

Sulfate ion (SO_4^{2-}) release from old and new cation exchange resins used in condensate polishing systems for power plants

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ABSTRACT

In this study, a dynamic cycle test, a static immersion method and a pyrolysis experiment were combined to examine the characteristics of SO_4^{2-} released from several new and old cation exchange resins used in condensate polishing systems for power plants. The results show that the quantity and velocity of SO_4^{2-} released from new and old resins tend to balance in a short time during the dynamic cycle experiment. SO_4^{2-} is released by 1500H (monosphere super gel type cation exchange resins) and 001 \times 7 (gel type cation exchange resins) new and old cation exchange resins, the quantity of which increases according to immersion time. In the pyrolysis experiment, the quantity of SO_4^{2-} released from resins increases and the pH of the pyrolysis solution transforms from alkaline to acidic with an increase in temperature.

Key words | cation exchange resin, dynamic cycle test, pyrolysis experiment, SO_4^{2-} release, the static immersion method

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INTRODUCTION

Cation exchange resin is a type of material used in condensate polishing treatment systems of power stations. Because its performance is directly related to the quality of the water used in power plant systems, the economy and safety of the operation units are directly affected by this substance (Ritter & Bibler 1992; Gong *et al.* 2000; Liu *et al.* 2011). Several short chains of oligomers are usually formed during the synthetic process of cation exchange resin to become organic sulfonate after sulfonation (Yarnell 2009; Leybros *et al.* 2010). When the resin is put into operation, the organic sulfonate will gradually dissolve out and will be further decomposed to produce SO_4^{2-} after entering the thermodynamic system (Stahlbush *et al.* 1987; Daucik 1994, 1996). Besides organic sulfonate, the dissolved cation exchange resin still contains inorganic sulfate, which is produced mainly by desulfonation of the benzene ring (Fisher *et al.* 1992; Fisher & Donnelly-Kelleher 2001; Fisher 2002). Previous research has reported the widespread problem of SO_4^{2-} leakage in a condensate polishing hydrogen mixed bed. Daya Bay and Ling Ao nuclear power stations in China have had similar issues (Tian 2009) with elevated SO_4^{2-} in the liquid phase of steam generation; these values even exceeded safe standards after the condensate polishing mixed bed merged

into a second loop. In addition to the SO_4^{2-} released from the strong acidic cation exchange resin, another reason for the elevated values may be the leaking of decomposed resin into the water vapour system at high temperature. For power plants, SO_4^{2-} poses a significant danger to the thermal system equipment by damaging the oxide protective film that forms on the surface of a water-wall tube. In this study, a dynamic cycle test is combined with a static immersion method and pyrolysis experiment to examine the characteristics of SO_4^{2-} released from several types of new and old resins that are commonly used in condensate polishing systems.

METHODS

Pretreatment method

The new and old styrene type strongly acidic cation exchange resins used in this experiment included 001 \times 7 gel type cation exchange resins (Jiangyin Su Qing Water Treatment Co., China), 1500H monosphere super gel type cation exchange resins (Rohm and Hass Co., USA) and

SP112H monosphere macroporous type cation exchange resins (Bayer Co., Germany), which were supplied by the power plants and the manufacturers. The ion exchange resin pretreatment method (GB/T 5476-1996) specifies that before testing the performance of ion exchange resin, the resin should be pretreated in a process that includes water scrubbing in addition to acid and alkali treatment before being altered into a fixed type, which usually involves a strongly acidic cation exchange resin changing to the sodium (Na) type. The pretreatment method used in the present study included the following steps: 150 mL samples of resins were first rinsed with deionized water two or more times until the water ran clear. The resins were then placed in a glass column (shown in Figure 1) and washed with 500 mL of deionized water at a speed of 25 mL/min. After washing, the resins were treated with alkali in the same manner, which changed the cation exchange resins to Na-type cation exchange resins.

Determination of sulfate ion (SO_4^{2-})

The steps for SO_4^{2-} determination taken are as follows: first a series of standard solutions of SO_4^{2-} were prepared, and then the solutions were determined with a Thermo Scientific Dionex™ ICS-900 ion chromatograph. The ion chromatograms were contrasted to make qualitative analysis of SO_4^{2-} according to the retention time. After the SO_4^{2-} qualitative analysis, its quantitative content was calculated based on peak area, so as to draw the corresponding standard

curve; finally, the sample solutions were determined to calculate the content of SO_4^{2-} . However, there are two points to note: the dynamic cycle test fluid and static immersion solution of cation exchange resins both contained some organic matter, especially those long-term immersion resultant solutions, so to prevent these organisms entering the ion chromatograph and contaminating the analytical column or clog pipes, the sample solution should be filtered with a 0.45 μm disposable syringe before injection. When the quantity of SO_4^{2-} released from cation exchange resins was too large, the sample solution should be diluted before determination or measured with a small injection volume.

Dynamic cycle test

The dynamic cycle test proceeded by using the styrene-type ion exchange resin organic dissolution determination method (dynamic method) (DL/T 1077-2007). The experimental apparatus diagram is shown in Figure 1. The experimental temperature was set to 40 °C, and the flow rate was 15 L/h.

The quantity of SO_4^{2-} released from the resins was measured using a Thermo Scientific Dionex™ ICS-900 ion chromatograph, and the amount of SO_4^{2-} released from the wet cation resins was obtained by using Equations (1) and (2)

$$\Delta G_N = [(C_N - C_{N-1}) \times V_N] / V_2 \quad (1)$$

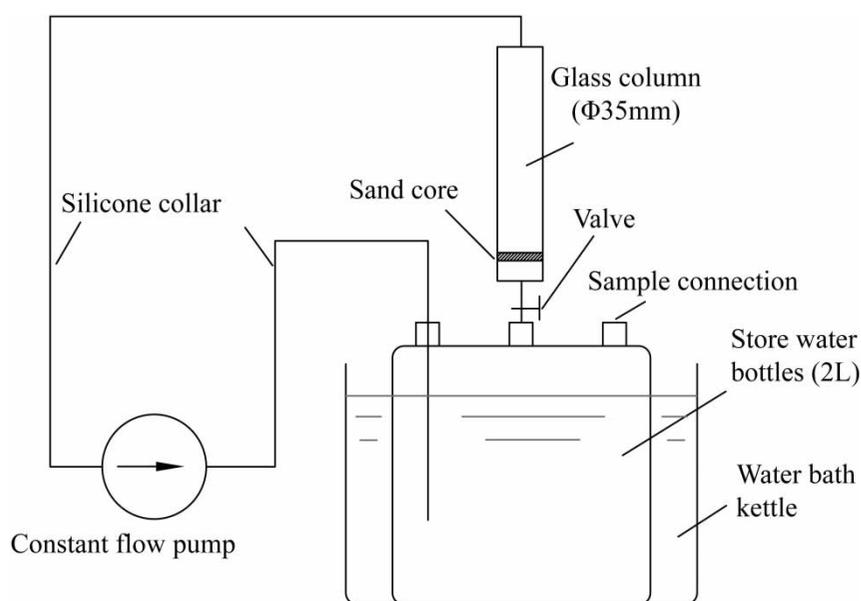


Figure 1 | Dynamic cycle test device for examining SO_4^{2-} released from resins.

$$G_N = \Delta G_1 + \Delta G_2 + \dots + \Delta G_N \quad (2)$$

where ΔG_N is the increased amount of SO_4^{2-} over the two-sampling interval time (mg SO_4^{2-} /L of wet resin); C_N and C_{N-1} are the SO_4^{2-} concentration of the n th and $(n-1)$ th sampling solution, respectively ($\mu\text{g/L}$); V_N is the cycle solution volume of the n th sampling ($\mu\text{g/L}$); G_N is the corresponding total amount of SO_4^{2-} released from resins of the n th time (mg SO_4^{2-} /L of wet cation resins).

The total average velocity of the SO_4^{2-} released from resins can be calculated by Equation (3)

$$v_t = G_t/t \quad (3)$$

where v_t is the corresponding total average velocity [mg/(L·d)] of the SO_4^{2-} released from resins, G_t is the total quantity of SO_4^{2-} released from resins at t time (mg SO_4^{2-} /L of wet cation resins) and t is the corresponding time (d).

Static immersion method

Fifty mL of pretreated resins were placed into two 500 mL brown reagent bottles into which 450 mL deionized water was added. The bottles were then soaked in a thermostatic water bath pot at $40 \pm 2^\circ\text{C}$; 10 mL samples of the resins were then placed in the bottles with 10 mL deionized water. The sample intervals increased with the extension of immersion time, usually every 7 days to 10 days in the initial stages of the experiment. The quantity of SO_4^{2-} released from resins was measured using the Thermo Scientific Dionex™ ICS-900 ion chromatograph and that for the unit volume of wet cation resins was obtained using Equation (4) after the specified immersion time

$$G_t = [C_N \times V_1 + (C_1 + C_2 + \dots + C_{N-1}) \times V_0]/V_2 \quad (4)$$

where G_t is the total quantity of SO_4^{2-} released from resins at time t (mg SO_4^{2-} /L of wet cation resins), C_N is the SO_4^{2-} concentration of leached liquor (n th sample; $\mu\text{g/L}$), $C_1 + C_2 + \dots + C_{N-1}$ is the concentration of SO_4^{2-} in the leached liquor from the first time to the $(n-1)$ th time ($\mu\text{g/L}$), V_1 is the total volume of the solution (450 mL), V_0 is the volume of each sample (10 mL), and V_2 is the wet cation resin volume of the static immersion test (50 mL).

The total average velocity of the SO_4^{2-} released from resins can be calculated by

$$v_t = G_t/t \quad (5)$$

where v_t is the corresponding total average velocity of the SO_4^{2-} released from resins [mg/(L·d)] and t is the corresponding immersion time (d).

Due to the long cycles of the static immersion test, each phase (i.e., every two-sample interval period) of the average velocity of SO_4^{2-} released from resins still needed to be calculated to gain a better understanding of the trend changes of the behaviour of SO_4^{2-} released from resins during the long-term immersion process. The specific calculation method is

$$v_N = (G_N - G_{N-1})/t_N \quad (6)$$

where v_N is the average velocity of SO_4^{2-} released from resins from the $(n-1)$ th to n th sample interval of time [mg/(L·d)], G_N is the corresponding total quantity of SO_4^{2-} released from resins in the n th time (mg SO_4^{2-} /L of wet cation resins), G_{N-1} is the corresponding total quantity of SO_4^{2-} released from resins in the $(n-1)$ th time (mg SO_4^{2-} /L of wet cation resins), and t_N is the sample interval time from $(n-1)$ th to n th (d).

Pyrolysis experiment

The pyrolysis experiment set the actual decomposition temperature of the resins as a starting point. Considering that the maximum temperature for Na cation exchange resins was 120°C , the autoclave temperatures for the pyrolysis experiment were set at 120, 160, 200, 240 and 280°C . Prior to the experiment, the resins and deionized water of a certain proportion were placed in the autoclave and were then heated to the setting temperature, which was maintained for 2 h. After being allowed to cool naturally to room temperature, the autoclave was opened to remove the resins and solutions, and its inner wall was rinsed with 20 mL 0.3% per weight NaOH dilute solution to remove the easily adsorbed SO_4^{2-} . The content of SO_4^{2-} was tested using the Thermo Scientific Dionex™ ICS-900 ion chromatograph, and the pH value of the solution was measured.

After the experiment, the concentration of SO_4^{2-} in the solution measured by the Thermo Scientific Dionex™ ICS-900 ion chromatograph was converted to determine the released quantity in the unit volume of wet resin. The specific calculation method was

$$G_T = [(C_T \times V_1 + C_l \times V_2)/V_T] \times 10^{-6} \quad (7)$$

where G_T is the corresponding quantity of SO_4^{2-} released by unit volume cation resins at $T^\circ\text{C}$ (g/L wet resins), C_T is the

corresponding SO_4^{2-} content in the decomposition solution ($\mu\text{g/L}$), V_1 is the volume of decomposition solution (mL), C_i is the content of SO_4^{2-} in the NaOH solution ($\mu\text{g/L}$), V_T is the volume of corresponding wet cation resins at $T^\circ\text{C}$ temperature (mL) and 10^{-6} is the unit conversion factor.

RESULTS AND DISCUSSION

New and old cation exchange resin dynamic cycle test

The curves for the dynamic cycle quantity and velocity of SO_4^{2-} released by 1500H and SP112H new and old resins, respectively, are displayed in Figures 2(a) and 2(b). As shown in the figure, SO_4^{2-} was released from both old and new cation exchange resins commonly used in condensate polishing treatment during the dynamic cycle experiment, and the quantity and velocity tended to balance in a short time during the experiment. However, the quantity of SO_4^{2-} generally displayed a growth tendency with the increase of time, and the velocity showed a tendency to decline. In addition, the quantity and velocity of released SO_4^{2-} were greater with the new resins than those with the old samples. One reason for this result is that the main released substances were less volatile organic iodo and SO_4^{2-} , which resulted in a trend that was difficult to balance. A second explanation is that the increased values may be associated with the synthesis progress of the cation exchange resin. In the sulfonation reaction process, several uncross-linked resin matrix short chain polymers were converted into organic sulfonate, which existed in the resin matrix and will release SO_4^{2-} after being put into operation.

New and old cation exchange resin static immersion experiment

The curves for quantity and velocity of SO_4^{2-} released by 001 \times 7 and 1500H new and old resins obtained through static immersion are displayed in Figures 3(a) and 3(b), respectively. The old resins were previously used in a fossil power plant. Figure 3(a) shows that the new and old resins both release SO_4^{2-} during the static immersion period and that the SO_4^{2-} quantity had an upward tendency with an increase in immersion time. These results are similar to those in numerous studies that have reported that the main released substance of cation exchange resin was SO_4^{2-} and that it was difficult to achieve a balance in the released trend. The quantities in the two types of new resins were greater than those of the old samples. In particular, the quantity in the 001 \times 7 gel type resins was largest, which may be related to the temperature of the cross-linking of the resin. Moreover, the quantity of the 001 \times 7 new and old resins was more than that of 1500H. Figure 3(b) shows that the velocity of SO_4^{2-} released by 001 \times 7 and 1500H new and old resins reduced gradually over the immersion time and eventually tended to balance.

New and old cation exchange resin pyrolysis experiment

Pyrolysis solution pH value change

Figure 4(a) shows the curves for the pyrolysis quantity of SO_4^{2-} released by 1500H and SP112H new and old resins at various temperatures. Figure 4(b) provides supplementary

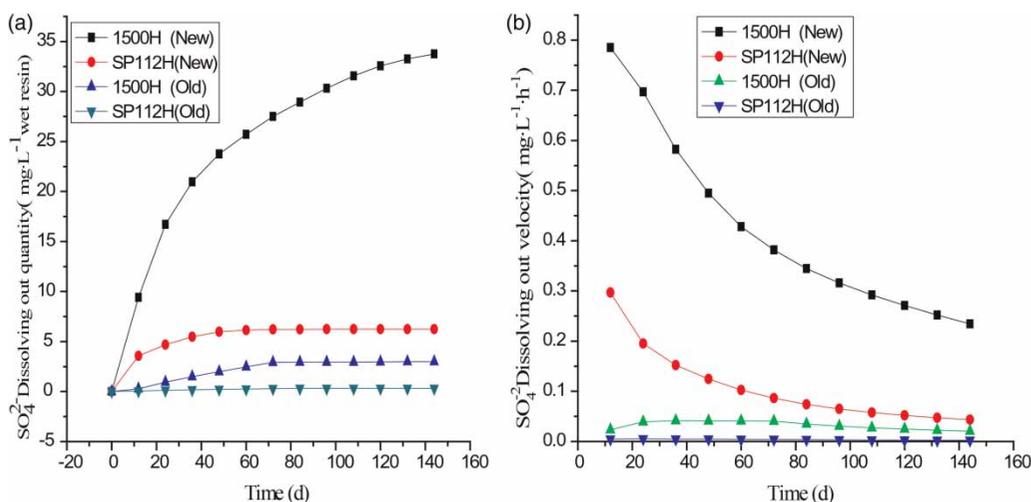


Figure 2 | Curves for dynamic cycle quantity (a) and velocity (b) of SO_4^{2-} released by 1500H and SP112H new and old resins.

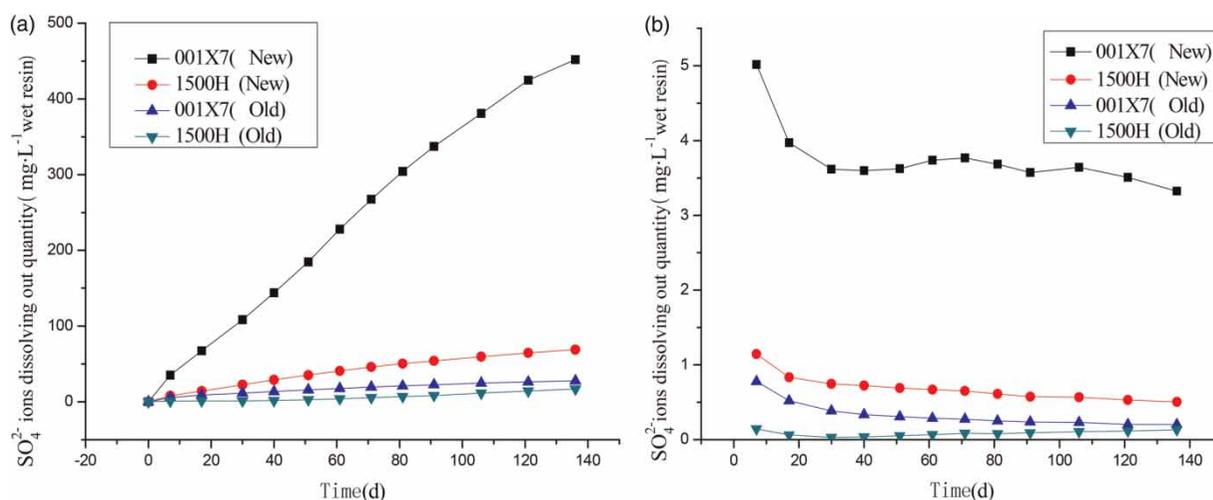


Figure 3 | The curves for static immersion quantity (a) and velocity (b) of SO_4^{2-} released by 001 × 7 and 1500H new and old resins.

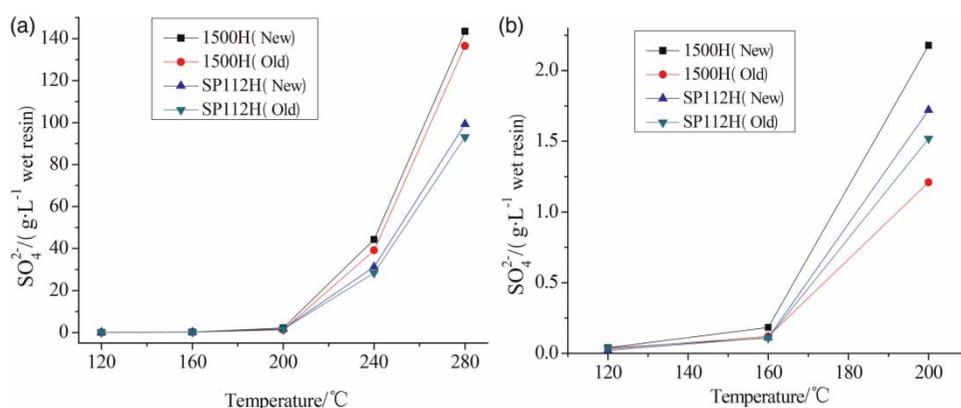


Figure 4 | The contrast curve for pyrolysis quantity of SO_4^{2-} released by 1500H and SP112H new and old resins.

information showing the variation tendency of SO_4^{2-} pyrolysis quantity between 120 and 200 °C in Figure 4(a). The SP112H resins were previously used in a supercritical unit condensate polishing treatment system.

As shown in Figure 4, 1500H and SP112H resins both release SO_4^{2-} during the pyrolysis experiment and the quantities in the new and old resins increased with an increase in temperature. The quantity of SO_4^{2-} released from new and old resins changed very little with temperatures between 120 and 200 °C. However, the quantity showed an abrupt increase when the temperature increased from 200 to 240 °C, which was related to the whole exchange volume of the resins. With the 1500H new and old resins, for example, the released quantity of new and old resins was 2.17 g/L and 1.72 g/L,

respectively, when the temperature was 200 °C. When the temperature changed to 240 °C, the values changed to 44.26 g/L and 39.9 g/L, respectively. This abrupt increase phenomenon still appeared when the temperature was 280 °C. For example, when the temperature was at 240 °C, the released quantity of SP112H new and old resins was 31.17 g/L and 28.37 g/L, respectively, whereas a temperature change to 280 °C resulted in values of 99.29 g/L and 93.12 g/L, respectively.

Figure 5 shows the curves for pH of pyrolysis solutions of 1500H and SP112H new and old resins at various temperatures; the pH values of the new and old resins both decreased with an increase in temperature, that is, the pH value declined from alkaline to strongly acid. Moreover, the pH values of the new resins were higher than

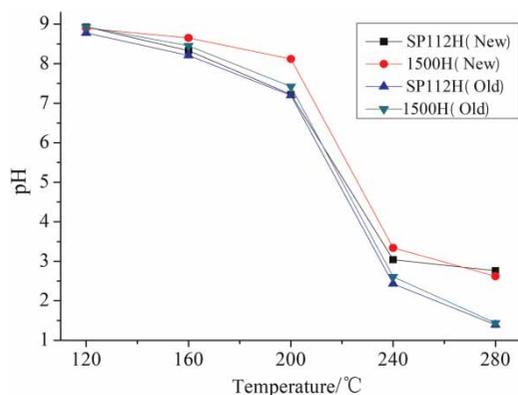


Figure 5 | Contrast curves for pH of pyrolysis solution of new and old resins.

those of the old samples, which indicates that the old resins generated more acidic material, particularly at high temperatures. The pH values changed little and remained alkaline when the temperature was between 120 and 200 °C. For example, the pH of the 1500H old resin was 8.93 when the temperature of the pyrolysis solution was 120 °C and 7.22 when the temperature rose to 200 °C. However, the abrupt increase phenomenon occurred when the temperature of the pyrolysis solution increased from 200 °C to 240 °C. The value was 2.43 for the 1500H old resins, which indicates that the solution transformed from slightly alkaline to strongly acidic. This tendency is consistent with the sudden increase in quantity of SO_4^{2-} released from resins, which indicates that large amounts of acidic substances are produced by cation exchange resin at 200 °C.

CONCLUSIONS

The results of this study are summarized in the following points:

1. The quantity of SO_4^{2-} released by 1500H and SP112H new and old resins has a growth tendency with an increase of time, whereas the velocity declines. However, both the quantity and velocity tend to balance in a short time during the dynamic cycle experiment.
2. Both 001×7 and 1500H cation exchange resins release SO_4^{2-} during static immersion. In addition, the quantity of SO_4^{2-} released from the two types of new resins is greater than that of the old samples.
3. During the pyrolysis experiment, the quantities of SO_4^{2-} released by 1500H and SP112H new and old resins are both low when the temperature is between 120 °C and

200 °C. However, an abrupt increase in quantity occurs when the temperature rises to 240 °C, and the phenomenon continues with a further increase in temperature.

4. The pH values of 1500H and SP112H new and old resins both decline from slightly alkaline to strongly acidic. In addition, the maximum reduction occurs when the temperature changes from 200 °C to 240 °C, which is inconsistent with the pyrolysis experiment results. The pH of the pyrolysis solution at 280 °C is acidic, which indicates that both new and old resins can release SO_4^{2-} to yield an abundance of acidic material.

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