Using Weak Acid Ion Exchange Resin to Neutralize & Remove Metals from Plating Rinsewaters – An Operational Perspective

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Operating experience using a sodium-form weak acid ion exchange resin to both neutralize and remove heavy metals from rinsewater is summarized. The technique utilizes the capability of the weak acid resin to be reneutralized with sodium hydroxide many times prior to regeneration with acid to remove accumulated metals. Data relating to resin capacity are given based on five installations in various electropolishing facilities. Operational issues, such as maximum metal concentrations handled, volumes of spent metal regenerant created, resin attrition, and automating reneutralization are covered.

For more information contact: Bruce Bishkin, PE APSI Inc. 205 E. Butterfield Rd. Elmhurst, IL 60126 USA electrolyteman@liquidsolid.com Operating experience has been acquired for the weak acid ion exchange resin operating to treat metal bearing wastewater streams. The mode employs simultaneous removal heavy metals and adjustment of pH. Experience includes 4 systems operating in printed circuit board manufacturing, 5 systems in electropolishing and 1 system in general job-shop plating. Total operating experience has reached approximately 35 years. The technology is novel and has met with satisfaction among these users. Valuable information on durability, operability has been gathered. This paper reviews some of the information gathered.

Chemistry

The common weak acid (polyacrylic or polymethacrylic) ion exchange resin can be converted to the sodium form, as given by the equation (1)

 $R-COO^{-}Na^{+} + H_2O(1)$

where R represents the backbone of the resin. In this form, when water bearing dissolved metal is passed over the resin, the exchange described in equation (2) will take place, removing the metals from the water.

 $2(R-COO^{-}Na^{+}) + M^{++} \rightarrow 2(R-COO^{-})M^{++} + 2Na^{+}(2)$

In addition, hydrogen ions in the water can exchange with resin according to equation (3), adjusting the pH of the water.

 $2(\text{R-COO}^{-}\text{Na}^{+}) + \text{HCl} \rightarrow \text{R-COOH} + \text{Na}^{+}\text{Cl}^{-}(3)$

The reaction in equation (3) will take place if the pH of wastewater is less than the corresponding pH of resin shown in Fig. 1 with a resultant rise in pH of effluent wastewater.



Fig. 1 pH v. Capacity of Typical Weak Acid Resin¹

As a result effluent wastewater from a column of such resin will have a pH higher than or equal to the resin and will be substantial free of metals.

Acidic Wastewaters

Rinsewaters from many common plating operations are quite acidic in nature and contain only small quantities of heavy metals. Our operating experience has shown that reaction (3) will predominate in many cases. The strategy of operating the resin column with simple reneutralization without regeneration allows the resin to continue operating without creating spent regenerant. Typically the column can be reneutralized between 30 and 60 times before regeneration is necessary.

Reneutralization

When pH of effluent falls below 6.0 the operator is alerted that resin column must be reneutralized. Column of resin must be taken out of service at this time. An automated reneutralization scheme has been developed that utilizes no fresh water and creates no waste effluent. Water is recirculated downflow through the resin column with pH measured on the effluent water. Sodium hydroxide is injected on the influent side of the column until a pH of 8.5 or greater is achieved. Water is continued to be recirculated and sodium hydroxide injection is reinitiated if pH again falls below 7.5.

Regeneration

Ultimately, enough heavy metals concentrate on the resin to hinder its ability to neutralize wastewater. This is noticed by the small amount of sodium hydroxide required to reneutralize. See above. Stripping of heavy metals is easily accomplished with the use of a strong acid. Nearly stoichiometric regeneration can be achieved. Typical acids used are nitric, sulfuric, sulfamic or hydrochloric at concentrations from 5 to 15% by weight. After regeneration with acid, the resin column must be thoroughly rinsed. Multiple rinses are recaptured and reused in the next regeneration. Typically, rinses are stored in 55 gallon drums. We have recommended that 6 drums be used with the strong acid added to the first rinse from last regeneration to create new regenerating solution. A small amount from the regenerating solution must be disposed of (typically off-site by others). Fresh water is added to the last rinse to keep it clean. Scrupulous attention to the above process can produce a concentrated acid of about 5% by metals. This is comparable to the concentration of metals from most filter cake from metal hydroxide precipitation.

Complexing agent	Cu	Ni	Zn	Cr	Cd
sodium gluconate	good	good	good	good	not tested
citric acid	good at low concentrations	good at low concentrations	not tested	good	not tested
ethanol amine	good	not tested	not tested	good	not tested
EDTA	no removal	no removal	no removal	not tested	no removal
tartaric acid	good removal	good removal	not tested	not tested	not tested
malic/succinic acid	not tested	no removal	not tested	not tested	not tested

1 able 1 – Removal of Metal with Complexing Ager
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Metal Removal Performance

Effluent concentrations of heavy metals have generally been very good although controlled testing has not been done. Properly running systems in electropolishing operations achieve chrome, nickel and copper concentrations in the range of 0.1 to 0.2 mg/l each. Units operating in the printed circuit board industry consistently achieve 0.2 mg/l copper in the presence of monoethanolamine. Units operating where citric acid pickling is done can still achieve good copper, removal possibly due to the large amount of iron also encountered in that wastewater. Results are shown in Table 1. Total metals removed before regeneration is needed amounts to approximately 1.5 meq/ml of resin.

Wastewater streams with total heavy metal concentrations above 100 mg/l have been treated by the above system but can exhibit heavy metal hydroxide precipitation at the top of the resin column, discussed in more detail below.

Neutralizing Performance

Although the maximum neutralizing capacity of the weak acid resin is up to 3.5 meq/ml (meq = mg mole equivalent), the practical reneutralizing capacity has been found to be much less. This is due to need to avoid running the resin down to fully the acidic conditions which would allow all the heavy metals to be stripped-off into the effluent water. Also, as more heavy metals build on the resin, between regenerations, there is less total neutralization capacity available. A practical neutralizing capacity per cycle would be closer to 1 meq/ml. In terms of sodium hydroxide (dry basis) this means 40 grams/liter of resin (2.5 lbs/cubic foot, dry basis). Attempts to neutralize the acidity of feed streams prior to treatment has not met with uniform success because of the possibility of creating large quantities of metal hydroxide particulate, which clogs the pre-filtration system.

Preferred Operating Configuration

All systems set up to this date have been constructed with the configuration illustrated in Fig. 2. They include

- pre-filtration to 5 microns
- lead weak acid resin column
- pH monitoring between columns
- lag weak acid resin column

All resin columns have been set-up for downflow service, downflow reneutralization, and downflow regeneration. Approximately 40% freeboard area has been provided for a reverse flow backwash. The lag and lead columns have been of identical design and are interchangeable. Reneutralization and backwashing are typically only required of the lead column since by the time the wastewater has passed through the first column it is substantially free of metal and neutral in pH. Columns must be taken off-line to be backwashed, regenerated, or reneutralized. When a column is taken-off line for such operations, the other column is operated alone on the wastewater stream.

When the lead column is finally regenerated it is placed in the lag position and the formerly lag column is placed in the lead position. In this way, each column is used to its maximum extent without compromising total system performance with respect to metal removal.



Fig. 2 – General Configuration

Resin Life

Unlike many other ion exchange resins the weak acid resin is one of the most durable available for metal finishing environments. Since it is hydrophilic it does not collect oil. Its carboxylic functionality is resistant to moderate quantities of oxidizing agents such as chlorine, persulfates, chlorates, nitric acid to 20%, and hydrogen peroxide, unlike iminodiacetic functionalities. Consequently we have had virtually no fouling or loss of functional sites. In fact, the resin never needs to be replaced *per se*.

Resin attrition is the major concern affecting resin life. This is due to dramatic swelling of the resin when converted from the hydrogen to the sodium form of the resin. To minimize resin attrition, a macroporous type resin has been employed. This prevents the swelling from creating undo mechanical stress on the particle and reduces attrition. The penalty is that macroporous resins have less capacity than their gel-type counterparts. Thus there is a balance between capacity and resin life. As mentioned above, the resin thus far employed in these systems has a capacity of 3.5 meq/ml. This is minimally macroporous weak acid resin and exhibits significant attrition.

Attrition creates resin bead fines which are backwashed from the column before every reneutralization. Consequently the bed volume is reduced by approximately 0.2% on every reneutralization. We have estimated that the average installation will loose approximately 20% of its resin to attrition each year.

Operating Cost

We have determined that the major operating costs for the weak acid resin system include:

- sodium hydroxide for reneutralization
- spent acid disposal
- pre-filter element replacement and disposal
- regenerant acid
- resin replacement
- pH probe replacement

A qualitative comparison of operating costs for the weak acid system versus the corresponding metal hydroxide precipitation system is shown in Table 2 below.

Cost Factor	Weak Acid	Hydroxide Precipitation
sodium hydroxide	low	higher
spent acid disposal	high	none
filter replacement	low	none
final polishing filtration	none	variable
flocculent usage	none	low
sludge disposal	minimal	high
probe maintenance	low	moderate
operator involvement	moderate	high
space requirement	very small	large
initial investment	moderate	moderate to high

 Table 2 – Cost Comparison

Sodium hydroxide usage is stoichiometrically equal to quantity of net acidity in the incoming wastewater. Since average pH of effluent is less than 8 we estimate that the quantity of sodium hydroxide used is less than would be needed for hydroxide precipitation which often requires pH values of 9 to 10.

Disposal costs are related to the concentration of metal that can be achieved in the spent acid. Careful management of spent regenerant rinses has demonstrated that 5% metals by weight is an achievable goal. The corresponding metal hydroxide precipitation system would have lower disposal costs because of the solid nature of the filter cake waste. Pre-filters have typically been cartridge type which present a minor disposal cost.

Operational Problems

The biggest problem relating to the operation of the weak acid system is the build-up of metal hydroxide at the top of the resin column. This problem becomes more pronounced as the influent concentration of metals increases. Ironically, the problem is reduced in the presence of complexing agent described in Table 1.

Hydroxide precipitation is not predicted by equation (2) at the head of the article because the resin theoretically contains no hydroxides. It is assumed that the bound water in the resin is the source of hydroxides and that hydroxide build-up at the front of the column is unavoidable.

Presently this problem is handled by thorough backwashing of the resin before each reneutralization. It is further believed that reneutralization with a mixture of sodium hydroxide and sodium gluconate could possibly alleviate this problem although the scheme has not been tried.

Operability

It is the author's opinion that the single biggest barrier to the general acceptance of ion exchange methods for the treatment of industrial wastewaters has been their typical lack of operator feedback concerning the condition of the resin column(s). This is addressed by the use of clear ion exchange columns, or windows in larger ion exchange columns. With clear columns the operator gets feedback concerning the condition of resin in Table 3 below.

Condition	Indicator
successful backwash has	resin is completely
been conducted	fluidized
resin is plugged or fouled	layer of sludge on top of
	resin
resin strainer has broken	resin is lost
resin inadequately	resin volume has not
reneutralized	swollen
resin is inadequately	resin has not returned to
regenerated	cream color

Table 3 – Visual Operator Feedback

Visual feedback has provided critical support for operator training that has allowed the weak acid ion exchange system to run without problems even when operated by newly trained personnel.

Proprietary Nature

The method for operating a weak acid ion exchange method is subject to U.S. Patent owned by APSI Inc.²

Summary

The weak acid system has proven to be an economical and reliable method for specific small plating operations to achieve wastewater treatment. Furthermore, the system has the capability to handle wastewaters with certain complexing agents in an efficient manner. We expect that acceptance of this method will grow in the future.

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¹Kunin, R., "Ion Exchange Resins" Krieger Publishing, Huntington, N.Y., 1972

²D. B. Bishkin, U.S. Patent No. 6,270,675 (2001)