Diameter, Surface area,
	Resistance, Porosity

Permeate flux  $(J_w)$  at transient condition in this model can be expressed as a function of net applied pressure, the membrane and cake (deposit) resistances,  $R_m$  and  $R_c$ respectively.

$$J_w = \frac{\Delta P}{\mu (R_m + R_c)} \tag{1}$$

The deposit resistance can be related to the specific cake resistance ( $\alpha$ ) as follows.

$$R_c = \alpha M_d \tag{2}$$

Substitution equation (2) into equation (1) yields.

$$J_w = \frac{\Delta P}{\mu (R_m + \alpha M_d)} \tag{3}$$

Where  $M_d$  is the mass deposited per unit area of the membrane.

It can be seen that build-up of salt (mass deposit) is inversely proportional to the permeate flux. Thus equation (3) can be rearranged as follows.

$$M_{d} = \left(\frac{\frac{\Delta P}{J_{w}\mu} - R_{m}}{\alpha}\right)$$
(4)

Equation (4) indicates that five parameters namely the pressure difference across the membrane ( $\Delta P$ ), permeate flux (*Jw*), viscosity of solution ( $\mu$ ), membrane resistance ( $R_m$ ) and the specific resistance of deposit ( $\alpha$ ) which strongly affect the build-up or deposit ( $M_d$ ) on the membrane surface.

The pressure difference ( $\Delta P$ ) can be calculated while feed pressure (Pf), rejection streams pressure (Pr), and permeate pressure (P<sub>p</sub>) are known [9].

$$\Delta P = \frac{Pf + \Pr}{2} - P_p \tag{5}$$

Permeate pressure is assumed to be constant at atmospheric pressure (101 kPa) and rejection streams pressure can be estimated as the difference between module pressure and pressure drop in the membrane channel. To calculate the osmotic pressure difference ( $\Delta \pi$ ) the following equation can be employed.

$$\Delta \pi = \overline{\pi} - \pi_r \tag{6}$$

$$\overline{\pi} = \frac{\pi_f + \pi_r}{2} \tag{7}$$

where  $\overline{\pi}$  is average osmotic pressure on the feed side and  $\pi_r$  is osmotic pressure of reject streams. The osmotic pressure of feed, permeate, and rejection stream can be calculated using the correlation from Pitzer [10].

$$\left(\frac{C}{\rho - CM/1000}\right)^{2} \frac{2(\nu_{M}\nu_{X})^{3/2}}{\nu} C_{MX}^{\varphi} \} + \left(\frac{2}{\nu_{M}} \nu_{X}}{\nu}\right) \left[\beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp\left(-\alpha I^{1/2}\right)\right]$$
(8)

The specific resistance of deposit ( $\alpha$ ) is depend on the cake porosity and water viscosity and can be calculated using the Carman-Kozeney equation [11]:

$$\alpha = \frac{45\mu_o(1-\varepsilon)^2}{\rho a_p^2 \varepsilon^3} \tag{9}$$

where  $\mu_o$  is water viscosity,  $\varepsilon$  is cake porosity ,  $\rho$  is cake density and  $a_p$  is the particle radius. For reverse osmosis system, porosity of cake can be estimated as 0.4 [7].  $R_m$  can be calculated by measuring the filtrate volume (V) from RO at interval of time with the following equation.

$$\frac{t}{V} = \left[\frac{R_m \mu}{\Delta P A_m}\right] + \left\lfloor\frac{C_b \alpha \mu V}{2 \Delta P^2 A_m}\right\rfloor$$
(10)

Where t is filtration time and V is filtrate (permeate) volume.

The intercept of t/V versus V at ranges of applied pressure will give the values of  $R_m$  [9]. Alternatively,  $R_m$  can be calculated by measuring the permeate flux over a range of applied pressures [6] with the following equation.

$$J_W = \frac{\Delta P}{\mu Rm} \tag{11}$$

In this work, flow rate and concentration of feed, permeate and rejection streams can be estimated using simple material (ions) balances as follow.

$$Q_f = Q_p + Q_r \tag{12}$$

$$Q_f C_f = Q_p C_p + Q_r C_r \tag{13}$$

Concentration of ions in bulk phase can be estimated as the average concentration of ions in feed and in the rejection streams [12,13].

$$C_b = \frac{C_f + C_r}{2} \tag{14}$$

$$\pi(C) = vRT \left(\frac{C}{\rho - CM/1000}\right) \left[1 - \left|Z_M Z_X\right| A \varphi \frac{I^{1/2}}{I + bI^{1/2}} + \left(\frac{C}{\rho - CM/1000}\right) \right] (15)$$

Concentration of ion in the membrane wall  $(C_m)$  is greater than both in the bulk phase and rejection streams



Figure 1. Membrane Resistance (R<sub>m</sub>) Versus Applied Pressure

due to concentration polarization. Therefore we assumed that build-up of ions  $(M_d)$  can be estimated with the following equations:

$$\% Md_{Na} = \frac{C_{Na(m)} - C_{Na(b)}}{C_{Na(f)}} x100$$
(16)

$$\% Md_{Ca} = \frac{C_{Ca(m)} - C_{Ca(b)}}{C_{Ca(f)}} x100$$
(17)

where subscripts *f*, *p*, *b*, and *m* refers to feed, permeate, bulk, and membrane wall.

Concentration polarization (CP) is strongly depends on the permeate flux (Jw) and mass transfer coefficient (k). Therefore, %M<sub>d</sub> can be simply estimated by measuring permeate flux (Jw) and using the available k in the literature. In this work, the mass transfer correlation for turbulent flow proposed by Sutzkover [14] was employed for calculation purposes.

Measurement of the membrane resistance were performed by collecting the permeate volume from RO system periodically at different times and pressures. Demineralized water (permeate from desalting of tap water) was used for this purpose. Figure 1 shows the  $R_m$  values for different applied pressures. The  $R_m$  values are found to be 6.64 x 10<sup>3</sup>, 4.51 x 10<sup>3</sup>, and 2.11 x 10<sup>3</sup> / m at applied pressures of 1000, 1500, and 2500 kPa, respectively.

From Figure 1  $R_m$  values for different applied pressure can be estimated with the following equation.

$$R_{\rm m} = 6 \ x \ 10^7 \ ({\rm P})^{-1.3071} \tag{18}$$

#### 3. Results and Discussion

In order to develop the empirical models for solute build-up on the membrane surface, series of experiment with NaCl and  $CaCO_3$  were performed. The data collected include applied pressure (P), feed characteristic (concentration, pH, TDS and EC), permeate flux (Jw), permeate characteristic (TDS, pH and EC), and rejection streams flux (Js) at constant temperature. Table 2 shows the range of experimental operating conditions for development of empirical model of solute build-up.

The membrane properties (length, area, porosity) were assumed to be constant except for the membrane resistances. The relationship between build-up (mass deposit) and operating pressure, feed, permeate, and membrane resistance in small-scale of RO can be expressed as.

$$\ln Y = a_0 + a_1 X_1 + a_2 X_2 + \dots + a_n X_n$$
(19)

$$Y = a_0 + a_1 \ln X_1 + a_2 \ln X_2 + \dots + a_n \ln X_n$$
 (20)

There are four independent variables and one dependent variable that can be expressed in natural logarithmic forms as follows.

$$\ln M_d = a_0 + a_1 \ln P + a_2 \ln J_w + a_3 \ln R_m + a_4 \ln C_f (21)$$

where  $M_d$  is dependent variable, P,  $J_w$ ,  $R_{m}$ , and Cf, are independent variables.

The regression coefficient  $a_0 a_1 \dots a_4$  can be obtained from the experiment data. The multiple linear regressions can be performed using sodium and calcium experiments data as shown in Table A1 to A5 (see Appendices).

The results of multiple linear regressions using sodium experimental data are presented in Table 3 and Figure 2. Figure 2 depicts the experimental and calculated  $\ln-M_d$  for NaCl. It can be seen that there is good agreement between the experimental data and calculated values. However, correlation coefficients ( $R^2$ ) are still low due to the relative small amount of data collected during the experiments.

Similar results of the multiple linear regressions of data in Table 2 are presented in Figure 3 and Table 4.

Table 2	. Experiments	Operating	Conditions
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Parameter	Minimum	Maximum
Operating condition		
- Applied pressure (kPa)	1000	4750
- Temperature (°C)	20	35
- Permeate flux $(m^3/m^2.s)$	1.44 x 10 <sup>-5</sup>	6.01 x 10 <sup>-5</sup>
Feed		
- NaCl (mg/L)	100	5000
- $CaCO_3$ (mg/L)	25	100
Membrane		
- Length (m)	1.01	1.01
- Width (m)	0.06	0.06
- Resistance (1/m)	382.81	6237.99

Table 3. Statistical Indicators for NaCl Experimental Data

Statistical indicators	Values	95% confidence
$a_0$	0	-
$a_1$	0.770	0.051
$a_2$	0.669	0.156
$a_3$	0.186	0.156
$a_4$	0.166	0.035
$R^2$	0.958	
Variance	0.046	



Figure 2. Calculated vs. Experimental M<sub>d</sub> for NaCl



Figure 3. Calculated vs. Experimental M<sub>d</sub> for CaCO<sub>3</sub>

 Table 4. Statistical Indicators for CaCO<sub>3</sub> Experimental

 Data

Statistical indicators	Values	95% confidence
$a_0$	0	-
$a_1$	0.963	0.059
$a_2$	0.752	0.146
$a_3$	0.207	0.147
$a_4$	-0.066	0.071
$R^2$	0.951	
Variance	0.020	

Statistical indicator also shows a good agreement between experimental data and calculated of ln  $M_d$  for CaCO<sub>3</sub> with coefficient regression (R<sup>2</sup>) of 0.95.

Based on the multiple linear regressions data from NaCl and CaCO<sub>3</sub> experiment; build-up of sodium and calcium can be expressed as simple equations:

$$\ln M_d \,NaCl = 0.77 \ln P + 0.67 \ln J_w + 0.19 \ln R_m + 0.17 \ln C_f$$
(22)

 $\ln M_d CaCO_3 = 0.96 \ln P + 0.75 \ln J_w + 0.2 \ln R_m - 0.07 \ln C_f$ (23)

Two models of build-up of solute have been proposed in the current work. An attempt has been made to validate the empirical model with the data reported in the literature. The accuracy of the proposed empirical model has been validated by comparing with selected experimental data of Avlonitis [15] with high concentration of NaCl for feedwater ranging from 25,000 to 40,000 mg/L and operating pressure from 5000 to 8000 kPa. Additionally, experimental data of Taniguchi were used to compare the model at relative low of NaCl concentrations [16]. Table 5 shows estimated values of  $C_p$ ,  $C_b$ , and  $C_m$  from Avlonitis et al and Taniguchi [15,16] experiments results. Figure 4 shows the plot between calculated and experimental values of  $\%M_d$  for NaCl. There is a good agreement between the model and literature data. Estimated error percentage between data and model are ranging from 1.40 to 10.97% for Avlonitis's data and from 1.07 to 6.57% with Taniguchi's data. Model also can predict build-up of NaCl for feed concentration up to 40,000 mg/L and applied pressure of 7000 kPa. Beyond this limit error percentage will reach 42%. Nevertheless, operation of membrane at applied pressure greater than 7000 kPa will leads to membrane compaction [17], increase the energy requirement, and unit cost.

To validate the empirical build-up of calcium model, experimental data from Arora et al [18] has been used as shown in Table 6.

Table 5. Estimated of C<sub>b</sub> and C<sub>m</sub> Values from Experimental data of Avlonitis and Taniguchi

Т	Р	C <sub>f</sub> (mg/L)	$J_{\rm w} \ge 10^{-5}$	Cp	$C_{\rm r} \ge 10^3$	C <sub>b</sub> **)	C <sub>m</sub> **)
(°C)	(kPa)		$(m^{3}/m.s)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)
20	5500	25,000	1.89	89	28.09	26545	29191
20	6000	25,000	2.09	89	28.43	26715	29378
20	6000	35,000	1.60	166	38.63	36815	40480
20	7000	35,000	1.96	141	39.49	37245	40955
20	7000	40,000	1.68	162	44.37	42185	46387
25	6000	35,000	1.76	182	39.00	37000	40682
25	6000	40,000	1.50	242	43.88	41940	46110
25	7000	40,000	1.88	200	44.68	42340	46554
30	6000	35,000	1.96	228	39.48	37240	40941
30	6000	40,000	1.64	289	44.25	42125	46309
35	6000	40,000	1.85	368	44.81	42405	46609
24.7 <sup>*)</sup>	3560	19,400	3.69	55.2	2.126	2033	2191
$25.1^{*)}$	3490	18,950	3.77	57.2	2.146	2021	2178
$24.8^{*)}$	3450	19,530	3.73	57.7	2.332	2143	2309

\*) Refers to experimental data of Taniguchi [16] an other data refers to Avlonitis et al. [18]

\*\*) Sample calculations for first data set in [19]



Figure 4. Calculated vs Experimental Percent Build-up (M<sub>d</sub>) for NaCl in Current Study (Δ), Taniguchi (□), and Avlonitis (○)



Figure 5. Calculated vs. Experimental Percent Build-up  $(M_d)$  for NaCl in Current Study ( $\Delta$ ), and Arora et al. ( $\circ$ )

Experimental Data of Arora et al. (2004)							
T (°C)	P (kPa)	C <sub>f</sub> (mg/L)	J <sub>w</sub> x 10 <sup>-5</sup> , m/s	C <sub>p</sub> (mg/L)	C <sub>r</sub> (mg/L)	C <sub>b</sub> (mg/L)	C <sub>m</sub> (mg/L)
25	2000	227.7	1.6	67	240	233.9	234.52
25	2000	24.8	1.6	4.9	27.7	26.3	26.34
25	2000	17.6	1.6	3.5	20.1	18.9	18.91
25	2000	15.2	1.6	4.2	17.7	16.5	16.50
25	2000	9.6	1.6	1.4	11.3	10.5	10.49
25	2000	63.2	1.6	17.2	70.3	66.8	66.95

Table 6. Estimated of C<sub>b</sub> and C<sub>m</sub> Values from

Figure 5 shows the plot of calculated and experimental data for build-up of calcium. Results show that model can predict the build-up of calcium with error percentage between 1.12 and 4.46%.

Empirical model for build-up of solute on membrane surface was developed based on the experimental results with simulated feedwater, secondary effluent, and groundwater in small-scale RO. The major parameters were considered in the study including operating condition, membrane and feed characteristics. Additionally, the model also has been validated with existing data in the literature. Overall empirical models proposed in the current work will be useful for predicting the membrane performance and build-up of solute.

# 4. Conclusion

Build-up of solute in small-scale of RO system was predicted using the empirical model proposed in this work. Two ions namely sodium and calcium in feedwater considered as dominant ions leading to buildup of solute on the membrane surface. Four main parameters namely applied pressure, permeate flux, membrane resistance, and feed concentration were considered as major parameters which strongly affect the overall membrane performance. One or two linier empirical models can be useful for predicting the buildup of solute on the membrane surfaces. However buildup of solute was calculated with indirect ways and only two ions were taken into account. Salts concentration in the experiments only represent for low concentration of salt in feedwater. Therefore the models are only recommended for brackish ground water and secondary effluent or other feedwater having low salt concentration (between 100 and 5000 mg/L). Furthermore, additional work with other solute (such as barium, magnesium, bicarbonate, sulfate, silica, iron, and barium) will be useful in arriving at a generalized empirical model suitable for various types of feedwater.

## Appendices

Table A1.	Estimated	Independent	Variables	for	NaCl
	Experimen	ts			

P (kPa)	$J_{\rm w} \ge 10^{-5}$ , m/s	$R_m (1/m)$	$C_{f}$ (mg/L)	(%M <sub>d</sub> )			
	100 mg/L NaCl						
1250	1.44	6238	42	1.41			
1750	2.72	3617	42	2.64			
2250	4.01	2407	42	3.61			
2750	5.13	1739	42	4.17			
	500 m	g/L NaCl					
1250	1.60	6238	197	1.56			
1750	2.56	3617	197	2.53			
2250	4.49	2407	197	4.29			
2750	4.97	1739	197	5.37			
3750	6.25	1052	197	8.17			
	1200 m	ng/L NaCl					
1250	1.44	6238	295	1.60			
1750	2.72	3617	295	2.96			
2250	4.00	2407	295	4.16			
2750	4.91	1739	295	6.12			
3750	6.25	1052	295	8.54			
	2500 m	ng/L NaCl					
1250	1.36	6238	209	1.55			
1750	2.56	3617	209	3.52			
2250	3.85	2407	209	4.09			
2750	4.97	1739	209	5.87			
3750	6.25	1052	209	8.23			
	5000 m	ng/L NaCl					
1250	1.28	6238	402	1.89			
1750	2.24	3617	402	3.53			
2250	3.74	2407	402	4.31			
2750	4.33	1739	402	6.04			

#### Table A2. Estimated Independent Variables for CaCO<sub>3</sub> Experiments

P (kPa)	J <sub>w</sub> x 10 <sup>-5</sup> , m/s	$R_m(1/m)$	$C_{f}$ (mg/L)	(%M <sub>d</sub> )
	100 mg/L Ca(	$CO_3 + 500 n$	ng/L NaCl	
1250	1.44	6238	5.10	1.14
1750	2.72	3617	5.10	2.5
2250	4.01	2407	5.10	3.53
2750	4.97	1739	5.10	5.05
3750	6.25	1408	5.10	8.74
	50 mg/L CaCO	$D_3 + 500 \text{ mg}$	g/L NaCl	
1250	1.44	6238	4.99	1.29
1750	2.72	3617	4.99	2.17
2250	4.01	2407	4.99	3.17
2750	4.97	1739	4.99	5.73
3750	6.25	1408	4.99	7.22
	100 mg/L CaCO	$D_3 + 1200 \text{ n}$	ng/L NaCl	
1250	1.28	6238	7.25	1.11
1750	2.40	3617	7.25	2.15
2250	3.53	2407	7.25	3.27
2750	4.49	1739	7.25	5.43
3750	6.25	1052	7.25	7.71
	50 mg/L CaCC	$P_3 + 1200 \text{ m}$	ig/L NaCl	
1250	1.28	6238	6.57	1.18
1750	2.24	3617	6.57	1.83
2250	3.37	2407	6.57	3.55
2750	4.33	1739	6.57	4.97
3750	5.93	1052	6.57	7.57

	100 mg/L CaCo	$D_3 + 2500 \text{ m}$	ng/L NaCl		
1250	0.96	6238	8.08	0.74	
1750	2.08	3617	8.08	1.52	
2250	3.04	2407	8.08	3.19	
2750	4.33	1739	8.08	3.66	
3750	5.61	1052	8.08	4.89	
$50 \text{ mg/L CaCO}_3 + 2500 \text{ mg/L NaCl}$					
1250	0.96	6238	6.19	1.21	
1750	2.08	3617	6.19	1.79	
2250	3.05	2407	6.19	3.28	
2750	4.33	1739	6.19	3.63	
3750	5.61	1052	6.19	4.97	
	100 mg/L CaCo	$D_3 + 5000 \text{ m}$	ng/L NaCl		
1750	1.28	3490	13.72	1.06	
2250	2.40	2511	13.72	2.33	
2750	3.21	1931	13.72	3.33	
3750	5.13	1052	13.72	6.12	
4750	4.65	717	13.72	5.31	
50  mg/L CaCO <sub>2</sub> + 5000 mg/L NaCl					
1750	1.28	3490	11.9	1.06	
2250	2.40	2511	11.9	2.53	
2750	3.21	1931	11.9	3.33	
3750	5.13	1052	11.9	6.12	
4750	4.65	717	11.9	5.31	
25 mg/L CaCO <sub>3</sub>					
1250	1.76	6238	1.67	1.24	
1750	2.89	3617	1.67	2.76	
2250	4.81	2407	1.67	4.03	
2750	5.77	1739	1.67	5.56	
$50 \text{ mg/L} \text{ CaCO}_2$					
1250	2.08	6238	2.02	1.11	
1750	3.21	3617	2.02	2.82	
2250	4.81	2407	2.02	4.92	
2750	6.09	1739	2.02	6.45	
	75 m	g/L CaCO <sub>2</sub>			
1250	1 76	6238	33	1.22	
1750	3 53	3617	33	2.84	
2250	4 81	2407	33	4 46	
2750	6.09	1739	33	6 68	
=,00	5.07	1,57	0.0	0.00	

Table A3.EstimatedIndependentVariablesforCombined of NaCl and CaCO3 Experiments

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$(M_d)$			
1250       1.28       6238       490       1.         1750       2.40       3617       490       3.         2250       3.53       2407       490       5.         2750       4.65       1739       490       6.         3750       6.25       1052       490       7.         500 mg/L NaCl + 50 mg/L CaCO3       128       6228       421       1				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.93			
2250 3.53 2407 490 5. 2750 4.65 1739 490 6. 3750 6.25 1052 490 7. 500 mg/L NaCl + 50 mg/L CaCO <sub>3</sub> 1250 128 6228 421 1	.41			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.39			
3750 6.25 1052 490 7. 500 mg/L NaCl + 50 mg/L CaCO <sub>3</sub>	.95			
500 mg/L NaCl + 50 mg/L CaCO <sub>3</sub>	.47			
1230 1.28 6238 431 1.	.90			
1750 2.24 3617 431 3.	.29			
2250 3.36 2407 431 5.	.11			
2750 4.33 1739 431 5.	.27			
3750 5.93 1052 431 6.	.20			
1200 mg/L NaCl + 50 mg/L CaCO <sub>3</sub>				
1250 0.96 6238 984 2.	.08			
1750 2.40 3617 984 4.	.40			
2250 3.54 2407 984 4.	.52			
2750 4.49 1739 984 7.	.17			
<u>3750</u> 5.93 1052 984 8.	.62			

250	00  mg/L NaCl + 3	50 mg/L C	aCO <sub>3</sub>	
1250	0.96	6238	1468	1.93
1750	2.08	3617	1468	3.46
2250	3.05	2407	1468	5.20
2750	4.20	1739	1468	7.69
3750	5.61	1052	1468	11.98
500	00  mg/L  NaCl + 3	50 mg/L/C	aCO2	
1250	0.96	6238	1027	1.83
1750	2.08	3617	1027	3 94
2250	3.05	2407	1027	417
2750	4 33	1739	1027	6.28
3750	5.62	1052	1027	9.36
100	$m_{\alpha}/L$ NaCl + 1	00  mg/I C	aCO.	
1750	1.60	3617	1941	2 82
2250	2.89	2407	1941	4 60
2250	3.85	1739	1941	7 13
3750	2.05 4.97	1052	1941	9.63
4750	5 77	717	1941	11 72
500	= 5.77	$\frac{1}{1}$	•00	11.72
1750	1  mg/L NaCl + I	00  mg/L C	$aCO_3$	2 47
1/30	1.00	2407	1551	2.47
2230	2.50	2407	1521	4.10
2750	5.55	1/39	1551	2.00
5750	4.03	1032	1521	0.90
4/30	5.45	/1/	1331	11.00
120	0  mg/L NaCl + 1	00  mg/L (	CaCO <sub>3</sub>	
1750	1.28	3617	1447	2.23
2250	2.40	2407	1447	3.89
2750	3.21	1739	1447	6.79
3750	4.80	1052	1447	9.54
4750	5.12	717	1447	12.47
250	0 mg/L NaCl + 1	00 mg/L (	CaCO <sub>3</sub>	
1250	3.21	6238	79	2.96
1750	4.07	3617	79	3.80
2250	5.13	2407	79	4.62
2750	6.01	1739	79	6.03
500	0  mg/L  NaCl + 1	00 mg/L C	CaCO <sub>2</sub>	
1250	1.44	6238	115	1.38
1750	2.57	2407	115	2.76
2250	3.21	2407	115	2.77
2750	3 53	1739	115	4 01

# Table A4. EstimatedIndependentVariablesforSecondary Effluent Experiments

P(kPa)	$J_{\rm w}  {\rm x10^{-5}},  {\rm m/s}$	$R_{m}(1/m)$	$C_{f}$ (mg/L)	(%M <sub>d</sub> )
1250	1.44	6238	10.6	1.26
1750	2.57	3617	10.6	2.50
2250	3.21	2407	10.6	2.89
2750	3.53	1739	10.6	3.47

# Table A5. Estimated Independent Variables for Ground Water Experiments

P(kPa)	J <sub>w</sub> x10 <sup>-5</sup> , m/s	$R_m (1/m)$	$C_{\rm f}$ (mg/L)	(%M <sub>d</sub> )
1250	3.21	6238	11.24	1.97
1750	4.07	3617	11.24	2.10
2250	5.13	2407	11.24	4.21
2750	6.01	1739	11.24	4.79

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