



APPLICATIONS BULLETIN

**PRODUCT PURIFICATION
RESOURCE RECOVERY
POLLUTION CONTROL**

Product Purification/Resource Recovery Pollution Control by Ion Exchange

Ion exchange techniques have been practiced for most of the twentieth century. The ion exchange resins developed to serve the needs required in the domestic and industrial markets were developed to react with the ions found in most common water supplies.

The most prevalent ions found in water include calcium, magnesium, sodium, sulfates, chlorides, bicarbonates, carbonates, and silica. Several other substances are sometimes found in water but usually in trace quantities, so not much application work has been directed towards them. These include iron, manganese, copper, ammonia, hydrogen sulfide and fluoride.

Following World War II, the growth of the petrochemical industry encouraged the use of exotic materials for more sophisticated chemical reactions. The effluents from these industrial operations and from the growing electroplating industry and other metal finishing operations presented a tremendous increase in metal and toxic organic ions in industrial effluents. This problem increased with the growth of the semiconductor and printed circuit board industries. Since these substances are not normally found in water supplies, there was very little information about how to use ion exchange resins to remove them from waste streams and it was found that traditional resins had only limited capabilities.

As industry and its waste volume grew, it became apparent that these ionic materials had to be removed from the waste water discharged by these industries. Today it is recognized that many of these materials are also relatively valuable. In some cases, therefore, it is economically rewarding to recover these materials. Most of these exotic substances are listed in the ResinTech product selection guide.

Over the last two decades much has been accomplished in developing ion exchange resins with greater capabilities to remove these substances. In response to growing environmental legislation and enforcement, there has been an increase in the need for economically removing these materials from process plant effluents. Recently, product recovery has become more widely recognized as a way of reducing waste treatment costs. Although a wide variety of specialized ion exchangers have been available for several years, until recently, applications technology, including product performance characteristics, was not well developed.

ResinTech has developed an application technology resource group that includes state-of-the-art laboratories, a dedicated group of scientists, and software developers. This technology is put to use whenever product or process recommendations are requested. This insures that our customers get the best solutions to their problems.

Many plants exist today that were built before environmental pressure or the technology for recovery at economical rates existed. Some companies want to remove certain materials from their plant discharges because of the economic benefits they can derive, while others are primarily driven to remove the same materials from essentially the same waste water streams because of environmental legislation. The technology is the same in either case.

Most ion exchange resins have ionic capacities that are equivalent to an equal volume of caustic or acid of a 5-10 percent concentration. Ion exchange is a regenerable process. The typical regeneration process (developed for traditional treatment) requires about 100 gallons of water per cubic foot of resin (15 bed volumes). Regardless of whether the goal is for compliance for profitable recovery, the operation is optimized when the ratio of regeneration waste water to the amount of water processed during the service cycle is minimized.

In order to get the most out of the ion exchange resin process, three steps should be considered carefully:

1. Optimize the process itself to take maximum advantage of the use of ion exchange resins.
2. Select the best resin for the specific situation.
3. Develop an optimal operating procedure for the performance of the ion exchange resin for the specific application.

These three steps are best done in the order in which they are stated. For example, as is stated in one of the case histories, ResinTech SIR-300 has the ability to remove copper in the presence of calcium and magnesium ions. Therefore, ResinTech SIR-300 would be ideal for removing copper from a waste stream containing copper in small quantities even in the presence of considerable quantities of hardness (calcium and magnesium).

Other resins, such as ResinTech CG8, also have a high affinity for copper but will remove calcium and magnesium to the same degree. The use of a standard cation resin like ResinTech CG8, while able to achieve the goals of copper reduction, would not give as high a throughput when treating a water containing hardness. ResinTech SIR-300, on the other hand, by ignoring the calcium and magnesium, would give much greater throughputs. So unless something was done to avoid the presence of hardness in the water used in the process, ResinTech SIR-300 is the clear choice. However, if the process were designed in such a way that the water used was free of ordinary hardness, then ResinTech CG8 (which is a less expensive product), would provide greater throughput capacity than ResinTech SIR-300. This could be achieved by installing a common water softener on the raw water makeup line to the process.

Not all situations are as straightforward as this, nor is it always feasible to accomplish the process modifications in as simple a manner as adding a common water softener.

All three of the process steps and selections must be reviewed properly to obtain maximum benefit. It is important that your resin supplier provide the necessary technical support for both process and application optimization.

The following case histories deal with instances where different parts of the above mentioned three processes were key to successfully meeting the customer's performance objectives.

Case History I (A)

Copper wastewater from a circuit board manufacturer

THE PROBLEM

An electronics company located in southern New England faced the problem of removing copper from the rinse water effluent from their ammonium persulfate etching process in their circuit board line. The circuit board rinsing operation was carried out with tap water supplied by the municipality which contained the following ionic contaminants:

City water used for rinsing (all constituents in ppm as CaCO₃)

Cations		Anions	
Calcium	45	Sulfate	17
Magnesium	22	Chloride	47
Sodium	30	Bicarbonates	33
Total Cations	97	Total Anions	97
		Silica	4

The circuit boards were etched with a solution of ammonium persulfate. This resulted in copper being dissolved into the etchant bath. Subsequent rinsing of the parts resulted in the addition of copper salts to the rinse water. Copper concentrations in the rinse water varied depending on the workload, the shape factor, and the amount of rinse water used. The typical copper loading was 4 ppm of copper as copper and an average flowrate of 5 gallons per minute (gpm).

ANALYSIS OF THE PROBLEM

The average copper concentration was only 4 ppm, about 4 percent of the total ions in solution. A normal or non-selective resin could have been used for removing the copper but it would have also removed calcium and magnesium (and to a lesser degree, some of the sodium) along with the copper. The end result would be that less than 5 percent of the total resin capacity would be utilized by copper due to competition from the “pre-existing” ions from the municipal water.

SOLUTION

ResinTech SIR-300 is a chelating resin with a very high affinity for copper and a total capacity that is about the same as standard resin. Unlike a standard “non-selective” resin, it is able to remove copper selectively in the presence of most other ions such as calcium, magnesium and sodium. In this case, the use of the selective resin increased the throughput per unit volume of ion exchange resin by a factor of 20 because copper utilized over 90 percent of the resin’s capacity despite the relatively high levels of calcium, magnesium and sodium.

Case History I (B)

Each installation is unique and has to be looked at on its own basis. All options must be weighed.

PROBLEM

In an installation similar to Case History I (A), the relative loading of copper, calcium and magnesium ions was almost the same. However, in this case, a water softener had been installed to treat all incoming water to the chemical process area. Therefore, the calcium and magnesium ions were all removed before the rinse tank and replaced with an equal number of sodium ions. The problem to be addressed now changed to the removal of copper from the rinsewaters in the presence of a larger concentration of sodium ions.

ANALYSIS OF THE PROBLEM

Copper has a much higher affinity than sodium for standard variety cation exchange resins. In the absence of hardness, a standard sodium form strongly acidic or weakly acidic (if the pH is greater than 6.5) cation resin will perform as efficiently as a selective resin when removing copper against relatively higher levels of sodium. In this particular case, the copper will also utilize the major portion of the capacity of the standard resin. It should be noted that in very high sodium waters or where it is not practical to pre-soften the water, a selective resin, such as ResinTech SIR-300, would be more effective.

SOLUTION

Since the resins are to be regenerated, ResinTech WACMP, a standard weakly acidic cation resin, was chosen because it has very high regeneration efficiency for copper and is regenerated at nearly 100 percent efficiency. If the resins had instead been used on a one-time throw-away basis (such as in a final polishing operation) then a less expensive resin like ResinTech CG8 would have provided about the same removal capacity at a lower cost.

Case History II

Treating contaminated combined rinse waters

PROBLEM

A plating shop was faced with the problem of eliminating or treating the contaminated rinse waters being discharged from their plant. The plant was configured so that each plating tank was followed by a “still” rinse which served occasionally as a reclaim tank to replace dragout and evaporation losses. Each still rinse was followed by two flowing water rinse tanks. Each had its own inlet, but all the effluents were combined before discharge. The combined rinse effluent contained traces of the chemicals used for the plating operation. This consisted of various acids, copper, nickel, chrome and various salts. The plating baths were replaced on a regular basis due to contamination, which ultimately interfered with the quality of the plating line.

ANALYSIS OF THE PROBLEM

In addition to the metallic contaminants, the wastewater contained the non-hazardous ions from the city water used to supply water to the rinse tanks. Although non-hazardous, these ions compete for and occupy ion exchange sites and thereby reduce the throughput capacity from a charge of resin. These ions can build up in concentration, having an adverse effect on finished work quality and can increase bath replacement frequency.

SOLUTION

The recommendation in this case was to use demineralized water to supply all water needs to the plating line, including the initial fill of the rinse tanks, still rinses, and to make up the plating bath chemicals.

Demineralized water was also to be used for the flowing rinses. The rinse waters were not recirculated. Instead, the rinse configuration was changed to a two-stage countercurrent rinse. Since demineralized water was used, bath contamination from tap water was avoided and the solution replacement frequency was significantly reduced. In addition to changing to countercurrent rinsing, fog style spray rinses were placed above the two rinse tanks. This changed the rinsing operation into a four-stage, countercurrent rinse and enabled a 90+ percent reduction in rinse water. Makeup for dragout losses from the plating baths was accomplished using only the still rinses, which now run at a higher concentration, reducing the demand for makeup chemicals. Occasional discharge and batch treatment of the still rinses replaced the need for a continuous wastewater overflow from the rinsewater treatment system.

The demineralizers operated on tap water and, therefore, only simple neutralization of the regenerant waste was required and the neutralized wastewater was discharged to the sewer.

Case History III

Purification of contaminated Hydrochloric acid

PROBLEM

A bulk storage tank containing concentrated technical grade (water white) hydrochloric acid had become fouled with iron which turned the acid to a tea-like color.

ANALYSIS OF THE PROBLEM

Iron forms a highly colored chloride complex (FeCl_4^{-1}) in the presence of hydrochloric acid. This complex turned the color of the acid which should have been “water white” to a strong tea-like color. The (FeCl_4^{-1}) complex has a tremendous affinity for the chloride form of ResinTech SBG1 ion exchange resin. ResinTech SBG1 removes the colored complex in exchange for an equivalent amount of chloride thus, maintaining acid purity.

SOLUTION

The hydrochloric acid was re-purified by filtering it through a bed of ResinTech SBG1. When the resin became saturated with iron, it was regenerated with water in a two-step process which involved draining the remaining acid out of the column by using pressurized air and then rinsing the column with demineralized water.

The demineralized water lowered the concentration of the remaining acid in the column to a level which caused the (FeCl_4^{-1}) complex to decompose to ferric chloride Fe^{+3} and

Cl^- ions. This caused the iron to leave the resin bed as soluble ferric chloride (FeCl_3). After the ferric chloride, which has a similar appearance to the tea-colored complex, was removed from the bed and the rinse (regenerant) water became colorless, the resin was ready to be returned to service. First air was used to blow the water out of the column so as not to dilute the incoming hydrochloric acid during the next treatment cycle. Then the unit was refilled with the contaminated acid and placed back into the service cycle.

In this case a relatively small amount of resin was all that was required. The resin was placed directly in the service line between the acid storage tank and the chemical process where the acid was used. The process was batch type as opposed to a continuous flow type. The acid was treated and regenerated in between process “batches.” The acid storage tank was drained to near empty without disrupting service. Before refilling the tank, the remaining contaminated acid was pumped through the resin bed into a smaller storage vessel. The acid storage tank was then cleaned out, partially refilled with the cleaned acid, refilled with fresh acid and returned to normal service. This approach eliminated the expense to either dispose of and treat the contaminated acid or to use a much larger resin bed to treat the entire acid storage tank at one time. The demineralized water was supplied by “exchange tank demineralizers” supplied by a local service company.

Case History IV:

Zinc is discharged from a metal finishing waste treatment plant

PROBLEM

A micro-electronics company in the Midwest had a problem with zinc effluent in the discharge from their combined metal finishing-waste treatment operation. The final treatment process involved precipitation, clarification and final filtration. Heavy metals and hazardous organics were reduced to acceptable levels. However, trace levels of zinc occasionally rose above the allowable limits.

ANALYSIS OF THE PROBLEM

Here the problem was caused by small levels of phosphates in the water that complexed with the zinc. The water was relatively free of hardness and other divalent ions.

SOLUTION

The effluent was treated by reducing the pH sufficiently to break the phosphate complex. Then the zinc was removed using ResinTech CG8 strong acid cation resin. By combining pH control and the use of sodium and hydrogen cycle ResinTech ion exchange resins, the zinc has been removed continuously below the effluent standard set by the EPA. Compliance has been maintained at 100 percent for 18 months and zinc loadings on the resins have averaged over 70 percent of the total capacities. This justified the use of a "non-selective" resin. In this case the most economical approach was based on using lower-cost non-selective resins.

Case History V:

Copper removal from a mixed metal finishing line

PROBLEM

Following the final treatment of the combined effluent from a metal plating operation which involved chlorine destruction of cyanides, it was found that copper was coming through at levels above the permit requirements, at times reaching several ppm.

ANALYSIS OF THE PROBLEM

Several hundred ppm of other dissolved metals were also present, including 80 ppm of hardness. The copper was present in an amount equal only to 1/2 to 1 percent of the total cations in the water supply. At first glance, ion exchange appeared to be uneconomical because of the requirement of removing 99 other metal ions for each ion of copper.

SOLUTION

ResinTech SIR-300, which is selective for copper even in the presence of hardness ions, came to the rescue. Despite the unfavorable concentrations, ResinTech SIR-300 provided complete removal of copper with little or no reduction in hardness and other ions and provided over 20,000 bed volumes between regenerations. Initially it was decided to dispose of the resin rather than to regenerate it when it was found that the throughput capacities were so high that resin replacement and disposal (solid) were less expensive than operating a regeneration process and disposing of the regenerant wastewater. The resins could be disposed of at a total treatment cost of less than \$3.00 per thousand gallons of water treated.

For more information, call: (410) 420-8001



COMPLETE ION EXCHANGE RESINS AND REGENERATION SERVICES

Recommended Resins for Specific Contaminants

CHEMICAL CONTAMINANT TO BE REMOVED	APPLICATION NATURE OF SOLUTION	RECOMMENDED RESIN	IONIC FORM	EFFECTIVE pH RANGE	COMMENTS
Aluminum	10-15% phosphoric acid	CG8-H/CG10-H	H	pH > 0	Regen w/ 20% H ₂ SO ₄ (also removes Fe)
	10-15% phosphoric acid	SACMP-H	H	pH > 0	Used for improved resistance to breakage
	All waters	CG8	Na/H	pH > 0	Works best at low pH
Ammonia & amines	Alcohol solutions	CG8-H/CG10-H	H	pH > 7	Acid regeneration
	Alcohol solutions	WACMP	H	pH > 7	Acid regeneration (only works when pH is > 7)
	Soft water	CG8-H	H	pH > 7	Resin swells in alcohol
Ammonia	Soft water	CG8	Na	pH > 5	Salt regeneration (limited capacity/poor removal)
	Hard water	SIR-600	Na	pH > 5	Salt regeneration
Antimony (Antimonite)	Concentrated hydrochloric acid	SBG1/SBG2	Cl	pH < 1	Forms chloride complexes/regen with water
Arsenic (Arsenate)	Soft or Hard water	SBG1/SBG2	Cl	pH < 10	Must be oxidized to arsenate
	Soft or Hard water	SBG1/SBG2	Cl	pH < 10	Present as anion, salt regeneration
	All waters	SIR-900	—	pH 6 to 8	
Barium	Soft or Hard water	CG8/CG10	Na	pH > 2	Salt regeneration
Boron (Borate)	Irrigation Supplies	SBG1	Cl	pH < 10	
	Semiconductor Plants	SIR-150	FB	pH > 3	Remove boron to nondetect levels
Cadmium	Soft or DI water	CG8	Na	pH > 2	
Calcium	Hard water	WACMP	Na	pH > 6.5	
	Hard water	SIR-300	Na	pH < 6.5	
	Cadmium cyanide plating effluents	SBG1/SBG2	Cl	pH < 10	
	Brine Purification	SIR-500	Na	pH < 11	Also removes other hardness ions
Cesium	All waters	SIR-600	Na	pH > 5	Salt regeneration (keep flow below 2 gpm/sqft)
Chromium Cr ³⁺	Soft or Hard water	CG10/SACMP	Na	pH > 4	Can be salt regenerated (also removes hardness)
	Soft or Hard water	WACMP	Na	pH > 6	Sodium form operation (also removes hardness)
	Hard water	SIR-300	Na	pH > 1.5	Best choice for high TDS solutions
Chromium Cr ⁶⁺	All waters	SBG1/SBG2	Cl	pH < 7.0	Salt regeneration
	All waters	WBMP(SO ₂)	FB/SO ₂	pH < 6.0	Best choice for regenerable applications
	All waters	SIR-700	SO ₂	pH < 6.0	Best choice for single use applications
Cobalt	Soft water	CG8	Na	pH > 2	Cannot remove cobalt past hardness break
	All waters	SIR-300	Na	pH > 1.5	Cobalt is non-ionized at high pH
Copper	Copper cyanide plating	SBG1/SBG2	Cl	pH < 10	
	Hard water	SIR-300	Na	pH > 1.5	
	Hard water	WACMP	Na	pH > 6.5	
	Soft water	CG8	Na	pH > 2	
Cyanide	Cyanide waste treated with ferrous salts	SBACR	Cl	pH > 7	Salt regenerated
	Hydroxide cycle	SBG1/SBG2	OH	pH < 11	
Ferrocyanide	Treated cyanide waste	SBACR	Cl	pH < 10	Salt regenerated
Fluorine (fluoride)	Waste water	SBG1/SBG2	Cl	pH < 10	
	All waters	SIR-900	—	pH 6 to 8	
Gold	Gold cyanide plating	SBG1/SBG2	Cl	pH < 10	Chloride cycle (not regenerated)
	Acid Gold plating effluents	SIR-400	H	pH < 10	
Iron	Weakly acidic solutions	CG8	Na	pH > 2	Intermediate & weak acids up to phosphoric
	Concentrated hydrochloric acid	SBG1	Cl	pH < 1	Regenerated by water rinse
Lead	Hard or Soft water	CG8/WACG	Na	pH > 2	Sodium or calcium form
	Waste water	SIR-300/WACG	Na	pH > 1.5	Preferred where mixed metals are present
	All waters	SIR-900	—	pH 6 to 8	
Magnesium	Brine Purification	SIR-500	Na	pH < 11	Also removes other hardness ions
Manganese	Potable water	CG8	Na	pH > 2	Sodium form (Mn is removed with other hardness)
Mercury (anionic)	Tap water, all pH ranges	SIR-200	Cl	pH < 10	SIR -> 1-10 ppb, -WBMP/CG8 -> 50 - 150 ppb.
Mercury (complexed)	When present as organic complex	SIR-200/SIR-300	Na	pH < 10	
Mercury (cationic)	Tap water, all pH ranges	WACMP/SIR-400	Na	pH > 4	In absence of Chlorides
Molybdenum	Anionic complexes	WBMP/SIR-700	SO ₂	pH < 7	
Nickel	Hard water	SIR-300	Na	pH > 1.5	Metal selective (does not remove hardness)
	Soft water	SIR-500	Na	pH > 1.5	Metal selective (also removes hardness)
	Hard water	WACMP	Na	pH > 6.5	Sodium form (also removes hardness)
	Soft water	CG8	Na	pH > 2	Limited to low TDS soft water
Nitrate	High sulfate waters	SIR-100	Cl	pH < 10	
	Low sulfate waters	SBG1/SBG2	Cl	pH < 10	
Organics (natural)	Decolorizing surface waters	SIR-22P	Cl	pH > 5	Can be salt regenerated
	Decolorizing surface waters	SBACR	Cl	pH > 5	Can be salt regenerated
Potassium	Wine stabilization	CG8	Na	pH > 5	Can be salt regenerated
Palladium	Anionic complexes	SBG1/SBG2	Cl	pH < 10	
Phenol	Waste water	WBMP	FB	pH < 4	
Phosphate	Soft or hard water	SBG1P/SBACR	Cl	pH < 10	Single bed salt regeneration or DI
Platinum	Anionic complexes	SBG1/SBG2	Cl	pH < 10	
Radium	Soft or hard water	CG8	Na/Ca	pH > 2	Can be salt regenerated
Selenium (selenite)	Soft or hard water	SBG1/SBG2	Cl	pH < 10	Single bed salt regeneration or DI
	Soft or hard water	SBG1/SBG2	Cl	pH < 10	Single bed salt regeneration or DI
Silver	Photographic wastes	SBG1	Cl	pH < 11	Regenerated with sulfuric acid
	Silver cyanide plating	SBG1	Cl	pH > 7	Use with WBMP for regenerable applications
Strontium	Soft water	CG8	Na	pH > 2	
Uranium (anion)	Groundwater	SBG1	Cl	pH < 10	Single bed salt regeneration
Uranium (cation)	Groundwater	CG8	Ca	pH > 2	Single bed salt regeneration
Zinc	Zinc cyanide plating effluents	SBG1/SBG2	Cl	pH > 7	
	Softened water	CG8	Na	pH 2 to 9	
	Hard water	WACMP	Na	pH 5 to 9	
	Hard water	SIR-300	Na	pH < 6.5	
	Concentrated acids	SBG1/SBG2	Cl	pH < 1	Removes zinc complexes/eluted with water

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