Cleaning of Hydrochloric Acid Pickling Baths

Hydrochloric acid is commonly used in pickling bath applications for cleaning of metal surfaces. Dissolved metals form chloride complexes in hydrochloric acid.
About Purolite

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 our customers’ needs, Purolite has the widest variety of products and the industry’s largest technical sales force. Globally, we have five strategically located research and development centers and eight application laboratories. Our ISO 9001 certified manufacturing facilities in the United States of America, United Kingdom, 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 team in the industry.

INNOVATIVE SOLUTIONS

Our continued investment in research and development means we are always perfecting and discovering innovative uses for ion exchange resins and adsorbents. We strive to make the impossible possible.
Cleaning of Hydrochloric Acid Pickling Baths

Hydrochloric acid is commonly used in pickling bath applications for cleaning of metal surfaces. In the pickling process, the acid becomes more and more concentrated with metals, which have been dissolved from the treated metal surfaces. When the efficiency of the pickling acid becomes too low it must be replaced by fresh acid.

Recycling of the spent acid after removing the metallic ions is common practice to minimize operating costs.

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Metals Removal By Ion Exchange

Dissolved metals form chloride complexes in hydrochloric acid that can be removed by using strong base type anion exchangers, such as Puromet™ MTA5000 or MTA5500. These anionic complexes are only stable in concentrated hydrochloric acid. Increasing the pH leads to hydrolysis. Therefore, regeneration can simply be carried out with water. To avoid neutralization of the hydrochloric acid, Puromet MTA5000 and MTA5500 are supplied and used in the chloride form.

Metals Removal From Concentrated Hydrochloric Acid

\[ R – Cl + (FeCl_4)^– \rightarrow R – FeCl_4 + Cl^– \]
\[ R – Cl + (ZnCl_3)^– \rightarrow R – ZnCl_3 + Cl^– \]

Regeneration with Water

\[ R – FeCl_4 \rightarrow R – Cl + FeCl_3 \]
\[ R – ZnCl_3 \rightarrow R – Cl + ZnCl_2 \]

Operating Capacity

As the anionic metal complexes' stability is very much dependent on HCl concentration and strong base type anion resins can only fix the metals when present as anionic complex, it follows that the operating capacity is a function of the acid concentration. The curves in Figure 1 illustrate the operating capacity of Puromet MTA5500 for the removal of Fe(III) as a function of the acid strength. The resins can be run in single column systems or in series of two or more columns.

In the first case the resin will be run to a leakage endpoint. In the second case the lead column will be run to saturation and the trail column to a leakage endpoint. Curve 1 shows the operating capacity to saturation, Curve 2 the operating capacity to leakage endpoint.
Figure 1 also shows that purification by anion exchange resins will be only economic from a minimum acid concentration. The minimum acid concentration depends on the stability of the anionic complex and is therefore different for different metals. Table 1 gives a rough guideline at which concentrations ion exchange treatment should be considered.

**TABLE 1** Recommended Minimum HCl Concentrations

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hydrochloric Acid Concentration, % w/w</th>
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</thead>
<tbody>
<tr>
<td>Iron (Trivalent)</td>
<td>&gt; 17</td>
</tr>
<tr>
<td>Iron (Divalent)</td>
<td>&gt; 25</td>
</tr>
<tr>
<td>Zinc</td>
<td>&gt; 7</td>
</tr>
<tr>
<td>Copper</td>
<td>&gt; 15</td>
</tr>
</tbody>
</table>
Regeneration

As already explained, the regeneration is carried out by eluting the metal complexes with water. Figure 2 shows a typical elution profile of an application where iron and zinc were removed from the pickling acid.

**FIGURE 2**

Typical Elution Profile
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