

Silver Recovery with Ion Exchange and Electrowinning  
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Silver cyanide complexes in wastewater from precious metals electroplating operations can be quite problematic, as the complexed cyanide is somewhat resistant to oxidation by conventional alkaline chlorination. Furthermore, silver is a valuable metal with a high market value and typical precipitation and clarification techniques do not readily allow recovery of the metal. It has long been recognized that ion exchange systems can be utilized to remove the silver cyanide complex from electroplating rinsewater. These metal complexes are strongly retained by anion resins and are difficult to remove with conventional strong base regeneration, so that often the exhausted resin is simply shipped off site for silver recovery by incineration, thereby resulting in high operating costs due to resin replacement. This paper will present the results of bench scale studies which examined the effectiveness of thiocyanate regeneration of the saturated resin for silver recovery. The spent regenerant was then treated by electrowinning to recover the eluted silver in a fairly pure state. Projected capital and operating costs for a 2 gpm regenerable ion exchange system were examined. Operating results of a full scale non-regenerated system are presented.

## BACKGROUND

A barrel-and-rack production electroplating facility specializing in high quality decorative and industrial finishes generates a contaminated rinsewater from its silver cyanide barrel plating line. Silver lost by dragout from the plating bath is partially recovered in a drag-out rinse tank. The silver in this tank is recovered by an electrolytic metal recovery unit. Metal parts leaving the drag-out rinse tank are rinsed in a two-stage counterflow rinse running at an average flow rate of 2 gpm. Silver cyanide that is not recovered in the drag-out rinse tank is currently treated in a wastewater treatment facility which utilizes alkaline chlorination for cyanide destruction, hydroxide precipitation, clarification, and filtration for metals removal.

Due to concern over the ultimate environmental fate of the silver cyanide complexes, and the economic loss of the silver metal, a study was commissioned to examine the applicability of ion exchange for silver recovery. The use of ion exchange for the removal of metal cyanide complexes has been reported by Gupta, et. al.<sup>1</sup>. Ion exchange is a process in which soluble, charged ions are removed from solution by exchange with similarly charged ions that are held by electrostatic charges on the surface of a solid (ion exchange resin)<sup>2</sup>. While most conventional ion exchange systems utilize regeneration techniques to recover the exchanged metals in a concentrated form, the metal cyanide complexes are strongly retained by anion resins

and are difficult to remove with conventional strong base (hydroxide) regeneration. For valuable metals such as gold and silver, difficulties with regeneration can be circumvented by simply selling the resin to a metals reclaimer who in turn burns the resin and recovers the precious metals. However, Gupta, et. al. <sup>1</sup> indicate that metal cyanide complexes can be effectively removed from anion exchange resin using thiocyanate as the regenerant. Because of the greater affinity for the thiocyanate anion (relative to hydroxide), the resin will give up the silver cyanide complex under the proper regeneration sequence. Regeneration allows reuse of the ion exchange resin, and can potentially offer significant savings in operating costs since the expensive resin can be reused.

Once removed from the ion exchange resin in a concentrated solution, the silver must be further converted to its elemental form. Electrolytic techniques such as electrowinning have been shown to be very efficient at converting silver cyanide ions to elemental silver.

The goals of this engineering study can be summarized as follows:

1. Verify the feasibility of ion exchange with regard to highly efficient silver cyanide removal from actual rinsewater from an electroplating facility.
2. Determine the effectiveness of thiocyanate regeneration for the removal of silver cyanide from exhausted anion exchange resin.
3. Optimize the regeneration sequence to achieve high silver cyanide capacities following thiocyanate regeneration along with high silver cyanide removal efficiencies.
4. Determine the effectiveness of electrolytic recovery of silver from spent thiocyanate regenerant solutions.
5. Prepare a budgetary cost comparison for thiocyanate regeneration/electrolytic recovery of silver versus resin disposal.

## Materials and Methods

### Ion Exchange

The bench scale apparatus utilized for the ion exchange studies is shown in Figure 1. An acrylic column was selected in order to provide visual information regarding the potential fouling or staining of the anion exchange resin, and to verify proper bed expansion during backwashing.

Rohm and Haas IRA-400 anion exchange resin was selected based on prior literature reports and field experience. Regeneration sequences and operating parameters were

selected based on suggested laboratory procedures from Rohm and Haas<sup>3</sup>. A summary of the service flow rates and regeneration flow rates and volumes is shown in Table 1. Distilled water was used for regenerant dilution and fast and slow rinse steps. Tap water was used for backwashing the resin prior to each regeneration. Fresh resin was placed in the hydroxide form by regeneration with 10 pounds per cubic foot of four percent sodium hydroxide solution prior to any testing.

Wastewater was formulated by diluting silver cyanide plating bath with tap water to produce a silver concentration of 16 mg/l. This represented a typical final rinsewater silver concentration, although tests were also run at 1.6 mg/l silver to determine the effect of influent concentration on the ion exchange system performance.

### Electrowinning

A bench scale electrowinning cell was utilized for the electrolytic recovery testing. A flow rate of 750 ml/min was maintained with a positive displacement pump to produce a recommended hydraulic retention time of 20 minutes. The rectifier amperage was set at 30 amps (2 volts DC). Copper reticulate cathodes with a total of six square feet were utilized in the test cell.

A "typical" spent regenerant solution was prepared as follows:

- 1.9 gallons silver cyanide plating bath
- 3.1 gallons distilled water
- 1600 grams sodium thiocyanate

The spent regenerant was made up to approximate the characteristics determined in the ion exchange bench testing. An artificial spent regenerant using plating bath had to be made up due to the small volume of actual spent regenerant produced in the lab column (1 liter) relative to the quantity needed for the electrowinner (20 liters). While the artificial solution was made up to approximate the silver and thiocyanate concentrations expected (6,300 ppm and 86,000 ppm, respectively), the free cyanide concentration was also high (41,000 ppm). This high free cyanide concentration will not be present in the actual spent regenerant since the resin will be saturated with mainly silver cyanide rather than free cyanide. Therefore, the electrowinning results may be somewhat different in actual practice, though the exact influence of the free cyanide is unknown at this time.

## Results and Discussion

### Ion Exchange Bench Test Results

One of the primary goals of this study was to verify the feasibility of silver cyanide removal by ion exchange. Figures 2 and 3 graphically depict the low effluent silver concentrations that can be achieved for this particular waste stream--especially with

fresh resin in the hydroxide form (Test Series 1). It is interesting to note that the silver leakage from the column increased substantially following thiocyanate regeneration. Leakage increased from below detection limits (.05 ppm) with fresh resin to 3.7 to 3.8 ppm following regeneration at 30 pounds sodium thiocyanate (NaSCN) per cubic foot of resin. Subsequent regeneration using 50 pounds NaSCN per cubic foot reduced the silver leakage to 1.2 ppm. An additional run using 40 pounds NaSCN per cubic foot followed by 10 pounds sodium hydroxide (NaOH) per cubic foot improved leakage slightly to 0.9 ppm. In general, it appears that a silver leakage of 1 ppm can be expected at a feed concentration of 16 ppm following thiocyanate regeneration at 40 to 50 pounds per cubic foot.

While much of the bench scale testing was conducted with a rinsewater containing 16 ppm silver, there are periods where the silver concentration is much lower. A rinsewater sample was diluted to 1.6 ppm and run through a thiocyanate-regenerated column of resin. The result of this test is shown in Figure 3. It is important to note that as the influent concentration is reduced, the silver leakage in the effluent is also reduced. However, overall removal efficiency decreased from 90-95 percent at 16 ppm influent silver to about 75 percent removal at 1.6 ppm influent silver. This relationship between influent concentration and overall removal efficiency has important full scale implications. A regenerable system may be applicable for rinsewaters containing greater than 10 to 15 ppm silver, but lower silver concentrations are best treated with virgin resin which can be removed following exhaustion.

Increased silver leakage following regeneration occurs primarily for two reasons. First, any regeneration procedure leaves some of the saturating ions within the resin. Since ion exchange is a reversible equilibrium, complete removal is virtually impossible. Virgin resin has no silver present and leakage is, therefore, negligible. Once resin has been saturated, some of the ions remaining after regeneration will leak into the effluent during the next service cycle. Leakage can be minimized by applying high dosages of regenerant, but complete regeneration is uneconomical and impractical. Second, because the silver cyanide complex is so tightly held in the resin, a strong regenerant is required to remove the complex. Unfortunately, the resin will also have a high affinity for the regenerant and the equilibrium exchange is shifted slightly away from the resin-silver complex bond. The resin's relative affinity for the silver complex is reduced accordingly, and more silver slips into the effluent during the next service cycle.

Besides silver removal efficiency, another important consideration for any ion exchange system is resin capacity, which can be expressed in pounds of the ion per cubic foot of resin. The service run time between regenerations is directly related to the resin capacity. Resin capacity was determined in the bench studies by making more concentrated "rinse" solution (1,100 to 1,300 ppm silver) in order to force silver breakthrough in a short period of time (5 to 6 hours). Using typical rinsewater would require weeks of continuous testing with hundreds of gallons of rinsewater. Unfortunately, capacity is a function of the influent concentration, so that this technique is somewhat problematic. However, a reasonable estimate of capacity can be obtained

in this manner. The capacity studies indicated favorable ion exchange kinetics and efficient resin utilization, as there was a rapid rise to exhaustion following initial breakthrough. In general, a capacity of about 3 - 4 lbs. silver/cu. ft. of resin was realized with either virgin resin or thiocyanate-regenerated resin. At a bulk resin density of 44 pounds per cubic foot, this capacity corresponds to 7 - 10 percent silver by weight. It is important to note that the resin capacity is also a function of the point at which the column is removed from service. That is, the capacity to complete exhaustion is higher than the capacity to initial breakthrough. By running columns in series, it is possible to fully exhaust the lead column without causing high effluent silver concentrations since the secondary (polishing) column will remove the excess silver.

Finally, the effectiveness of silver cyanide removal from the resin during regeneration is an important consideration in a regenerable system. Gupta et. al.<sup>1</sup> indicate that approximately 85 percent of the exchanged metal-cyanide complexes can be eluted by thiocyanate regeneration. The results from this study are in agreement with this finding.

Figure 4 illustrates the elution of silver from the anion exchange resin during regeneration. The integrated area under the elution curve indicated that 85 - 87 percent of the silver retained in the exhausted resin was removed during regeneration. These results indicate that the resin can be effectively regenerated using sodium thiocyanate. Because of the efficient elution of silver using thiocyanate, the resin capacity remained high during subsequent loading steps.

#### Electrowinning Bench Scale Test Results

Results of the electrowinning bench tests showed that silver electrowinning was outstanding, with virtually all the silver converted to elemental silver within two hours of testing. Analysis for copper (also present in the silver plating bath as a contaminant at a silver-copper ratio of 4:1) was conducted after 16 hours of electrowinning. Approximately two-thirds of the copper could be removed from solution. It is not known how soon copper equilibrium is achieved, but presumably it is less than 16 hours of operation under the conditions of this test.

An analysis of thiocyanate was run following 28 hours of operation. The electrolytic action of the electrowinner reduced thiocyanate from approximately 86,000 to 69,000 ppm (20 percent reduction). This fairly minimal loss indicates that the treated spent regenerant could most likely be reconstituted with additional thiocyanate and reused. Eventually the dissolved solids content would be problematic and, therefore, only one reuse would be recommended. It also bears mentioning that a considerable amount of ammonia was generated following extended periods of electrowinning. The effect of the ammonia on the treated regenerant is unknown. Since the silver is recovered so quickly, ammonia production can be minimized by minimizing the electrowinning treatment time.

### Full Scale Silver Recovery - Preliminary Design and Costs

The two basic flow schemes for ion exchange recovery of silver cyanide complex are shown in Figures 5 and 6. Figure 5 depicts the simplest recovery scheme, in which the silver cyanide is captured on hydroxide-form anion exchange resin. When the lead column reaches silver breakthrough, the column is taken off-line and the exhausted resin is sluiced to a spent resin holding tank. The silver-laden resin is shipped to a reclaimer, and fresh resin is loaded into the exchange vessel, which is then placed in the polishing mode. Fresh resin is always used in the secondary column to achieve the lowest silver leakage possible. Drawbacks of this system are 1) the high cost of resin replacement (\$250 to \$300 per cubic foot IRA-400), 2) the reclaimer's handling fee (approximately \$2 per pound of resin), and 3) shipping costs.

Figure 6 shows an alternative system in which the lead column is regenerated with sodium thiocyanate. The spent regenerant and slow rinse volumes are directed to an electrowinner storage tank. The silver in the spent regenerant is then reclaimed by electrolytic recovery. The secondary (polishing column) is always used with fresh hydroxide-form resin. When this column becomes spent, the resin is removed and sent to recovery. Because of the higher silver leakage that occurs following regeneration, the polishing column is not regenerated and is always filled with virgin resin only. The treated spent regenerant and the effluent from the ion exchange system are directed to the existing wastewater treatment system. The advantage of the regenerated system is the lower operating cost since the resin is reused following exhaustion. Disadvantages result from increased capital cost (additional piping, valves, regenerant storage tanks, electrowinner, transfer pumps, etc.) and greater operational complexity, though operating manhours are minimal due to the long run times between regenerations. Preliminary budget capital and operating costs for a regenerable vs. non-regenerable ion exchange system were prepared based on the following design considerations:

Rinse Flow Rate = 2 gpm  
Silver Concentration = 10 ppm  
Shop Production: 16 hours/day  
                                  250 days/year  
Silver Mass Loading = .16 lb/day  
Resin Capacity = 3 lb silver per cu. ft.  
Ion Exchanger Size = 2 cu. ft. (6 lb silver)  
Regeneration/Replacement Frequency =  $6 \text{ lb} \div .16 \text{ lb/day} \approx 30 \text{ days}$   
Resin Cost = \$250/cu. ft.  
Silver Reclaimer's Processing Fee = \$2/lb resin  
Labor to Empty/Refill Vessel = 4 hours @ \$20/hr  
Sodium Thiocyanate Cost = \$1.30/lb  
Labor to Regenerate/Electrowin = 6 hours @ \$20/hr

A budgetary installed capital cost of a regenerable ion exchange system was estimated to be \$30,000. Operating costs were estimated to be \$4,500 per year which assumes that the lead (regenerable) column is refilled with new resin twice/year and the polishing column is refilled once/year. The other major operating costs are for regenerant chemicals and labor.

A non-regenerable system was estimated to cost \$15,000 (installed). The simplicity of the system results in major capital savings compared to a regenerable system. However, the operating costs are primarily due to the high cost of replacement resin, which can be as much as \$6,000/year.

It is imperative to recognize that the operating costs of the two systems are largely a function of the mass loading of silver. Should lower silver mass loadings be realized, the annual operating cost savings that can potentially be obtained with a regenerable system will also be reduced. Given the above design conditions, a regenerable ion exchange/electrowinner system may have a 3 to 4-year payback. However, at lower silver mass loadings, the payback period will increase and a non-regenerable system will clearly be the most cost-effective approach.

#### Full Scale Ion Exchange Results

Based on the economic evaluation discussed previously, a non-regenerable ion exchange system was installed at the electroplating facility. Due to low silver concentrations that existed in the final rinsewater (less than 10 ppm expected) due to the use of electrolytic metal recovery in the drag-out rinse tank, a non-regenerable system was deemed to be most cost-effective. The results of approximately seven months of full scale operation at a nominal flow rate of 2 gpm are depicted in Figure 7. At an average influent silver concentration of 4.9 ppm, the effluent has averaged .07 ppm, which represents 98.6 percent removal of silver under actual field conditions. Mass balance and spent resin assays indicate that the resin contains 1% - 2% silver by weight. This is somewhat lower than silver content predicted by bench scale testing (7% - 10% by weight), and is no doubt related to the fact that the influent silver concentration is quite low compared to the high concentration (in excess of 1,000 ppm) used in the bench scale treatability testing. Nevertheless, valuable silver is recovered and recalcitrant metal cyanide complexes are removed from solution, while easily-treated free cyanide is passed through to waste treatment.

#### Summary and Conclusions

The following conclusions may be drawn from this study.

- Bench scale tests have shown that greater than 99% of the silver cyanide can be removed from electroplating rinsewater using strong base anion exchange resin. Full scale system test results confirmed this finding as seven months of operation yielded an average removal of 98.6%.

- The ion exchange resin can be effectively regenerated using sodium thiocyanate at a dosage of 40 to 50 pounds per cubic foot of resin, though subsequent removal efficiency falls to 90% - 95%.
- Bench scale tests indicated that a resin capacity of 3 - 4 pounds of silver per cubic foot of resin could be expected. Preliminary scale results indicate that a capacity of only 0.5 - 1 pounds of silver per cubic foot are actually realized. The lower capacity is probably due to the fairly low influent silver concentration (4 - 5 ppm) that is realized in actual practice.
- Silver can be completely recovered from spent thiocyanate regenerant by using electrowinning. Copper, which is also present in the plating bath, can be practically recovered (67% recovery) using electrowinning. Thiocyanate destruction during electrowinning is fairly minimal (less than 20% destruction), so that regenerant can be reconstituted for reuse.
- Budgetary estimates for a 2-gpm treatment system indicate that a 3 to 4-year payback is possible for a regenerable ion exchange system compared to a non-regenerable system. The higher capital cost of a regenerable system is offset by the savings in annual disposal costs of the anion exchange resin. This payback is applicable for a rinsewater with a 10-15 ppm silver concentration. As the rinse silver concentration decreases, the payback period will increase, and vice versa.

#### Acknowledgements

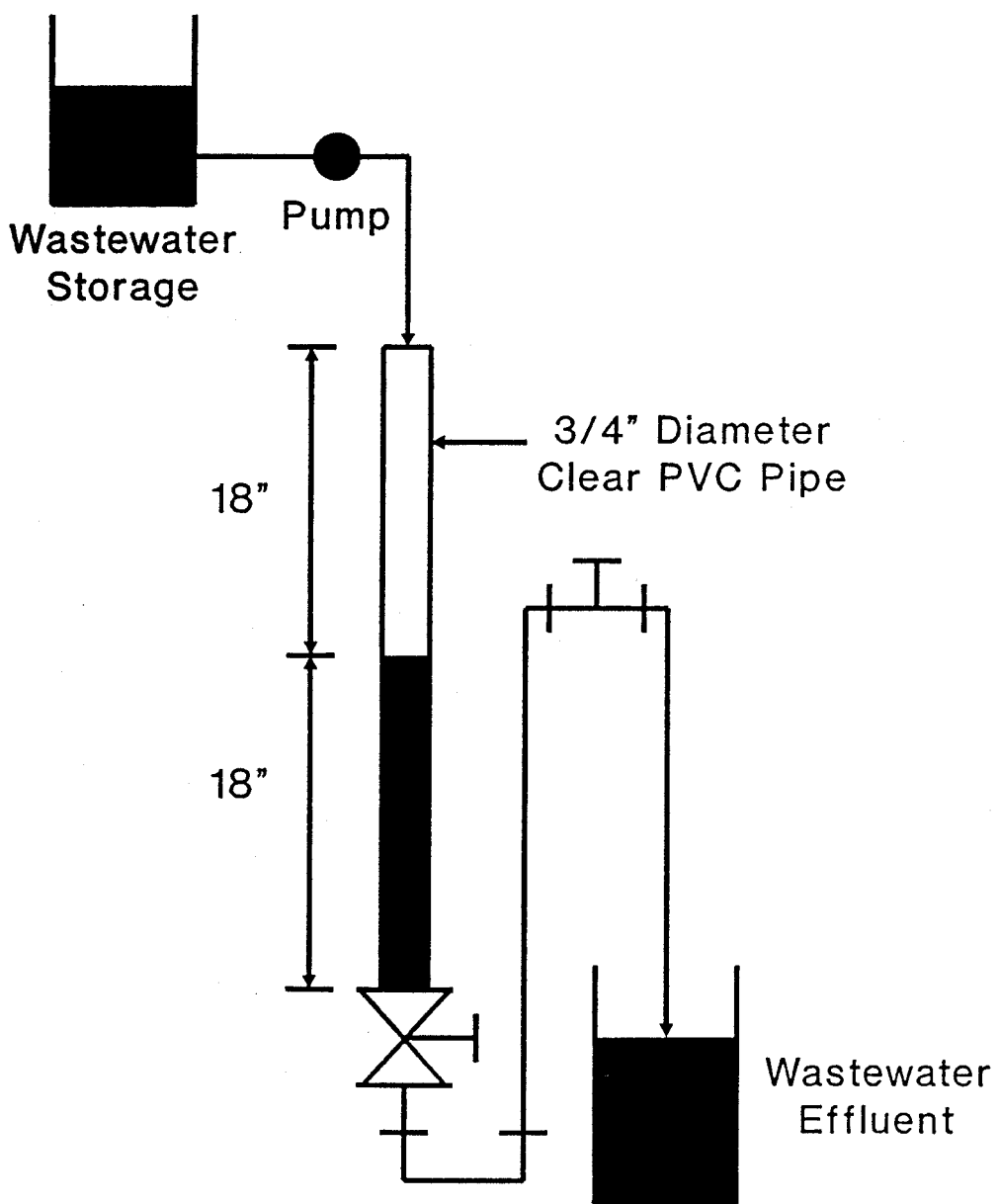
This study was funded in its entirety by Artistic Plating Company, Inc. Bench scale treatability was conducted by Triad Engineering, and wastewater analyses were performed by the Artistic Plating Company analytical laboratory.

#### References

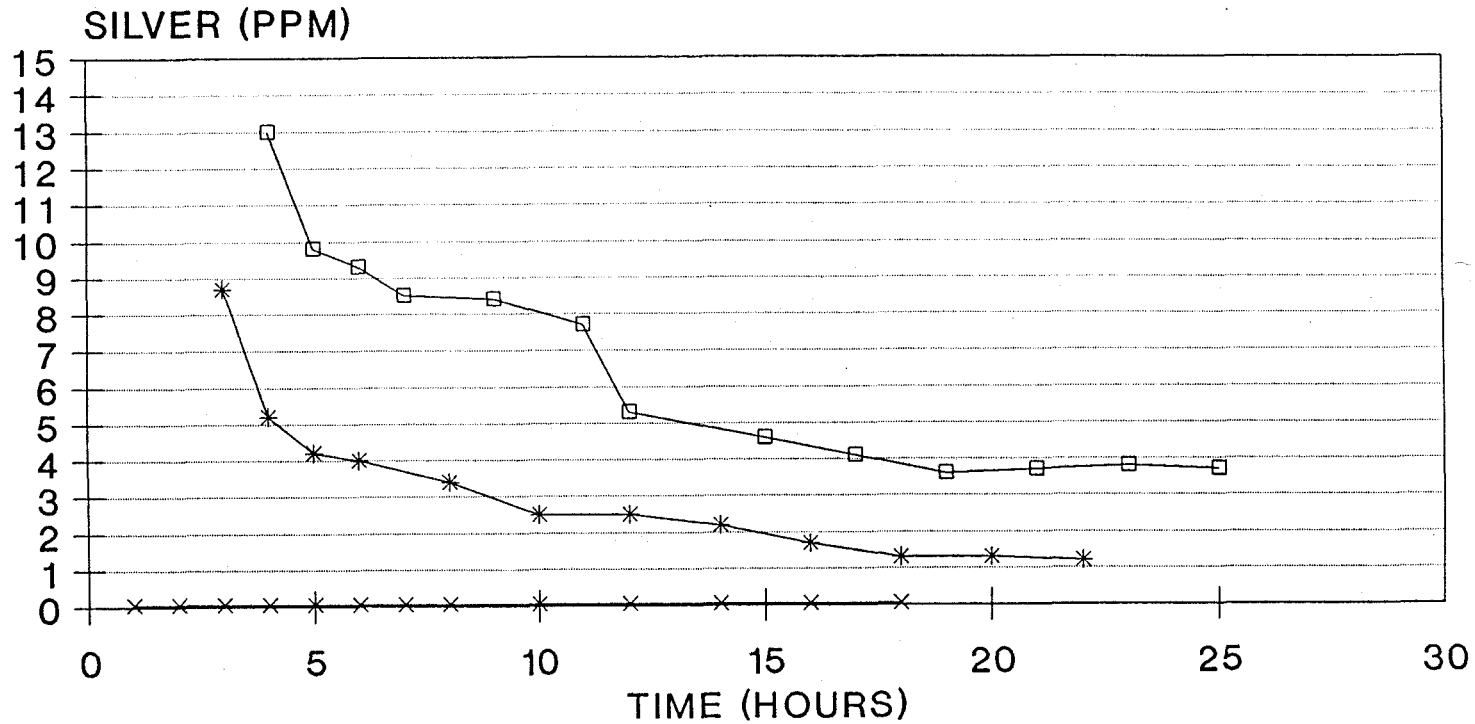
1. Gupta, A., Johnson, E.F., Mindler, A.B., and Schlossel, R.H., "The Use of Ion Exchange for Treating Wastewaters and Recovering Metal Values from Electroplating Operations." AICHE Symposium Series, No. 243, V.81.
2. Weber, W.J. Jr., "Physicochemical Processes for Water Quality Control." John Wiley and Sons, Inc. Publishing, 1972.
3. Rohm and Haas Company. Amberlite Engineering Manual.



FIGURE 1  
COLUMN APPARATUS



# FIGURE 2 SILVER LEAKAGE



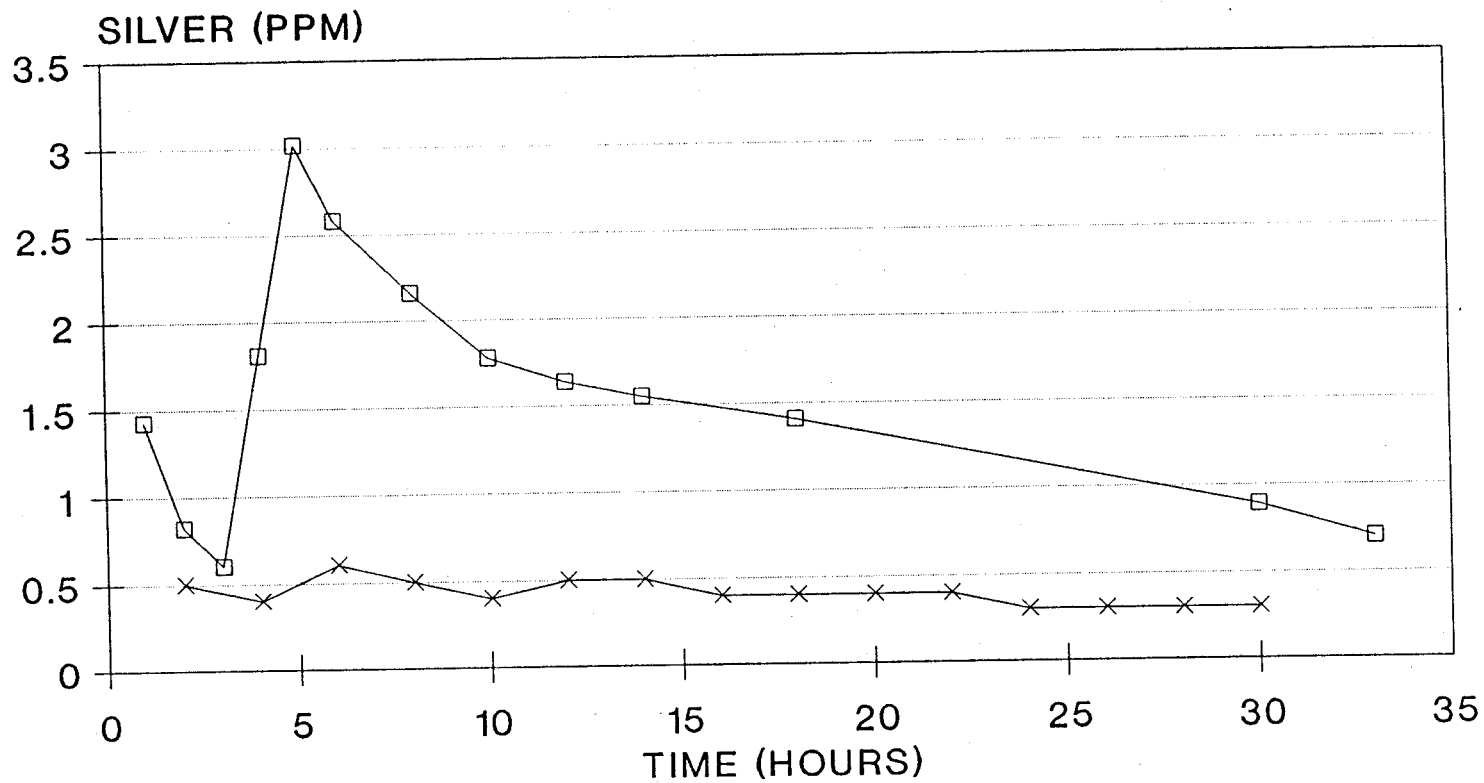
—x— Test Series 1  
Hydroxide Form

—□— Test Series 4  
Regeneration at  
30 lb NaSCN/cu.ft.

—\*— Test Series 7  
Regeneration at  
50 lb NaSCN/cu.ft.

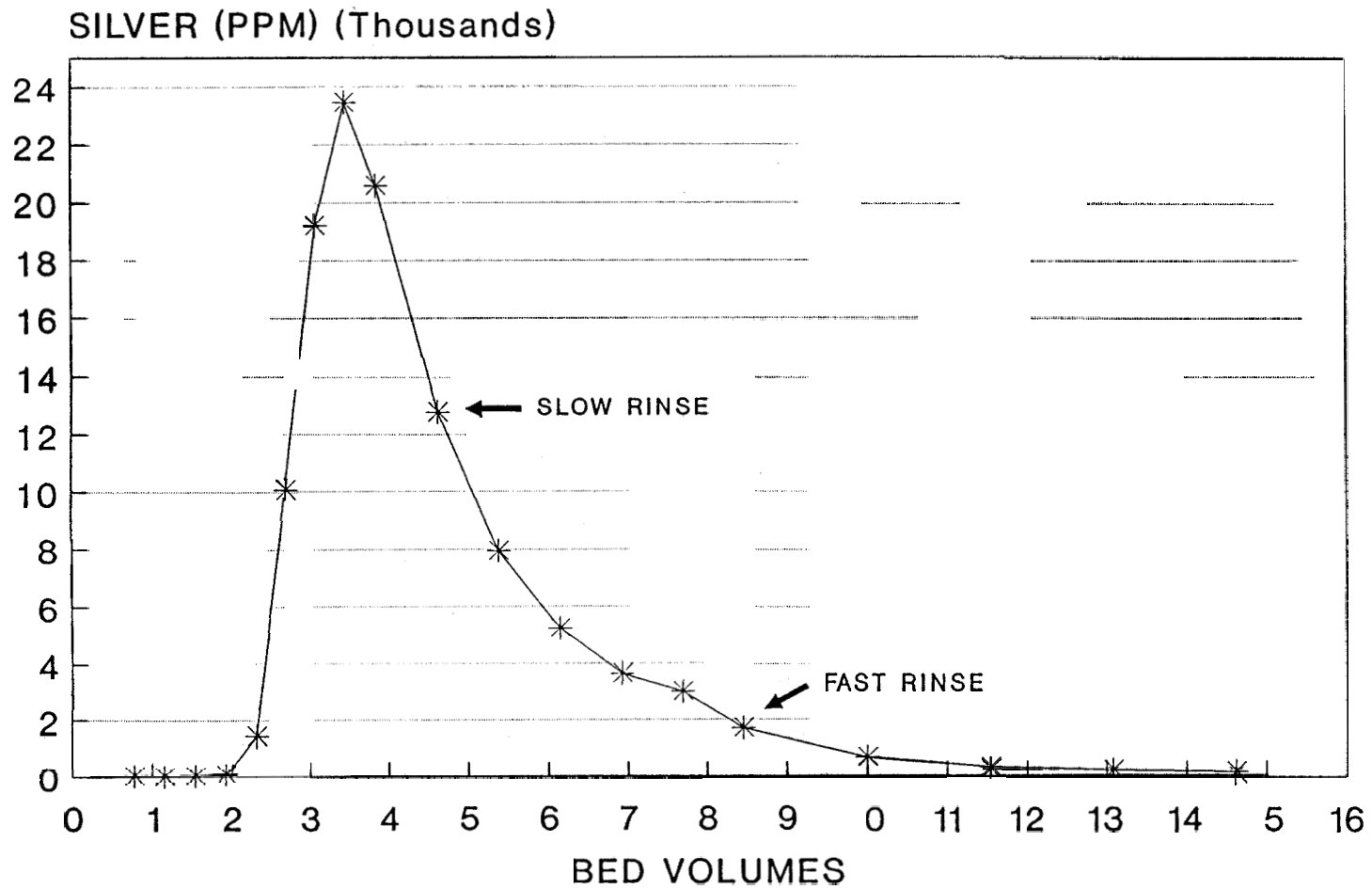
Rinse Concentration = 16 ppm Silver

**FIGURE 3**  
**SILVER LEAKAGE VS. INLET CONCENTRATION**



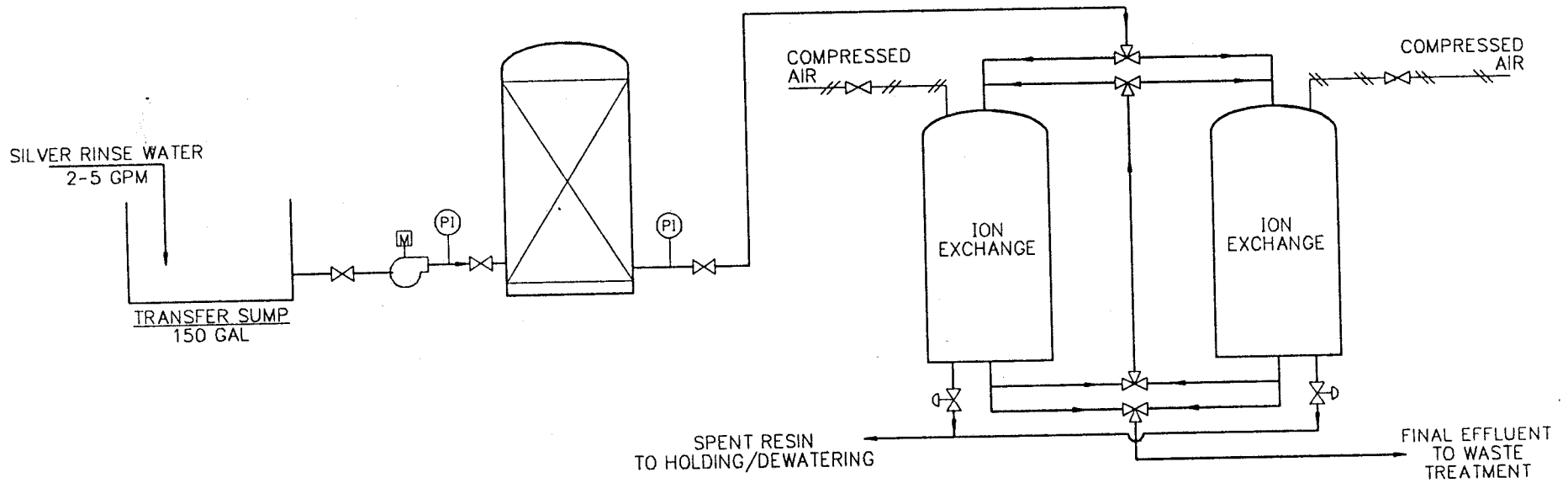
—□— Test Series 10A      —×— Test Series 10B  
RINSE = 16.60 PPM      RINSE = 1.66 PPM

**FIGURE 4**  
**REGENERATION CURVE: TEST SERIES 6**

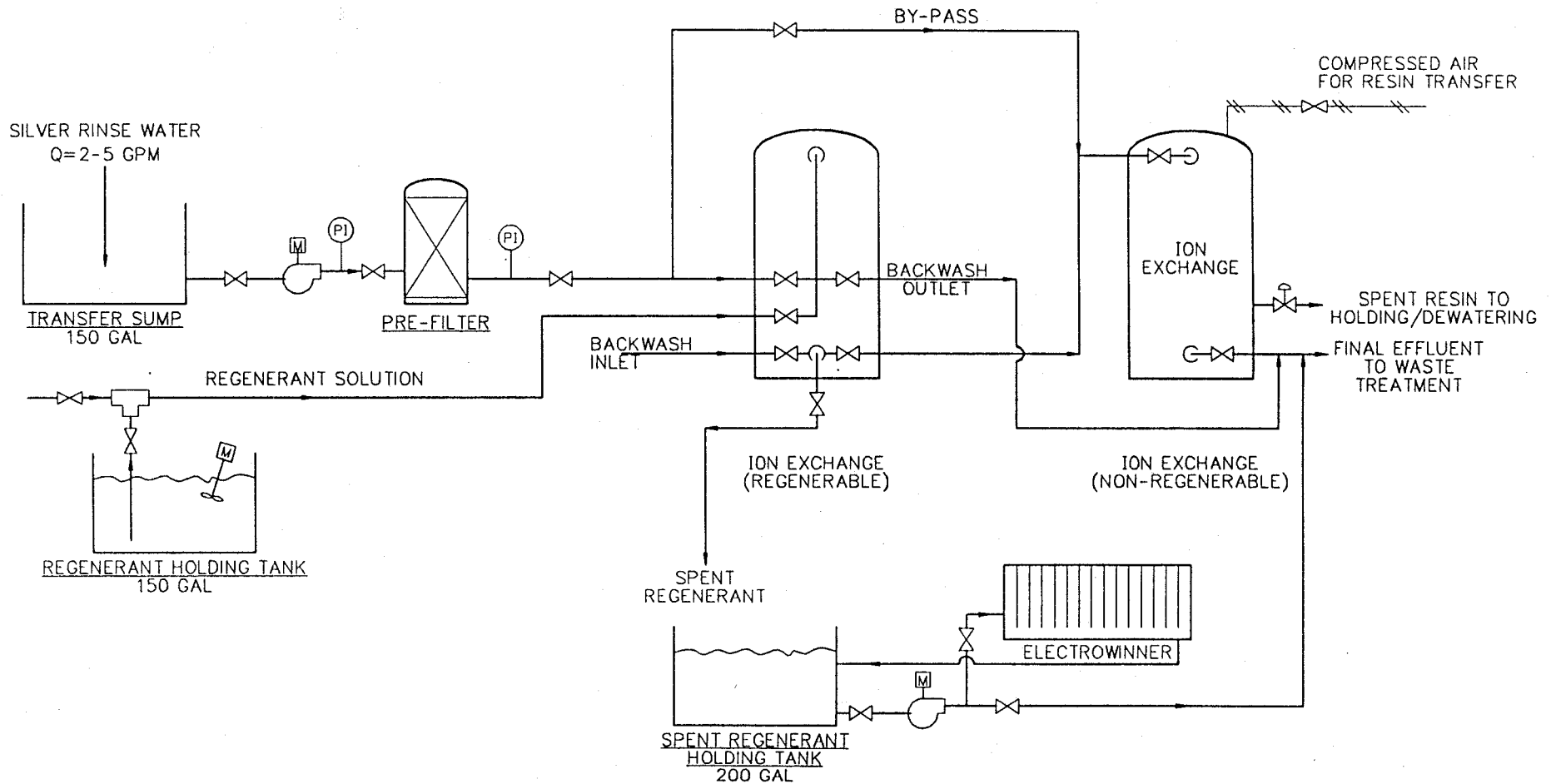


Regeneration at 50 lb NaSCN/cu.ft.

# FIGURE 5 SILVER RECOVERY FLOW SCHEMATIC- NON-REGENERABLE SYSTEM



**FIGURE 6**  
**SILVER RECOVERY**  
**FLOW SCHEMATIC- REGENERABLE SYSTEM**



**FIGURE 7**  
**SILVER RECOVERY WITH ION EXCHANGE**  
**FULL SCALE RESULTS**

