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Sulfate removal from the sea by anion exchange process combined with K_2SO_4 precipitation

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ABSTRACT

Sulfates can be removed from seawater by weak base anion exchanger which is regenerated with concentrated potassium chloride solution. The potassium sulfate was removed from the regeneration solution by adding solid KCl, which reduced the solubility of K_2SO_4 causing its precipitation. Dilution of the regenerated solution was substantially reduced by using three displacement solutions with different KCl concentrations. Precipitation of potassium sulfate in the column during regeneration was prevented by heating the regeneration solution to 55°C. After the regeneration solution exited the column, it was cooled to achieve maximum precipitation of the K_2SO_4. The weight of the K_2SO_4 obtained was about the same as that of the KCl used for regeneration. The concentration of sulfate in seawater was reduced from 34 mM to less than 15 mM. To produce one ton of potassium sulfate about 250 tons of seawater is needed. The volume of the solution disposed of to the drain approached zero.

Keywords: Sulfate removal; Seawater; Anion exchanger; Recycled regeneration

1. Introduction

Water designated for desalination typically has a high concentration of calcium sulfate that significantly reduces the potential desalinated water recovery rates and that increases the problem of a brine disposal. Sulfate ions can be removed from concentrated chloride solution by exchanging them with chloride ions using weak base anion exchangers, which have a high selectivity for sulfates over chlorides [1–5]. However, regeneration of the weak base anion exchanger, typically done using large amounts of concentrated sodium chloride solution, is expensive, and the subsequent disposal of the sodium chloride causes ecological problems. Alternatively, the concentrated brine rejected by an evaporation desalination unit can, theoretically, be exploited to regenerate the weak base anion exchangers [1–5]. However, generally chloride concentration in a brine of RO plants may be too small to enable effective exchanger regeneration.

Recently it was shown [6] that sulfate can be removed from brackish water which has a high level of Cl concentration (0.2–0.3 M), by a weak base anion exchanger which is regenerated with concentrated KCl solution and is combined with a K_2SO_4 precipitation process. It was shown in this study that the selectivity of the weak base anion exchanger (Purolite A-830, Purolite Co., England) to sulfate relative to chloride is high and it is possible to remove sulfate from seawater in spite of the fact that it has a high level (0.65 N) of Cl concentration To prevent scaling of calcium sulfate in the desalination units, Zannoni et al. [5] used a weak base anion exchange resin to remove sulfate from the seawater. Concentrated brine of 1.1–1.6 N Cl was used to regenerate the weak anion exchange resin. In this study regeneration of the anion exchanger was carried out with a concentrated KCl solution (3.5–4.0 N + 0.15 M K_2SO_4). After the regeneration, this solution contained 2.5 M KCl + 0.45 M K_2SO_4. Sulfates were removed from this solution by adding solid KCl which caused salting out of K_2SO_4 crystals. The price of potassium sulfate is about twice (or more) that of potassium chloride and it is widely used as fertilizer for tobacco, certain fruits, and vegetables, and provides the soil with both potassium and sulfur. In the desalination process of seawater, $CaSO_4$ can precipitate on the membranes or heat exchangers' surface and thus increase the maintenance price of the unit. To prevent calcium sulfate precipitation the concentration of brine must be controlled and it is necessary to use expensive additives that prevent scaling. As most sulfate is removed in this process, problems associated with $CaSO_4$ scaling during desalination of seawater, are eliminated. In solutions containing both K_2SO_4 and KCl, the solubility of K_2SO_4 decreased as the concentration of KCl increases as shown in Fig. 1. In our study, we used concentrated (3.5–4.0 M) KCL at 55°C to regenerate the anion exchanger and thus a rejected regeneration solution of about 2.5 M KCl + 0.45 M K_2SO_4 was obtained from the anion exchange column. During regeneration, the hot KCl solution was diluted when it was passing through the column and it was necessary to evaporate about 2%–4% of its volume by vacuum evaporation. This operation reduced the temperature of the regeneration solution to 20°C–25°C and helped K_2SO_4 precipitation. When solid KCl was added to the cooled regeneration solution (up to 4.0 M) it caused precipitation of pure K_2SO_4 which was removed from the solution by filtration (Fig. 1). The new concentrated KCl solution (3.5–4.0 M) with a low concentration of K_2SO_4 (about 0.15 M), was heated to 55°C and then re-used to regenerate the anion-exchange column. As the weak-base anion exchanger is used it is necessary to acidify the seawater to pH 3.3–4.0. When the chloride concentration of the seawater was 0.65 M the operation capacity of the resin to sulfate was 0.75–0.80 eq./L. The sulfate concentration of the seawater was decreased from 34 to 6–15 mM (Fig. 2). The weight of K_2SO_4 obtained in the regeneration process was similar to that of the solid KCl that was added. The substantially higher price of the former compared to that of the latter compound, therefore indicates that the regeneration steps proposed here are economically viable. The potassium sulfate crystals obtained in this process were 99% pure and their sizes were in the range of 0.1–1 mm.

2. Experimental

The research was carried out in a pilot plant unit that comprised two PVC columns, each with a height of 2.2 m and a diameter of 10 cm. Every column contained 16 L of Purolite-A 830 (Purolite Co., England) a weak base anion exchange resin. The two columns were operated in alternating fashion so that while one column was in operation mode, the second was being regenerated. Two hundred liters of seawater with a concentration of 34 mM sulfates and at pH 3.3–4.0 were loaded into the top of the column, from where the water flowed to the bottom at a flow rate of 240 L/h for a period of 50 min (Fig. 2), at the end of which the ion-exchange resin was partially saturated with sulfate. The saturated column then underwent regeneration while the second column was put into operation.

To prevent the concentrated (3.5–4.0 M), hot (55°C) KCl solution from becoming diluted while it is loaded into the column, three displacement solutions (at volumes of 3 L, initial KCl concentrations of about 0.4–0.5, 0.9–1.1, and 1.8–2.1 M) were loaded sequentially in the reverse direction, that is, from the bottom to the top of the column. The loading of 25 L of concentrated (3.5–4.0 M) KCl regeneration solution from the bottom of the column forced the three displacement solutions out of the column. The displacement solutions were collected in their original containers for later reuse. The excess regeneration solution that remained in the column was displaced by the displacement solutions, which were loaded from the top to the bottom of the column in the order of most to least concentrated. Finally, the column was flushed with feed water,

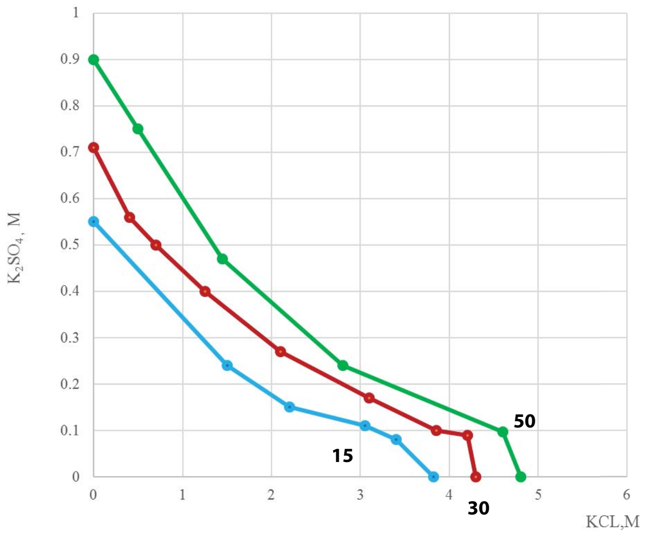

Fig. 1. Sulfate solubility at different temperatures vs. KCl concentration.

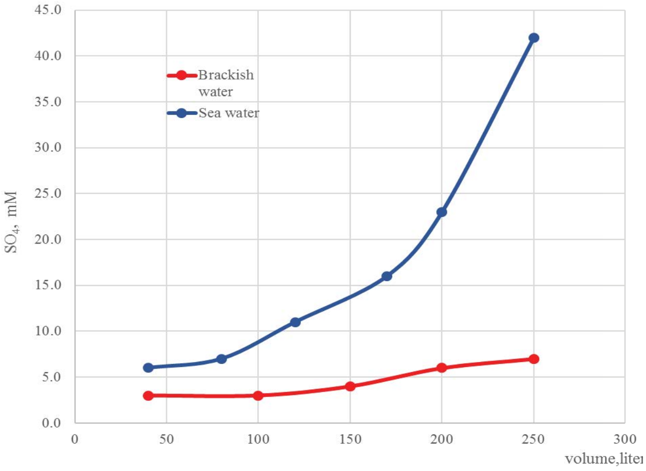

Fig. 2. Sulfate concentration in seawater (Cl-0.64 M, SO_4-34 mM) (*) and brackish water (Cl-0.22 M, SO_4-0.32 m M) (**) exiting anion exchange column vs. solution volume.

displacing the remaining volumes of the displacement solutions, which were again collected in their containers. This procedure ensured that dilution of the regeneration solution and losses of potassium salts during the regeneration cycle were substantially minimized.

The sulfate concentration of the regeneration solution exiting the ion-exchange column was 0.42–0.6 M. It was oversaturated [1,7] and immediately potassium sulfate began to precipitate in the container as fine crystals at size 0.1–1.0 mm. It was cooled by vacuum evaporation from 55°C to 25°C. About 1.1 kg solid KCl was added to the container, which then underwent strong agitation for 30 min (Fig. 3). About 1.0–1.1 kg potassium sulfate precipitated out of solution and was filtered by centrifugation. The concentration of sulfate in the regeneration solution after precipitation was in the range of 0.12–0.15 M. Concentration of sulfate in seawater is between 27 to 35 mM. The seawater used in our study comprised 650 mM Cl, 34 mM SO_4, 14 mM Ca, 11 mM K, and 69 mM Mg. The unit was operated automatically and continuously for 170 cycles.

3. Results and discussion

In this study, when a concentrated KCl (4 M) regeneration solution was passed through a column containing an anion exchanger in SO_4 form, a highly concentrated K_2SO_4 solution was obtained. Due to the low solubility of the K_2SO_4 in the regeneration solution (Fig. 1), it was heated to 55°C to prevent its precipitation in the column and it was passed through the column for a short time of less than 10 min. Because the column was made of transparent PVC, it was possible to verify that no precipitation occurred even after the continuous operation of 170 cycles. The exit of the regeneration solution from the column was accompanied by a change in the hydrodynamic conditions, from laminar to turbulent flow, and K_2SO_4 started immediately to precipitate in the mixing container (Fig. 3). The influence of agitation on the time stability of the potassium sulfate oversaturation solution was examined in the laboratory with 2.4 M KCl + 0.5 M SO_4 (Fig. 4). It showed that with laminar flow high potassium sulfate oversaturation can be maintained. The solubility of potassium sulfate in the KCl solution depended on the temperature and on the KCl concentration (Fig. 1). The addition of solid potassium chloride to an oversaturated potassium sulfate solution led to K_2SO_4 precipitation as a result of salting out, in the form of pure crystals. The time needed to complete the precipitation process was about 20–30 min (Fig. 3). To ensure maximum K_2SO_4 precipitation, the regenerating solution was cooled to 20°C–25°C by vacuum evaporation, which caused an approximately 4% decrease in solution volume. Therefore, although the regeneration solutions (K_2SO_4 and KCl) became slightly diluted by the passage through the ion exchange column, due to the subsequent decrease in their volumes by evaporation, their concentrations remained unchanged. The composition and temperature of the regeneration solution at the column exit are given in Figs. 5 and 6. From Figs. 1 and 5, it was possible to calculate K_2SO_4 concentration at saturation and to compare this to the over-saturation concentration in the regeneration solution exiting the ion exchange column (Fig. 6). The oversaturation concentration of K_2SO_4 in the regeneration solution showed that it was very high at the beginning of the regeneration cycle, after which it declined (Fig. 6).

Concentration of sulfate in the seawater exiting the anion exchange column is given in Fig. 2. It showed that at the beginning the sulfate concentration was reduced from 34 mM down to about 6 mM and after 11 BV (170 L) the sulfate concentration increased up to 15 mM. In previous experiments when we used brackish water (0.22 mM Cl) instead of seawater the sulfate concentration was reduced to less than 3 mM. The average sulfate reduction in seawater of the whole cycle was reduced from 34 mM to less than 10 mM and average sulfate recovery was 71%. By reducing the flow rate the concentration of sulfate in solution exiting the column was reduced (Fig. 7).

The concentration of KCl at the end of the regeneration was high both in the solution that remained in the column

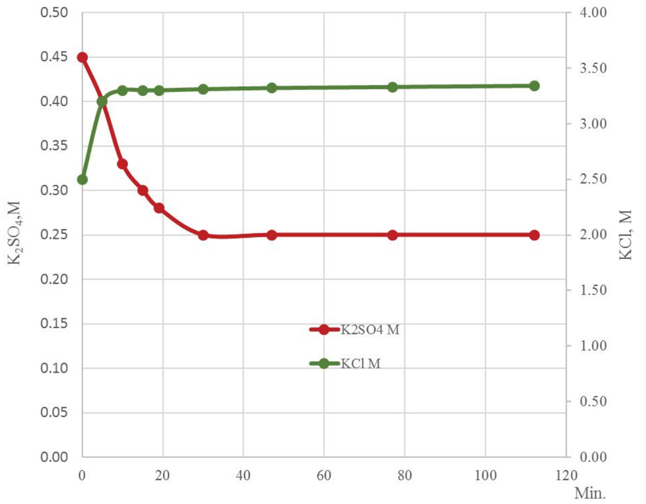

Fig. 3. Changes in concentration of K_2SO_4 (*) and KCl (**) after addition solid KCl to regeneration solution at 22°C.

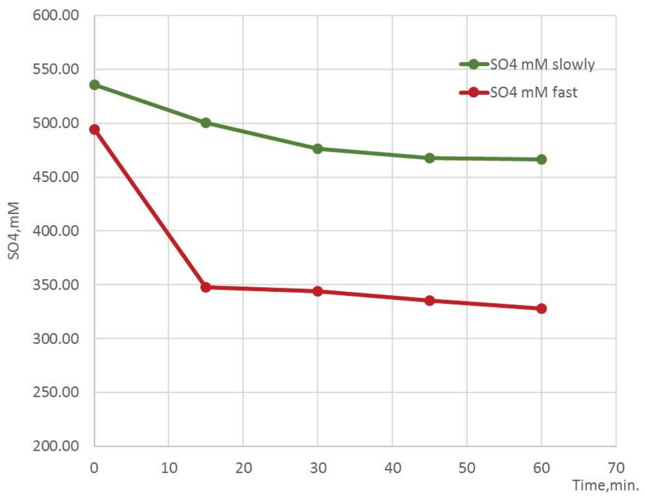

Fig. 4. SO_4 concentration vs. time with a solution containing 2.4 M KCl + 0.4 M Na_2SO_4 with fast and minimal agitation.

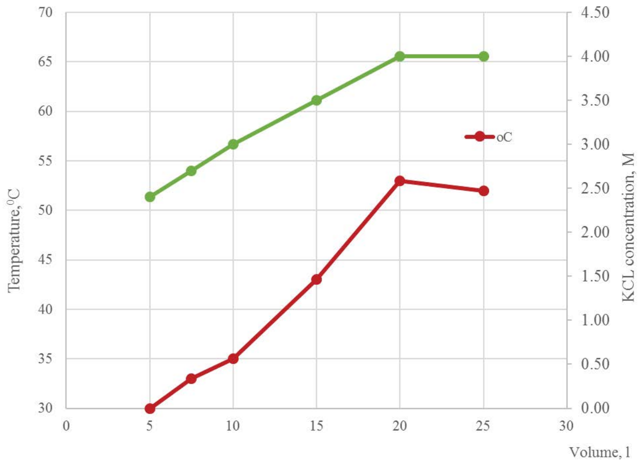

Fig. 5. Temperature (and KCl concentration) vs. regeneration solution volume exiting ion exchange column.

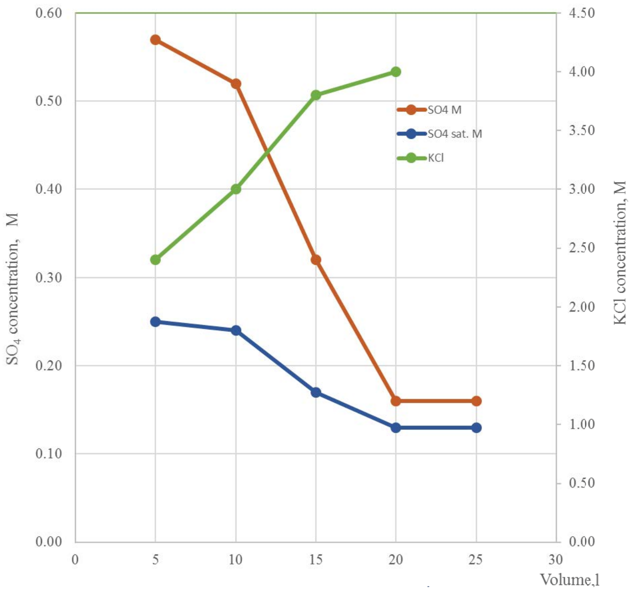

Fig. 6. Sulfate concentration in saturated (*) and oversaturated (**) regeneration solution leaving the ion exchange column vs. solution volume and KCl (***) concentration.

and that within the anion exchange beads. To recover this remaining KCl, displacement solutions at different concentrations were used. Mixing between the solutions of different concentrations was negligible because the more concentrated (higher density) solutions were pushed down by the more diluted (lower density) solutions. The KCl concentration of each of the three displacement solutions (2, 1, and 0.5 M) decreased when they passed through the column before regeneration and increased when they passed through the column after regeneration. In addition, column temperature after regeneration was 55°C, and the heat was absorbed by the displacement solutions and then used to preheat the column prior to the next cycle of regeneration.

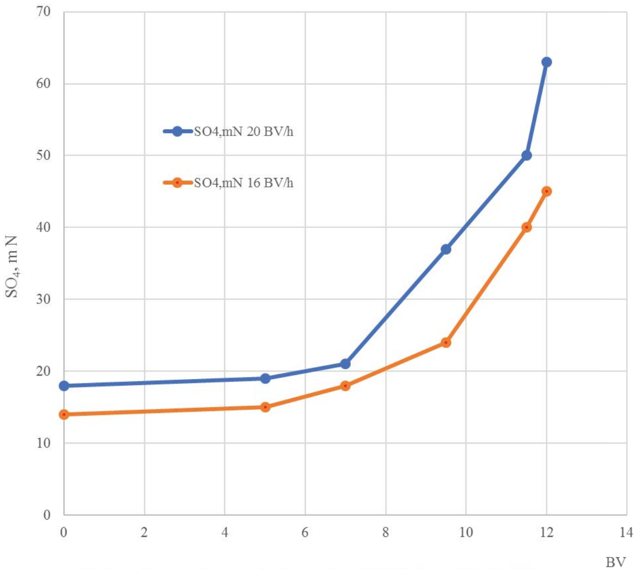

Fig. 7. Influence of seawater flow rates measuring bed volume (16 BV/h* and 20 BV/h**), on sulfate concentration in seawater existing anion exchange column.

After collecting the displacement solutions, the column was rinsed with 4 L feed water. Because both the volume and concentration of the KCl solution remaining in the column at this stage were low, it could either be sent to the desalination unit or disposed of in the drain. The salting-out precipitation technique can be exploited to recycle the regeneration solution. In addition, the combination of salting out with the use of displacement solutions ensured that very small amounts of potassium salt were disposed of to the drain. The flow rate of water through the column influenced the level of sulfate leakage as can be seen from Fig. 7. The ion exchange capacity with seawater was 0.75–0.80 eq./L compared to that of brackish water (220 mM Cl) where it was 1.0–1.1 eq./L. The molar fraction (XSO_4) of sulfate in the anion exchange resin depended on [Cl]/[SO_4] concentration as can be seen in Fig. 8.

4. Conclusions

- The results of this study show that the ion exchange process can be used to reduce the sulfate concentration in seawater from 34 to 6–15 mM. By removing sulfates from seawater the risk of $CaSO_4$ precipitation in desalination units is eliminated.
- Sulfates are removed from the regeneration solution by dissolving more KCl in the solution to cause K_2SO_4 oversaturation and precipitation. The time required to complete K_2SO_4 precipitation was less than 30 min.
- The potassium sulfate that precipitated in the regeneration solution as pure crystals were filtered off and the remaining solution which contained 2.5 M KCl + 0.14 M K_2SO_4 was reused in the next cycle.
- To prevent precipitation of potassium sulfate in the ion exchange column the regeneration solution was heated to 55°C and the time of regeneration was kept short at less than 10 min.

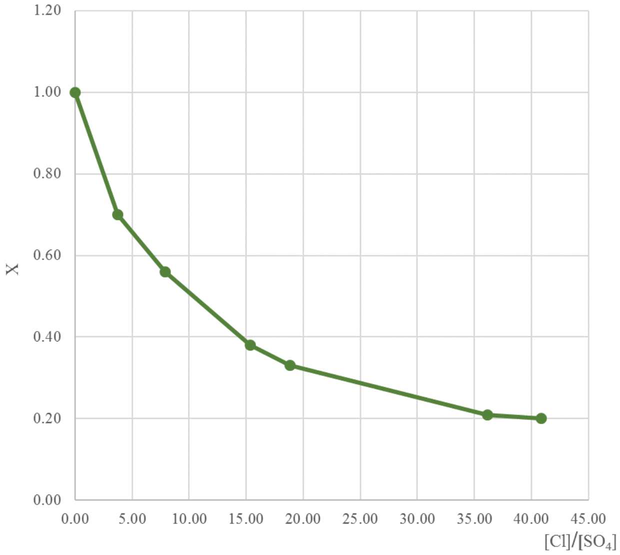

Fig. 8. Sulfate molar fraction (X) in resin vs. molar ratio in solution between Cl and SO_4 [CL]/[SO_4].

- Using the displacement solution technique results in minimal losses of solutions containing potassium salts.
- Using the salting-out process the obtained potassium sulfate was in a solid-state and its quantity is the same as the added quantity of potassium chloride.

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