**Ion Exchange Resins**
Regenerating strong acid cation resins with sulfuric acid

**Introduction**

Sulfuric acid is commonly used to regenerate strong acid cation resins. However, when the feed water contains a significant concentration of calcium salts, there is a potential for exceeding the solubility of calcium sulfate during regeneration. This will result in calcium sulfate crystals being deposited within the resin structure and throughout the resin bed. In order to control the precipitation of calcium sulfate, regeneration with reduced concentrations of sulfuric acid at selected flow rates is necessary.

Regeneration with sulfuric acid is most effectively done by gradually increasing the regenerant concentration, either step-wise or continuously. If the percentage of calcium relative to total cations is greater than 75 %, the first portion of acid should be applied at a concentration in the range of 0.8 to 1.0 %.

A way to limit the risk of precipitation is to avoid long contact of the acid with the calcium in the resin bed. Therefore in general the injection time should not exceed about 45 minutes. With properly adjusted concentration and flow rate it is not unusual to see precipitation occurring outside of the resin vessel.

**WAC resins**

As weakly acidic resins (WAC) usually contain no sodium, and there is normally no or very little excess, all acid must be passed at a concentration of about 0.7 % only. There is no exception. For couples of WAC + SAC resins, regeneration is done in thoroughfare, but a secondary dilution of the acid must be done between both columns or compartments so that the concentration is no higher than 0.7 % before hitting the WAC resin. This is possible only for separate vessels or compartments.

In **layered beds**, all acid is passed at 0.7 % or 0.8 %, in one step. A second step would be possible only if the global regenerant ratio were greater than about 150 %, which is unusual. That second step could then be applied to the excess only. Cation layered beds with $\text{H}_2\text{SO}_4$ regeneration are not recommended.

In **double chamber packed beds**, a secondary dilution is possible.

**SAC resins Precise method**

When regenerating strongly acidic cation (SAC) exchange resins, the concentration is not exactly the same with co-flow (CFR) and reverse flow (RFR) regeneration. The reason is the location of the calcium ions in the resin at the end of the exhaustion run. With co-flow regeneration, the $\text{Ca}^{++}$ ions are on the top, where the fresh acid first contacts the resin. With reverse flow regeneration the acid is first in contact with the least exhausted resin layers.

Regenerant ratio

The parameter used in this method for the regeneration steps is:

\[ \text{RegRatio} / \text{pCa} \]
The regenerant ratio is defined as the ratio between regenerant quantity and ionic load per liter of resin — which is the operating capacity:

\[ \text{RegRatio} = \frac{\text{Regenerant quantity [eq/L]}}{\text{Exchange capacity [eq/L]}} \]

For instance, if the regenerant quantity is 120 g H₂SO₄ per liter resin, this is 120 / 49 = 2.45 eq/L, 49 being the equivalent mass of sulfuric acid and if the operating capacity is 1.05 eq/L, the regenerant ratio is 2.45 / 1.05 = 2.33

And \( p\text{Ca} \) is the ratio between calcium and total salinity in the feed (both in meq/L or other equivalent units).

So that for instance if there is 57 % calcium in the feed the parameter RegRatio/pCa is 2.33 / 0.57 = 4.09

The first concentration step \( C_1 \) is read from figure 1 or figure 2 depending on the mode of regeneration. In the second step the initial concentration is doubled and in the third step, if any, a concentration equal to three times the initial concentration \( C_1 \) is used.

The number of steps and quantity of the acid in each injection step are calculated from table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity at concentration ( C_1 )</th>
<th>Quantity at concentration ( C_2 = 2 \times C_1 )</th>
<th>Quantity at concentration ( C_3 = 3 \times C_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( &gt; 6 )</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
</tr>
<tr>
<td>4 to 6</td>
<td>1/2</td>
<td>1/2</td>
<td>1/3</td>
</tr>
<tr>
<td>3 to 4</td>
<td>2/3</td>
<td>1/3</td>
<td></td>
</tr>
<tr>
<td>( \leq 3 )</td>
<td>3/3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Injection steps, in proportion of the total quantity, in grams or pounds
The idea is that if you have a large excess of regenerant, i.e. a high regenerant ratio, you can pass more regenerant at the higher concentration, because most of the calcium will have been eluted before.

**Important:** if C$_2$ or C$_3$ > 6 %, use 6 %.

**Example**

Using the preceding data:
- pCa = 57 % (= 0.57)
- Dosage 120 % g/L = 2.45 eq/L
- Reverse flow regeneration (RFR)
- Operating capacity (from engineering data or software) 1.05 eq/L
- RegRatio = 2.45 / 1.05 = 2.33
- RegRatio / pCa = 2.33 / 0.57 = 4.09

We get
- C$_1$ = 1.6 % from graph B thus C$_2$ = 3.2 %

From table 1 we have half of the regenerant at 1.6 % followed by the second half at 3.2 %

**Bed volumes and flow rate**

1. The first concentration is 1.6 %, which is about 16 g H$_2$SO$_4$ per liter solution. If we need 60 g acid per liter resin for the first step, the volume is 60/16 = 3.75 bed volumes
2. The second concentration is about 32 g H$_2$SO$_4$ per liter solution, thus the second half of the regenerant has a volume of 60/32 = 1.88 BV.

The total volume of regenerant is thus 5.62 BV.

Assuming an injection time of 40 minutes and a constant flow rate for the dilution water, we will have a specific flow rate of 5.62 × 60 / 40 = 8.4 BV/h.

**Working mixed bed units**

Working MBs are those units fed with feed water than may contain all sorts of cations including calcium. Therefore the concentration of sulfuric acid must be adjusted to the Ca content of the water.

Only in polishing units downstream a main demineralization train can it be assumed that the feed water contains no calcium at all. In this case, and only in this case, any H$_2$SO$_4$ concentration can be used, 6 % being a reasonable value.

**Method 1**

For working mixed bed units, the percentage of calcium in the feed water must first be calculated, as a percentage of the total cations concentration in meq/L or mg/L as CaCO$_3$, and the concentration can be read from figure 3.
Method 2

An alternate method allows the use of higher concentrations, provided the injection flow rate is high enough so that precipitation of calcium sulfate, which is a relatively slow reaction, does not have time to occur in the resin bed.

The concentration and flow rate can be read from figure 4.

Example: if your feed contains 50 % calcium, you can use in principle 2.5 % concentration, but you must pass the acid at a flow rate of at least 9 BV/h.

In doubt, it is safer to use method 1.