Acid Recovery with Diffusion Dialysis


The minimization of industrial waste and the recovery and reuse of chemical resources is the most cost-effective way to abate pollution for many industries. The costs and liability associated with routine disposal have a major impact on a shop’s operation. This trend will continue. In addition, consistency of product is dependent upon bath uniformity. Diffusion dialysis can be used to recover mineral acids, such as hydrochloric, nitric, hydrofluoric, phosphoric and sulfuric acids from acid solutions containing dissolved metals.

WHAT IS DIFFUSION DIALYSIS?

Diffusion dialysis is a membrane separation process (see Fig. 1). For diffusion, material in high concentration (the solute) moves to an area of low concentration using the thermal energy of the system. Dialysis is the process in which a solute permeates through a diaphragm. When used together and combined with a selective diaphragm, certain solutes can be separated from others.

An ion exchange membrane makes an excellent selective diaphragm for diffusion dialysis. The acid solution (solute) is on one side of the membrane; deionized water (solvent) is on the other. The acid passes or diffuses through the membrane into the water. Movement is based solely on the difference in concentration on either side of the membrane.

Electroneutrality must be maintained in each ion exchange membrane compartment. This physical law allows for no imbalance in ionic charge. When a negative charge moves across the membrane, a negative charge must move in the opposite direction or a positive charge such as hydrogen, must follow.

Anion membranes are used for the recovery of mineral acids from an acid salt environment. The choice has also been influenced by the membranes’ strong affinity for acid absorption without salt absorption.

The anion membranes in theory repel and otherwise prevent certain positive ions from passing into the recovery stream. The process works because the membranes don’t act as a significant barrier for hydrogen. The hydrogen ion is too small and mobile for the membrane to inhibit its movement with an anion. The anions (chlorides, sulfates, nitrates, phosphates, etc.) migrate in response to the difference in concentration. Hydrogen also moves because of this gradient. As this happens the law of electroneutrality is satisfied. Both ionic species can then exchange through the membrane into the recovery side of the system.

Metal ions are much larger than hydrogen. They are repelled and can’t pass through the membrane. Size and ionic charge keep the unwanted mate-

Fig. 1. Diffusion dialysis cell pair.
Acid recycling flow diagram.

Filter

Water

In

Acid

Water

Acid

Membrane Stack

Pump

Acid Bath

Metal Contaminants

To Treatment or Recovery

Recovered Acid

Recycled To Bath

Acid Recovery Module

Water

Acid

Fig. 2. Acid recycling flow diagram.

rial on the spent side of the membrane. Membranes are not 100% efficient. This inefficiency is known as "leakage." Leakage is a consideration in system design that affects recovery rate in a complex interaction of concentration, membrane area and flow. During design, conditions are optimized to provide the desired results at minimum cost with the widest possible operational window.

DIFFUSION DIALYSIS IN OPERATION

Acid is pumped from the active process tank or bulk storage tank to a storage reservoir in the recovery module (see Fig. 2). It flows from the storage reservoir through the system on one side of the anion exchange membrane stack. Water flows from a similar reservoir in the opposite direction on the other side of the membrane. Level controls and pumps maintain the proper liquid levels in the storage reservoirs. The acid diffuses into the clean water producing a clean acid solution at nearly the same normality as the original acid. The spent stream still has the metal and other contaminants and a small amount of the original acidity. The recovered acid is transferred to the operating bath. The spent stream is sent for further treatment, volume reduction or recovery.

The operating tank needs to be monitored for acid strength. Additions must be made to compensate for the percentage of acid that was not recovered. This can be done manually or automatically depending on the size of the operating window and the degree of change.

SYSTEM SIZING AND APPLICATION

To size a system properly, the removal rate should be equal to or greater than the rate of contaminant introduction. In practice it appears that the minimum requirement is a system sized to process the entire tank volume in the same time interval that dumping had been traditionally scheduled.

For some situations, this can be an over simplification. The user or proprietary chemical manufacturer can do things to the basic chemistry that impacts recovery and metal removal efficiencies. Changes in recovery rates from organic inhibitors, oil and grease and anionic metal complexes have been monitored. For safe applications, design expectations are confirmed through pilot testing. These tests have yielded acid recovery efficiencies as high as 99% with 98% metal removal obtained. In the manufacturing environment, 80–95% of the initial acid can be recovered economically with 60–90% of the metal contaminants removed. As an example, Table I relates results of hydrochloric acid chromium rack strip and sulfuric acid anodize applications.

The technology has been effective for hydrochloric and nitric acid rack strips as well as mixtures of nitric and hydrofluoric acids, ferric chloride etchants, nitric-chromic passivation solutions, sulfuric acid anodizing solutions and other acid solutions. Most industrial acids and acid mixtures are good candidates.

Membrane life is excellent and not a significant factor in the operational economics except when dealing with certain highly concentrated acids. Membranes can last as long as 20 years.

EQUIPMENT FEATURES

Systems are compact and use space efficiently. A 100-gallon-per-day system would occupy about 15 square feet. They can be located near the related processes minimizing installation costs.

Operation is highly automated without much instrumentation. Systems run unattended 24 hours a day, 7 days a

Table I. Typical Recovery Results

<table>
<thead>
<tr>
<th></th>
<th>Acid (N)</th>
<th>Aluminum (ppm)</th>
<th>Chrome (ppm)</th>
<th>Copper (ppm)</th>
<th>Iron (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Rack Strip</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Concentration</td>
<td>4.7</td>
<td>NA</td>
<td>900</td>
<td>NA</td>
<td>1700</td>
</tr>
<tr>
<td>Recovered Concentration</td>
<td>4.3</td>
<td>NA</td>
<td>200</td>
<td>NA</td>
<td>400</td>
</tr>
<tr>
<td>Spent Concentration</td>
<td>0.4</td>
<td>NA</td>
<td>700</td>
<td>NA</td>
<td>1300</td>
</tr>
<tr>
<td>Removal Efficiency</td>
<td>91.5%</td>
<td>NA</td>
<td>77.8%</td>
<td>NA</td>
<td>76.4%</td>
</tr>
<tr>
<td>Sulfuric Acid Anodizing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Concentration</td>
<td>3.4</td>
<td>5200</td>
<td>NA</td>
<td>35</td>
<td>150</td>
</tr>
<tr>
<td>Recovered Concentration</td>
<td>3.0</td>
<td>30</td>
<td>NA</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Spent Concentration</td>
<td>0.4</td>
<td>5150</td>
<td>NA</td>
<td>34</td>
<td>140</td>
</tr>
<tr>
<td>Removal Efficiency</td>
<td>88.2%</td>
<td>99.0%</td>
<td>NA</td>
<td>97.1%</td>
<td>93.3%</td>
</tr>
</tbody>
</table>
week. The only maintenance required
is the periodic cleaning or replacement
of prefilters. Constant use assures
maximum system use. This minimizes
the system size and the capital invest-
ment.

Utility requirements are small. No
chemicals are required. Although
deonized water is the recommended
solvent, city water may be used. The
only use of electricity is related to
solution transfer. Operating cost is
very low.

The extremely low pressure feed
puts minimal stress on the stack com-
ponents. This further enhances the
reliability and longevity of the system
components.

**BENEFITS**

The typical payback for a diffusion
dialysis recycling system generally
ranges from 3 months to 2 years. It is
most rapid if acid wastes are currently
being manifested and hauled away.

Diffusion dialysis for acid recycling
has many benefits. It reduces acid
purchases by up to 95%. The process
eliminates or lessens neutralization or
hazardous waste hauling costs and
related liability. Toxic chemical use
is reduced and the required reporting, and
handling of hazardous materials and
associated labor is greatly reduced.

Consistent bath strength yields greater
product uniformity and better quality.
Diffusion dialysis can dramatically
improve a facility’s quality and eco-
nomic performance.

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