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The use of the dose gradient method for evaluating reverse osmosis membrane scale inhibitors

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ABSTRACT

This paper describes the dose gradient method for assessing the relative inhibitory effectiveness of various reverse osmosis membrane scale inhibitors. Five scale inhibitors were chosen as examples for the examination of the dose gradient method's feasibility in evaluating the relative inhibitory effectiveness of different scale inhibitors. The results show that pH, R_{ej} (desalination rate), and ΔK_{Ca} (increase in cycles of concentration) can be used as indicators with ΔK_{Ca}, being the most suitable indicator; the sensitivities of three indicators are, from greatest to smallest, $\Delta K_{Ca} >> \text{pH} > R_{ej}$, and their relative standard deviations are, respectively, 73.07, 1.89, and 0.17%; and the scale suppression effectiveness of the five tested scale inhibitors by three judgment indicators are all, from stronger to weaker, RO-4 > RO-5 > RO-2 > RO-3 > RO-1.

Keywords: Dose gradient; Reverse osmosis; Anti-scalant; Evaluation method introduction

1. Introduction

During the operation of a reverse osmosis (RO) system, initially feed water enters the RO device and a fraction of the water molecules move through the RO membrane and become permeate (pure) water, but the solutes are unable to permeate the membrane. Thus, causing the ratio of solutes in feed water to increase, which turns the feed water into a concentrate. The RO process can be seen as a concentrated process, where the feed water flows along the RO membrane surface and the ratio of water continuously decreases and the ratio of solutes continuously increases. The concentration of solute i in the concentrate can be calculated by Eq. (1) [1]:

$$C_{bi} = C_{fi}\frac{1 - yp_i}{1 - y} \tag{1}$$

where C_{bi} and C_{fi} are the concentrations of solute i in concentrate and feed water, respectively; y is the recovery rate of water, defined as the ratio of permeate to feed water; and p_i is the percentage of solute i which has permeated the RO membrane, which value can be obtained from the instruction manual of the membrane.

The cycles of concentration of solute i in concentrate (K_i) are calculated by Eq. (2):

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$$K_i = \frac{C_{bi}}{C_{fi}} = \frac{1 - yp_i}{1 - y} \tag{2}$$

Generally, the degree of saturation of the concentrate can be represented by the cycles of concentration of non-fouling substances (e.g. Cl) such as K_{Cl}.

Obviously, the higher the water recovery rate is, the higher the cycles of concentration of solute i, which means that there is a strong tendency for sparingly soluble salts (e.g. $CaCO_3$) to form scales. To prevent a scale layer precipitate on the membrane after concentrated by sparingly soluble salts, it is necessary to add scale inhibitors into the feed water.

The desalination rate is an important performance indicator for RO devices. The desalination rate, designated as R_{ej}, is defined as the percentage of decrease of salt content from feed water to permeate through the RO process, calculated by Eq. (3):

$$R_{ej} = \frac{C_f - C_p}{C_f} \times 100 \tag{3}$$

where C_f is the feed water salt content, mg/L and C_p is the permeate salt content, mg/L. In water processing, C_f is often represented by the total dissolved solids (TDS) or the conductivity of the feed water, and C_p by TDS or conductivity of permeate. In this investigation, the R_{ej} is calculated using conductivities.

There are roughly over 100 RO membrane scale inhibiting products available. Users of RO devices need to select high-performance products suited to their water conditions. Such selections should be made on the basis of comparative testing, where the scaling prevention capacities of different inhibitors are tested under the same water conditions, and a suitable inhibitor is chosen according to its performance. Therefore, it is of practical value to investigate the evaluating methods of RO membrane scale inhibitors. Such methods also play an important role in the development of inhibitors and troubleshooting of RO systems.

At present, the test methods for evaluating RO membrane scale inhibitors can be divided into two categories: static methods and dynamic methods. Static methods are commonly used for circulating water coolant scale inhibitors. There are many methods used for rapid evaluation in laboratories, including the heating method [2], the limiting of carbonate hardness method [3], the turbidity method [4], the critical pH method [5], the pH shift method [6], the conductivity method [7], and the constant composition method [8]. Dynamic methods select inhibitors using dynamic simulations in RO devices, including the feed water one-pass method, the full-amount circulation method, etc. [9].

Static methods have the advantage of rapidness and low water usage. For each experiment, generally, the time required is not more than 12 h and water usage is less than 2 L. However, these tests do not take into account the interactions between inhibitors and RO membranes, as well as the effects of hydrodynamics on inhibitor performance. So, there is a relatively large difference between conditions of the experiment in a laboratory and the real conditions in a production environment.

Dynamic methods are free from the disadvantages of static methods, but require longer testing times and higher water usage. In particular, the one-pass method directly utilizes the user's water source as feed water to simulate the actual operating conditions, and passes the feed water through the RO system in one go, while rejecting the concentrate and recycling the permeate generated from the test, which is a complete simulation of actual operations, but this generally requires three months and over 3,000 t water. The full-amount circulation method feeds all the permeate water and concentrate from RO system back into the feed water to pass through RO system again, which generally requires not more than 10 h and 1 t. However, there are two disadvantages to the full-amount circulation method:

(1) The scaling tendency is lowered, if sparingly soluble salts are precipitated during the RO process. Each time the feed water passes through the RO system, the concentration of sparingly soluble salts in the feed water will be lowered, i.e. the solubility of insoluble salts (e.g. $[Ca^{2+}][CO_3^{2-}]$) will be lowered. This is different from the actual operations, where the solubility of sparingly soluble salts in feed water is constant, i.e. the scaling tendency is unchanged.

(2) Multiple tests are required. For each test, only the scale inhibitor performance data specific to one cycle of concentration can be obtained. However, in actual operations, it is often necessary to know the allowed cycles of concentration range for one particular scale inhibitor, or the maximum recovery rate for the RO system. Therefore, a series of tests are required in order to obtain the performance of scale inhibitors under different cycles of concentration or recovery rates.

Some simple laboratory techniques have been developed for characterizing the scaling propensity of RO feed waters and for assessing anti-scalants inhibitory effectiveness [10–12]. The basic concept is the recycling of the concentrate and permeate to a feed vessel and periodic withdrawal of permeate to cause increased concentration of all species; the laboratory technique for characterizing scale suppression effectiveness, which based on full recycling of concentrate and permeate to feed vessel, is of no significant difference between scale suppression results measured in full recycle and in once-through flow systems. We use dose gradient method in which recycling of concentrate and permeate to feed vessel and solutes are added into the feed water to increase the cycles of concentration [13] to screen RO membrane scale inhibitors.

2. Principles

Fig. 1 shows the flow chart and device used in the test. The system consists of a feed vessel, a security filter, a feed water pump, thermostatic apparatus, an RO tubular membrane, online meters, etc. In the diagram, K1 and K2 are the intake and output valves for feed water; K3 is the circulation valve for concentrate; K4 is the circulation valve for permeate; and P, F, T, D, and pH represent the pressure meter, the flow meter, the thermometer, the conductivity meter and the pH meter, respectively.

The dose gradient method is an improvement on the basis of the full-amount circulation method. As the main feature of this method, instead of withdrawing the concentrate or permeate, solutes are added into the feed water to increase C_{bi} resulting in increasing the cycles of concentration, in order to obtain performance data of inhibitors under different cycles of concentration or recovery rates.

In this method, the experiment tests water with the same composition as the feed water. For every fixed amount of time (called "dose gradient period"), fixed amount of solutes are added to the feed water. Then, the concentrate and permeate are fully circulated. When the circulation reaches a point, where the non-fouling substances (e.g. Cl^-) in the concentrate have stabilized, measurements are taken of the concentrate's composition parameters such as Ca^{2+}, HCO_3^-, conductivity, and pH, as well as operation parameters such as flow and pressure. Each time solutes are added, the solute content in feed water increases (equivalent to feed water being condensed). With multiple doses, the cycles of concentration in feed water rises step by step, allowing multiple sets of data on (K_j, K_{Cl}), (R_{ej}, K_{Cl}), and (pH, K_{Cl}) to be obtained. The K_j–K_{Cl}, R_{ej}–K_{Cl}, and pH–K_{Cl} curves can be plotted based on the data, and the scaling propensity on the RO membrane and performance of scale inhibitors can be evaluated,

(1) The basis for evaluating inhibitor performance with cycles of concentration is as follows. As K_{Cl} increases, prior to any precipitation out of solution, the cycles of concentration K_j of the scaling substances j (e.g. Ca^{2+}, $j \neq Cl^-$, the same below) are equal to K_{Cl}; when K_{Cl} reaches a certain level, j participates in precipitation reactions, therefore, $K_j < K_{Cl}$. As shown in Fig. 2, when K_{Cl} reaches Point a, $K_j < K_{Cl}$, i.e. $0 < \Delta K = K_{Cl} - K_j$, indicating j starting to participate in precipitation reactions. The stronger the inhibitor's capacity is, the more effective it is at preventing the scaling of j, and ΔK is smaller. Therefore, by comparing the ΔK values corresponding to the different inhibitors, their comparative strengths can be evaluated. So we can know the scaling prevention capacities of the five tested inhibitors order from Figs. 3 and 4.

(2) The basis for evaluating inhibitor performance with pH is: during the feed water circulation and condensation process, the direction of change in the pH of concentrate is dictated by two opposing trends: on one hand, the content of alkaline substances (e.g. HCO_3^-) is increased,

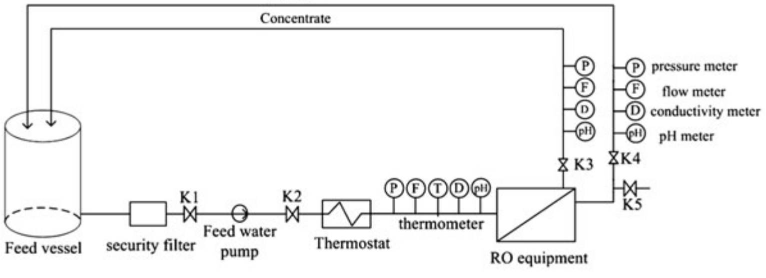

Fig. 1. Experimental system.

Table 1
Five types of RO membrane scale inhibitors

Serial number	RO-1	RO-2	RO-3	RO-4	RO-5
Trademark	Tion ASD 200/SC	SJ-881	Flocon 260	PTP-0100	WHRO
Manufacturer	Professional Water Technologies Corporation	Dolong Water Chemistry Corporation	Great Lakes Chemical Corporation	KingLee Technologies Corporation	Wuhan University

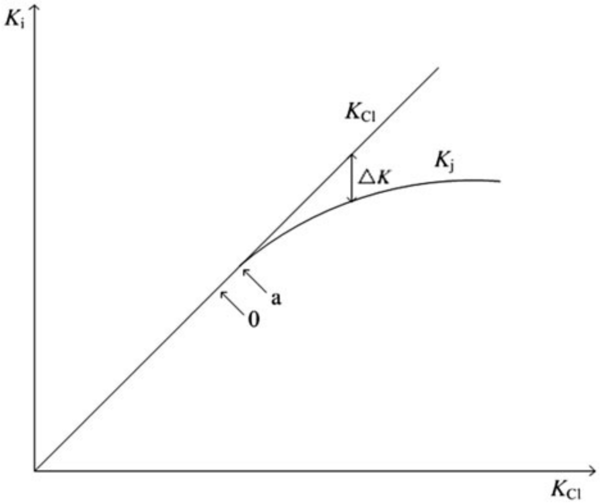

Fig. 2. Variation of K_j from K_{Cl}.

while the concentration of CO_2 decreases, causing the pH of the concentrate to increase with K_{Cl}; on the other hand, when K_{Cl} rises past a certain value, the precipitation reaction $Ca^{2+} + HCO_3^- \rightarrow CaCO_3\downarrow + H^+$ occurs, releasing acidic CO_2 molecules, and the greater K_{Cl} is, the more H^+ will be released, therefore, the scaling from $CaCO_3$ decreases the pH of the concentrate. The two factors add up to the plots of $pH - K_{Cl}$ as shown in Figs. 5 and 6. Obviously, the faster the pH decreases with K_{Cl}, more precipitation reactions occurr and worse the inhibitor performance.

(3) The basis for evaluating inhibitor performance with R_{ej} is: during the circulation process, as the salt content in feed water rises, the difference in concentrations between the concentrate and permeate water on the two sides of RO membrane increases, resulting in an increase of the amount of solutes passing through the RO membrane, therefore, R_{ej} decreases with K_{Cl}. The slower R_{ej} decreases with K_{Cl}, the better the inhibitor performance.

To summarize the above, fluctuations in K_j, R_{ej} and pH from K_{Cl} can be plotted, in order to compare and evaluate the different scale inhibitors.

3. Materials and methods

3.1. Materials

(1) RO membrane scale inhibitors. Five types of RO membrane scale inhibitors were chosen as candidates (denoted as RO-i, $i = 1, 2, \ldots 5$), see Table 1.

(2) Feed water. The chemical composition of feed water in the test was based on the average chemical composition of raw water supply from thermal power plants in Shanxi Province, China (Table 2). The feed water was prepared by mixing distilled water with chemicals ($CaCl_2$, $MgSO_4$, $NaHCO_3$, etc.), in order to simulate the main solutes shown in Table 2 (Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-).

3.2. Dose gradient

The amount of dose gradient is calculated by Eq. (4):

$$\Delta G_{ni} = M_i V_w \Delta K_n C_{Si} \tag{4}$$

where ΔG_{ni} is the dosage at the nth gradient for i (i represents $CaCl_2$, $MgSO_4$, $NaHCO_3$, etc.); M_i is the molar mass of i, which is 110.99, 120.36, 84.01, and 58.44 g/mol, for $CaCl_2$, $MgSO_4$, $NaHCO_3$, and NaCl, respectively; V_w is the water amount for the test device in Fig. 1, measured to be 0.6515 m^3; and ΔK_n is the cycles of concentration difference of the nth gradient. Smaller ΔK_n values allow for a more accurate curve in Fig. 2, while increasing the number of does and prolonging the test time. Generally, the ΔK_n is taken to be 0.2–1.5, using a greater value when the cycles of concentration are relatively small, and

Table 2
The chemical composition of feed water

Parameter (mmol L^{-1})	Feed water	Parameter (mmol L^{-1})	Feed water	Parameter	Feed water
Total hardness	5.43	HCO_3^-	3.95	Conductivity/μS cm^{-1}	979
$1/2Ca^{2+}$	3.28	$1/2SO_4^{2-}$	2.35	pH	7.92
$1/2Mg^{2+}$	2.15	Cl^-	1.928		

smaller when the multiplier is greater, especially when nearing Point a. C_{Si} is the concentration of the ion corresponding to i (e.g. Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-) from Table 2, mmol/L.

3.3. Parameters of operation

The main parameters of operation in the test are as follows:

- Concentrate flow: 1,000 L/h;
- Permeate water flow: 150 L/h;
- Water temperature: 25 ± 1℃;
- Gradient dose period: 50 min;
- Inhibitor dosage: 2 and 4 mg/L.

3.4. Test method

The main steps of the test were as follows:

(1) Preparation of feed water: To save time during the test, the initial feed water can be at any point (such as Point O) in Fig. 2 where the two curves overlap (i.e. prior to Point a). Based on calculation results of feed water in Table 1 using RO software from Dow Chemical, as well as preliminary tests, the cycles of concentration at Point O, K_{Cl0}, can be taken to be 2.5. The feed water corresponding to Point O is called feed water K_{Cl0}.
(2) A predetermined scale inhibitor dosage added into the feed vessel.
(3) Circulation: After the feed water K_{Cl0} is prepared, the feed water pump is started, running for 50 min at full-amount circulation mode (i.e. both permeate and concentrate recycled to feed vessel).
(4) The parameters of concentrate and permeate are recorded, such as conductivity, temperature, pH and flow.
(5) A sample of concentrate are taken to measure its conductivity, alkalinity, hardness, $[Ca^{2+}]$, and $[Cl^-]$. Calculations are made according to Eq. (2) for cycles of concentration K_i (i standing for Ca^{2+}, HCO_3^- and Cl^-).
(6) A curve is plotted with K_{Cl} as the horizontal axis and K_j as the vertical axis.
(7) If $K_j \approx K_{Cl}$ ($j \neq Cl^-$), solutes of the amount ΔG_{ni} is added to the feed vessel, and another full-amount circulation process is started for 50 min.
(8) Repeat steps (3)–(6); if $K_j << K_{Cl}$ ($j \neq Cl^-$), the experiment ends.

4. Results

The following parameters can change due to scaling in the RO device: (1) increase in pressure differences between intake and output of feed water, and between both sides of the membrane; (2) decrease in R_{ej}, as well as concentrate's pH, Ca^{2+} concentration and hardness. Theoretically, any of these parameters can be used for determining whether scaling has occurred. However, the differences in pressures are insensitive to such changes, and also dependent on cycles of concentrations. Calculating them requires standardization processes. For these reasons, this investigation has not chosen them as indicators. Among the solutes related to hardness, Mg^{2+} generally does not partake in scaling, making it also less sensitive to Ca^{2+}, so it is also not chosen. In the end, R_{ej} and concentrate's pH and Ca^{2+} are chosen as indicators.

The relationships of the concentrate's K_j, pH and R_{ej} to K_{Cl} are shown in Figs. 3–8, where K_{Cl}, blankness, and "RO-i" represents curves of K_{Cl}, K_{Ca} of feed water in the absence of inhibitors, and feed water in the presence of RO-i to K_{Cl}, respectively. The numbers in the parentheses are the dosage of RO-i added.

In Figs. 3 and 4, the straight line K_{Cl} has a slope of 1. It serves as the basis for determining the occurrence of scaling. The closer an inhibitor's curve is to straight line K_{Cl}, the smaller the ΔK is and better the inhibitor performance is. As can be seen in Figs. 3 and 4, the curves for RO-i (i = 1, 2, … 5) are convex curves. Taking the RO-4 curve in Fig. 3 as example, as K_{Cl} increased, the initial RO-4 was close to K_{Cl}, then as Ca^{2+} participated in precipitation reactions, the RO-4 curve became lower from K_{Cl}, as ΔK_{Ca} kept increasing. When

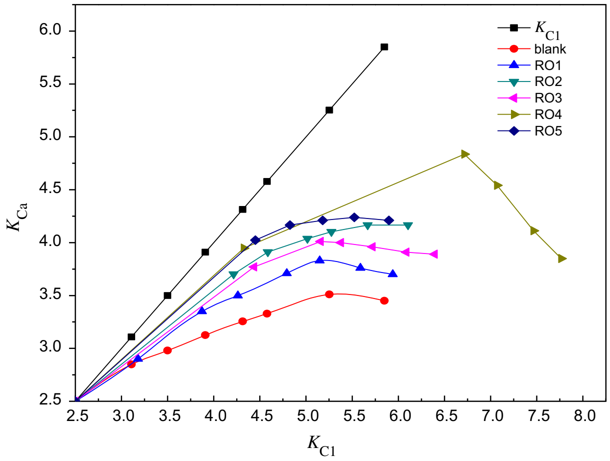

Fig. 3. The relationship of K_{Ca} to K_{Cl}.
Note: Dosage:2 mg/L.

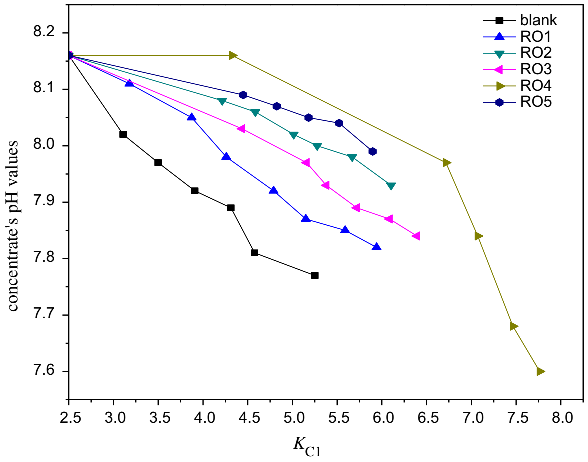

Fig. 5. The relationship of brine's pH values to K_{Cl}.
Note: Dosage:2 mg/L.

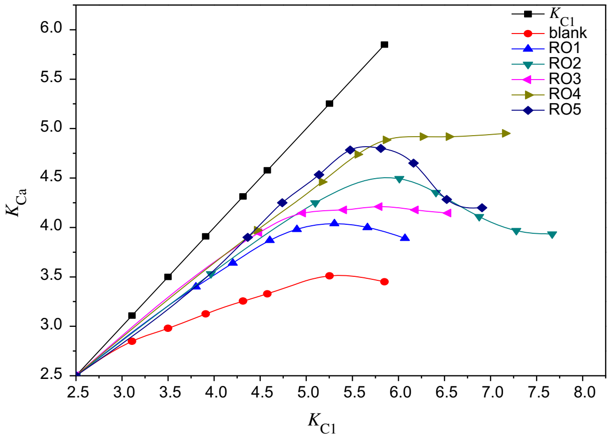

Fig. 4. The relationship of K_{Ca} to K_{Cl}.
Note: Dosage:4 mg/L.

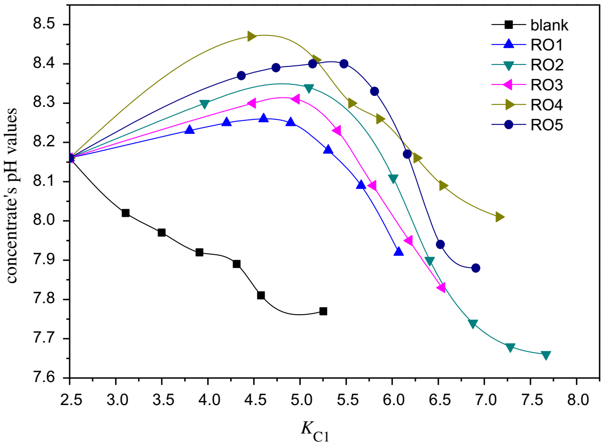

Fig. 6. The relationship of brine's pH values to K_{Cl}.
Note: Dosage:4 mg/L.

K_{Cl} reached 6.5, as large amount of Ca^{2+} was precipitated, the RO-4 curve fell sharply. Thus, the performance of inhibitors can be compared based on the closeness to the straight line K_{Cl} of their curves. Thus, it is evident known from Figs. 3 and 4 that the scale suppression effectiveness of the five tested scale inhibitors are, from stronger to weaker, RO-4 > RO-5 > RO-2 > RO-3 > RO-1.

In Figs. 5 and 6, the pH varies with the cycles of concentration for two reasons: the pH increase caused by the process of condensation and pH decrease from $CaCO_3$ scaling. Using Fig. 5 as an example, initially the condensation effect was more pronounced causing the RO-4 curve to rise. Afterward, the scaling effect was more pronounced, causing it to fall. The curves corresponding to the other four inhibitors were falling throughout, indicating for them the scaling effect was always more pronounced, and their performances were not as good as RO-4. However, when the dosage of inhibitors was increased from 2 to 4 mg/L, the pH for all five inhibitors rose at the beginning, only falling down after the K_{Cl} was approximately 4.5–5.5, indicating that an increase in inhibitors can enhance their performance for preventing $CaCO_3$ scaling. Thus, it is evident known from Figs. 5 and 6 that the scale suppression effectiveness of the five tested scale inhibitors are, from stronger to weaker, RO-4 > RO-5 > RO-2 > RO-3 > RO-1.

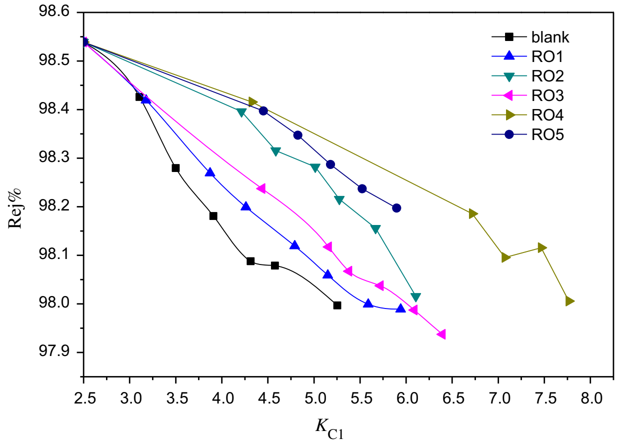

Fig. 7. The relationship of R_{ej} to K_{Cl}.
Note: Dosage:2 mg/L.

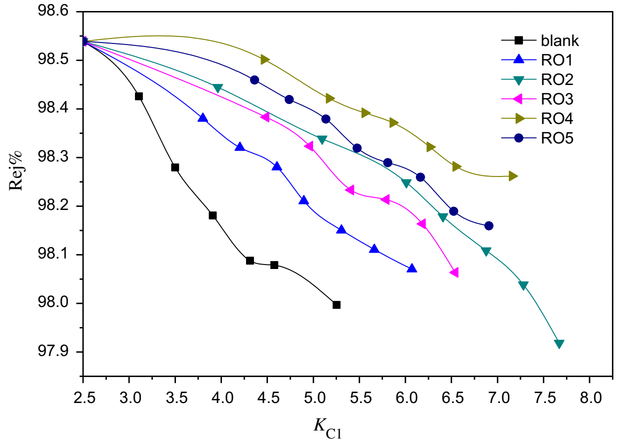

Fig. 8. The relationship of R_{ej} to K_{Cl}.
Note: Dosage:4 mg/L.

For any RO membranes, the R_{ej} will decrease when salinity (or conductivity) of feed water increases, accompanied by the scale layer precipitate. This is reflected in Figs. 7 and 8, however, the $R_{ej} - K_{Cl}$ corresponding to different inhibitors are different, due to differences in their capacities. The slower R_{ej} decreases with K_{Cl}, the better the inhibitor performance. Thus, it is evident known from Figs. 5 and 6 that the scale suppression effectiveness of the five tested scale inhibitors are, from stronger to weaker, RO-4 > RO-5 > RO-2 > RO-3 > RO-1.

Table 3 shows the relative standard deviations (RSD) of $\Delta K_{Ca} - K_{Cl}$, $R_{ej} - K_{Cl}$, and $\text{pH}_j - K_{Cl}$ curves. The greater the RSD is, the more sensitive an indicator (e.g. ΔK_{Ca}) is to scaling.

Table 3
The evaluation index of RSD%

Scale inhibitors	Dosage/mg L^{-1}	pH	R_{ej}	ΔK
Blank	0	1.66	0.20	79.16
RO-1	2	1.58	0.20	76.57
RO-2	2	0.93	0.17	66.63
RO-3	2	1.39	0.21	62.97
RO-4	2	3.01	0.21	78.45
RO-5	2	0.70	0.13	72.39
RO-1	4	1.42	0.16	73.46
RO-2	4	3.47	0.21	74.66
RO-3	4	2.22	0.16	68.71
RO-4	4	1.91	0.10	67.54
RO-5	4	2.46	0.13	83.18
Average		1.89	0.17	73.07
Sensitivity order	$\Delta K \gg \text{pH} > R_{ej}$			

Note: Remarks: $\Delta K = K_{Cl} - K_{Ca}$.

5. Conclusion

The dose gradient method can be used for evaluating RO membrane scale inhibitors; the difference in performances between scale inhibitors can be found through this method, and the scaling-scale suppression effectiveness of the five tested scale inhibitors are, from stronger to weaker, D > E > B > C > A. ΔK_{Ca}, pH, and R_{ej} can be used as indicators, with ΔK_{Ca} being the most suitable indicator. If ΔK_{Ca} is chosen as the scaling indicator, the total test time for using the dose gradient method on five anti-scalants, at one dosage amounts to approximately 29 h, using approximately 3.3t of water. Therefore, the dose gradient method is a simple and reliable method for assessing the relative inhibitory effectiveness of various RO scale inhibitors.

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