Reviews operating conditions for chromatographic separations involving Purolite® WCA100 for the removal of sulfate from concentrated brine solutions.
Inside this Technical Report you will find a review of lab-scale trials for removing sulfate from concentrated brine solutions using Purolite® WCA100. For more detailed information on any product or to find a product for an application not mentioned, please go to www.purolite.com or contact the closest Purolite regional office to you listed on the back cover.

INTRODUCTION

Founded in 1981, Purolite is a leading manufacturer of ion exchange, catalyst, adsorbent and specialty resins. With global headquarters in the United States, Purolite is the only company that focuses 100% of its resources on the development and production of resin technology.

Responding to the needs of our customers, Purolite has built the largest technical sales force in the industry, the widest variety of products and five strategically located Research and Development groups. Our ISO 9001 certified manufacturing facilities in the U.S.A, Romania and China combined with more than 40 sales offices in 30 countries ensure complete worldwide coverage.

PREMIER PRODUCTS

The quality and consistency of our products is fundamental to our performance. Throughout all Purolite plants, production is carefully controlled to ensure that our products meet the most stringent criteria, regardless of where they are produced.

RELIABLE SERVICE

We are technical experts and problem solvers. Reliable and well trained, we understand the urgency required to keep businesses operating smoothly. Purolite employs the largest technical sales organization in the industry.

INNOVATIVE SOLUTIONS

Our continued investment in research & development means we are always perfecting and discovering innovative uses for ion exchange resins and adsorbents. We strive to make the impossible possible.
Purpose

Investigate the operating conditions necessary to use Purolite® WCA100 amphoteric resin to chromatographically separate sulfate from concentrated brine as an aqueous solution of sodium sulfate.

Background

Amphoteric ion exchange resins are ideal candidates for chromatographic separation as the polymer support structure contains both strong base anion and strong acid cation functionalities. Because of this, low TDS water can be used to elute a sample of aqueous salts across a column of this type of resin. In the case of separation of sulfate from concentrated brine solutions, the very high chloride concentration results in high selectivity for chloride relative to sulfate. For this reason the sulfate will elute off of the resin first, as sodium salt. Within a well-defined set of operating conditions, a process of intermittent pulses of brine on the resin—combined with a continual flow of eluent (softened water)—can achieve effective removal of sulfate from the starting brine solution.

Results

Lab trials performed in this investigation focused on two specific operating parameters, elution flow rate and brine dosage. Data was evaluated in terms of elution time, brine dilution and percent removal of sulfate. The impact of each of these keys factors is critical to the successful implementation of the proposed ion exchange treatment system.

Operating costs are directly related to system dwell time. The amount of time it takes to elute the brine sample impacts the amount of brine that can be treated, as well as the amount of softened water necessary to perform the elution. The volume of softened water also contributes to brine dilution during treatment, which can have a negative impact on effective operation of downstream processes.

Figure 1 shows elution times under various conditions, ranging from low flow and low brine dosage to high flow and high brine dosage.

Figure 1 – Comparing elution times to flow rate and brine dosage
The ultimate measure of a successful process, however, is whether or not an adequate amount of sulfate is removed from the influent brine.

Below you will find graphical representations of the elution of sulfate as Na₂SO₄ and chloride as NaCl from Purolite WCA100 using a 100 ppm NaCl solution as the eluent. Careful tracking of the effluent refractive index results in the collection of a distinct fraction of sodium sulfate almost entirely free of chloride and a concentrated sodium chloride stream with as much as 50% less sulfate concentration than the pulsed brine.

The trials pulsed 0.3 to 0.4 BV of customer supplied concentrated brine at 26% NaCl by weight and 18,000 ppm of sulfate. The resulting recovered brine solution is diluted between 2 to 4.5 times, depending on eluent flow rate and brine dosage onto the media. The recovered brines produced from the various trials represent an average sulfate reduction from 18,000 ppm to less than 4,700 ppm. The overall reduction in sulfate concentration is a function of both segregation of the sulfate in the sodium sulfate elution as well as overall dilution of the recovered brine solution.

When comparing the green trace in Figure 1 to the blue trace, it is obvious to see the impact of eluent flow rate on elution time of the dosed brine. Not only does a faster eluent flow rate shorten the time it takes to treat the brine dose, but the faster rate also reduces the quantity of eluent necessary by approximately half and reduces the dilution factor on the recovered, treated brine.

However, a modest 33% increase in brine dosage at the same increase in eluent flow rate shows a loss of elution efficiency of nearly 50%, as represented by the red trace. The benefit of the faster flow rate is no longer realized as increased eluent usages, elution time and treated brine dilution are all experienced.

The following data represents a series of lab trials that were run under the conditions described in Figure 1. Trials 1 through 3 represent the 3 BV/h and 0.3 BV brine dosage. Trials 5 through 7 coincide with the 4 BV/h eluent flow rate and 0.3 BV brine dosage. Finally trials 8 through 10 represent the 4 BV/h flow and 0.4 BV brine dosage.

<table>
<thead>
<tr>
<th>TRIAL</th>
<th>RECOVERED BRINE (%)</th>
<th>RECOVERED BRINE SO₄ (ppm)</th>
<th>TOTAL SO₄ RECOVERED BRINE (mg)</th>
<th>SO₄ FRACTION CONCENTRATION (ppm)</th>
<th>SO₄ FRACTION Cl⁻ CONCENTRATION (ppm)</th>
<th>SO₄ REMOVAL</th>
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<tbody>
<tr>
<td>1</td>
<td>5.68</td>
<td>3211</td>
<td>1419.60</td>
<td>8842</td>
<td>913</td>
<td>36.6%</td>
</tr>
<tr>
<td>2</td>
<td>5.71</td>
<td>3197</td>
<td>1142.57</td>
<td>8793</td>
<td>926</td>
<td>36.4%</td>
</tr>
<tr>
<td>3</td>
<td>5.69</td>
<td>3154</td>
<td>1202.04</td>
<td>8811</td>
<td>895</td>
<td>36.5%</td>
</tr>
<tr>
<td>Average</td>
<td>5.69%</td>
<td>3187.33</td>
<td>1254.74</td>
<td>8815.33</td>
<td>911.33</td>
<td>36.5%</td>
</tr>
<tr>
<td>5</td>
<td>13.21</td>
<td>4731</td>
<td>794.81</td>
<td>11670</td>
<td>521</td>
<td>48.4%</td>
</tr>
<tr>
<td>6</td>
<td>13.5</td>
<td>4653</td>
<td>781.70</td>
<td>11878</td>
<td>556</td>
<td>49.2%</td>
</tr>
<tr>
<td>7</td>
<td>13.42</td>
<td>4871</td>
<td>818.33</td>
<td>11296</td>
<td>617</td>
<td>46.8%</td>
</tr>
<tr>
<td>Average</td>
<td>13.38%</td>
<td>4751.67</td>
<td>798.28</td>
<td>11614.60</td>
<td>564.67</td>
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<tr>
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<td>8.56</td>
<td>2176</td>
<td>1043.78</td>
<td>10123</td>
<td>542</td>
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<tr>
<td>9</td>
<td>8.61</td>
<td>2254</td>
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<td>10057</td>
<td>581</td>
<td>41.7%</td>
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<tr>
<td>10</td>
<td>8.35</td>
<td>2097</td>
<td>1041.43</td>
<td>10092</td>
<td>562</td>
<td>41.8%</td>
</tr>
<tr>
<td>Average</td>
<td>8.51%</td>
<td>2175.76</td>
<td>1045.24</td>
<td>10090.67</td>
<td>561.67</td>
<td>41.8%</td>
</tr>
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</table>
The overriding factor affecting sulfate removal efficiency, as represented in the data, is the dilution factor realized from the use of additional eluent necessary for trials 1 – 3 and 8 – 10.

In Figure 1, the more gradual slope of the front side of the elution curve seen for trials 1 – 3, compounded by the overall extended elution time for the same trials, results in a double negative impact for the sulfate removal for this set. When examining the two sets of trials run at the faster flow rate, trials 5 – 7 and trials 8 – 10 respectively, one can see a maintained level of sulfate removal, which coincides with the sharp sulfate elution displayed by the leading edges of both curves in Figure 1. However, extended elution time, this time a result of the additional dose of brine in trials 8 – 10, yields unfavorable brine recovery.

It is also important to recognize that the chloride concentration in the recovered sodium sulfate fraction represents no more than 0.35% of the total chloride dosed onto the column.

**Conclusion**

Based on lab scale trials it has been determined that at an eluent flow rate of 4 BV/h and brine dosage of 0.3 BV approximately 50% of the sulfate present in the starting concentrated brine can be reproducibly removed without sacrificing sodium chloride solids.

**Figure 2: Overlays of brine and sulfate elutions with a 0.3 BV brine dose and 4 BV/h eluent flow**

These conditions represent the most ideal parameters evaluated for the removal of sulfate from concentrated brine solutions. Faster eluent flow rate results in sharp elutions of both the sulfate and chloride fractions of the brine. Also, the lower dosage of brine pulsed results in reduced brine dilution and improved sulfate removal efficiency.

Repetitive injection of brine samples was also trialed to carry this process further. Only one trial was conducted for this approach, yet appropriate timing of the second and third brine injections showed very promising results.
Injection of secondary and tertiary brine samples onto the resin bed, just at the beginning of the previous brine elution, results in repetitive elutions of the sulfate and chloride fractions, as shown in Figure 3.

Optimization of the timing of the additional brine injections should result in a return to baseline in between elutions and therefore more efficient recovery of both sulfate and chloride. This type of process development is beyond the scope of this study. Further arrangements can be made with Purolite and its associates to generate the necessary data.