

Ion Exchange for Recovery of Precious Metals

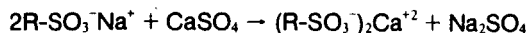
By W. H. Waitz Jr.

In this review of procedures for recovering precious metals by ion exchange, resins are discussed and techniques for gold, silver and the platinum-group metals are highlighted. A regeneration process involving electrolysis of an eluate is described for silver. Incineration is customary for recovery of gold from exhausted resin.

With the rapid rise that has occurred in the prices of precious metals during the past few years, recovery of even minute amounts of these elements has become of greater interest to metal finishers.

Although precious metals are recovered easily from concentrated solutions by reduction and precipitation or electrolysis, solutions containing a few parts per million are difficult to handle by these methods. However, the use of ion-exchange resins makes it possible to concentrate dilute solutions economically so that they can be subjected to common refining procedures to recover the metal. Also, the purity of the wastewater is improved to facilitate disposal.

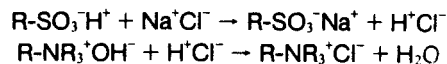
Ion exchange is well known for its use in water softening, where resins are used to replace the calcium and magnesium in "hard" water with sodium, thereby producing "soft" water. The resin used in this operation consists of a polymeric water-insoluble anion with a water-soluble cation attached to it (in this case, sodium). At low concentrations, the anion prefers large ions with higher valences and therefore readily exchanges the sodium ions for calcium and magnesium ions, according to the following equation:



The equilibrium of this reaction is shifted to the left by contacting the resin with a high concentration of sodium ions. Thus, the resin can be returned to the sodium form, or regenerated, by passing a concentrated sodium chloride solution through it. This practice makes it possible to reuse the resin.

Ion-exchange resins also are used to deionize water for a great variety of applications, including plating rinsewater. To accomplish deionization, the cation-exchange resin is placed in the hydrogen form by passing an acid such as hydrochloric or sulfuric through it. The resin will then exchange the hydrogen ions for metal ions in the water. The anions are removed from the water by an anion-exchange resin, which consists of a polymeric water-insoluble cation and the soluble OH⁻ anion. This resin then exchanges the hydroxide anion for chloride, sulfate, nitrate, and other anions, yielding water that is essentially triple-distilled in

terms of purity. These deionization reactions are illustrated by the following equations:



When exhausted, these resins can be regenerated: The cation exchange resin is regenerated with acid; the anion exchange resin with a base such as sodium hydroxide.

Ion-Exchange Resins

For the most part, the resin backbones used today consist of styrene or acrylic polymers crosslinked with divinylbenzene. Resins with cation-exchange functionality are available as either strongly acidic or weakly acidic ion exchangers. The strongly acidic resins have sulfonic acid functionality while the weakly acidic resins have carboxylic acid functionality. Anion-exchange resins also are available with strongly or weakly basic functionality. The strongly basic resins have quaternary ammonium functionality, whereas the weakly basic resins are primary, secondary, and tertiary amines.

Resins can differ in porosity. Gel-type resins are not truly porous. Therefore, exchangeable ions in solution must diffuse through the bead structure to exchange sites. The ability of the ions to do this is governed by their size and by the level of crosslinking agents present. The greater the crosslinking, the higher the physical strength of the resin and the slower the diffusion. In macroreticular resins, the individual beads consist of many small beads stuck together like a popcorn ball (Fig. 1). Therefore, the resin has discrete pores between the small beads, making possible a high-porosity resin with good physical stability. These resins are useful when large ions are exchanged or when the resin is subjected to a strongly oxidative solution or severe physical stress.

The equipment required for the recovery of precious metals is similar to that used in water softening or deionization—i.e., a tank to hold the resin, a distributor and collector to assure even contact of the stream with the resin bed, and the tanks and pumps necessary to store the regenerants and move the wastestream, regenerants and rinsewater through the resin bed. The tank holding the resin should have sufficient freeboard to permit expansion of the bed during backwashing so that resin fines and suspended solids that collect at the top of the bed can be removed. A number of equipment manufacturers specialize in designing, building, and installing these systems.

Because of their preference for large ions with a high valence, ion-exchange resins are useful for recovering low

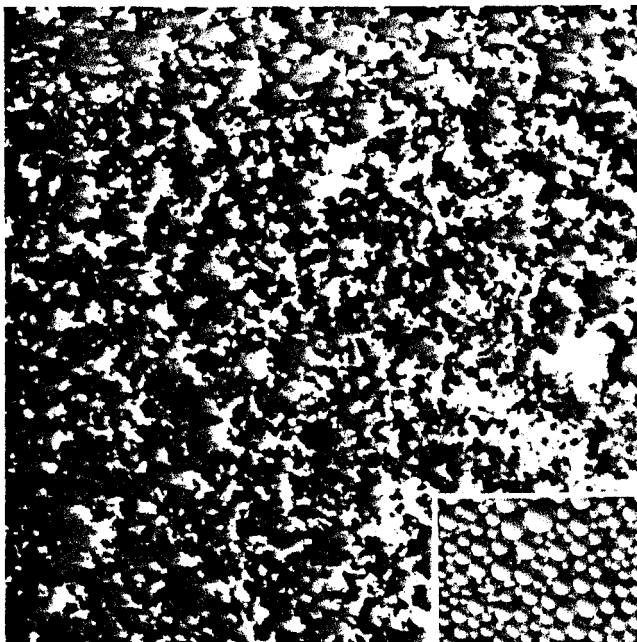
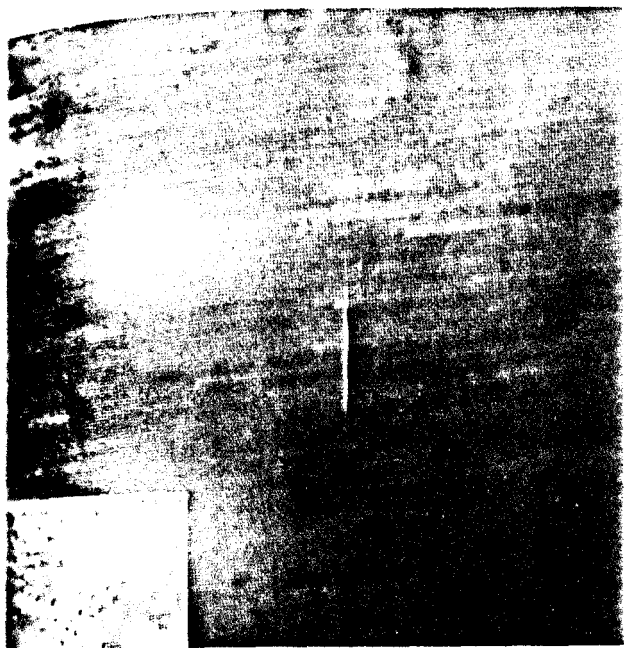


Fig. 1—Comparison of resin structures: (left) gel-type and (right) macroreticular, both at 25,000 X.

concentrations of heavy and precious metals from wastestreams and have been used for this application for a number of years. With the escalating price of precious metals and the imposition of discharge restrictions, interest in the recovery of trace quantities has increased substantially. As a result, considerable work has been done in the recovery of metals from plating rinsewater, not only to recover the metal values but to make the water suitable for discharge or recycling to the rinse tanks.

In most cases, precious metals exist in solution as anionic complexes. Because these complexes are large and often have a valence greater than one, the resins employed are quite selective compared with those used for other anions commonly found in water.

Recovery of Gold

Some of the earliest studies in the recovery of precious metals by ion exchange were reported in 1945 by Sussman, Machod and Wood,¹ who worked with a solution of gold chloride. Studies on the recovery of gold from the more common cyanide solutions were first done by Hussey in 1949² using a weakly basic phenolic resin. In 1953, Burstall, Forrest, Kember and Wells³ reported the adsorption of gold from a cyanide solution using a strongly basic resin. They attained a capacity of up to 0.297 g of gold per gram of resin. They found the presence of sulfate had no adverse effect on the adsorption of gold, but the capacity of the resin for gold was decreased by the presence of thiosulfate or thiocyanate ions.

By eluting with various agents, Burstall et al. were able to separate gold and silver from mixtures containing nickel, zinc, cobalt and iron cyanides. Using 400 mL of acetone containing 5 percent HCl and 5 percent water, they were able to elute 99.9 percent of the gold from 1 g of resin while 96.2 percent of the gold was eluted with 100 mL (Fig. 2). But, because this elution system results in a very dilute solution and because acetone is hazardous from a flammability standpoint, incineration has become the most popular method of recovering gold from ion-exchange resins.

Gel-type strongly basic anion-exchange resins continue to be recommended for the recovery of gold from plating rinsewater. Incineration of the resin to reclaim the gold is justified by the high price of the metal in today's market. Capacity of the resin is dependent on the amount of gold in the wastestream and the presence of interfering anions. The theoretical capacity of a strongly basic gel-like resin for gold is 276 g/L (20.9 troy lb/ft³). It is impossible, of course, to attain a capacity of this level under normal operating conditions.

Average experience gives a capacity of 22 to 220 g/L (20 to 200 troy oz/ft³) with 93 g/L (85 troy oz/ft³) most commonly reported. Before designing a unit to recover gold, a laboratory study to evaluate the particular stream in question should be conducted. This will determine whether a strongly basic resin alone will do the job and whether there are any interfering anions in the stream that will adversely affect the capacity of the resin for gold.

Many waste streams contain only a small amount of gold, and the generators do not have laboratory facilities required to conduct studies and design a system to handle them. In this case, water-treatment equipment manufacturers who specialize in deionization can be helpful. Also, there are a number of firms who specialize in gold recovery and supply resin-filled cartridges for this specific purpose. They will install the necessary equipment and supply new cartridges as the old ones are exhausted.

To recover the gold by incinerating the resin, the exhausted resin generally is sent to a metal refiner. A temperature of 500 to 600° C (900 to 1100° F) is required in an air-enriched atmosphere to burn the resin. Without sufficient oxygen, the resin chars but is not reduced to ash. There are reports that some of the gold can volatilize while the resin is being ashed. Precautions should be taken, therefore, to prevent the loss of gold up the exhaust stack.

Silver Recovery

Extensive work on the recovery of silver by ion exchange is relatively recent. For years, silver-containing wastestreams were discharged to sewers because the cost of recovering the last few parts per million did not justify the expense. Both plating waste and photographic effluent were involved.

A common method used to treat silver-containing wastestreams is the metal replacement process. With this method, steel wool is placed in a cartridge, through which the wastestream is passed. As the silver solution contacts the steel, the silver oxidizes the iron and precipitates as the iron goes into solution. This is a good method for gross silver recovery, but the exiting stream still contains small amounts of silver and a considerable amount of precipitable iron. At \$6/troy oz of silver and no local, state, or federal regulations, it was hard to justify a polishing step. When the price rose to more than \$35/troy oz, however, it was obvious that even incineration of the resin to recover the metal would be economical.

As a result, a number of laboratories began to investigate the use of ion exchange in the recovery of silver from both plating and photographic waste. In plating waste, silver gen-

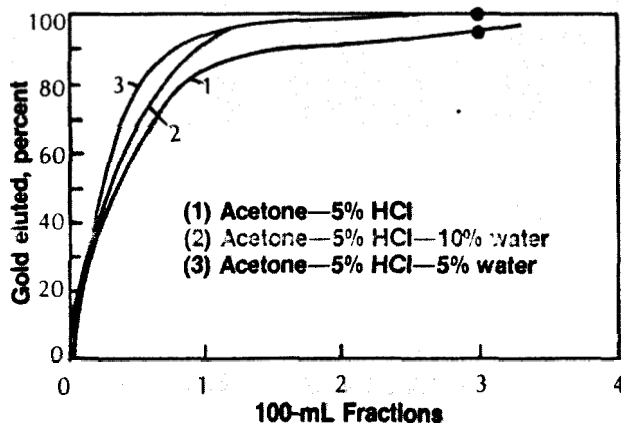


Fig. 2—Elution of gold cyanide with a mixture of acetone and hydrochloric acid from 1 g of resin.

erally is present as the anionic cyanide complex, $\text{Ag}(\text{CN})_2^-$. In photographic waste, it is present as the anionic thiosulfate complex, AgS_2O_3^- . Both strongly basic and weakly basic resins have been found useful in the recovery of these silver ions. Even though silver chloride is insoluble in water, 5 M NaCl has been used successfully to elute the silver. However, the ammonium, sodium or potassium salts of cyanide, thiocyanate, and thiosulfate ions seem to offer the best approach to elution.

Burstall et al. used a strongly basic gel-type resin and found a maximum capacity for silver of 0.15 g/g of resin (6.6 lb/ft³) when adsorbing silver cyanide from solution. Using 2N potassium thiocyanate (19.4 percent solution in water), they recovered 100 percent of the silver, but did not report the amount of potassium thiocyanate required to accomplish this. The latter point is important because the silver then is recovered from the solution by electrolysis. Strongly basic resins also have been used with incineration for recovery of the metal.

In our laboratory, it was found that a weakly basic acrylic resin could be used to recover silver cyanide efficiently. Potassium thiosulfate was used to regenerate the resin. Weakly basic anion-exchange resins will not split neutral salts such as sodium silver cyanide, so it is necessary to convert the resin to a salt form (e.g., bisulfate) prior to treating the silver-containing waste. This is accomplished by passing a 4 percent sulfuric acid solution through the resin until the pH of the effluent is equal to that of the influent. At this point, the excess acid is rinsed from the resin and the silver solution is introduced. Because of the large size of the silver cyanide ion, the resin has a high selectivity for it, resulting in a high

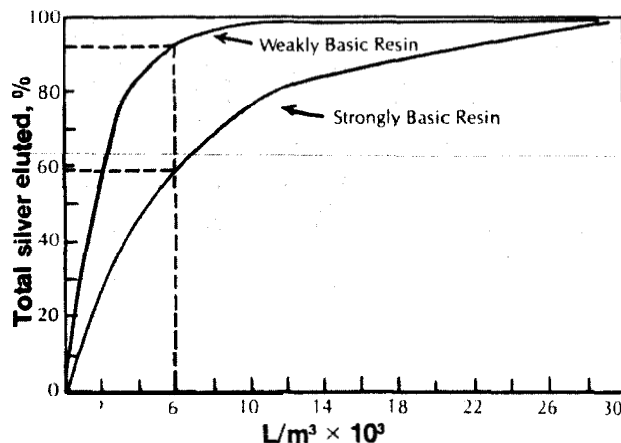


Fig. 4—Elution rate of silver as a function of the volume of eluting solution.

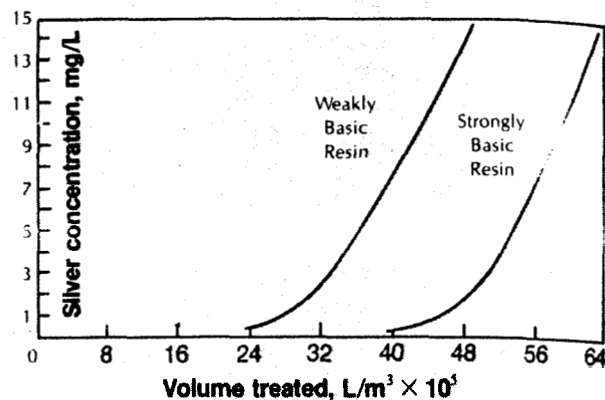


Fig. 3—Exhaustion curves for treatment of silver-containing wastewater per (L of rinsewater per m³ of resin).

capacity. The ease of regenerating the weakly basic resin makes complete recovery more likely.

During recent studies by Howard W. Chou of the Eastman Kodak Co.,⁴ a weakly basic acrylic resin was used to remove silver from washwater used for processing photographic paper. Dr. Chou eluted approximately 85 percent of the silver with a solution of 30 percent ammonium thiosulfate in water and regenerated the resin with 5 percent sulfuric acid. Silver

Table 1
Amine-Borane Resin Selectivity
For Metal-Ion Species

Reactive		Non-reactive	
Metal ion	Source	Metal ion	Source
Au ³⁺	AuCl ₄ ⁻	Group IA*	Chloride salts
Pt ²⁺	PtCl ₄ ⁻	Group IIA*	Chloride salts
Pt ⁴⁺	PtCl ₆ ⁻	Group IIIA*	Chloride salts
Pd ²⁺	PdCl ₂	Group IVA*	Oxides/nitrates
Ag ⁺	AgNO ₃	Cr ³⁺	CrCl ₃
Ir ³⁺	IrCl ₃	Mn ²⁺	MnCl ₂
Rh ³⁺	RhCl ₃	Fe ²⁺	FeCl ₂
Hg ⁺¹	Hg ₂ Cl ₂	Fe ³⁺	FeCl ₃
Hg ²⁺	HgCl ₂	Co ²⁺	CoCl ₂
CH ₃ Hg ⁺	CH ₃ HgCl	Ni ²⁺	NiCl ₂
As ³⁺	As ₂ O ₃	Cu ⁺	CuCl
Sb ³⁺	Sb ₂ O ₃	Cu ²⁺	CuCl ₂
Bi ³⁺	Bi(NO ₃) ₃	Zn ²⁺	ZnCl ₂
		Cd ²⁺	CdCl ₂
		Ru ³⁺	RuCl ₃
		Sn ⁴⁺	SnCl ₄
		Pb ²⁺	Pb(NO ₃) ₂
		Tl ³⁺	Tl ₂ (SO ₄) ₃

*Periodic table of the elements.

Table 2
Saturation Capacities of Amine-Borane Resins

Metal	Source	Grams of metal per g of dry resin	Troy oz per ft ³ of wet resin
Platinum	K ₂ PtCl ₆	0.6	210
Platinum	K ₂ PtCl ₄	1.2	420
Gold	HAuCl ₄	0.8	280
Palladium	PdCl ₂	0.64	220

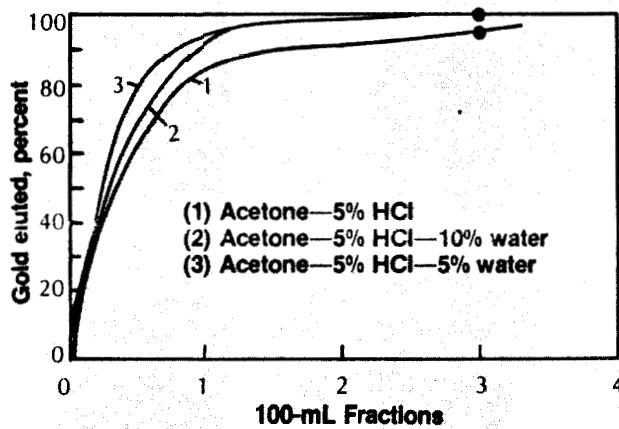


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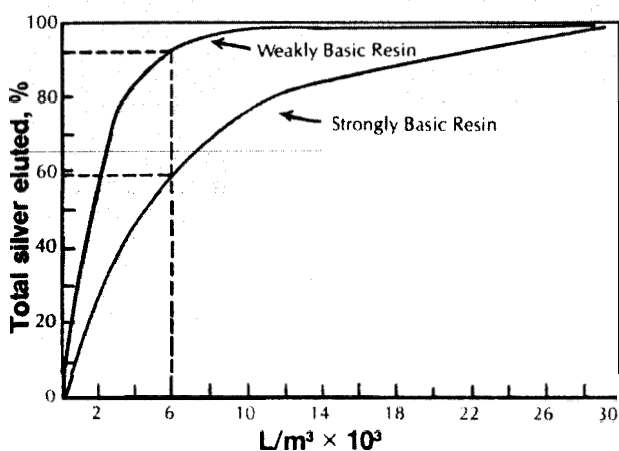


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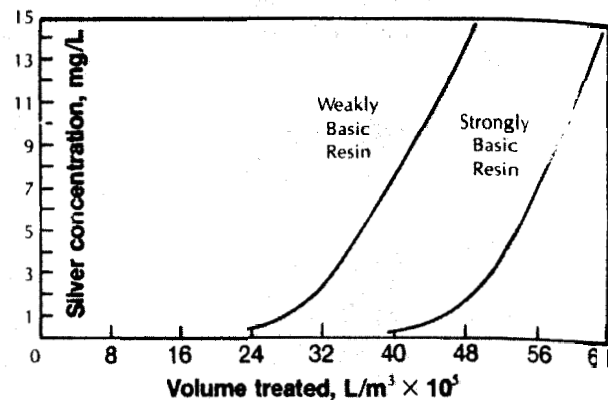


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Pd ²⁺	PdCl ₂	Group IVA*	Oxides & nitrates
Ag ⁺	AgNO ₃	Cr ³⁺	CrCl ₃
Ir ³⁺	IrCl ₃	Mn ²⁺	MnCl ₂
Rh ³⁺	RhCl ₃	Fe ²⁺	FeCl ₂
Hg ¹⁺	Hg ₂ Cl ₂	Fe ³⁺	FeCl ₃
Hg ²⁺	HgCl ₂	Co ²⁺	CoCl ₂
CH ₂ Hg ⁺	CH ₃ HgCl	Ni ²⁺	NiCl ₂
As ³⁺	As ₂ O ₃	Cu ⁺	CuCl
Sb ³⁺	Sb ₂ O ₃	Cu ²⁺	CuCl ₂
Bi ³⁺	Bi(NO ₃) ₃	Zn ²⁺	ZnCl ₂
		Cd ²⁺	CdCl ₂
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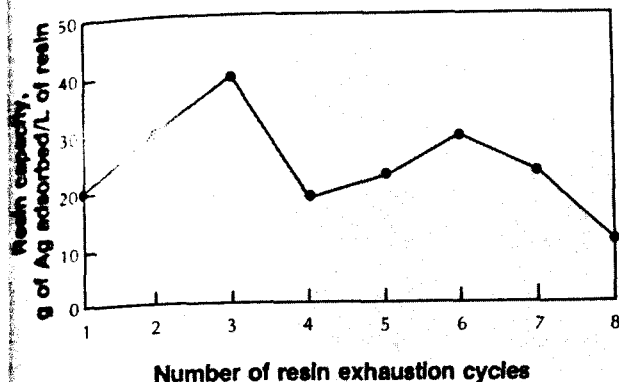


Fig. 5—Capacity of weakly basic anion-exchange resins regenerated by 30 percent ammonium thiosulfate.

from the ammonium thiosulfate solution was recovered by electrolysis. This system may give similar results with silver cyanide solutions from plating rinsewater.

It is interesting to note that Dr. Chou used countercurrent (upflow) regeneration. This gives a high degree of regeneration to the bottom of the column, eliminating early leakage when the column is returned to service. The weakly basic acrylic resin was found to have a lower capacity for silver than the strongly basic resin (Fig. 3). Leakage from the strongly basic resin was less than 0.5 mg/L through 2,700 bed volumes, when a sharp breakthrough was noted. Breakthrough occurred after only 1,700 bed volumes when using the weakly basic acrylic resin. In regenerating the weakly basic resin, however, only six bed volumes of regenerant removed 90 percent of the silver. With the strongly basic resin, only 60 percent of the silver was removed with this same amount of regenerant (Fig. 4). The capacity of the weakly basic acrylic resin using 30 percent ammonium thiosulfate is shown in Fig. 5. Over eight cycles, the capacity averaged 22.4 g/L of resin (1.7 lb/ft³). After removing silver from regenerant electrolytically, the ammonium thiosulfate can be reused.

Platinum-Group Metals

Strongly basic gel-type resins also have proven useful in recovering platinum-group metals from plating wastestreams when they are present as chlorides. One stream studied was a combined primary and final rinse containing 565 mg/L of palladium and 1.54 mg/L of copper at a pH of 2.04. Because palladium was present as the anion complex (most probably a complex palladous chloride), it could be separated from the copper cation by passing the stream through a strongly basic anion-exchange resin. Excellent removal was indicated by the palladium concentration of the column effluent, which was only 0.1 mg/L. Unfortunately, insufficient quantities of the wastestream were available to carry this work to completion, but we would expect to treat in excess of 1,000 bed volumes before any significant leakage would be observed. Regeneration was accomplished with 4 percent sodium hydroxide solution. Even though insufficient material was available to fully load the resin, it was possible to account for 73.9 percent of the palladium.

New Development

The latest development in the recovery of precious metals with resins in the free-base form involves the use of amine-borane reducing agents. These mild reducing agents are comparable to monomeric amine-boranes but offer greater stability, selectivity and process advantages for precious metal recovery. The advantage of these resins is that they combine very high capacity with excellent selectivity for precious metals in the presence of base metals.

These resins remove the ionic metal from solution by reduction, concentrating the reduced metal within the highly porous bead. The metals that can be recovered with these resins are shown in Table 1. Table 2 shows the saturation capacity of one of the resins.

To recover the metal values, the resin is slowly roasted at 500° to 800° C (932 to 1472° F) in a well-ventilated area. If high-purity metal is desired, any unreacted borane functionality should be removed from the resin prior to roasting. This will minimize the formation of borate glass in the recovered metal. This is accomplished by treating the resin with an acidic acetaldehyde solution.

Summary

Ion exchange provides an economical and practical method for concentrating dilute solutions of precious metals so that they can be readily recovered by conventional refining methods. In addition, the greater purity of the treated water reduces disposal problems. Before designing a system to handle a given waste stream, laboratory studies should be conducted in order to choose the best resin and regenerating system for the job.

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