Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1080450

57 (2016) 14364–14368
July

Taylor & Francis
Taylor & Francis Group

Sulfate removal from brackish water using an anion exchanger with recycled regeneration

Emanuel Korngold*, Tony Tuvia Bejerano

Zuckerberg Institute for Water Research, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 8410501, Israel, Tel. +972 86461940; Fax: +972 86472960; email: korngold@bgu.ac.il (E. Korngold)

Received 13 May 2015; Accepted 10 June 2015

ABSTRACT

The removal of excess sulfate from brackish water was carried out using a weak anion exchanger that was regenerated with a potassium chloride solution. The potassium sulfate was removed from the regeneration solution by adding solid KCl, which reduces the solubility of K_2SO_4. 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 it to 50–60˚C. After the regeneration solution exited the column, it was cooled to achieve maximal 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 volume of the solution disposed to drain approached zero.

Keywords: Sulfate removal; Brackish water; Anion exchanger; Recycled regeneration

1. Introduction

Water designated for desalination typically has a high concentration of calcium sulfate that significantly reduces potential desalinated water recovery rates and that increases the problem of brine disposal. Sulfate ions can be removed from the water by exchanging them with chloride ions using weak base anion exchangers, which have a high selectivity for sulfates over chlorides [1]. 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 [2–5]. However, generally chloride concentration in brine of RO plants may be too small to enable effective exchanger regeneration. The goals of this research, therefore, were to devise a methodology for the recycling of the regeneration solution and to substantially reduce its disposal.

In solutions containing both K_2SO_4 and KCl, the solubility of K_2SO_4 decreases as the concentration of KCl increases [6]. Shown in Fig. 1, this dependence is the basis for the process we propose. In this study, we used a highly concentrated (e.g. 3.0–4.0 M) KCL solution at 50–60˚C to regenerate the anion exchanger. The rejected solution obtained from the ion-exchange column contained about 2.0 M KCl and 0.45 M K_2SO_4. The addition of solid KCl to the cooled, regenerated solution caused pure K_2SO_4 to precipitate from the solution until the concentration of KCl was in the range of about 3.5–4.0 M (Fig. 1) [6]. The resulting solution, with a high concentration of KCl and a low

---

*Corresponding author.

1944-3994/1944-3986

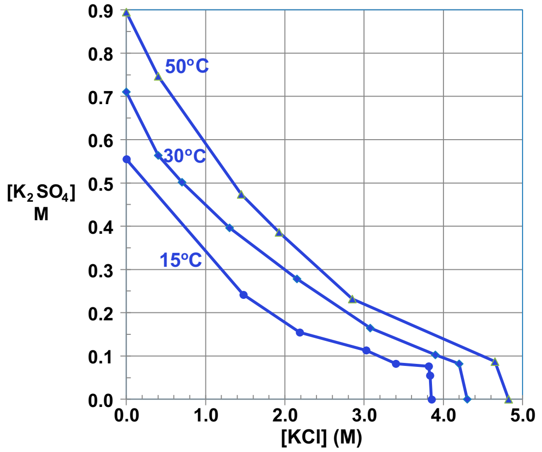

Fig. 1. Saturation concentrations of K_2SO_4 in KCl solutions at 15, 30 and 50˚C.

concentration of K_2SO_4 (about 0.18 M), was then re-used to regenerate the ion-exchange column. The process as a whole is highly complex [7], and therefore, Fig. 2 presents a simplified schematic illustration of its steps. The weight of K_2SO_4 obtained in the regeneration process is similar to that of the solid KCl that was added. The substantially higher price of the former than that of the latter compound, therefore, indicates that the regeneration steps proposed here are economically viable.

During the regeneration process, dilution of the KCl solution by the rinse necessitates that about 3–4% of the water be evaporated. In addition, because a weak-base anion exchanger is used, the brackish water must be acidified to pH ≤ 4.0. The operational capacity of the resin for sulfates was 0.7–1.1 eq/L at chloride concentrations of 0.6–0.2 M, respectively. The potassium sulfate crystals obtained in this process were 99% pure and their sizes (i.e. diameters) were in the range of 0.1–1.0 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, 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. Brackish water with a high concentration of sulfates (25–30 mM) and at pH 3.5–4.5 was loaded into the top of the column, from where the water flowed to the bottom at a flow rate of 6 L/min for a period of 30 min, at the end of which the ion-exchange resin was saturated with sulfate. The saturated column then underwent regeneration while the second column was put into operation.

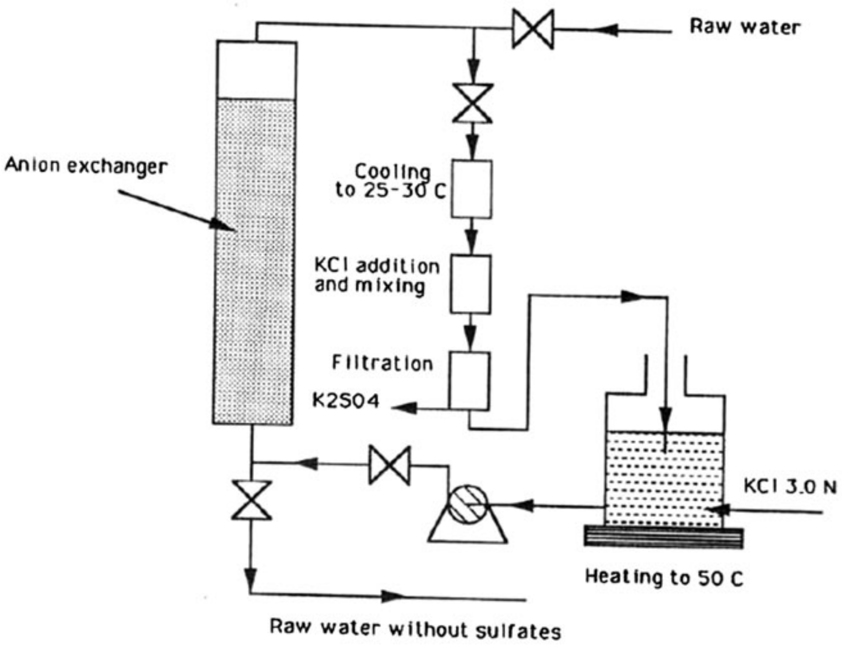

Fig. 2. Schematic depiction of the experimental setup for K_2SO_4 removal from brackish water.

To prevent the concentrated (3.0–4.0 M), hot (50–60˚C) KCl solution from becoming diluted before it was loaded into the column, three displacement solutions (at volumes of 3 L and concentrations of about 0.4–0.5, 0.9–1.1, and 1.8–2.1 M) were loaded sequentially in the reverse direction, i.e. from the bottom to the top of the column. The loading of 25 L of concentrated (3.5–4.0 M) KCl regeneration solution at low dilution 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. At the conclusion of the regeneration process, 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, 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 minimized substantially.

The sulfate concentration of the regeneration solution exiting the-ion exchange column was 0.45–0.5 M, and it was cooled by vacuum evaporation from 50 to 25˚C. About 1.1 kg solid KCl was added to the container, which then underwent strong agitation for 30 min. 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 0.17–0.20 M. The water used in our study comprised Cl (220 mM), SO_4 (31 mM), Ca (2 mM), and Mg (1.5 mM). The pilot plant unit was operated automatically and continuously for 95 cycles.

3. Results and discussion

In this study, when a concentrated KCl regeneration solution was passed through a column containing an anion exchanger of the $SO_4^=$ 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 50–60˚C to prevent its precipitation in the column and it was exposed to the column for short times of about 10 min. Because the column was made of transparent PVC, it was possible to verify that no precipitation occurred even after continuous operation of 95 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 to precipitate in the mixing container. The solubility of potassium sulfate in the KCl solution depends on temperature and on the concentration of KCl (Fig. 1). The addition of potassium chloride to a saturated 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 30–40 min (Fig. 3). To ensure maximal K_2SO_4 precipitation, the regenerating solution was cooled to 20–25˚C by vacuum evaporation, which caused an approximately 4% decrease in solution volume. Therefore, although the K_2SO_4 and KCl solutions became diluted by their passage through the ion-exchange column, due to the subsequent decreases in their volumes, their concentrations remained unchanged. The composition and temperature of the regeneration solution at the column exit is given in Figs. 4 and 5. From Figs. 1, 4, and 5, it was possible to calculate K_2SO_4 oversaturation concentration, the results of which are depicted in Fig. 6. The oversaturation concentration expressed as a percentage of the saturation concentration shows that it was very high at the beginning of the cycle (210%), after which it declined to 11% (Fig. 7).

The concentration of KCl at the end of the regeneration was high both in the solution that remained in the column and in that within the anion exchange beads. To recover this remaining KCl solution, 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 KCl passed through the column before regeneration and

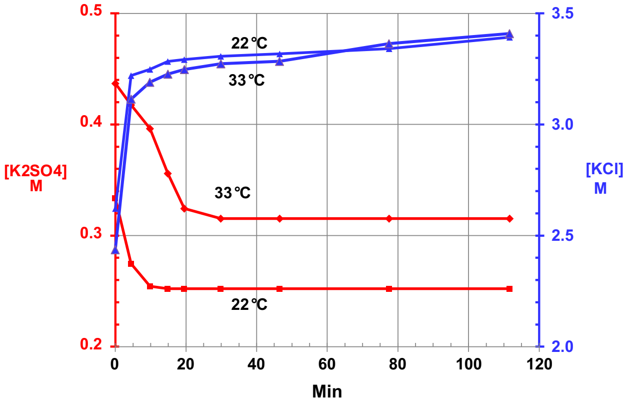

Fig. 3. Change in the concentrations of K_2SO_4 and KCl over time after the addition of solid KCl at two temperatures.

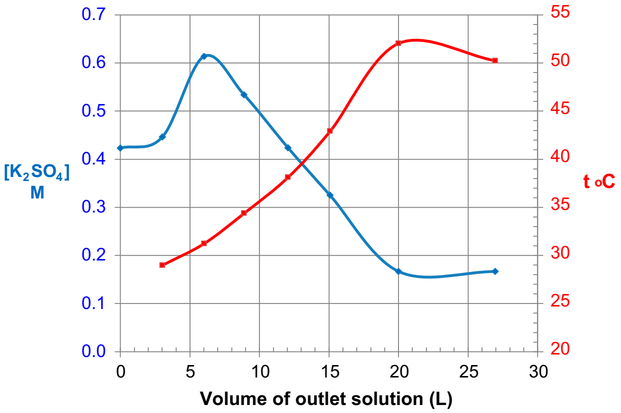

Fig. 4. Regeneration outlet effluent K_2SO_4 concentration and temperature vs. its volume. The corresponding values at the inlet were 0.145 M and 60˚C.

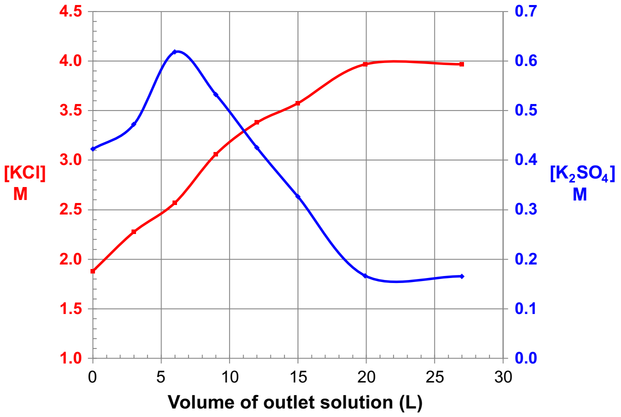

Fig. 5. Regeneration outlet effluent K_2SO_4 concentration and temperature vs. volume. At the inlet, the regeneration solution contained 4 M KCl.

increased when it was loaded after regeneration. In addition, column temperature after regeneration was about 50˚C, and the heat was absorbed by the displacement solutions and then used to preheat the column prior to the next cycle of regeneration. 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 ensures that very small amounts of salt are disposed to the drain. The efficiency of this process depends on the following parameters.

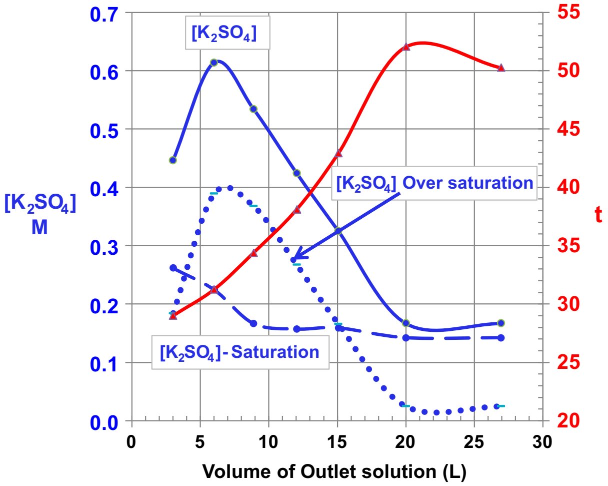

Fig. 6. Concentration and temperature of K_2SO_4 in the regeneration solution at the column outlet. Saturation and over-saturation concentrations are shown using dashed and dotted lines, respectively.

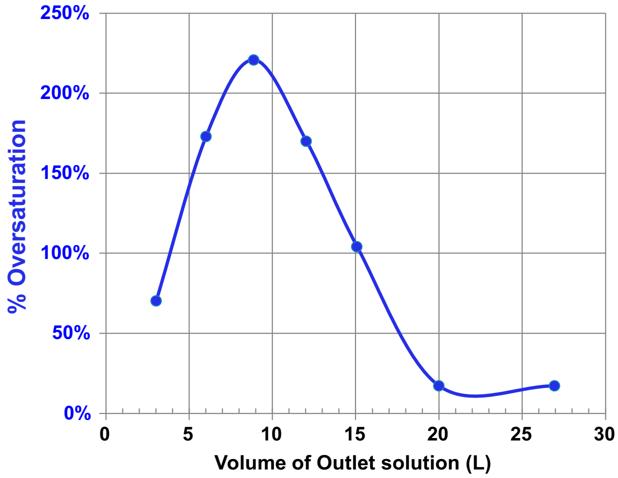

Fig. 7. K_2SO_4 oversaturation in the regeneration solution at the outlet, expressed as % of the saturation values of the same solution.

3.1. *Anion exchange resin capacity*

A weak base anion exchange resin, Purolite A-830, was used in all the experiments. The neutralization curve of the resin shows that its capacity increases as the pH of the treated water decreases (Fig. 8). At a pH of 3.5, the capacity is 2.7 eq/l.

3.2. *Chloride concentration*

The higher the chloride concentration in the feed water (e.g. brackish water), the lower the efficiency of

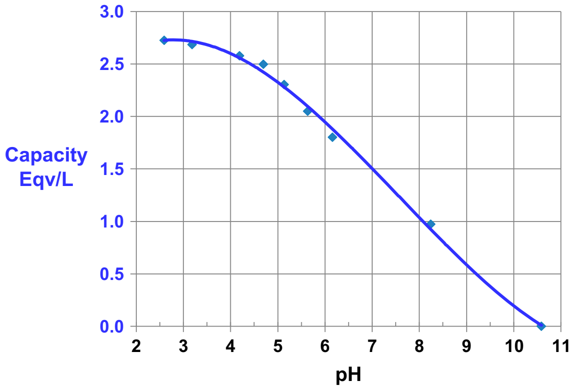

Fig. 8. Dependence of Purolite A830 capacity on pH in a 0.5 M NaCl solution.

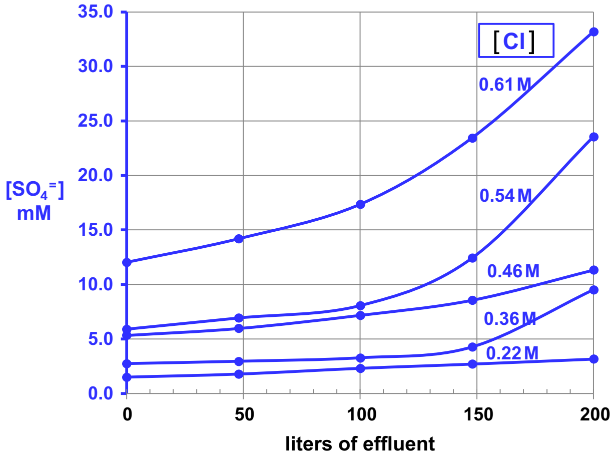

Fig. 9. Concentrations of $SO_4^=$ in effluents with different $[Cl^-]$ and passing through an anion exchange column. The inlet $[SO_4^=]$ was 30–39 mM and column capacity was 12–14 eqv.

sulfate absorption by the anion exchange resin and therefore, the lower the overall efficiency of the recovery process (Fig. 9). When Cl concentrations were in the range of 0.22–0.36 M, the sulfate concentration in the effluent decreased from 30 to 3.0 mM and the column capacity was 1.0–1.1 eq/L. At the higher chloride concentration of 0.54 M, the sulfate concentration in the effluent increased to 6–9 mM and column capacity decreased to 0.7–0.8 eq/L.

4. Conclusion

(1) The results of this study show that the ion-exchange process can be exploited to reduce the sulfate concentration in brackish water from 30 to 2.5 mM.

(2) The efficiency of the process decreased as the chloride concentration in the brackish water increased. This was particularly relevant when feed water chloride levels were above 0.5 M.

(3) Sulfates can be precipitated as K_2SO_4 from the regenerating solution by dissolving more KCl in the solution to cause K_2SO_4 oversaturation. The time required to complete K_2SO_4 precipitation was about 30 min. The K_2SO_4 that precipitated as pure crystals was filtered off and the remaining KCl solution was reused in the next cycle.

(4) To prevent K_2SO_4 precipitation in the ion-exchange column, the duration of the regeneration time was kept short (about 10 min) and the regenerating solution was heated to 50–60˚C.

(5) Using the displacement solution technique results in minimal losses of potassium salts (KCl and K_2SO_4), about 4–5%, and the increase in the volume of the regeneration solution is less than 4%. The volumes of the solutions disposed to the drain are negligible.

Acknowledgments

This research was partly supported by Dead Sea Works Ltd.

References

[1] G. Boari, L. Liberti, C. Merli, R. Passino, Kinetics of sea water desulfation on a weak anion exchanger resin, Environ. Protect. Eng. 6(2) (1980) 251–256.
[2] G. Boari, L. Liberti, M. Santori, L. Spinosa, Advanced evaporation plants with sulfate removal by ion exchange, Desalination 19 (1976) 283–298.
[3] A. Aveni, G. Boari, L. Liberti, M. Santori, B. Monopoli, Sulphate removal and dealkalization on weak resins of the feed water for evaporation desalting plants, Desalination 16 (1975) 135–149.
[4] G. Boari, L. Liberti, C. Merli, R. Passino, Sulfate ion/chloride ion exchange on a weak anion resin, Ion Exch. Membr. 2 (1974) 59–66.
[5] R. Zannoni, A. De Maio, G. Odone, F. Fioravanti, G. Boari, L. Liberti, M. Santori Desulphation new applications: Doha east (Kuwait) and Gela (Italy) desalination plants, Desalination 47 (1983) 93–102.
[6] K. Maeda, H. Kuramochi, T. Shinkawa, K. Fukui, Solubility of two salts containing sulfate and chloride ions in water for ternary systems at 313 K, J. Chem. Eng. Data 47 (2002) 1472–1475.
[7] E. Korngold, V. Freger, N. Belayev, L. Aronov, J. Freiman, Manufacturing of K_2SO_4 from KCl and sulfate which are in water Internal BGU Report No. BGUN-ARI-4-97.