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Oxidation-reduction potential in saline water reverse osmosis membrane desalination and its potential use for system control

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ABSTRACT

Chlorination and dechlorination are required in most saline water (brackish and seawater) reverse osmosis membrane desalination processes, regardless of whether a membrane or conventional chemical conditioning is employed as a pre-treatment. Wastage of chemicals occurs when the dosing process is not automated. Titrations of chlorinated water (using sodium hypochlorite) with sodium meta-bisulfite were undertaken using water of different salinities, which were obtained by varying volume ratios of seawater to deionized water (4:0, 3:1, 2:2, 1:3 and 0:4). Changes in reduction and oxidation potential (ORP) were studied with variations in chlorine doses (0 to 5 mg L^{-1}NaOCl) and salinities. As expected, the ORP values were greater at higher than at lower chlorine doses for any given water. The greater the ratio of seawater to deionized water, the lower was the ORP value, with a difference of greater than 100 mV between the deionised water and the seawater at a high chlorine dosage. The results suggest that the ORP level would be lower for seawater than for brackish water in control of chlorine dose. The ORP decreased with sodium meta-bisulfite addition at high chlorine dosages ≥2 mg l^{-1}) while the opposite was observed at low chlorine dosages (≤1 mg L^{-1}). Free chlorine disappeared instantly following sodium meta-bisulfite addition. As more than 80% of the added chlorine was diminished in the seawater, 2 mg L^{-1} sodium meta-biosulfite was sufficient to reduce free residual chlorine to less than 0.1 mg L^{-1} as required for most of the cellulose acetate RO membrane in seawater desalination. To be safe and cost-efficient, a chemical dose controller can be developed using the ORP titration information.

Keywords: Chlorination; Dechlorination; Free residual chlorine; Ionic strength; Activity coefficient; Seawater; RO membrane

1. Introduction

In water treatment, oxidation-reduction potential (ORP) has several applications: (1) to assess the disinfection potential of a system—a high ORP normally indicating an effective disinfection environment and low viable counts of microorganisms, (2) to determine the dose of a disinfectant [1], and (3) to guide manipulation of oxidation-reduction condition of a system by dosing an oxidant or a reductant for a particular need [2–8].

In preparation of secondary effluent, brackish water and seawater for reverse osmosis (RO) membrane process,

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chlorine in the form of sodium hypochlorite (NaOCl) is used as a disinfectant to control bio-fouling of the RO membrane [9]. However, most of the RO membranes currently in use are made of cellulose acetate and are sensitive to chlorine, a strong oxidizing agent which can deteriorate the integrity of the membranes [10–13]. To prevent membrane fiber damage caused by chlorine, operators limit the life-time exposure of cellulose acetate or polyamide RO membranes to chlorinated solution to less than 1,000 mg L^{-1} h [10,12,13] and implement intermittent chlorination [11]. To be safe, dechlorination is required to reduce chlorine concentration to less than 0.1 mg L^{-1}. In practical applications, sodium biosulfite, sodium metabisulfite or similar chemicals is the preferred dechlorination agent [14,15] and their dose is normally controlled at 1.5 parts for every part of free residual chlorine present in the water. Excessive concentration of bisulfite that is used for dechlorination may facilitate scale formation [16].

RO membrane desalination of brackish water and/or seawater has become an important strategy to provide water for municipal and industry use. In pretreatment, disinfection is necessary for control of biofouling [15]. Currently, chlorination is the common choice for disinfection although ultraviolet [17] has the potential of becoming a future disinfectant in the seawater RO membrane desalination. Control of chemical dosing in the desalination process is primarily done by fixing the flow rate of a chemical solution and continuously feeding the solution to the system. This has two disadvantages: (1) over dose; and (2) excessive and unnecessary loading of chemicals/contaminants to the environment-natural system [9,11].

Addition of both chlorine and the dechlorination reagents affects oxidation and reduction potential (ORP) [14]. Breakpoint chlorination, quality of the water matrix and the level of required free residual chlorine (FRC) determine the dose of chlorine. The breakpoint chlorination is primarily related to ammonia and natural organic matter in the water [18]. Therefore, high chlorine dose is required to achieve disinfection for water with high concentrations of ammonia and natural organic matter. Higher chlorine dose results in more production of disinfection by-products [19–21] and demands a higher dose of a dechlorination agent for complete chlorine removal [22]. Information on FRC concentration and ORP is also useful in predicting the corrosion potential of metal pipes in water distribution network and metal components that are in contact with the saline water. Normally, high concentrations of FRC and disinfection by-products and high ORP are associated with significant corrosiveness [7,23] which requires inhibitive measures to prevent it from happening.

In an aqueous environment, ORP together with pH determines the proportions of the chemical species of a substance in the water [24]. For most of the metals having high and multi-valences, such as Fe and Mn, the most oxidizing states are responsible for scale formation. This trades off the merits that a high ORP improves the effectiveness of disinfection.

Seawater is known to have an ORP between 150 and 400 mV in sallow columns [14,25–27]. There is a lack of knowledge, however, on how chlorination and dechlorination and salinity might influence ORP quantitatively. The importance of understanding such relationships will benefit (1) dose determination of the chlorine chemicals and dechlorination agent with high confidence and minimum chemical wastage; and (2) robust control of the chlorination/dechlorination unit operations. The objectives of this study were to quantify the relationship between the dose of chlorine and ORP, to assess the impact of salinity on the ORP, and to explore possible application of the titration curves of sodium meta-bisulfite and sodium hypochlorite for process control.

2. Materials and methods

2.1. Seawater sample

Seawater samples were collected at a low tidal time in January 2004 at the coast of near Tanah Merah ferry terminal, Singapore, at the spot E 103°59.2′ N 1°18.8′ where the sampling point was about 50 m from the shore, 1 m below the water surface and 1 m above the seabed. The seawater samples were placed in 20 L polyethylene containers and stored at room temperature (25°C). Subsamples were analysed for physical and chemical characteristics following standard analytical procedures [28]. Selected characteristics of the seawater are presented in Table 1.

2.2. ORP titration

Water samples of different salinities were obtained by addition of deionized water to the seawater at different ratios (Table 2). Sodium hypochlorite (12% NaOCl) solution was used to make a stock solution of 1,000 mg L^{-1} NaOCl. While it was still "fresh", aliquots of 1,000 mg L^{-1} NaOCl solution were added to the saline water to achieve initial concentrations of 0, 1 to 5 mg L^{-1} NaOCl. Solid-state sodium meta-bisulfite ($Na_2S_2O_5$, reagent grade) was used to make the titratant at 500 mg L^{-1}.

The ORP titration was conducted by slowly titrating the chlorinated saline water with the titratant using a 50 mL burette and a 500 mL Erlenmeyer flask in which the saline water (initially mL) was mixed continuously using a magnetic stirring bar after each addition of 1 mL aliquot of the titratant. The changes in ORP were monitored using

Table 1
Characteristics of the seawater collected and analyzed in January 2004

Parameters	Unit	Value	Parameters	Unit	Value
pH	—	8.2	Carbonate	mg L^{-1}	<2.0
Fe	mg L^{-1}	<0.3	Bicarbonate	mg L^{-1}	110
Al	mg L^{-1}	<1.9	SiO_2	mg L^{-1}	0.36
Na	mg L^{-1}	10,300	TOC	mg L^{-1}	1.55
K	mg L^{-1}	476			
Ca	mg L^{-1}	439	Oil and grease	mg L^{-1}	1.8
Mg	mg L^{-1}	1,300	Total alkalinity	mg L^{-1}	112
Mn	mg L^{-1}	0.46	Total hardness	mg L^{-1}	6,450
Sr	mg L^{-1}	9.00	Conductivity at 25°C	μS cm^{-1}	47,500
Ba	mg L^{-1}	0.44	TDS (drying method)	mg L^{-1}	35,700
B	mg L^{-1}	3.92	UV absorbance (254 nm)	cm^{-1}	<0.05
Cl	mg L^{-1}	14,800	Mode of particle size	μm	18.4
F	mg L^{-1}	2.00	Total suspended solid	mg L^{-1}	34.4
Ortho-P	mg L^{-1}	<2.61	Turbidity	NTU	0.1
SO_4^{2-}	mg L^{-1}	2,700	Temperature	°C	28
NO_3-N	mg L^{-1}	<1.00			
NH_4-N	mg L^{-1}	<0.05	HPC	cfu ml^{-1}	22

Table 2
Ionic strength and activity coefficient as related to the salinity of titration water

SW:DW (volume)	TDS (mg L^{-1})	I (M)	OCl^-	Cl^-	$S_2O_5^=$	$SO_4^=$	H^+	Na^+
			Radius, λ (nm)					
			0.35	0.3	0.45	0.4	0.9	0.4
			Activity coefficient, γ					
0:100	50	0.00125	0.961	0.961	0.854	0.854	0.963	0.961
25:75	8,490	0.212	0.737	0.723	0.335	0.315	0.835	0.749
50:50	16,900	0.423	0.712	0.692	0.310	0.284	0.849	0.730
75:25	25,400	0.634	0.710	0.685	0.321	0.288	0.875	0.732
100:0	33,800	0.845	0.718	0.689	0.348	0.307	0.908	0.745

an ORP meter (CyberScan 510) and the ORP was recorded after each addition for data analysis. The titration for saline water was stopped after the consumption of 30 and 40 mL of the 500 mg L^{-1} $Na_2S_2O_5$ solution and/or when the titration passed the ending point. The changes in pH of the water before and after the titration were observed to be less than 0.2 units as a result of the small doses of the NaOCl and $Na_2S_2O_5$ and the buffering capacity of the saline water.

The reaction of sodium meta-bisulfite with sodium hypochlorite in the water can be written as:

$$Na_2S_2O_5 + 2NaOCl + H_2O \rightarrow 2NaHSO_4 + 2NaCl \qquad (1.1)$$

or

$$Na_2S_2O_5 + 2NaOCl + H_2O \rightarrow 2Na_2SO_4 + 2HCl \qquad (1.2)$$

On a weight-to-weight basis, approximately 1.34 parts of sodium meta-bisulfite are required to remove 1 part of free chlorine.

The equilibrium-constant expression for reaction Equation [1] is derived as:

$$K = \frac{\left[a_{NaCl}\right]^2 \left[a_{NaHSO_4}\right]^2}{\left[a_{NaOCl}\right]^2 \left[a_{Na_2S_2O_5}\right]\left[a_{H_2O}\right]} \qquad (2)$$

2.3. Free chlorine measurement

One-liter stocks of saline water with initial NaOCl concentrations of 1, 3 and 5 mg L^{-1} were prepared. The changes in FRC concentration of chlorinated saline water with times were determined using colorimetric method (i.e., the N,N-diethyl-p-phenylenediamine-DPD method) [29].

Several clean and dry 10 mL sample vials were filled with 10 mL chlorinated saline water and spiked with DPD free chlorine reagent powder. A few minutes were allowed for the reaction between the reagent and chlorine to take place. The vial was inserted into the colorimeter for measurement of free residual chlorine concentration. The colorimeter was zeroed with the same saline water without the addition of sodium hypochlorite. The duration from the time of adding the DPD free chlorine reagent powder to the time at which the measurement was made was kept constant. The same chlorinated saline water was determined for free residual chlorine concentration at several time intervals to examine whether it changes with time.

2.4. Oxidation-reduction potential

For redox reaction described by Eq. (1), the ORP (E, in volts) can be expressed using the Nernst expression as follows:

$$\begin{aligned} E &= E^0 + \frac{2.30RT}{nF}\log K = E^0 + \frac{0.591}{n}\log K \\ &= E^0 + \frac{0.0591}{n}\left(\log\frac{\left[a_{\text{NaCl}}\right]^2\left[a_{\text{NaHSO}_4}\right]^2}{\left[a_{\text{NaOCl}}\right]^2\left[a_{\text{Na}_2\text{S}_2\text{O}_5}\right]}\right) \end{aligned} \qquad (3.1)$$

During titration, changes in concentrations of NaCl and $NaHSO_4$ can be negligible. Eq. (3.1) yields the following:

$$E = E^0 + \frac{0.0591}{n}\left[A - 2\log\left(a_{\text{NaClO}}\right) - \log\left(a_{\text{Na}_2\text{S}_2\text{O}_5}\right)\right] \qquad [3.2]$$

Before the titration took place, the concentration of NaOCl had a fixed value. Eq. (3.2) is thus simplified to:

$$\begin{aligned} E &= E^0 + \frac{0.0591}{n}\left[A + B - \log\left(a_{\text{Na}_2\text{SO}_5}\right)\right] \\ &= \frac{0.0591}{n}\log\left(a_{\text{Na}_2\text{S}_2\text{O}_5}\right) + D \end{aligned} \qquad (3.3)$$

In the above equations, E^0 is the ORP of the reaction at the standard conditions; A, B and D can be treated as constants and n is the number of moles of electrons transferred during the reaction. F is Faraday's constant, with a value of 96,500 J (V-mol $e^-)^{-1}$, R the gas constant (R= 0.082057 $L\cdot atm\cdot K^{-1}\cdot mol^{-1}$) and T the absolute temperature.

The molar activity (a_i) is the product of the activity coefficient (γ_i) and the molar concentration (C_i) for a reactant or a product, i.e.,

$$a_i = \gamma_i \times C_i \qquad [4]$$

The activity coefficient (γ) of an ion in a dilute solution is a function of the ionic strength, charge and radius of the ion. The concentration of $Na_2S_2O_5$ during the titration was calculated by subtracting the normality of $Na_2S_2O_5$ from that of NaOCl, a negative value indicating residual $Na_2S_2O_5$ in the water. The normality of the remaining $Na_2S_2O_5$ was subsequently converted into molality for data analysis.

2.5. Activity coefficient

The activity coefficient (γ_i) of an ion in a diluted aqueous solution (i.e. ionic strength I <0.1 M) was calculated using the extended Debye–Hückel approximation of the Debye–Huckel limiting law:

$$-\log\gamma_i = \frac{\alpha Z_i^2\sqrt{I}}{1+\beta\lambda_i\sqrt{I}} \qquad (5)$$

in which α is a constant that relates to the solvent and varies with temperature [$\alpha = 1.82 \times 10^6\,(\varepsilon T)^{-3/2}$, and ε is the dielectric constant. α = 0.5 at 15°C and 0.509 at 25°C]; β is a constant that relates to the solvent and varies with temperature ($\beta = 50.3\,(\varepsilon T)^{-1/2}$: $\beta = 0.326 \times 10^8$ at 15°C and 0.328×10^8 at 25°C); λ_i = a constant that relates to the diameter (nm) of the hydrated ion; Z_i the valence of the ion; and I is the ionic strength (M).

For ionic strength greater than 0.1 M (e.g., seawater), the activity coefficient can be calculated from the modified Debye–Hückel equation with modification [30,31]:

$$-\log\gamma_i = \frac{0.511\times z_i^2\times\sqrt{I}}{1+3.29\times\lambda_i\times\sqrt{I}} - 0.1\times z^2\times I \qquad (6)$$

The ionic strength was calculated from the relationship between ionic strength and total dissolved solids (TDS) using Eq. (7):

$$I = 2.5 \times 10^{-5} \times \text{TDS (mg L}^{-1}\text{)} \qquad (7.1)$$

or

$$I = 1.6 \times 10^{-5} \times \text{specific conductance } (\mu\text{S cm}^{-1}) \qquad (7.2)$$

in which I is the ionic strength (M).

3. Results and discussion

3.1. Ionic strength and activity coefficient

The ionic strength of the seawater, a non-idea solution, is about 0.8 M, and the value decreased with increasing dilution using de-ionized water (Table 2). Dilution of seawater using de-ionized water produces brackish water of various salinities. With changes in total dissolved solids from 8,500 mg L^{-1} to 25,000 mg L^{-1}, the ionic strength varied from 0.2 M to 0.6 M. Such variations would have an impact on a variety of reactions in the aqueous system because the activity coefficient of a reactant in a system of high ionic strength became smaller than unity. These reactions include dissolution-precipitation [16,32], oxidation–reduction [25], sorption–desorption [33], etc.

The analysis showed that the activity coefficient of an ion in the aqueous was primarily a curvy linear function of the ionic strength (Fig. 1). Numerical simulation using Equation [6] showed that the smallest activity coefficients were 0.710, 0.686, 0.310, 0.285, 0.835 and 0.729 for OCl$^-$, Cl$^-$, $S_2O_5^{2-}$, SO_4^{2-}, H$^+$ and Na$^+$, respectively. The corresponding ionic strengths were 0.550, 0.634, 0.423, 0.465, 0.212 and 0.465 M and the SW:DW ratios 2.6:1.4, 3.0:1.0, 2.0:2.0, 2.2:1.8, 1.0:3.0, and 2.2:1.8. These results indicated that for same concentrations of the reactants, their activities in brackish water were lower than those in fresh water or seawater. The activity coefficients were comparable with those recorded in the literature [34–36] although they differed in the equations which were used to calculate the activity coefficient. Of the Pitzer, Debye–Huckel, extended Debye–Huckel and Davies equations, the Pitzer equation gives an activity coefficient significant lower than the other three; the latter generated similar values for the same ion when ionic strength was less than 0.15 M. The difference escalated when ionic strength was greater than 0.5 M because the Pitzer equation takes into account pairs of ions [36–38] while the others do not.

The implication of the low activities is that operations (e.g. chlorination/dechlorination, anti-scaling, and clean-in-place) associated with brackish water would require higher doses of a chemical than with either the fresh water or pure seawater to have the same effectiveness. The activity coefficients were remarkably low for ions with high charges which are frequently responsible for scale formation. This explains the fact that to remove scales from the surfaces in contact with saline water, the scale-stripping reagent must be of high strength to effectively strip the scale off the surface and recover the reversible flux in the case of membrane filtration.

In the desalination process, a conductivity sensor and transmission system could be installed and the salinity of the water acquired online at real-time and processed for ionic strength and activity coefficients of relevant ions. The solubility products of possible scaling substances would be evaluated using the activity coefficients. An algorithm could be developed and implemented and subsequently a controller constructed on basis of the calculated ionic strength, the activity coefficients and solubility products and used to formulate the solutions required for the clean-in-place of a membrane system. A robust CIP reagent preparing mechanism could substantially reduce the consumption of the chemicals and make the CIP a more environmentally friendly process in RO membrane desalination.

3.2. Oxidation-reduction potential

Before adding the titratant, the raw water had ORP values that varied from 270 mV for deionzed water to 54 mV for seawater. Addition of NaOCl increased ORP and the increment ranged from 100 mV to 650 mV depending on the salinity and the dose of the oxidant. In general, the lower the salinity, the higher the dose of NaOCl, the higher the ORP (Fig. 2). There were interactions between the salinity and the NaOCl dose. Salinity suppressed ORP most when NaOCl was dosed at 1 mg L^{-1}. The reduction became less with increasing

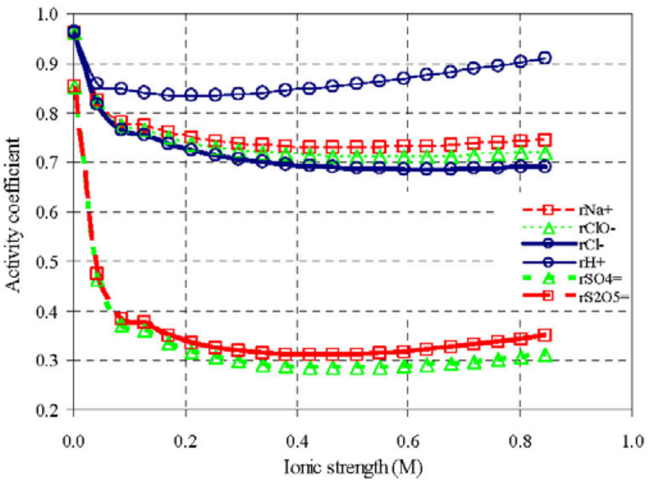

Fig. 1. Activity coefficient of selected ions as related to ionic strength.

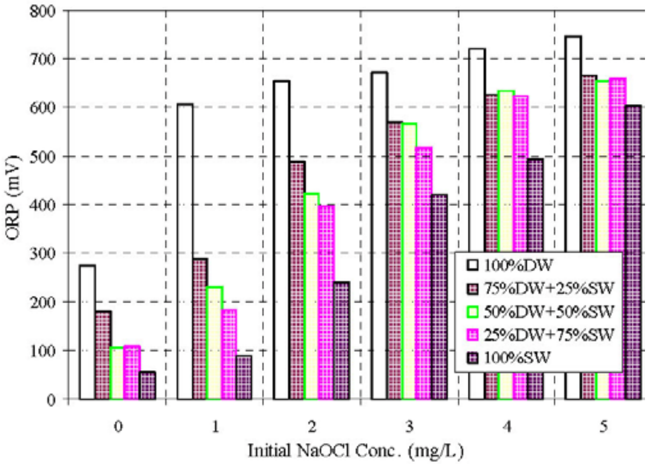

Fig. 2. Oxidation-reduction potential as related to initial chlorine concentrations in water of various salinities.

NaOCl dose. At a NaOCl dose of 4 or 5 mg L^{-1}, the TDS change from 8,490 to 25,400 mg L^{-1} resulted in little difference of ORP values (Fig. 2).

With zero or 1 mg L^{-1} NaOCl, ORP of deionized water in general decreased with the additions of $Na_2S_2O_5$. For saline water, however, ORP increased slightly as the titration continued (Fig. 3: 0, 1, 2 mg L^{-1}) and greater increments were observed with higher salinities. With NaOCl dose of 3 mg L^{-1} and above, the ORP values decreased with increasing $Na_2S_2O_5$ additions and the decrements were similar for water with different salinities (Fig. 3: 3, 4, 5 mg L^{-1}). For the same amounts of $Na_2S_2O_5$ addition, the decrements were greater at the early (before reaching the end-point) than at the late stage of titration.

Of a titration curve, there was no clear-cut of the end-point (Fig. 3), probably because of the presence of the other reduction–oxidation pairs in the sweater [25]. The "end-points" were obtained by dividing a titration curve into two segments that could be approximated best using two linear equations. The segments before the "end-

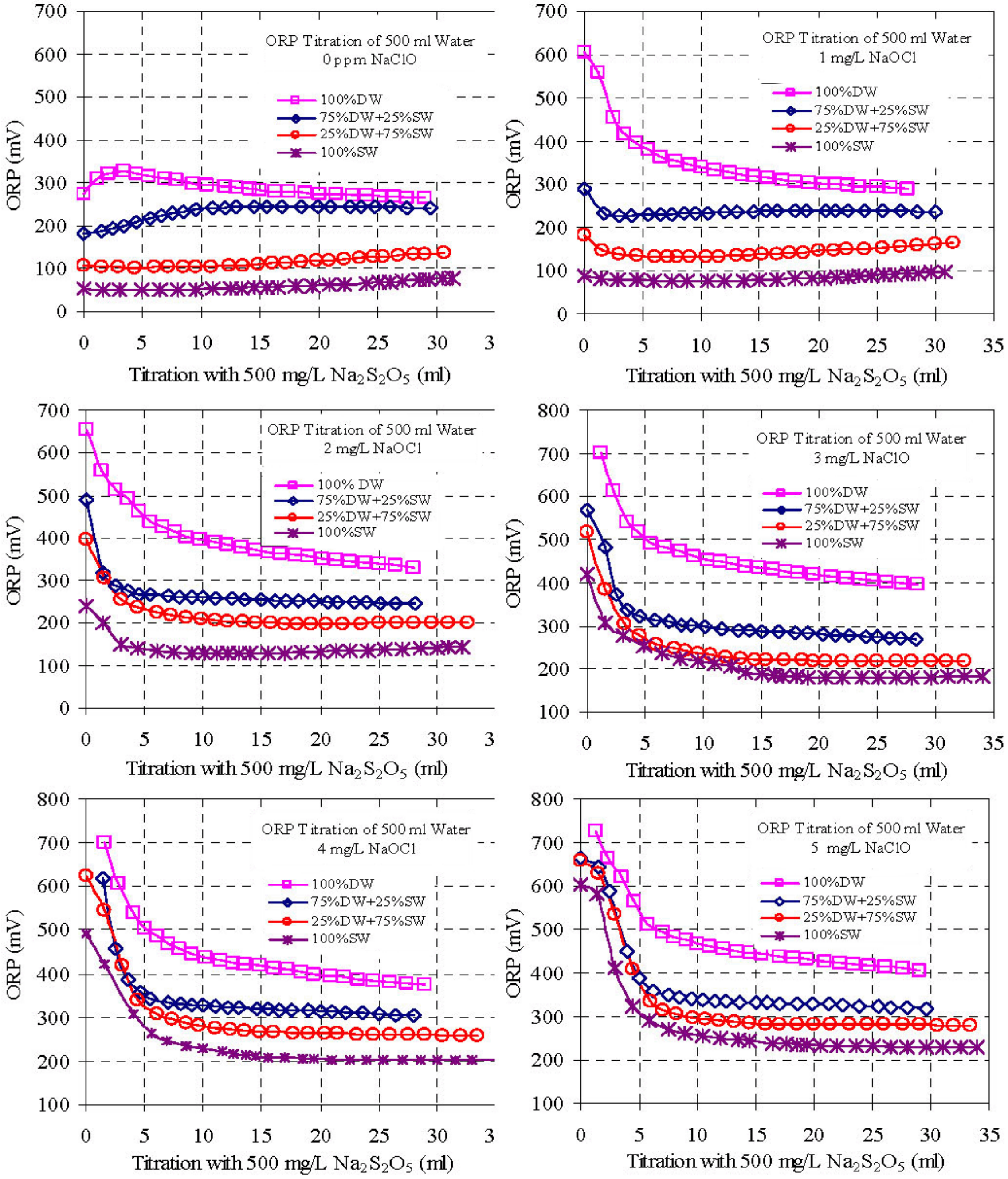

Fig. 3. $Na_2S_2O_5$–NaOCl titration curves as influenced by water salinity.

points" have steep slopes in comparison with those after the end-point (Fig. 3). The cross point of the two lines was taking as the proxy of the "end-point" of the titration, which showed that the higher the salinity of the water, the greater the volume of the titrant was required to reach the end-point, and the higher the dose of NaOCl, the greater amount of the reducing reagent was consumed to remove the oxidant (Table 3).

To protect membranes that are sensitive to strong oxidants, dechlorination of the feed is required [15]. The common practice for processing non-saline water is that for every part of NaOCl, approximately 1.5 parts of $Na_2S_2O_5$ are used to remove the FRC. The data of titration end-point (Table 3) indicated that a greater amount of $Na_2S_2O_5$ (up to 2.5 parts for every part of NaOCl) might be required to remove the oxidant from the saline water. When ORP which might be associated with deterioration of the RO membrane under defined conditions becomes available, a robust $Na_2S_2O_5$ or another effective anti-oxidation agent (a reductive chemical) dosing system can be developed to prevent the membrane from being destroyed.

Saline water itself is highly corrosive because of high concentrations of active ions, such as Cl^- and $SO_4^=$ [7,39]. In the presence of a chlorine compound, such corrosion potential could be greatly enhanced [23]. For RO membrane desalination under tropical conditions, the corrosiveness of the saline water could be further enhanced because of the high pressure, stress, and relatively high water temperature. System components made of iron, copper and other metals and/or metal alloys in saline water desalination process could be corroded slowly when in contact with the feed water for an extended period. Observations from a pilot study [40] showed that the high pressure stainless steel pipe and the accessories of the flow switch meters could all become rusted within several months of operation. Anti-corrosion materials and regents, high pH, reduction of ORP and disinfection [23, 41,42] could be sound options to prevent and/or slow down the corrosion.

Table 3
Estimated titration end-point for water with various salinities

Chlorine dose (NaOCl, mg L^{-1})	SW:DW (volume)				
	0:100	25:75	50:50	75:25	100:0
	Titratant volume (500 mg L^{-1} $Na_2S_2O_5$, ml)				
1	5.5	2	2	2.5	3.5
2	5	2	3.5	—	4
3	4.5	3.5	4	4	4
4	6	4	—	5	6
5	6.5	5.5	—	6	5.5
	ORP (mV)				
1	340	225	145	125	75
2	410	270	205	—	120
3	470	310	265	225	180
4	450	335	—	280	210
5	470	340	—	290	250

When added to saline water, NaOCl dissipated quickly at room temperature (25°C) as indicated by the decreases in free chlorine concentrations (Fig. 4). The decrement was greater and faster with higher than with lower NaOCl additions. This might have been contributed to the decreases in ORP during the titration although such contribution could not be separated from the decreases resulted from $Na_2S_2O_5$ (Fig. 3). In addition to the consumption in inactivation of microbes, the reduction of FRC could be related to four mechanisms: (1) reaction with ammonia forming chloramines and with organic materials forming organo-chlorine compounds during breakpoint chlorination [15,18,43,44]; (2) decomposition of the hypochlorite to chloride under ambient conditions as a result of exposure to light, an increase in temperature, or because of the relatively high concentration of the compound [7, 45]; (3) decreases in NaOCl activity in saline water due to the influence of high ionic strength (Table 2); and (4) the presence of metals pairs, such as iron and manganese [25,46,47]. The nature of self-decomposition of NaOCl has two contradictory but practical implications: a higher dose might be required to achieve an effective disinfection if the hydraulic retention time is short, and a lower dose of $Na_2S_2O_5$ to remove the FRC from the feed water to protect the chlorine sensitive membrane.

3.3. Regression slopes and intercept of the Nernst equation

When the ORP was plotted against $Na_2S_2O_5$ concentration after each addition of the reducing aliquot, the

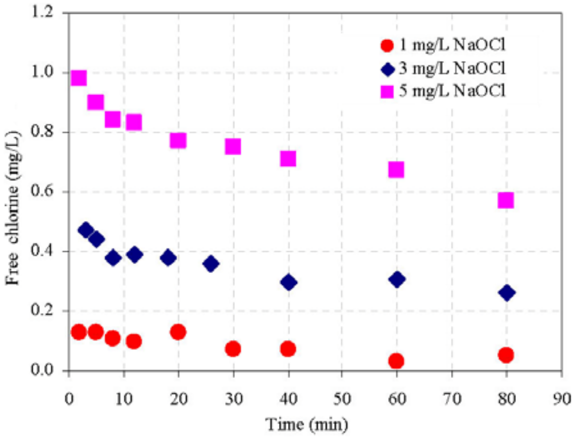

Fig. 4. Changes in free NaOCl concentration in seawater as related to initial chlorine addition.

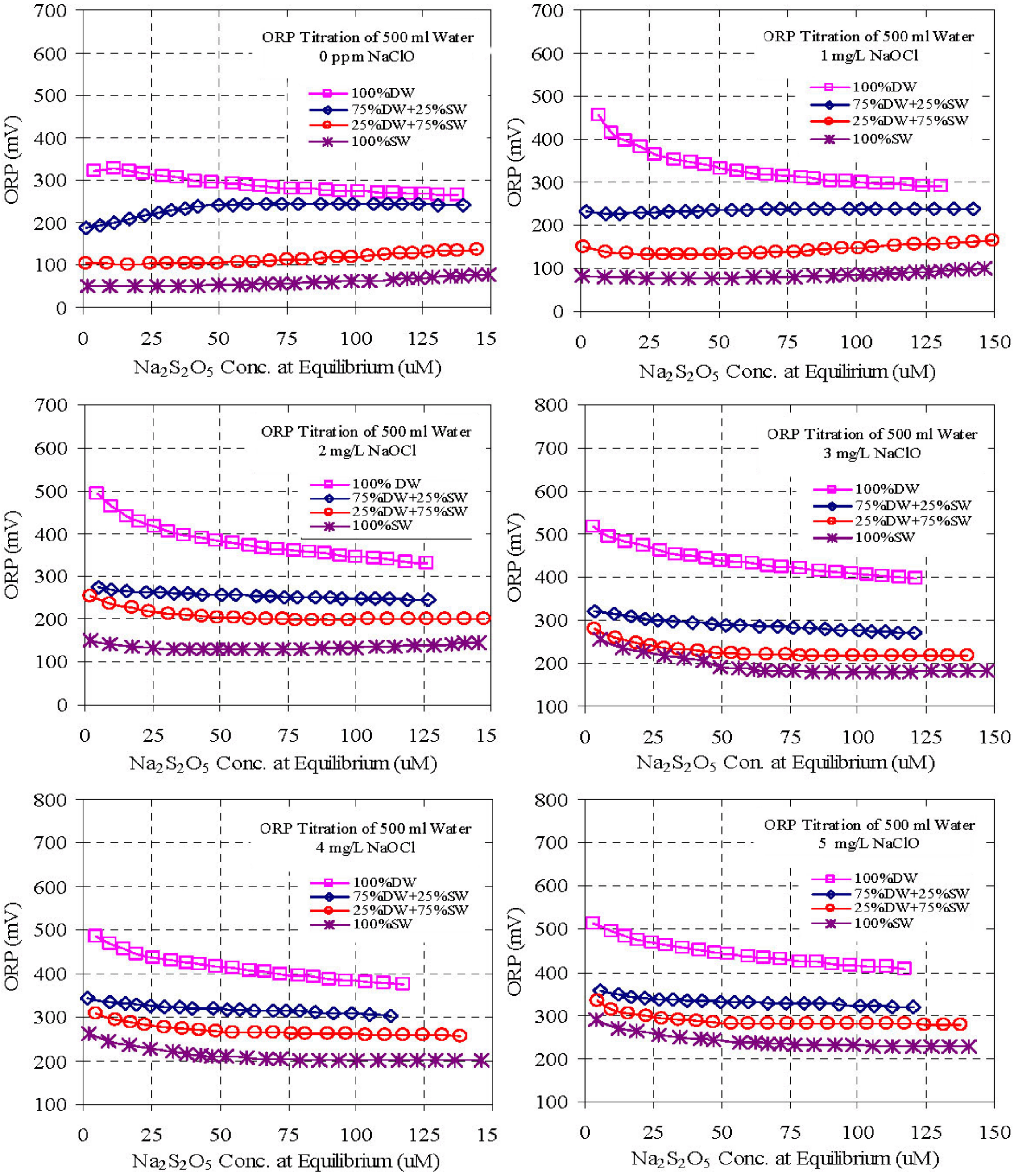

Fig. 5. Changes in oxidation-reduction potential (ORP) during titration as related to $Na_2S_2O_5$ concentration at equilibrium and water salinity.

shape of the plot (Fig. 5) was smooth in comparison with that of the titration curve (Fig. 3). Regression of ORP on concentration of $Na_2S_2O_5$ at equilibrium was conducted following Eq. (3.3). Significant R^2 values were obtained for all of the titrations except three occasions of low chlorine dose and high salinity (Table 4).

The simple regression equations gave significant slopes and intercepts. The slope in Eq. (3.3) is related to electrons transferred in and out of the titration domain as defined by Eq. (1). The slope (Table 4) was converted into the electrons transferred by equaling the slope value to $-0.0591\times n^{-1}$ and solving the equation for n, a quantity of electrons transferred. The calculation (Table 5) indicated that the electron transport in the titration domain defined by Eq. (1) took place. For deionized water with added chlorine, the electron transfer ranged from 0.481×10^{-3} mmole L^{-1} for 1 mg L^{-1} NaOCl to 0.848 mmole L^{-1} for 5 mg L^{-1} NaOCl. The number of electrons transferred was

Table 4
Regression of ORP (E) on activity of $Na_2S_2O_5$ at equilibrium as related to dose of sodium hypochlorite and volume ratio of seawater to deionised water

Chlorine dose (NaOCl, mg L^{-1})	SW:DW (volume)	Regression of E (mV) on activity of $Na_2S_2O_5$ (mM) at equilibrium	R^2
0	0 : 100	$E = -48.75 \times \log(a) + 223.8$	0.9057
	25 : 75	$E = 34.29 \times \log(a) + 294.5$	0.8857
	75 : 25	$E = 17.12 \times \log(a) + 145.6$	0.4870
	100 : 0	$E = 14.29 \times \log(a) + 84.74$	0.4946
1	0 : 100	$E = -122.75 \times \log(a) + 168.4$	0.9942
	25 : 75	$E = 7.14 \times \log(a) + 247.6$	0.6284
	75 : 25	$E = 8.79 \times \log(a) + 159.0$	0.1644[a]
	100 : 0	$E = 6.37 \times \log(a) + 95.45$	0.2277[a]
2	0 : 100	$E = -115.00 \times \log(a) + 176.5$	0.9979
	25 : 75	$E = -21.44 \times \log(a) + 217.5$	0.9761
	75 : 25	$E = -31.16 \times \log(a) + 153.0$	0.9046
	100 : 0	$E = -3.04 \times \log(a) + 129.9$	0.0423[a]
3	0 : 100	$E = -78.00 \times \log(a) + 328.2$	0.9654
	25 : 75	$E = -36.04 \times \log(a) + 224.2$	0.9569
	75 : 25	$E = -37.83 \times \log(a) + 161.3$	0.9467
	100 : 0	$E = -56.64 \times \log(a) + 99.48$	0.9067
4	0 : 100	$E = -80.71 \times \log(a) + 301.4$	0.9788
	25 : 75	$E = -21.93 \times \log(a) + 278.8$	0.9165
	75 : 25	$E = -34.37 \times \log(a) + 209.1$	0.9774
	100 : 0	$E = -37.50 \times \log(a) + 147.9$	0.9612
5	0 : 100	$E = -69.67 \times \log(a) + 345.9$	0.9639
	25 : 75	$E = -27.02 \times \log(a) + 283.6$	0.9891
	75 : 25	$E = -33.34 \times \log(a) + 229.3$	0.9048
	100 : 0	$E = -41.54 \times \log(a) + 170.3$	0.9859

[a] Not significant.

Table 5
Electrons transferred [among the reactants, Eq. (1)] during the titration of saline water with $Na_2S_2O_5$[a]

Chlorine dose (NaOCl, mg L^{-1})	SW:DW (volume)			
	0:100	25:75	75:25	100:0
	$\times 10^{-3}$, mmole			
0	1.212	−1.723	−3.452	−41.36
1	0.481	−8.277	NS	NS
2	0.514	2.757	1.897	NS
3	0.758	1.640	1.562	1.043
4	0.732	2.695	1.719	1.576
5	0.848	2.187	1.773	1.423

[a] Negative values denote that electron transfer took place among components other than those specified in Eq. (1).

generally greater in saline water than that in the deionized water. This could have been due to the facts that metal couples such as Fe^{3+}/Fe^{2+} and MnO_4^-/Mn^{2+} might have facilitated the travel of the electrons [48]. However, smaller numbers were noted with higher than with lower salinity, implicating that electron transfer might have been slowed down in the titration domain of high salinity because many of the side reactions might have taken place. In these reactions, electron self-exchange within the couples and/or among the reactants could have occurred [49]. The negative values of electron transfer associated with titrations of zero or low chlorine dose suggest that other components in the water might have contributed to the changes in ORP during the titration.

The values of the intercept showed clearly that the higher the salinity, the smaller the contribution of the other constituents was in the titration system. The dose of chlorine increased the intercept, which was consistent with observations that greater ORP values were with higher chorine additions. The intercept captured contributions from a range of components in the ORP titration system, including the standard ORP [$E°$ in Eq. (3)] value, the other redox reactions that were not shown in Eq. (3.3), the water matrix (Table 1) and temperature influence.

In seawater, there is a variety of compounds or elements that could have involved in oxidation and reduction processes. These include O_2/H_2O, O_3/OH^-, H_2O_2/H_2O, Fe^{3+}/Fe^{2+}, I_2/I^- IO_3^-/I^-, MnO_4^-/Mn^{2+}, $NO_3^-/NH_3/N_2$ [25]. Although occurring in very low concentrations, they could have either scavenged the electrons or acted as shuttles in transporting the electrons to various destinations [49]. Their importance is keeping the reaction chain "alive" in the reacting domain.

The significant linear regression between the ORP and the concentration of residual $Na_2S_2O_5$ should make it easy to develop a comprehensive OPR based controller for saline water chlorination, RO feed dechlorination and for robust control of the clean-in-place for the RO membrane. Implementation of such controller is beyond the scope of the present paper.

4. Conclusions

Ionic strengths and activity coefficients of electrolytes were evaluated for water of salinities ranging from 50 to 33,500 mg L^{-1} TDS. Ionic strengths ranged from 0.001 M for the deionized to 0.85 M for the seawater. In general, ions in water of high salinity have smaller activity coefficients than those in water of low salinity. This suggests that chlorine doses for saline water application need to be higher than those for fresh water in order to achieve the same efficacy.

ORP increased with decreasing salinity. Dosing of NaOCl increased ORP and the increment was smaller at higher than at lower salinity. The $Na_2S_2O_5$–NaOCl titration curves showed that $Na_2S_2O_5$ effectively removed FRC and brought down ORP of the saline water. This has three practical implications: (1) to minimize membrane deterioration in RO membrane desalination and to reduce the corrosiveness of the chlorinated water; (2) to reduce membrane loads, and (3) to optimize the use of dechlorination reagent for the protection of the environment.

The $Na_2S_2O_5$–NaOCl titration in water of various salinities was described well using the Nernst equation [Eq. (3)]. The slope reflected electrons transferred during the ORP titration while the intercept revealed the impact of the salinity and the initial dose of NaOCl and other water characteristics. The amount of electrons transferred was generally greater in the saline water than that in the deionized water.

Using the ORP information and the $Na_2S_2O_5$–NaOCl titration curves, it is possible to develop a controller for a range of applications of automation, including chlorination and/or dechlorination, oxidation and/or reduction, and dissolved oxygen control.

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