Desalination 437 (2018) 100–107

Contents lists available at ScienceDirect

Desalination

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

Study on inhibitors' performance under the condition of high concentration ratio in MED system

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ARTICLE INFO

Keywords:
Scale
Inhibitor
Performance
High concentration ratio
MED

ABSTRACT

Improving the concentration ratio to reduce the emission of concentrated brine is required in some desalination plants. However, scaling problem will be aggravated with higher concentration. In this study, scaling tendency was analyzed according to two indexes including the Langelier Saturation Index and the Ryznar Stability Index. Four kinds of inhibitors were analyzed. Their inhibition performance under the condition of high concentration ratio in MED system was studied by both static jar tests and experiments on a small-scale falling film evaporation apparatus. Results indicate that severe scaling problems would occur when high concentration ratio encounters high temperature. Under the experimental condition, for which the temperature was 70 °C and the concentration ratio was 2.5, the alkaline scales were calcium carbonate. No magnesium hydroxide was formed. Calcium sulfate began to appear and increase when the concentration ratio exceeded 2. All inhibitors showed controlling effect on scale formation. Inhibitor A with its main constituents of HPAA and polymaleic acid showed the best inhibition performance. Better inhibition performance was achieved with higher inhibitor dosage, but no obvious improvement was observed when inhibitor dosage exceeded 5.5 ppm. The present study is helpful to the MED system under the condition of high concentration ratio.

1. Introduction

With the development of society and increasing demand for fresh water, water shortage has become a prominent issue in many parts of the world. As an effective technique for fresh water production, seawater desalination has been widely used in solving this problem due to its improvements in cost effectiveness and breakthroughs in technical limitations in the last decades [1].

Concentrated brine as well as fresh water is produced at the same time in desalination process. The properties of concentrated brine such as temperature and salinity are quite different from that of natural seawater. Environmental damage would occur if large amounts of concentrated brine were discharged back to the ocean directly. Problems are more serious in enclosed sea areas like Bohai Bay in China.

To reduce the negative environmental impact, transporting concentrated brine to nearby Salt Works for salt production provides a new way. However, sometimes there are conflicts in the process of concentrated brine being used as raw material for salt production with the development of desalination industry, for the Salt Works can't digest so much concentrated brine. If the concentration ratio is higher, there might be a better balance between the production and utilization of concentrated brine. What's more, utilization efficiency of raw seawater is higher and the specific cost for seawater intake might be lower. Brine with higher salinity is preferred in Salt Works as well. Therefore, sometimes it's required to increase the concentration ratio to reduce the emission of concentrated brine and increase its salinity at the same time.

Due to its advantages of low operating temperature, full utilization of low grade energy, low fouling tendency, high thermal efficiency and large elasticity of operation, multiple-effect-distillation (MED) has gained wide attentions [2]. In China, More and more MED desalination plants are being established around the Bohai Bay to balance the industrial water demand and supply. The concentration ratio in current MED desalination plants is around 1.5, providing wide improvement spaces.

However, scales would deposit in various parts along the path of concentrated brine especially when the concentration ratio is high. It should be noticed that inferior thermal efficiency, decreased production and quality, even unanticipated shutdown would occur if scales appear on the heat exchanger tubes in distillation plants [3]. Measures are taken to prevent and dispose these scaling problems. Current methods of disposing scaling problems in MED system mainly include: (a) acid treatment, (b) additive treatment, and (c) mechanical cleaning [4].

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https://doi.org/10.1016/j.desal.2018.02.019
Received 21 November 2017; Received in revised form 14 January 2018; Accepted 18 February 2018

Acid treatment is effective to alkaline scales but has a number of drawbacks such as corrosion problem, CO_2 gas removal, security issues and so on. Additive treatment is mainly inhibitor treatment, which has attracted much attentions in last decades due to its advantages of easy handling, low dosage rate, minimal corrosion problems and relatively lower cost [5]. Mechanical cleaning is usually used in combination with inhibitors to wipe heat exchanger tubes and prevent the adherence of scales [6].

Scales will appear on the surface of heat exchanger tubes in MED system due to variable parameters such as over-saturation, mixing conditions, impurities, the effect of additives and so on [7]. It's necessary to research the scaling phenomenon and inhibition technologies in MED systems.

There are already some studies related to the deposition of calcium carbonate, calcium sulfate, and magnesium hydroxide in different conditions [8–12]. Most researches are focused on the bulk solution with conventional concentration ratio. In the case of improving the concentration ratio, scaling tendency would be aggravated. What's more, studies related to the scales on the surface of heat exchanger tubes are rare. Therefore, study on inhibitors' performance under the condition of high concentration ratio in MED system is necessary.

In this paper, scaling tendency was analyzed according to two predicting indexes including the modified Langelier saturation index (LSI) and Ryznar stability index (RSI). Besides, four available inhibitors which have shown good performance in controlling scale formation at present desalination plants were analyzed. Their inhibition performance under the condition of high concentration ratio in MED system was studied by both static jar tests and experiments on a small-scale falling film evaporation apparatus. The inhibition efficiency, the scaling particle size in bulk solution and scaling crystal morphology on the surface of heat exchanger tube were adopted to evaluate inhibitors' performance. The effect of inhibitor dosage on inhibition performance was also studied according to the variation of the apparent calcium scaling amount with the increase of inhibitor dosage.

The present study is helpful to the MED system under the condition of high concentration ratio.

2. Experimental descriptions

2.1. Predicting indexes for scaling tendency

Two indexes are adopted to predict calcium carbonate depositing from solution in seawater desalination: the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI).

The LSI is defined as

$$LSI = pH - pH_s \tag{1}$$

The RSI is defined as

$$RSI = 2pH_s - pH \tag{2}$$

where pH is the actual pH value and pH_s is the pH value of calcium carbonate saturation solution with the formula of [13].

$$pH_s = pK_2 - pK_{sp} + pTA + p[Ca^{2+}] + 5pf_m \tag{3}$$

where K_2 is the second dissociation constant of carbonic acid, K_{sp} is the solubility product of calcium carbonate, TA is the total alkalinity, $[Ca^{2+}]$ is the concentration of calcium ions and f_m is the activity coefficient of monovalent ions. The p-function designates the negative logarithm of the variables.

There are three polymorphic forms of calcium carbonate crystals: vaterite, aragonite, and calcite. Calcite is the least soluble over a temperature range between 0 °C and 90 °C [14]. The solubility of calcite in seawater is related to the temperature (T) and salinity (X). It can be calculated by the following formula:

$$\begin{aligned} -\log K_{sp,cal} &= 171.945 + 0.077993 \times T - \frac{2903.293}{T} - 71.595 \times \log T \\ &\quad - \left(-0.77712 + 0.0028426 \times T + \frac{178.34}{T}\right) \times X^{0.5} \\ &\quad + 0.07711 \times X - 0.0041249 \times X^{1.5} \end{aligned} \tag{4}$$

with T in K, X in g/kg and $K_{sp,cal}$ in $mol^2/(kg^2$ seawater).

Millero [15] proposed a correlation for the second dissociation constant K_2 of carbonic acid in seawater as followed:

$$\begin{aligned} \ln K_2 &= -0.84226 - \frac{3741.1288}{T} - 1.437139 \times \ln T \\ &\quad + \left(-0.128417 - \frac{24.41239}{T}\right) \times X^{0.5} \\ &\quad + 0.1195308 \times X - 0.0091284 \times X^{1.5} \end{aligned} \tag{5}$$

where K_2 with the unit of mol/(kg seawater), T in K and X in g/kg.

The value of f_m is related with temperature and ion concentration as the following formula:

$$pf_m = A \times \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \times I\right) \tag{6}$$

where A is a constant relevant with T. I is ionic strength, which is relevant with salinity.

For the LSI, when the value is above zero, there is risk of scaling.

As for the RSI, an evaluation standard is given in Table 1.

Table 1
Evaluation standard of the Ryznar Stability Index [16].

RSI value	Indication
4.0–5.0	Severe scaling
5.0–6.0	Moderate to slight scaling
6.0–7.0	Stable water, slight tendency for dissolving of scale
7.0–7.5	Dissolving of scale, corrosive
7.5–9.0	Intense dissolving of scale and corrosion
> 9.0	Very intense dissolving of scale and corrosion

2.2. Characterization and evaluation

2.2.1. Characterizations of inhibitors

The inhibitors used in this study came from real desalination plants. All chosen inhibitors are commercial chemical additives whose exact compositions are unknown, which constrains us to know the exact inhibitor dosage and their potential functions according to physical and chemical characteristics.

In order to determine the elemental compositions, these inhibitors were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) technique and Elemental Analyzer.

In order to determine the main characteristics and constituents of these inhibitors, a variety of testing techniques were employed, including ion chromatography, infrared spectrometry, mass-spectrography, thermo-gravimetric analysis, etc.

2.2.2. Evaluation of inhibition performance

In order to evaluate inhibition performance of different inhibitors, various testing techniques or instruments were adopted.

The possible scales formed in desalination plants could be divided into alkaline scales and non-alkaline scales. Calcium carbonate and magnesium hydroxide are alkaline scales which usually exist in thermal desalination [17]. The non-alkaline scale is calcium sulfate which exists in three forms: anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot H_2O$) and dehydrate ($CaSO_4 \cdot 2H_2O$) [18].

Main scaling ions include Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$ and $CO_3{}^{2-}$. The only scale to which $SO_4{}^{2-}$ is related is calcium sulfate. Scales in which Ca^{2+} is involved include calcium carbonate and calcium sulfate. The concentration of scaling ions reflects the scaling tendency and inhibition