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The Application of Ion-Exchange and Modified Rinsing Procedures to Minimize Treatment Costs

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INTRODUCTION

The capital cost of treating wastewater generated from a metal finishing operation is primarily a function of the rinse water volume to be treated. Many wastewater treatment systems installed during the 1970's were oversized since water conservation measures were not always fully exploited. It is anticipated that systems designed during the 1980's in response to the pretreatment regulations will be less costly due to the increased awareness of this factor.

However, the approach of minimizing water usage does not necessarily result in the lowest cost treatment system. It would be more cost-effective to focus on minimizing the quantity of process chemicals lost in the drag-out and to segregate residual drag-out loads into small rinse volumes that can be recovered or treated in a simple and inexpensive batch treatment system. By reducing pollutant loads discharged from the process line, operating costs as well as capital costs can be minimized. Background information on this approach is described below with an example of a system design to illustrate the application of in-line process controls.

DRAG-OUT CONTROL

The most effective pollution control measure is to keep the process chemicals in the process bath. This is most frequently accomplished by incorporating more effective drainage of drag-out from the work with longer drain times or modifying the position of the work. Methods to decrease the quantity of process chemicals lost in drag-out include reducing the chemical concentration in the process bath and installing exit sprays.

The actual reduction in drag-out losses that can be realized is strongly dependent on existing plant practices and the ability of plant management to initiate corrective action. It is not unreasonable to anticipate reductions in process chemical losses in the 25-50% range along with corresponding reductions in capital and operating costs. Because of these potential opportunities it would be prudent for plant management to initiate a process assessment to identify feasible alternatives that would be practical to implement. A more detailed description of point source controls has been recently published by EPA[1] which would provide background for this assessment.

DRAG-OUT SEGREGATION

The next line of defense to keep the process chemicals out of the rinse water is to segregate the drag-out in a still rinse or a slow rinse. The rinse concentrate can be returned to the process as evaporative make-up or batch treated. This approach requires the use of multiple rinse stations, however, space constraints can be a limiting factor. Off-line concentration of the drag-out can be accomplished by evaporation, electrolytic deposition, ion-exchange, or with membrane processes such as reverse osmosis and electrodialysis. These processes are relatively expensive and before they are seriously considered, a thorough evaluation of in-line process controls should be completed. Frequently, the addition of one or two rinse tanks in the process line can achieve similar results at far lower capital and operating costs.

The use of a drag-out recovery still rinse, followed by a fast rinse, is widely employed to recover process chemicals in the drag-out from a heated plating bath. It is less widely applied to control the contamination levels in the fast rinse to minimize the size and cost of a treatment system. A slow rinse can be used to remove the major fraction of the process chemical in a drag-out followed by a fast rinse to reduce the residual drag-out load to acceptable contamination levels for quality control purposes. If the residual load in the fast rinse is sufficiently low, it can be discharged without treatment since other non-contaminated rinses would provide a dilution factor. Alternatively, the lightly contaminated fast rinse can be economically treated by an ion-exchange process.

Generally a minimum of three and preferably four rinse tanks would be necessary to provide sufficient flexibility to adjust flow rates to achieve an acceptable degree of rinsing in the final or fast rinse and concentrate the pollutants in the slow rinse. Examples of alternative rinsing modes that could be considered under different process conditions are shown in Figure 1.

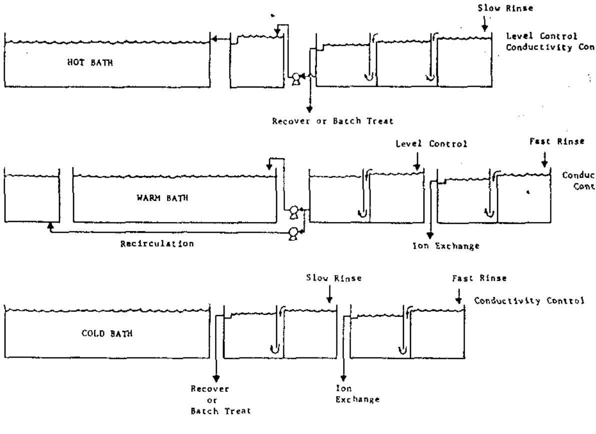

Fig. 1—Alternative Rinsing Modes.

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With a cold bath, the slow rinse concentrate can not be returned to the bath as evaporative make-up and would be discharged for batch treatment unless it was economical to consider an off-line process such as an electrolytic recovery unit. With a heated bath a closed loop rinsing system is shown where a sufficient degree of rinsing is achieved in the final rinse and all of the process chemicals are returned to the plating bath. Insufficient evaporation occurs with a warm bath to achieve high recovery by returning the slow rinse as evaporative make-up. In the example shown in Figure 1, a pre-dip in the rinse concentrate increases the recovery efficiency since process chemicals rather than rinse water are dragged into the plating bath.

To illustrate how drag-out losses can be reduced for a heated bath alternative rinsing modes are shown in Figure 2 for a heated Watts nickel bath. These baths are generally operated at 140-145° C with nickel salt concentrations in the 40-45 oz/gal range and typically have one drag-out recovery tank followed by one or two fast rinses. As shown in the first example, this would result in about one pound of nickel discharged into the final rinse assuming a drag-out loss of 1 gph over one shift.

The quantity of nickel discharged for treatment can be reduced by a factor of approximately 10 by decreasing the salt concentration and increasing the bath temperature by 10° F which almost doubles the evaporation rate. By operating the three rinse tanks as a 2-stage CF slow rinse followed by a single stage fast rinse 97% of the nickel can be recovered and 54 grams of nickel will be discharged compared to 520 grams in the first example. However, the nickel concentration in the final rinse is 14 mg/l versus 1.1 mg/l at the 2 gpm flow rate.

Another rinse tank can be added as shown in the third example to reduce the concentration. The evaporation rate could be doubled by increasing the bath heating time or by adding air agitation. The resulting 80 gpd flow in the 2-stage CF slow rinse would result in 99.8% nickel recovery and a residual nickel level of approximately 4 mg/l in a single stage 2 gpm rinse.

END-OF-PIPE TREATMENT

The driving force to control drag-out losses is to avoid the high cost of treating large volumes of lightly contaminated rinse water in a large treatment system that consumes valuable floor space in a non-productive activity. The capital cost for a conventional treatment system involving metal hydroxide precipitation is shown as a function of flow rate in Figure 3. These costs range from about $4000/gpm at the low flow rate, decreasing to about $2000/gpm at the high flow rate. Lower costs are associated with the batch reaction tanks that are made of plastic instead of coated steel.

Ion-exchange represents an end-of-pipe alternative to a conventional treatment process that can achieve a higher quality effluent. However, it has not been widely employed in the metal finishing industry because of higher overall costs that are associated with regenerating the spent resin.

A comparison of the capital costs curves shows that the ion-exchange treatment system is approximately one third the cost of a conventional treatment system. A relatively smaller cost would need to be added for a small bath treatment system to process ion-exchange regenerate, spent process solutions, floor spills, and other miscellaneous low volume, concentrated process discharges.

The higher operating costs for ion-exchange can be offset by taking a credit for the lower water usage by recycling the deionized water produced during treatment. With this credit, ion-exchange can be less costly than a metal precipitation process particularly in those cases where the cost of water includes a sewer use fee. A detailed cost evaluation and an in-depth description of the application of ion-exchange in the metal finishing industry has recently been published by EPA.[2]

ION-EXCHANGE POLISHING

The operating cost of ion-exchange can be significantly reduced if the system is operated as a polishing process rather than a primary treatment process. This can be accomplished by modifying the rinsing procedures in the process line to include the following:

1. Slow rinse - utilize a slow rinse to remove the majority of the ionic contaminant load in the drag-out; recover the rinse concentrate or treat the small volume in an inexpensive batch treatment system.
2. Fast Rinse - utilize a fast rinse to reduce the residual contaminant load in the drag-out to acceptable levels; process the lightly contaminated rinse water in an ion-exchange unit with periodic batch treatment of the regenerate.

This approach allows the major fraction of the hydraulic load to be treated with a lower capital cost compared to that by conventional treatment.

The operating cost is directly related to the regeneration

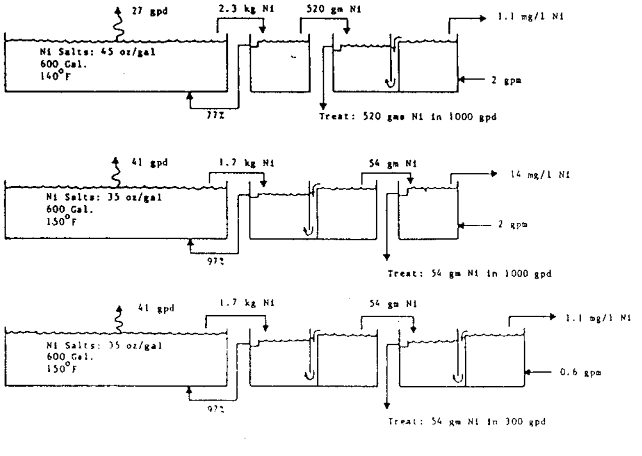

Fig. 2—Nickel Rinsing Alternatives.

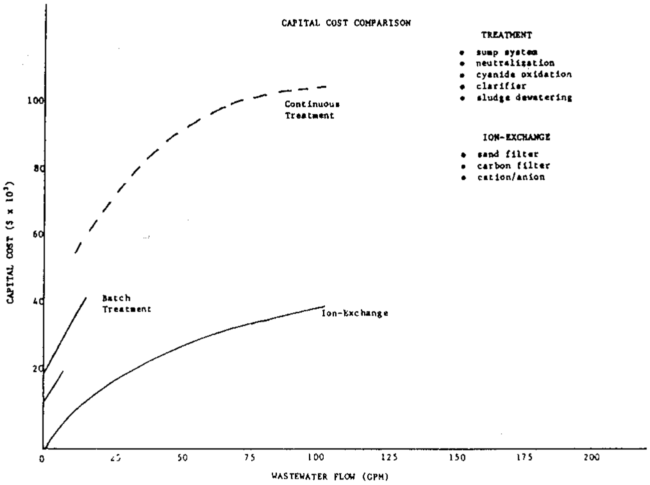

Fig. 3—Capital Cost Comparison.

frequency which in turn is a function of the flow rate set in the slow rinse. As shown by the curves in Figure 4 for a single and 2-stage CF chrome rinse, the regeneration frequency can be readily reduced by a factor of 10 or greater, along with corresponding reductions in operating costs.

In this example, one cubic foot of resin would saturate in approximately 2.5 hours if a 1 gph drag-out from a 40 oz/gal chrome plating bath were processed through the resin. (Resin capacity: 30 equivalents/ft^3). With a slow rinse set at 70 gpd, for example, the regeneration frequency would increase by a factor of 10 for a single stage rinse and a factor of 90 with a 2-stage CF slow rinse.

One objective in setting a slow rinse rate is to minimize the regeneration frequency and therefore the operational costs. A second objective is to minimize the volume of wastewater to be treated to minimize the capital costs. This volume consists of the slow volume and the ion-exchange regenerate. The latter includes the acid and caustic used to regenerate both the cation and anion columns and the slow and fast rinses. Typically about 10 column-volumes or about 150 gallons/ft^3 of contaminated wastewater are generated during cation and anion regeneration and require treatment. This volume can be reduced because not all of the fast rinse volume requires treatment. This, however, is offset somewhat by the need to periodically treat backwash water from the filter that precedes the ion-exchange column.

The average daily volume of regenerate per cubic foot of resin that would require treatment is shown as a function of the regeneration frequency in Figure 3. The point of intersection with the slow rinse curves represents the point where the total volume requiring treatment is minimized. For example, with a drag-out of 1 gph, a volume of 100 gpd or 50 gpd would require treatment depending on whether a single or 2-stage CF slow rinse is employed.

The data in Figure 3 illustrate that the operating cost of an ion-exchange process can be significantly reduced by using a slow rinse to reduce the ionic load discharged to the ion-exchange system. By coupling point source controls to minimize drag-out losses with ion-exchange treatment to

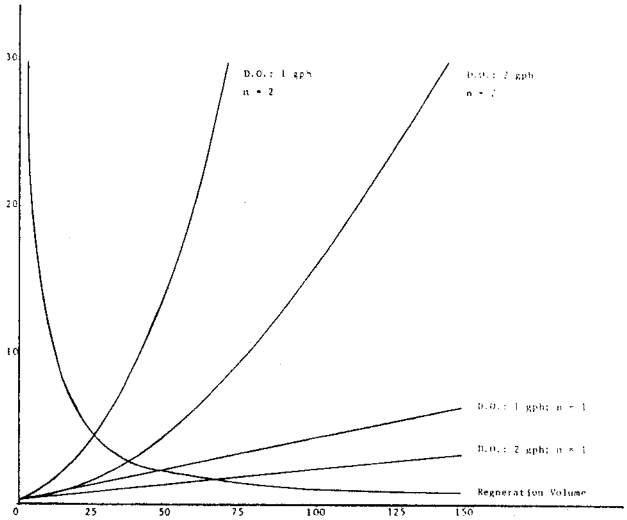

Fig. 4—Ion-exchange Regeneration Frequency as a Function of Slow Rinse Flow Rate.

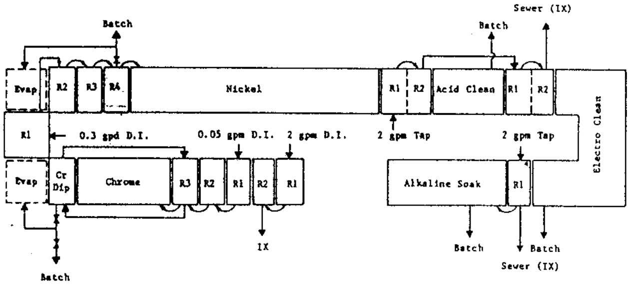

Fig. 5—Automated Line.

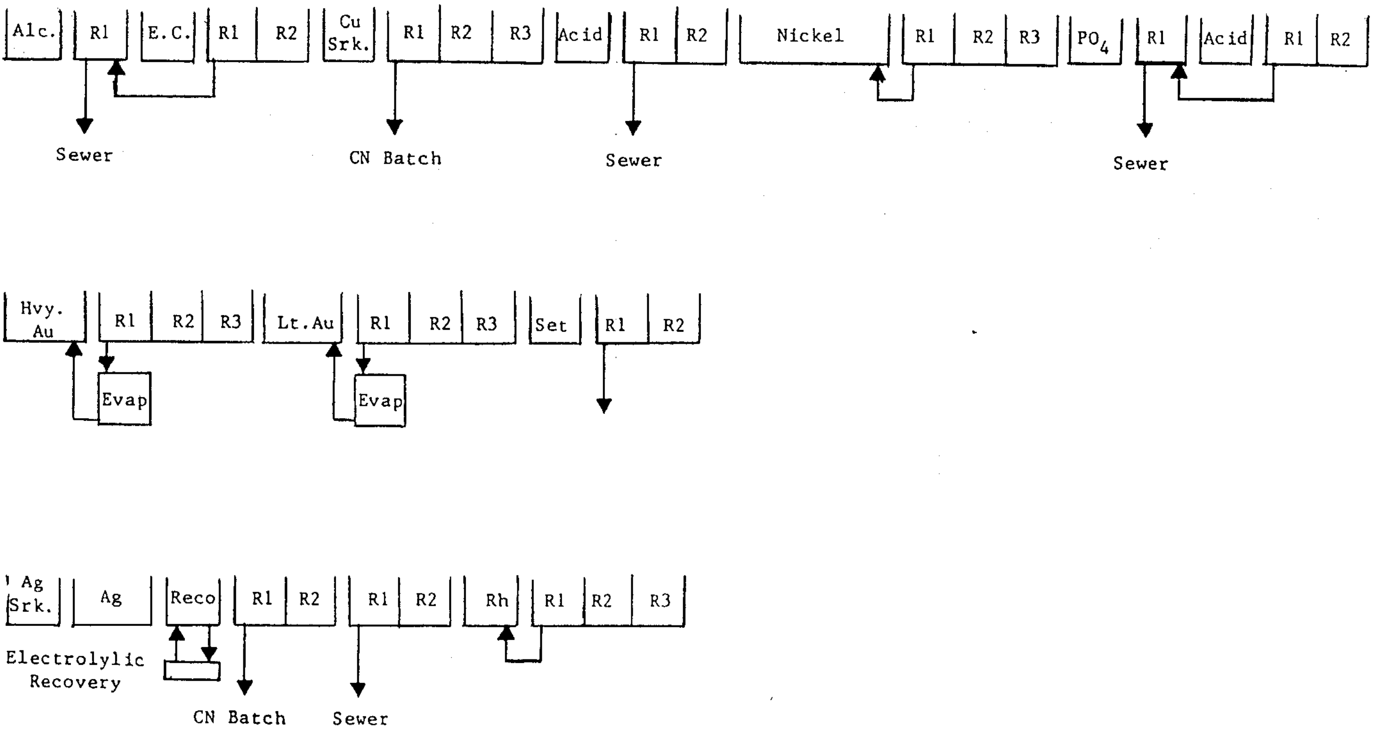

Fig. 6—Precious Metal Line.

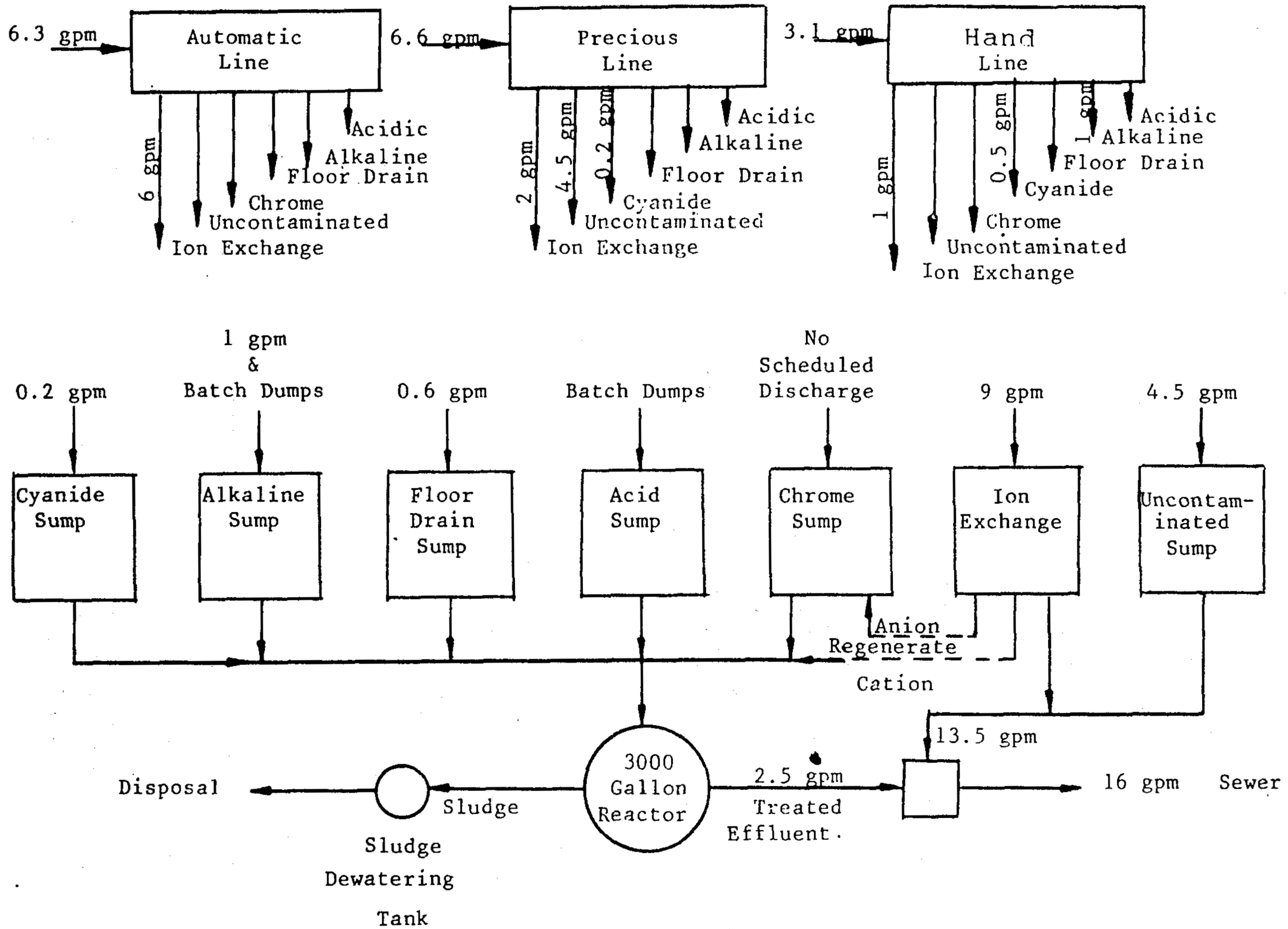

Fig. 7—Wastewater Flow Schematic.

remove residual process chemicals in the rinse water, a cost-effective treatment system can be designed.

DESIGN OF A POINT SOURCE CONTROL SYSTEM

An example of how point source controls can be applied to minimize treatment costs has been demonstrated in one facility design for a plant that manufactures mechanical pens and pencils. The existing metal finishing operation incorporated an automated chrome line and a low volume hand line that included copper, brass, nickel, and chrome plating. The operation was to be moved to a new location and expanded to include a manual precious metal line. The company required a wastewater treatment system to be designed to satisfy the sewer use ordinance which included the following limits (mg/l): CN - 0.5; Cu - 1.0; Ni - 3.0; Cr - 3.0; Ag - 0.03).

A systematic evaluation of each process bath was conducted to define process specifications that would minimize treatment costs and process chemical losses. The approach focused on reducing drag-out losses and the use of counterflow rinsing to minimize the volume of wastewater requiring treatment.

Automated Line

The automated chrome line involves rack plating of a variety of brass components that include tubular pieces. Drag-out rates in the existing line were measured to be 1 - 1.5 gph. It was determined that the majority of the drag-out could be more effectively drained by tilting the rack and a redesigned rack will be used for rack replacements.

The layout of the new automated line is shown in Figure 4 and consists of a single stage rinse after the alkaline soak and a 2-stage CF rinse after the acid cleaning bath with the discharge used as the supply for the 2-stage CF rinse after the electroclean bath. The soluble copper concentration in the cleaning bath was found to approach 150 mg/l near the end of the 2-3 week cleaning cycle. It was calculated that this would result in a copper concentration in the combined discharge in excess of the 1 mg/l limit toward the end of the cleaning cycle. To offset this factor, exit sprays were specified in each of the three cleaning baths which would enable the rinse water to be discharged to the sewer without treatment. As a precaution the discharge could be directed to an ion-exchange unit which was sized to process the rinse water from all the cleaning baths in the automated and manual lines.

Four CF rinses were used after the 1800 gallon nickel bath (heated at 150° F) to close the rinsing loop and recover 100% of the nickel salts. The standby capacity in the off-line evaporation tank and facilities for air agitation in the nickel tank would enable the slow rinse to be increased if required. All of the slow rinse concentrate is returned to the bath as evaporative make-up via the exit spray by pumping from R4. A conductivity flow control in R1 would enable additional water to be added if necessary and any excess rinse water that could not be returned as evaporative make-up would be pumped to the evaporation tank or discharged to batch treatment.

The chrome rinsing sequence consists of a 3-stage CF slow rinse (0.05 gpm) with recirculation from R3 to a chrome pre-dip tank. A stand-by tank provides additional holding capacity to evaporate any excess slow rinse that can not be returned to the chrome bath via an exit spray pumped from R3. Over 95% recovery is expected. The 2-stage CF final rinse would remove the residual chrome in the drag-out to achieve a final calculated chrome concentration of 1 mg/l. The final rinse would be discharged to an ion-exchange unit to remove the residual chrome which is estimated to be less than 250 gms/day.

Precious Metal Line

The precious metal line involves manual rack plating of gold, silver, and rhodium. The rinsing system in this line was directed at achieving the following objectives:

1. close loop rinsing after the nickel bath
2. recovery of greater than 99% of the gold and rhodium
3. segregation of greater than 90% of the cyanide load from the copper strike and silver baths into a slow rinse
4. reduction of water usage by inter-loop rinsing where feasible.

A drag-out rate of 0.5 gph was assumed in the calculations to determine concentrations, flow rates, and optimum arrangement of rinsing tanks.

In the cleaning line it was established that a 3-stage CF rinse after the copper strike and nickel baths would be adequate to satifsy the rinsing objectives. A conductivity flow control would be used to ensure that acceptable concentration levels would be maintained in R3. With a slow rinse flow rate set 25 gpd to match the evaporation rate in the nickel bath essentiallly 100% of the nickel salts would be recovered. Back-up evaporation capacity in the 150° F nickel bath is available through air agitation if an increase in the slow rinse flow is required.

In the gold line an off-line air agitated evaporation tank was used to further concentrate the slow rinse from the 3-stage CF rinse after the heavy and light gold baths. By returning the concentrate to the heated gold baths (110-120° F) as evaporative make-up, 99% of the gold could be recovered. This approach eliminated the need to use an off-line gold recovery process. If it is established that gold leakage from inefficient rinsing occurs, it would accumulate in the set rinse and an ion-exchange unit would be installed to recover the residual gold.

The rinsing sequence after silver plating consists of an electrolytic recovery rinse followed by a 2-stage CF slow and fast rinse. The slow rinse flow of approximately 25 gpd was calculated to segregate over 99% of the cyanide load. The residual cyanide load in the fast rinse would result in an acceptable effluent concentration after dilution with the other rinse water.

A 3-stage CF closed loop rinse was employed after the rhodium bath to recover over 99% of the rhodium by returning the slow rinse to the bath as evaporative make-up. The evaporation rate is maximized by employing air agitation in the bath at elevated temperatures during periods of non-plating activity.

WASTEWATER TREATMENT SYSTEM

As shown in the wastewater flow scheme in Figure 7, 16 gpm of wastewater is expected to be generated from the three process areas. The only sources that require treatment are:

- 2 gpm of lightly contaminated chrome rinse water
- approximately 100 gpd of cyanide contaminated rinse water

The remaining wastewater can be discharged to the sewer without treatment as the residual contamination levels would be below the EPA limits promulgated in the Electroplating Pretreatment Regulations and the more stringent local sewer use limits.

The 100 gpd of cyanide contaminated rinse water would be discharged to a 600 gallon reaction sump and batch treated on a weekly basis. The contaminated chrome rinse water would be processed in an ion-exchange unit which has an anion resin capacity (4 ft^3). This would enable the unit to be operated for over four weeks before regeneration would be required. The regenerate would be batch treated in a 500 gallon reaction sump to reduce the hexavalent chrome to chrome III.

The ion-exchange system which costs approximately $16,000 is a skid mounted semi-automatic unit that consists of a sand filter, a carbon column, and a cation and anion column each containing 4 ft^3 of resin. The system which has a hydraulic capacity of 8-12 gpm was sized to process rinses from the cleaning, chrome, and silver baths. Initially the deionized water (DI) produced in the system will be discharged to the sewer and the installation of a DI water recirculation system will be delayed until after the metal finishing operation is brought on-line in the new facility. Plant management elected to install a second back-up ion-exchange system which will be used initially to provide DI water for the metal finishing operation using town water rather than wastewater as the supply source.

The remaining wastewater sources include:

• schedule batch dumps (normalized over cleaning cycle):	300 gpd
• vibrator discharge (design specification):	500 gpd
• floor spills (estimated):	300 gpd
Total	1100 gpd

These discharges would be directed to the acid, alkaline, and floor drain sumps and pumped to a 3000 gallon batch reaction tank to neutralize the combined discharge and remove metallic fines and soluble metal.

SUMMARY & CONCLUSIONS

The facility design described above illustrates that in-process controls can be integrated into a process line to maximize recovery of process chemicals and significantly reduce treatment costs. The success of this approach is highly dependent on plant management initiating a detailed process evaluation to identify procedures to minimize drag-out losses and to locate sufficient space in the process line to incorporate additional rinsing. This approach would enable ion-exchange to be considered as an economical alternative to conventional treatment involving metal hydroxide precipitation.

REFERENCES

1. Control and Treatment Technology for the Metal Finishing Industry, In-Plant Changes. EPA Summary Report, January, 1982. Industrial Environmental Research Laboratory. EPA 625/S8-82-008.
2. Control and Treatment Technology for the Metal Finishing Industry, Ion Exchange. EPA Summary Report, June, 1981. Industrial Environmental Research Laboratory. EPA 625/S8-81-007.

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