Desalination 344 (2014) 357–361

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

The use of the drainage gradient method for evaluating reverse osmosis membrane anti-scalants

Jiaqiang Wei [a], Juan Liu [b], Maodong Li [b], Lin Yang [b], Baiqing Zhou [a,*]

[a] School of Power and Mechanical Engineering, Wuhan University, People's Republic of China, No.8 South East lake Road, Wuchang District,Wuhan City, Hubei Province, 430072, People's Republic of China

[b] Guangzhou Special Pressure Equipment Inspection and Research Institute, No.97 Baiyun Road, Yuexiu District, Guangzhou City, Guangdong Province, 510199, People's Republic of China

HIGHLIGHTS

- The drainage gradient method is simple and reliable for screening anti-scalants.
- Gradient was concentrated by a fixed amount of permeate withdrawn at regular intervals
- pH, ΔK_{Ca} and LSI can be used as indicators, and ΔK_{Ca} is the most suitable indicator.

ARTICLE INFO

Article history:
Received 1 December 2013
Received in revised form 15 March 2014
Accepted 17 March 2014
Available online 3 May 2014

Keywords:
Drainage gradient
Reverse osmosis
Anti-scalant
Evaluation method introduction

ABSTRACT

This paper describes the use of the drainage gradient method for assessing the relative inhibitory effectiveness of various reverse osmosis (RO) anti-scalants. Five different anti-scalants were selected for the examination of the drainage gradient method's feasibility for evaluating their relative inhibitory effectiveness. The results show that pH, ΔK_{Ca} (increase in cycles of concentration) and Langelier's saturation index (LSI) can be used as indicators and that ΔK_{Ca} is the most suitable indicator. The sensitivities of the three indicators from greatest to least are: ΔK_{Ca} > LSI ≫ pH, with relative standard deviations (RSD) which are 38.39%, 14.22%, and 1.45%, respectively. The order of the scale suppression effectiveness of the five tested anti-scalants, based on the three judgment indicators, is D > E > B > C > A.

1. Introduction

During the operation of a reverse osmosis (RO) system, the feed water enters the RO device. As purified water permeates the RO membrane, the dissolved species are concentrated. Generally, the degree of saturation of the concentrate can be represented by the cycles of concentration of non-fouling substances (e.g., Cl) as K_{Cl}.

Obviously, the higher the water recovery rate, the greater the economic benefit. However, when the cycles of concentration of solute *i* are high, 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 the concentration of sparingly soluble salts, it is necessary to add anti-scalants to the feed water.

There are over 100 RO anti-scalants available. RO device users should select high-performance anti-scalants that are suitable for their water conditions. These selections should be made on the basis of comparative testing, where the scale suppression effectiveness of different anti-scalants is tested under the same water conditions, and suitable anti-scalants are selected according to their performance. Therefore, it is of practical value to investigate the methods used to evaluate anti-scalants. Additionally, these methods play an important role in the development of anti-scalants and in troubleshooting RO systems.

At present, the methods used for evaluating RO membrane anti-scalants can be divided into two categories: static methods and dynamic methods. Static methods are commonly used to test circulating water coolant anti-scalants. There are many static methods used for rapid evaluation in laboratories, including the heating method [1], the limiting of carbonate hardness method [2], the turbidity method [3], the critical pH method [4], the pH shift method [5], the conductivity method [6], and the constant composition method [7]. Dynamic methods, including the feed water one-pass method and the full amount circulation method, are used to select anti-scalants using dynamic simulations in RO devices [8].

Static methods have several advantages, including speed and low water usage. For each experiment, the time required is approximately 12 h, and water usage is less than 2 L. However, these tests do not consider the interactions between the inhibitors and the RO membranes

* Corresponding author. Tel.: +86 27 68772264.
E-mail address: zhoubaiqing5@163.com (B. Zhou).

http://dx.doi.org/10.1016/j.desal.2014.03.023
0011-9164/

or the effects of water streams on inhibitor performance. Hence, there is a relatively large difference between the experimental conditions in a laboratory and the real conditions in a production environment.

Dynamic methods are free from the disadvantages of static methods but require extended testing times and greater 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 only once, while rejecting the concentrate and recycling the permeate water generated from the test. This process fully recapitulates the actual operation but generally requires 3 months and over 3000 t of water. The full amount circulation method feeds all the permeate and concentrate from the RO system back to the feed vessel and recycles it through the RO system, which generally requires approximately 10 h and 1 t of water. However, there are two disadvantages of the full amount circulation method:

(1) The scaling propensity 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 the sparingly soluble salts (e.g., [Ca^{2+}] and [CO_3^{2-}]) will be lowered). In actual operations, however, the solubility of sparingly soluble salts in feed water is constant (i.e., the scaling propensity does not change).
(2) Multiple tests are required when using this method because only the anti-scalant performance data that is specific to one cycle of concentration can be obtained in each test. However, in actual operations, it is often necessary to determine a range of allowed cycles of concentration for one specific anti-scalant or the maximum recovery rate for the RO system. Therefore, a series of tests is required to obtain the performance of the anti-scalants under different cycles of concentration or recovery rates.

Several simple laboratory techniques have been developed for characterizing the scaling propensity of the RO feed water and for assessing the anti-scalants' inhibitory effectiveness [9-11]. The basic concept is the recycling of the concentrate and permeate to a feed vessel with the periodic withdrawal of permeate, which increases the concentrations of all species. The drainage gradient method, which we used to screen anti-scalants, is similar to these techniques.

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, a thermostatic apparatus, an RO equipment, and online meters. In the diagram, K1 and K2 are the intake and output valves for the feed water, K3 is the circulation valve for the concentrate, K4 is the circulation valve for the permeate, K5 is the withdrawal valve for the 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.

In the drainage gradient method, a fixed amount of permeate is withdrawn at regular intervals while the RO equipment is running to concentrate the feed water gradient. During the period in which the permeate is no longer being withdrawn, both the permeate and the concentrate are recycled to a feed vessel; i.e., the test water through the circulating loop ("feed vessel → security filter → feed water pump → thermostatic apparatus → RO equipment → feed vessel") returns to the feed vessel and is then mixed into the tested water before it is concentrated. This process actually prolongs the contact time of the concentrate and membrane. When the circulation reaches a point where the non-fouling substances (e.g., Cl^-) in the concentrate have stabilized, the measurements of the concentrate's composition parameters, such as Ca^{2+}, HCO_3^-, conductivity, and pH are recorded, along with operation parameters such as flow and pressure. Each time the permeate is withdrawn, the number of cycles of concentration in the feed water increases by one. Therefore, for multiple withdrawals of the permeate, the cycles of concentration in the feed water increase in step-wise fashion and allow multiple sets of data for (K_j, K_{Cl}), (pH, K_{Cl}) and (LSI, K_{Cl}) to be obtained. The K_j–K_{Cl}, pH–K_{Cl} and LSI–K_{Cl} curves can be plotted based on the data, and the scaling propensity on the RO membrane and the performance of anti-scalants can be evaluated.

(1) The basis for evaluating the anti-scalant performance with the cycles of concentration is as follows: as K_{Cl} increases prior to any precipitation out of the solution, the cycles of concentration K_j of the scale-forming ions 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. Thus, $K_j < K_{Cl}$. As seen in Fig. 2, when K_{Cl} reaches Point a, $K_j < K_{Cl}$ (i.e., $0 < \Delta K = K_{Cl} - K_j$) and indicates that j is starting to participate in precipitation reactions. The stronger the inhibitor's capacity is, the more effective it is at inhibiting the scaling of j, and ΔK is smaller. Therefore, by comparing the ΔK values that correspond to different anti-scalants, the relative inhibitory effectiveness of the anti-scalants can be evaluated. Therefore, we can determine the relative scale suppression effectiveness of the five tested anti-scalants based on Figs. 3 and 4.
(2) The basis for evaluating the anti-scalant performance using the pH is as follows: during the feed water circulation and concentrated process, the direction of change in the pH of the concentrate is determined by two opposing trends. In one case, as the content of the alkaline substances (e.g., HCO_3^-) increases, the concentration of CO_2 decreases because the CO_2 molecules permeate through the RO membrane, enter the permeate, and cause the pH of the concentrate to increase with K_{Cl}. However, when K_{Cl} is greater than a certain value, the scaling precipitation

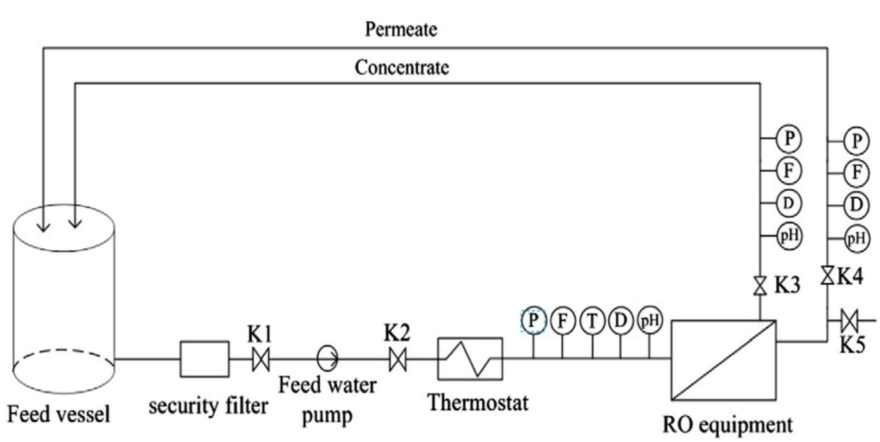

Fig. 1. Experimental system.