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Alkaline Noncyanide Zinc Plating and Reuse of Recovered Chemicals

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Alkaline Noncyanide Zinc Plating with Reuse of Recovered Chemicals

by

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NOTICE

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FOREWORD

Today's rapidly developing and changing technologies and industrial products frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure their impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis to support the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research. It provides a vital communication link between the researcher and the user community.

This document presents the results of an experiment conducted to compare reductions in the volume and toxicity of wastes that resulted from the change from a cyanide-based to an alkaline noncyanide-based plating operation. This material substitution facilitated recovery and reuse of both rinsewater and plating bath chemicals. An assessment of the economic impact resulting from this modification is also provided.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

A metal finishing process can create environmental problems because it uses chemicals that are not only toxic but also resistant to degradation or decomposition. A study was undertaken at a zinc electroplating operation to achieve zero discharge of wastewater and total recycle of recovered precipitates. The first step in this project was to change an existing zinc cyanide (CN) plating line to one that used an alkaline noncyanide (ANC) zinc bath. The project then investigated a closed-loop system to treat plating rinsewater from the ANC zinc plating line so the plating chemicals were recovered and the water purified. The goal was to return both the recovered zinc hydroxide and the clean water to the plating line for continued use. The system that was designed and installed, at P&H Plating Co., a Chicago area operation, used precipitation by pH adjustment to remove the zinc from the rinsewater. The precipitated zinc hydroxide was collected on filters, dewatered using a filter press, and stored for reuse in the plating line as needed. Once filtered, the water was recirculated to the rinsing portion of the plating line. The recovery/recycle system successfully purified the rinsewater and facilitated the recycling of the cleaned water and the precipitated zinc hydroxide. Eliminating cyanide from the plating process meant the line workers were dealing with a less toxic plating bath, made compliance with regulations easier, and reduced treatment and disposal costs for the company. The recycling of the recovered water and the zinc hydroxide further reduced the costs for treatment and disposal. The replacement of this single CN line with an ANC line resulted in an annual savings to P&H Plating of $14,000 from the elimination of the need to pretreat the plating line rinsewater to oxidize cyanide. The addition of the recovery/recycle system increased the company's savings to $62,000/year. The reuse of 30% of the recovered zinc hydroxide and 70% of the treated rinsewater reduced annual water usage and wastewater discharge by 841,911 gallons and reduced the amount of sludge disposed annually by 14 cubic yards. The payback period for the recovery/recycle system is slightly less than 18 months. Installation and use of this system for other ANC plating operations would result in reductions in wastes and increased economic benefits similar to those experienced by P&H Plating Co.

This report was submitted in partial fulfillment of Cooperative Agreement No. CR815829 by the Hazardous Waste Research and Information Center under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from January 1990 to December 1992. The work was completed as of December 18, 1992.

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SECTION 1

INTRODUCTION

The Waste Reduction Innovative Technology Evaluation (WRITE) Program was implemented by the USEPA in 1989. In May of that year the Illinois Hazardous Waste Research and Information Center (HWRIC) began its participation in the program with the initiation of a three year project to evaluate a minimum of five pollution prevention technologies currently used by Illinois industries. One of the industries targeted for investigation was the electroplating industry. For the project, *Alkaline Noncyanide Zinc Plating with Reuse of Recovered Chemicals*, HWRIC staff worked with contractors hired by an electroplating company to evaluate the feasibility of using an innovative closed-loop rinsewater treatment system to precipitate the plating chemicals for recovery and reuse and to produce cleaned water that could be recirculated to the rinsing tanks and sprayers. The system uses pH adjustment to precipitate zinc hydroxide from the rinsewater from an alkaline noncyanide zinc plating process making the precipitate available for reuse in the plating bath. After precipitation, the treated rinsewater is of sufficiently high quality to be used again in the plating line.

This project represents a joint research effort of P&H Plating Co. (P&H) and the Center for Neighborhood Technology (CNT), both of Chicago, Illinois; HWRIC, Illinois Department of Energy and Natural Resources (ENR), Champaign, Illinois; and the U.S. Environmental Protection Agency (EPA), Office of Research and Development, Cincinnati, OH.

The wastes generated from the electroplating processes are carefully regulated to eliminate or at least reduce the threat that their disposal may pose to human health and the environment. Treatment is almost certainly required before disposal. There are many publications available that discuss the regulations and suggest technologies to meet the regulatory requirements (Spearot 1993, USEPA 1987, USEPA 1985b, USEPA 1982). Researchers have explored the feasibility of a centralized treatment facility for metal finishing wastes (Comfort et al 1985). Others have examined technologies to reduce or recover and reuse electroplating process wastes (Foecke 1986, USEPA 1985a, USEPA 1990, Walton and Loos 1992, CDHS 1990, HWC 1990). Simple process changes such as slowing down the withdrawal of the workpiece and increasing drainage time to reduce dragout can result in significant reductions in the amount of plating bath chemicals found in or transferred to the rinsewater wastes. Since the largest volumes of plating wastes are contaminated rinsewaters, adoption of methods to reduce the volume and/or toxicity of these rinsewaters is desirable

(USEPA 1990). Ideally, efforts should be made to recycle the rinsewater and to recover the metals it contains so they too can be reused in the plating process or reclaimed for other uses. Developing a closed-loop system to achieve this end would be beneficial both economically and environmentally (Walton and Loos 1992). The design, installation, and testing of one type of closed-loop system to reduce electroplating process wastes was the primary objective of this study.

For this project, P&H Plating replaced one zinc cyanide-based barrel plating line with one that used an alkaline noncyanide zinc plating bath. This new line was used to evaluate the effectiveness of the recovery/recycle system designed by CNT engineers. The goal was to recover zinc from the process rinsewater, recirculate the cleaned water, and approach zero water discharge. Once precipitated, the zinc hydroxide was collected through filtration, transferred to a filter press to remove residual water, then stored in a barrel until it was needed to replenish the plating bath. The purified rinsewater was recycled through a closed-loop system, developed and installed by CNT engineers, for reuse in both spray and counterflow rinse tanks. Recovery of the zinc hydroxide and its reuse in the bath coupled with the reuse of the cleaned rinsewater resulted in reduced operational and disposal costs.

HWRIC staff evaluated the effectiveness of the system in achieving waste reduction by:

- quantifying the effectiveness of the removal of zinc through precipitation by pH adjustment, the basis of the recovery system;
- determining the quality of the precipitate and the cleaned water that were recovered;
- comparing the plating quality of the cyanide-based process to that achieved with the alkaline noncyanide-based process which used both the recycled chemicals and the treated rinsewater; and
- analyzing the costs associated with the change in the process and the installation and use of the recovery/recycle system.

Evaluation of the system continued for nearly two years. An initial 4 week analysis of the recovery process indicated that it would indeed be effective in producing both zinc hydroxide and water that could be reused in the plating line. After the system was in place for three months, however, the plating quality had deteriorated and the system was bypassed until the cause of the problem was determined. The persistence of the company and their desire to employ recovery and recycling in their facility resulted in resolution of the problem. Once the problem was corrected, another period of evaluation of the recovery/recycle system was undertaken to document the metal removal efficiencies and to determine the treated water and precipitated zinc hydroxide quality. Data from these evaluations are included in Section 4 and Appendix B of this report. The original CNT recovery/recycle (R/R) system has been modified slightly to accommodate larger volumes and flow rates than were anticipated in the original design discussions. The modified R/R system continues to be used at P&H Plating on a single plating line. The new design will accommodate the use of the R/R system to clean rinsewater from two lines. It is anticipated that this two line system could be operational within two years.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The CNT designed R/R system proved quite successful in meeting the project objectives. By converting from a cyanide-based (CN) to an alkaline noncyanide-based (ANC) plating bath, the company eliminated one step from the treatment cycle, i.e. the destruction of cyanide which was no longer present in the wastewater from this plating line. The removal of cyanide from the system also reduced the risk to employees by eliminating a highly toxic substance from their work environment. The treatment of the wastewater proved so successful that nearly all of the recovered water could be recycled as well as much of the precipitated zinc hydroxide. As a result of installation of this recovery unit in the facility, operational costs, including treatment and disposal costs, raw material purchases, and water usage fees were reduced by approximately $62,000/year. The cost to design and install a R/R system like the one in use at P&H Plating is recovered during 18 months of operations. The reuse of 30% of the recovered zinc hydroxide and 70% of the treated rinsewater reduced annual water usage and wastewater discharge by 841,911 gallons and reduced the amount of sludge disposed annually by 14 cubic yards. Similar economic benefits are anticipated from installation of this type of recovery unit in other plating operations.

The goal of zero discharge and total recycle was not achieved for two reasons. The rectifier that converts alternating current to the direct current required for the plating process is tap water cooled (Cambria 1989). This cooling water flows into the counter flow rinsing tanks on the plating line. As a result of this continuous addition of fresh water, only 70% of the treated rinsewater is needed for the line. The company is currently exploring the possibility of using the treated water in the rectifier cooling operation which if successful, would meet the project goal of zero discharge.

Only 30% of the recovered zinc hydroxide is returned to the line for it is not a totally suitable replacement for the zinc ingots traditionally used to replenish the plating bath zinc. At present this precipitate can only be used on this test line as it is not suitable at all for the CN lines; however, as the company converts to an all ANC zinc operation the precipitate can be a raw material source for all of the lines. Additionally this precipitation process is partially serving as a pretreatment step; the cost of the precipitation pretreatment is less than would have been the cost of pretreating the cyanide containing rinsewaters. The compliance criteria that need to be met by the final treatment are only those for zinc, since there is no longer cyanide in this rinsewater. The maximum discharge levels for metals are generally easier to achieve than those for cyanide, resulting in reduced treatment costs and fewer compliance problems.

All of the precipitate produced is passed through the filter press which greatly reduces its volume. The unused portion is stored for later use or disposed as a hazardous waste. While it would be possible to petition to delist this waste, the amount being produced is less than 5% of the total metal waste that the company produces and must routinely dispose. Since much of the other metal waste was from cyanide-based lines and probably contained residual amounts of cyanide, even after treatment, it was disposed as a hazardous waste. It is currently more economically advantageous to simply add the zinc hydroxide to that waste and dispose of it as hazardous rather than separating it, storing it, and attempting to have it delisted (Anderson 1993). As the company converts all of its plating lines from cyanide-based to noncyanide-based it will experience even greater economic and environmental benefits. This change will eliminate the need for cyanide destruction in the company's treatment operations. One major compliance problem will also be eliminated as will potential health risks associated with cyanide exposure.

Although the goals of the project were not totally achieved, the use of this system has proven to be economically beneficial to the company. The change to an alkaline noncyanide bath has reduced the toxicity of the plating line and its resulting wastes. The water and chemical recycling made possible by the CNT designed R/R system has reduced operational costs. Direct results of this recycling effort are reduced water usage, fewer raw material purchases, lower treatment costs, and smaller volumes of waste needing disposal. This system is simple and functions well. It is in use at P&H Plating today and its use in other similar electroplating operations would result in economic benefits comparable to those experienced by P&H.

RECOMMENDATIONS

Cyanide-based plating baths are still the most widely used type of bath, despite the costs of pretreatment, treatment, and disposal. The tightening of discharge limits and the ban on land disposal of cyanide containing wastes have made their replacement by less toxic, more easily treated bath chemicals desirable. Cyanide-based systems are well defined, making analysis and control of the concentration of plating bath chemicals relatively simple processes. Extensive pretreatment or cleaning of the parts to be plated is not required. The final products are generally of very high quality with uniform, hard, bright, corrosion resistant plated deposits. This process, however, requires the use of highly toxic chemicals and produces equally toxic wastes that are difficult and expensive to treat and dispose (Cushnie 1985).

While the toxicity and waste treatment problems inherent in zinc cyanide plating can be substantially reduced by changing to the use of noncyanide plating bath chemicals, there are significant obstacles to changing the plating process. In terms of product quality, the alkaline noncyanide zinc plating finish is not as lustrous nor is its color the same as that produced by a cyanide zinc process. This can be a serious problem since customers frequently equate quality with appearance and find the noncyanide finish unacceptable aesthetically. Also, the alkaline noncyanide plating process requires the plating surface to be much cleaner than the surface being plated by a cyanide-based process. Many shops are unable to provide this more stringent parts cleaning (Kansupada 1985).

Despite these problems, alkaline noncyanide plating produces a hard, corrosion resistant finish which at least equals and may exceed that produced by the cyanide zinc process. The potential reduction in toxicity and operating costs that result from making this plating process change warrants increased efforts to overcome customer concerns about the luster and color of the finish and encourage their acceptance of the alkaline noncyanide zinc plated products (Kansupada 1985).

HWRIC and USEPA agree that there are many pollution prevention opportunities for the electroplating industry left to explore (USEPA 1992). HWRIC continues to work with electroplaters to develop and document other waste reduction technologies. Documented case studies of process modifications and technology evaluations that lead to source reduction are available but more should be prepared (Kohl et al 1985, Kirsch and Loobey 1991, NCDNRCD 1985, USEPA 1993, Lindsey and Peden 1994). Distribution of this information to the appropriate audience can be achieved with the assistance of trade groups for the electroplating industry. Continued association with these industry organizations is essential to identify new pollution prevention options and to promote adoption of those that have succeeded. This continued interaction can only benefit all parties involved. Economic benefit could be substantial to the companies willing to work toward source reduction. The environmental benefits that could result from the reduction in toxicity and volume of this industry's wastes would be significant and would be reason enough to continue to support the research that will bring about those reductions.

SECTION 3

PROJECT DESCRIPTION

In this section, general information about the electroplating industry and P&H Plating Co.'s operation is provided. Also discussed briefly is the bench scale study that was used to develop the CNT recovery/recycle (R/R) system and the information that was used to formally evaluate its performance. A detailed description of the CNT R/R unit and how it operates are provided.

INDUSTRY BACKGROUND

Electroplating is a process used to coat metal or plastic objects with one or more metals. This is achieved by submersing an object into a solution of dissolved metal ions and passing an electrical current through the solutions. The result is the deposition of the metal onto the surface of the object. The most commonly used plating metals are: brass, bronze, cadmium, chromium, copper, lead, nickel, tin, and zinc. The plating solution or bath may contain metal salts, alkaline compounds, and additives designed to reduce irregularities in the plating finish and increase the brightness of the finished surface (EMPE, Inc. 1986).

Waste reduction in the electroplating industry is important to achieve for several reasons. The metal finishing process can create several environmental problems for it uses chemicals that are not only toxic but also resistant to degradation or decomposition (UNEP 1989). The electroplating wastewater pollutants of greatest concern are toxic metals, cyanide, toxic organics, and conventional pollutants such as suspended solids, oil, and grease (USEPA 1985).

Many opportunities exist in electroplating operations to achieve waste reduction. The design and operation of the system used to move the parts through the plating line will determine how much plating solution is dragged out into the wastewater. Simple steps such as submerging the plating barrel half way, which will generally still ensure complete submersion of the parts being plated; increasing drain time; and installing sloped drain boards can mean significant differences in the amount of dragout. Other options include recovering bath chemicals, cleaning and recycling rinsewater, using less toxic chemicals when possible, and using technologies such as ion exchange to clean and maintain plating baths (USEPA 1990, USEPA 1985a). Adoption of these types of process modifications are generally not only environmentally advantageous, but also result in economic benefits from their implementation.

Federal and state regulations have been developed to eliminate or reduce these pollutants in the environment by setting limits on the amounts of toxic plating line constituents that can be discharged (USEPA 1985b). The current federal standard for the maximum discharge level of zinc is $\leq$4.5 mg Zn/L for daily discharge and $\leq$2.6 mg Zn/L for a 4 day average discharge, and for total cyanide it is $\leq$1.9 mg/L/day and $\leq$1.0 mg/L for a 4 day average (Martin 1992). Local compliance standards may be even more restrictive. For example, P&H must comply with the discharge standards for the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC 1991) which are 0.10 mg CN^-/L and 1.0 mg Zn/L for discharge to waters and 5.0 mg CN^-/L and 15.0 mg Zn/L for discharge to sewage systems. The cost to the electroplating industry to comply with these regulations can be considerable. These costs include not only those for disposal of the waste stream but also the expense of pretreatment to reduce the volume and/or toxicity before disposal is even possible.

Cyanide is a particularly difficult contaminant to treat. It readily combines with iron to form very stable complexes which may not be completely precipitated by standard treatment methods. The treatment process may not always be functioning efficiently resulting in incomplete cyanide removal from the company's effluent (Martin 1992). Enforcement efforts on both the state and federal levels are well coordinated. Inspector training and information sharing are on the rise in local communities, the states, and the federal government. The penalty for violators will certainly include monetary fines, sometimes in the millions of dollars, and may also include a prison sentence (Krukowski 1992). It therefore becomes essential for electroplaters to develop an integrated approach to waste management that meets compliance standards and includes waste reduction as a vital component.

The Harris Directory (1992) lists 5,200 companies under the Standard Industrial Classification (SIC) Code 3471, plating and polishing, in the United States with 331 residing in Illinois. A review of the County Business Patterns for 1989-1990 (Bureau of the Census 1993) indicates that there are 174 plating operations (SIC 3471) located in Cook County. In these Chicago facilities, one can find a wide variety of metals being plated on an assortment of surfaces. The plating of zinc on steel parts is common to many Chicago plating companies. While the majority of these companies use cyanide-based plating baths, operations employing noncyanide plating baths with zinc hydroxide and zinc chloride as the plating bath chemical are growing in number (Kansupada 1985). The parts that are plated range from nuts, bolts, and other common hardware items to automobile parts and metal furniture. Zinc plating is designed to be both functional (preventing corrosion) and decorative (providing an attractive appearance).

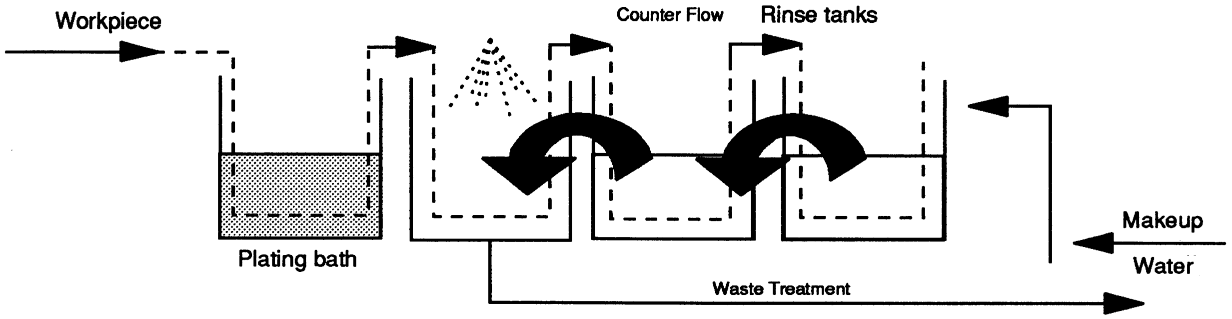
P&H PLATING CO. OPERATION

HWRIC researchers worked with P&H Plating Co., a large Chicago plating job-shop that operates 16 hours a day, 6 days a week and employs 100. It uses barrels, hoists, and racks to move parts through the plating operations. For this study a barrel line that plates zinc on small steel parts such as washers, nuts, bolts, and hinges was used. Although the project concentrated on zinc plating, the shop is capable of and does plate nickel, brass, copper, and cadmium on a variety of surfaces. The facility contains a waste treatment area which receives effluent at an average rate of 150 gallons per minute (gpm). Pretreatment of the wastewater is required for effluent from the cyanide and chromate plating lines. The cyanide wastewaters are treated with hypochlorite to destroy cyanide complexes and comply with current standards for discharge of metals and cyanides into the sewer. The pretreated wastewaters are combined and the metals are removed principally by precipitation. The precipitate is collected as sludge and disposed according to current regulations. The treated wastewater is tested and discharged, if all of the regulatory criteria are met, and returned for additional treatment if they are not.

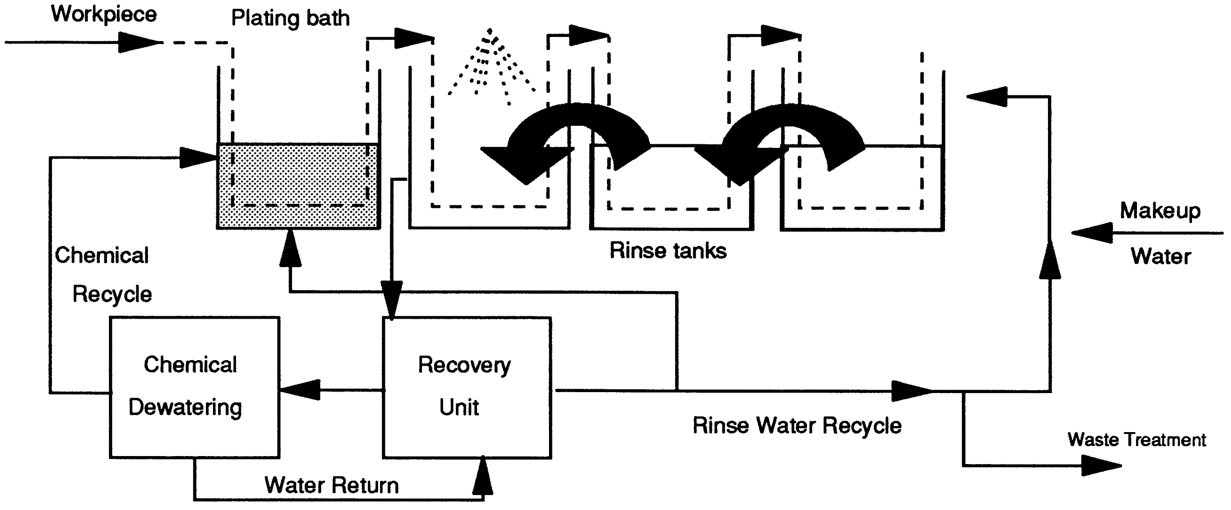
In this project, two changes were made to one of the zinc barrel plating lines. First, the plating solution was changed from a zinc cyanide (CN) bath to an alkaline noncyanide (ANC) zinc bath. Although there are examples of successful plating operations replacing CN baths with ANC baths (FM 1992, CDHS 1990) there was still concern at P&H that the plate achieved with the ANC process would not meet their customers' satisfaction. By changing to the ANC process, the company could explore the possibility of implementing a waste reduction technology to recover the plating line wastes. Once the change to ANC actually occurred, a rinsewater purification system was installed to recover both water and zinc hydroxide for reuse in the plating line. The objectives of this project were to evaluate these changes by examining the reduction in toxicity and volume of the waste and assessing the effectiveness of the recovery of zinc hydroxide from the waste water. The feasibility of using the treated water and the precipitated zinc hydroxide in the plating lines was also explored and the economic benefits resulting from the use of the CNT R/R system determined.

THE PLATING PROCESS

In the original operation of the plating line (which is the current operation of the 5 plating lines that were not modified for this project), workpieces were placed in the barrel and subjected to several precleaning steps before plating. The plating tank for the modified line is divided into 8 stations each capable of holding one barrel. The barrels with the workpieces (in this study generally small steel items such as washers and nuts) inside were dipped into the plating tank for approximately 25 minutes (time and current will vary somewhat by job). From the plating tank, the barrel and its contents moved to the spray rinse tank where 4 nozzles sprayed water into the barrel for 20 seconds at a rate of 7 gallons per minute. The barrel then moved on to two additional counterflow rinse tanks where it was submerged for approximately 2 minutes. The rinse spray and overflow from the counterflow tanks were collected, pretreated to oxidize the cyanide (Cushnie 1985) then sent to the waste treatment area where they were treated to comply with state and local effluent requirements before being discharged. Figure 1a is a very general schematic of the plating and rinsing operation. The change that was evaluated for this project is represented in Figure 1b. The modification was to direct the rinse water through a closed loop recovery system and return the treated water to the counterflow rinse tanks instead of simply sending the effluent stream to the waste area for treatment and disposal.



A. Typical Plating Line Schematic



B. Plating Line with Closed Loop Recovery System

Figure 1. Plating lines with and without Closed Loop Recovery System

THE CNT RECOVERY/RECYCLE (R/R) SYSTEM

The principles involved in the design of the CNT R/R system were relatively simple and similar to the standard wastewater treatment of flocculation to remove metals prior to disposal of water and sludge wastes. Once the change was made from the cyanide plating bath to one that used noncyanide compounds, the zinc that was "dragged out" into the rinsewater could be easily precipitated as zinc hydroxide by simply adjusting the pH of the solution. Most of the precipitated zinc hydroxide settled to the bottom of a clarifying tank. From there it was collected and returned to the plating bath. Water from the clarifying tank was pumped through filters to remove and collect suspended zinc hydroxide. The filtered water was returned to a holding tank for reuse in the rinsing process and the zinc hydroxide collected on the filters was returned to the plating bath.

Figure 2 is a schematic of the R/R system that was finally installed and is currently in use at P&H. Ideally, 100% of the zinc in the rinsewater would be recovered and returned to the plating bath. Additionally, all rinsewater would be recycled. The projected result would be substantial savings for the company in plating chemicals and water from this rinsewater purification that both recovers and reuses as well as treats.

Bench Studies

Two bench scale studies were needed to determine the optimum pH for complete precipitation and the correct pore size for maximum retention of the zinc hydroxide. To determine the optimum pH for the zinc hydroxide precipitation, the pH of aliquots of a known concentration of zinc hydroxide solution were adjusted at intervals of 0.2 pH units from a pH of 9.5 to pH 11.1. Approximately 50 minutes (the residence time of the rinsewater in the continuous stirred reactor (CSR) and clarifying tank based on the size of the tanks and system flow rate) after the pH adjustment, the solutions were filtered. The percent of zinc precipitated and the zinc concentration of the filtrate were determined. These tests indicated that a pH between 10 and 10.5 was ideal and a pH monitor and a controller were purchased and placed on the CSR to determine the pH of the rinsewater and to adjust and maintain it between pH 10 and 10.5.

The original standard that was used to determine whether the water was suitable for return to the rinse tank was that its zinc content should be less than the minimum discharge level for zinc allowed by the Water Reclamation District of Greater Chicago which is ≤4.5 mg/L daily and ≤2.6 mg/L for a 4 day average. During the bench studies, however, it was found that the recovery system could successfully remove the zinc to concentrations of ≤0.5 mg/L. This concentration (0.5 mg/L) became the new standard used in the bench study in both the determination of the optimum pH range for maximum precipitation and the proper pore size selection for complete removal of the precipitate.

The system design employed a dual filtration unit. A pump, placed approximately 2 feet above the bottom of the clarifying tank, was used to draw the rinse water through the

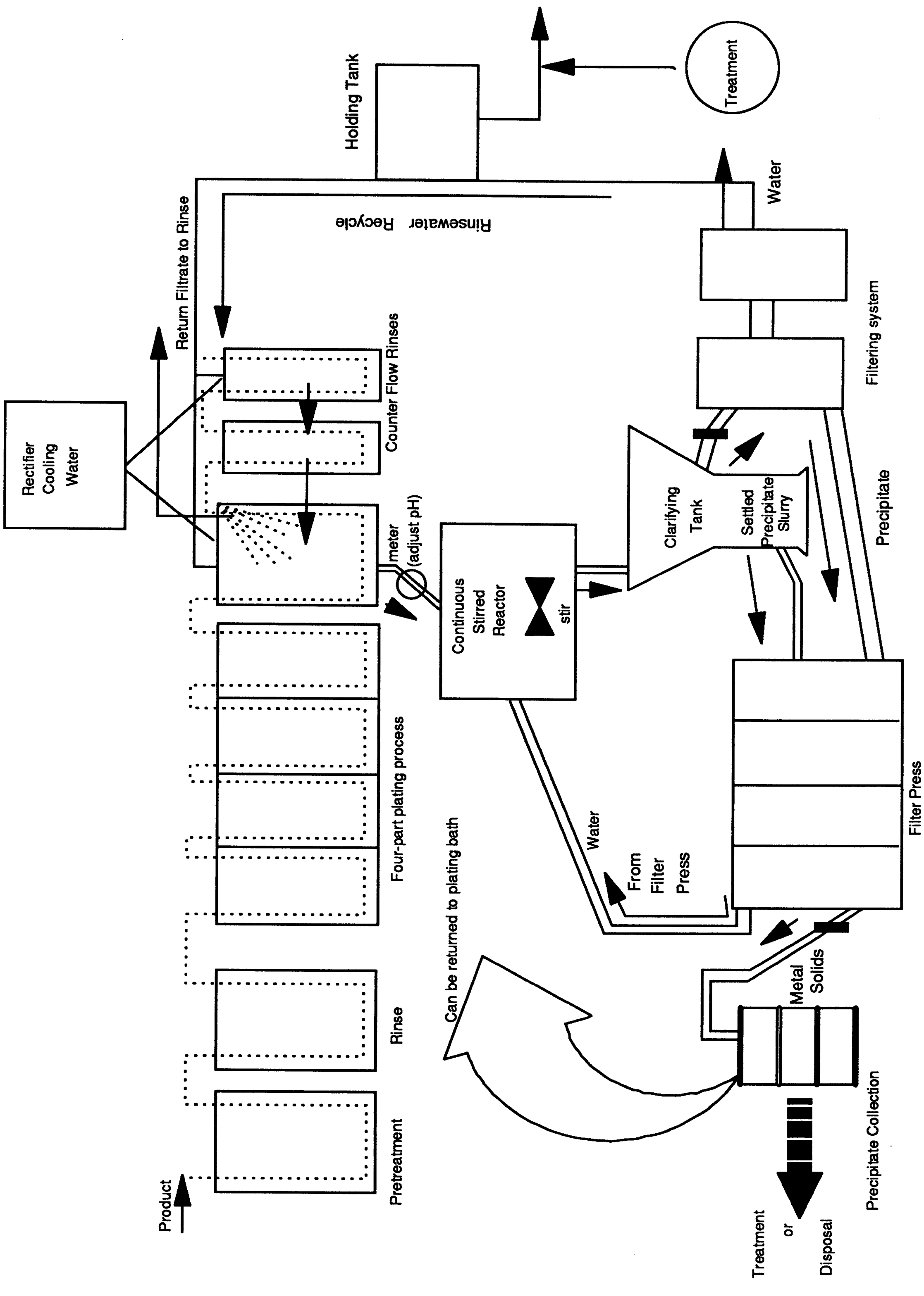


Figure 2. P&H Plating alkaline noncyanide plating line with CNT designed recovery/recycle system.

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dual filter unit. A series of tests using filters varying in pore size by 2 micron were made to determine the proper pore size to use to best accommodate the projected flow rate of 10 gallons per minute (gpm) and meet the ≤0.5 mg/L of zinc standard. As a result of these tests the unit consists of two consecutive filters with the first having a pore size of 12-15 microns to remove the coarser particles and the second, a pore size of 3-4 microns to remove the finer fraction of the precipitate.

R/R System Description

In the plating process at P&H there is the usual parts pretreatment or cleaning, followed by plating spray rinsing, and finally, submerging into two counterflow rinse tanks. Although cleaning requirements for ANC plating are generally more stringent than those for CN plating, no change was required to the pretreatment portion of the line at P&H. The company had already installed a very stringent cleaning component to their plating lines to ensure good parts cleaning and, presumably, better plate quality. This cleaning was more than was needed on the CN lines and quite acceptable for the new ANC line. The CNT R/R system was plumbed from the spray rinse tank into which the counter flow tanks ultimately overflowed. The rinsewater flows from the rinse tank (CFSR) into the reactor tank where the pH is measured and automatically adjusted.

This pH monitoring and control tank is a continuous flow stirred reactor. It is designed to allow adequate mixing to stimulate precipitation. Compressed air from an air sparger at the bottom of the tank is used for mixing in the R/R system. The flow rate through the reactor is set at 10gpm. The next step is to allow settling of the precipitated zinc hydroxide. This is accomplished in a flat bottomed clarifying tank. To facilitate the settling process, the tank is baffled. A recirculating pump pulls water from the clarifying tank through the dual filtering system to remove suspended hydroxide. The treated water is then either sent to the storage tank for reuse or to the waste treatment area for additional treatment prior to discharge. The settled precipitate is removed through a port near the bottom of the clarifying tank and combined with the precipitate collected on the filters. This composited hydroxide is put through a filter press to remove as much water as possible. The water that is removed is returned to the precipitation reactor and the de-watered hydroxide is analyzed and stored for future use or disposed if not needed. Figure 2 shows the system components and the way the water and solids flow through the system.

R/R System Performance

The initial testing of the system took place over 4 weeks. The design engineer ran the system from 8-16 hours a day during that period. The initial design differed somewhat from that depicted in Figure 2 and it was this 4 week test period that exposed the design flaws and allowed the time to implement the changes that made the system perform as desired.

The early design flaws were the result of planning a system for a rack operation, but ultimately implementing it on a barrel line. The original concept was proposed for use by another plating company. The bench studies and subsequent system components selection were based on calculations of dragout that would be expected from a rack plating operation. Financial problems forced the first industrial participant to withdraw. P&H agreed to participate, but was considering the change to the alkaline noncyanide process for one of their barrel lines. The original system design could use components P&H already had available which would mean minimal additional costs to P&H. This first system had many mechanical problems. It was modified to include: separate precipitation and settling tanks, stirring capabilities for the precipitation tank, baffles in the settling tank, a valve in the settling tank to facilitate removal of the settled precipitate, a valve in the water recycling line and the water storage tanks to bleed off excess water to the treatment area, and a filter press to dewater the hydroxide.

These changes were needed for several reasons. The dragout from the barrel was much greater than that from the rack which meant more precipitate to be filtered and frequent clogging of the filters ultimately resulting in considerable downtime. Sparging in the precipitation tank hastened the precipitation process, so a minimal amount of zinc hydroxide remained suspended in the water. The sparging coupled with the installation of the settling tank and the valve to remove the settled material, dramatically reduced the filter clogging and the system downtime. Inclusion of a filter press to dewater the recovered hydroxide reduced the volume of the precipitated solids, making the precipitate a more suitable additive to the plating bath and reducing the cost of disposal of the material that couldn't be used. The water recovered from the press operation could then be returned to the R/R system and ultimately recycled. These component changes did not eliminate all of the problems, but solved the major ones so that the system has remained in use for almost 3 years without needing further modification. Additionally, downtime for extensive system maintenance has been eliminated. A schedule has been established for routine checks of the mechanical components and the filters are replaced and cleaned every few weeks as needed. (The maintenance schedule is dependent on the number and types of jobs that are run on the line.)

Another major concern resulting from the change to an ANC-based system and the use of recovered materials was that of maintaining the plating quality. There has been a problem with customer satisfaction with the parts plated by this new process. Quality is typically linked to appearance. Because the plating luster is not quite as bright as with a cyanide-based process, the customer assumes that the corrosion resistance and other protective features for which the plate is applied have been adversely affected. Salt spray corrosion tests were performed to ensure protection was not compromised, but customers are not always easily convinced. This is a problem that is difficult to resolve. When changes in product appearance are equated with negative changes in product quality, one tactic to overcome this customer dissatisfaction has been to highlight the environmental and economic benefits resulting from reduced plating costs for the company due to the new ease in meeting compliance limits which also translate into reduced costs to the customer. These are very real problems for platers considering the switch from cyanide to less toxic materials and the potential loss of customers may prove to be too large of an uncertainty for some platers to risk by changing to safer plating process alternatives.

While the initial testing of the system showed promise, it was not without problems. It was through the persistence of the facility chemists that success was finally achieved. After several months of returning the precipitated zinc hydroxide to the plating bath, a noticeable and unacceptable change in plating quality was observed. HWRIC staff were concerned that the probable cause of the problem was the buildup of organic brighteners and their byproducts that were being collected with the zinc hydroxide precipitate and returned to the plating bath. Analysis by HWRIC's chemist, however, found no measurable organic carbon in either the treated water or sludge.

During the system shutdown to resolve the plating quality problems recovered zinc hydroxide was not used. The bath was adjusted as usual with new materials. Testing by the analytical laboratory normally used by P&H discovered that the problem actually was caused by excessive iron levels in the zinc anode balls used in the bath. These were replaced and the CNT R/R system was again put to full use. The system continues to operate and function as designed.

Although in this instance brightener buildup did not play a role in plating quality deterioration, it has the potential to affect the plate. Monitoring of the chemicals used in the bath is important. The recycling efforts may mean different additives are needed to ensure a high quality product. The willingness of the chemical supplier to assist the plating operation with this monitoring is critical to the implementation of new systems that employ a recycling option.

PERFORMANCE SUMMARY

This project began as a short term evaluation of a new technology to reduce electroplating wastes. Had it remained that, important information would have been lost and the evaluation would have been basically correct but flawed. Since the resolution of the plating quality problem, the CNT R/R system has been in continuous use at P&H. Maintenance of the system is minimal, consisting of proper care of mechanical parts and periodic replacement and cleaning of the filters. Zinc hydroxide is removed from the rinse streams with an efficiency averaging 84%. The amount of precipitate recycled to the system varies depending largely on the number of jobs that will require use of that line. On average, the company recycles 30% of the zinc it recovers. The quality of the treated rinsewater is generally acceptable for recycling and/or discharge. Essentially, the system works and is in use providing both environmental and economic benefits to P&H.

SECTION 4

RESULTS AND DISCUSSION

The use of the CNT R/R system has indeed been beneficial to the company, its employees, and the environment. Comparisons of plating wastes and other operational factors prior to and after installing the system clearly show the benefits. The comparisons examined: product quality, toxicity/safety differences, amounts and types of wastes produced, quality of the products of the R/R system, and use of the recovered materials.

P&H routinely collects and analyzes samples to assess the bath and the plating quality. While these analyses are vital to the successful operation of the plating lines, they did not really provide the information that was needed to evaluate the recovery/recycle capabilities of the CNT system. HWRIC staff used four full day sampling opportunities to obtain the samples used for the CNT R/R system assessment. The sampling took place over a month and occurred approximately 1 year after the system had been installed. During the first 6 months after installation, there were several problems, including previously discussed design flaws, that had to be resolved. By the time the HWRIC sampling effort took place, all of the system problems had been corrected and the unit had been in successful, routine operation for 6 months. The data from the analyses of samples taken from the early testing and those taken during this one month effort were used to quantify the effects of the change in the plating operation.

PLATING BATH CONVERSION

If a company were to start up a new plating line, it would begin the process by determining the cost of the bath chemicals for each alternative - the cyanide (CN) or the alkaline noncyanide (ANC) zinc plating solutions. This assessment would show that the total costs of make-up chemicals for each plating solution option were essentially the same - $1,771 for the CN bath and $1,860 for the ANC bath. These costs are broken down by cost/bath chemical in Table 1. Labor and water used in the bath preparations would be essentially identical, so those costs were not included in the calculations.

P&H, however, was not starting a new line but replacing an existing line. Since the company was still operating other CN zinc lines, the plating bath could be stored and used as needed in those other lines. Had this storage option not been available, the 1,800 gallon CN zinc bath that was being replaced would have to be treated and then disposed at a cost of $16-20/gallon. Additionally, the ANC system does not function properly in the presence of cyanide. Since the equipment in the line had previously handled CN zinc it had to be thoroughly washed. No attempt was made to quantify the amount of water used in this rinsing process. It was simply treated as wastewater from the line and piped to the waste treatment area for processing and disposal. This water was not considered in the economic evaluation presented in Section 5.

TABLE 1. COMPARISON OF COST FOR PLATING BATH MAKEUP CHEMICALS FOR 1800 GALLON SOLUTIONS

Zinc Cyanide Bath		Alkaline Noncyanide Zinc Bath	
Chemical	Cost $	Chemical	Cost $
NaCN	404		
NaOH	249	NaOH	560
Zn	1064	$Zn(OH)_2$	1100
Brightener	54	Brightener	200
Totals	1771		1860

R/R SYSTEM EVALUATION

To evaluate the effectiveness of the system, the amount and quality of zinc recovered from the rinsewater were determined. Additionally the quality of the recovered water was determined. Finally, the amount of the recovered materials that were recycled was calculated. The monetary value of the recycled chemicals and the water were calculated and used to determine the time required to recover the costs associated with the bath chemical substitution and the development, construction, and implementation of the CNT R/R system. Data used to assess recovery and quality are summarized in this section. The raw data are available in Appendix B.

Zinc Hydroxide Quality

Grab samples were taken from the filters and the bottom of the clarifying tank and analyzed for metal content. Metal concentrations were determined using atomic absorption spectroscopy following the sample preparation and analyses methods described in SW-846 (USEPA 1986) in accordance with the quality assurance plan for the project. The company routinely analyzes metal sludge samples prior to disposal. The contract laboratory that it uses for these determinations performed the analyses of the zinc hydroxide precipitate during CNT's testing of the R/R system. Since the most likely contaminants in the precipitate were oxides of iron from the parts being plated and calcium and magnesium from the tap water used throughout the system, concentrations of these metals were determined in addition to the concentration of zinc. The contract laboratory analyzed 32 samples for total solids content to assess the amount of water in the zinc hydroxide from the R/R system. Water content was consistent ranging from 86% to 93% and averaging 88% (see Table B-1). The samples were dried to a constant weight (a change of <0.2mg) then analyzed for zinc, iron, calcium, and magnesium at HWRIC's laboratory. Table 2 summarizes the data from these analyses. The standard deviations are included to indicate the variation that existed within the sample set. The data used to generate Table 2 are found in Appendix B (Table B-2).

TABLE 2. COMPARISON OF CONCENTRATIONS OF ZINC, IRON, CALCIUM, AND MAGNESIUM IN DRIED ZINC HYDROXIDE FROM THE CNT SYSTEM

Analyzing Laboratory	N*	Zinc		Iron		Calcium		Magnesium	
		Mean %	SD	Mean %	SD	Mean %	SD	Mean %	SD
HWRIC Lab	32	64.4	8.02	0.93	0.78	3.27	2.43	1.61	1.20

*N=Number of samples analyzed

The analysis of the recovered zinc hydroxide led to the following actions. Although iron, calcium, and magnesium are present in the precipitate, the concentrations of these materials were found to be at levels that should not effect plating quality; therefore, analysis of these three contaminants was not performed on subsequent samples. Zinc concentrations alone were used to assess quality and recovery. The percentage of zinc in pure zinc hydroxide is 66% and the mean found in the dried R/R system precipitate is 64%, so the precipitate is very suitable for recycling in the plating bath. The major problem with the R/R system precipitate was the amount of water it contained. The company preferred not to use heat to dry the precipitate and chose instead to purchase a filter press for dewatering. The press was added to the recovery unit and effectively dried the precipitate. Because the precipitate was then stored prior to being returned to the plating bath, additional drying through evaporation to the air took place. Water from the pressing operation was recycled through the R/R system.

A subset of these 32 samples was used to investigate the cause of the deterioration in plating quality that occurred approximately 6 months after the system became operational. Six samples were selected at random and analyzed for TOC following the method prescribed in SW-846 (USEPA 1986). It was suspected that the plating quality problem resulted from a buildup of brightener being carried into the bath on the recovered precipitate. Appreciable levels of TOCs (>1%) (Table B-3) were found in only one of the six samples analyzed. Other analytical anomalies were found in this sample, such as reduced levels of zinc (~45%) and high levels of iron (>5%) (Table B-2), which raised questions about its integrity. During the time the analyses were being performed, P&H's chemist discovered that the zinc ingots used in the plating process were not the purity required by the system. These were replaced and plating quality improved immediately, so no further investigation of the problem was undertaken. Since organic carbon was not present on these samples taken when there were problems, it was assumed this would be the case for the other samples and TOC was eliminated as one of the test parameters.

Zinc Hydroxide Recovery and Recovered Water Quality

The CNT engineer had originally planned to use the amount of zinc measured in the rinsewater and the amount of precipitate produced by the R/R system to calculate the percent removal of zinc. This assumed a constant flow through the system at a known flow rate or an accurate measurement of the volume of water passed through the system in a run. Unfortunately, the flow through the system is variable and could not be used to calculate the volume of water passing through the system. There were also no devices installed in the system to measure the rinsewater volume, so another means of calculating zinc recovery was used. The concentration of zinc in the rinsewater before entering the R/R system was determined and compared to the concentration of zinc in the water leaving the system. The difference was divided by the amount of zinc originally measured in the rinsewater, multiplied by 100% and reported as %Zn removed.

During the initial period of testing by CNT, two types of samples were taken, the rinsewater and the zinc hydroxide precipitate. The analysis of the precipitate samples was discussed in the previous section on recovered metal quality. Like the precipitate samples, the rinsewater samples were grab samples. They were taken from a sampling port in the piping to the R/R system (input samples) and from the overflow valve on the purified water holding tank (output samples). These rinsewater samples were analyzed by HWRIC's laboratory for zinc and iron. Four samples were randomly selected and analyzed for total organic carbon (TOC) as well. The zinc concentrations were to be used in the calculation of the %Zn recovered. The analyses for iron were to determine the levels of possible contaminants. Although the presence of contaminants such as iron and organic carbon compounds would not affect plating quality since the cleaned water would be recycled to the rising portion of the plating line, it was useful to obtain some indication of their concentrations to assess whether the cleaned water could be used for other purposes such as replenishing the plating baths. Table 3 summarizes the analyses for zinc and iron for this set of samples (see Tables B-4 and B-5 for raw data). TOC values were at the method detection limit (1.0 mg/L) (Table B-6) and are not included on the table. Since the amount of iron and TOC were so small, they were not analyzed in the samples taken later in the evaluation.

TABLE 3. ZINC AND IRON RECOVERY FROM INITIAL TESTING OF CNT SYSTEM

Analyte	N*	Input Mean (SD) mg/L	Output Mean (SD) mg/L	% Recovered
Zinc	16	190 (± 61)	19 (± 23)	90
Iron	16	0.48 (± .18)	0.38 (± .38)	21

*N=Number of samples analyzed

Theoretically, measuring the concentration of the metal in the rinsewater being put into the R/R system and then measuring the concentration of the metal in the water that has passed through the system and is about to be recycled should allow you to calculate the percent of zinc removed. In practice this technique is not totally accurate. The difficulty is how do you compare what went in to what came out? How long do you wait from the time you start up the system and take the input sample to grab the output sample? Again, because there were no devices in the system to measure flow, this period could not be calculated. Additional factors also play a role here.

When the plating bath is not in use, the R/R system is turned off. Whatever solution remains in the lines and tanks of the system sits until it is again activated. Because of the need to cool the rectifier there is a period after the plating operation stops when clean water is being added to the rinse tanks. There is another period at the start of a plating run where the dragout has just begun and the metal levels have not built up as they will later when several barrels have been through the plating and rinsing steps. What this leads to is a cycling of metal concentrations in the input and output waters. HWRIC laboratory staff tried to account for these factors in the sampling effort made towards the end of the project. Input samples were taken after the first barrel of parts was rinsed and the output sample was taken approximately half an hour later. Table 4 is the data from the analyses of the samples taken on September 19, 1992. The input samples are rinsewater from the ANC line before it entered the R/R system and the output samples are water that had passed through the system and was about to be recycled. These data are a good example of the changes in the zinc concentrations as the plating operation progressed from start-up, through the plating of parts, to shutdown of the line.

TABLE 4. CONCENTRATION OF ZINC IN WATER SAMPLES TAKEN SEPTEMBER 19, 1992

Input mg/L	Output mg/L
250	10
180	21
290	32
270	69

It is interesting to note that the zinc levels in the output sample (which had passed through the recovery process) increased with time. This was normal for the system. Since the levels are fine for rinsewater reuse, no attempt was made to determine why this occurred. It is probably because the precipitate remains in the clarifying tank from the start of the run through the end of the run. Precipitate removal takes place once the line is shut down. The concentrations of zinc in the water could easily show this level of increase simply as a result of the stoichiometry of the precipitation reaction and the amount of precipitate present in the tank at the end of the run. While the water being recycled may not have always been suitable to discharge, it was acceptable for reuse in both the rinsing portion of the plating line and in the plating bath itself where zinc was present in concentrations >50%.

To determine zinc recovery, four sets of samples were taken. These samples were grab samples taken from sampling ports in the input and output lines of the R/R system. Each sample set consisted of four input and four output samples. The first input sample was taken after the first barrel with parts had passed through the plating line. The approximate time of the plating operation for the day was determined and the second, third, and fourth input samples were taken at quarterly intervals. A fairly typical sequence would be: start up, first sample at one and one half hours, second sample at three and one half hours, third sample at five and one half hours, and final input sample at seven and one half hours. Output samples were all taken at about one half hour after each input sample. The percentage of zinc recovered by the system was calculated by determining the concentration of zinc in the input sample, subtracting the concentration of zinc in the output sample collected ~one half hour later, dividing that difference by the input concentration and multiplying by 100%. Using this method, the %Zn recovered ranged from 55% to 99%. The large range for the percent recovery is a factor of the cyclical nature of the system input and output that was just discussed. Because of this variability, it was decided to use each data set as a whole calculating % recovery as the [(mean input)-(mean output)] ÷ mean input x 100% rather than calculating the recovery between individual input/output pairs. This approach should more accurately portray the % recovery for each plating run.

Blank problems were encountered during the analysis of one sample set which could not be resolved, so only three data sets were used to calculate % recovery of zinc. Table 5 presents the percentage of zinc that was recovered by the R/R system and also provides mean input and output zinc concentrations used for the calculation. The standard deviation about each mean is provided to indicate the variability of the zinc concentrations within the set. The actual data sets used are found in Tables B-7 and B-8. When the data are evaluated in this way, the %Zn recovery ranges from 75% to 89% and averages 84%. Although 100% recovery of zinc from the rinsewater was not achieved, the amount that was recovered is reasonable. Additionally while not all of the samples of the outflow had measured zinc concentrations low enough to discharge, the average output levels for each set of samples was within the discharge limits or very close to them. Since these means would more closely approximate the composite sample that would be tested for metal concentrations before further treatment or discharge, these data suggest that the system could generally generate recovered water that could be discharged without additional treatment.

TABLE 5. PERCENT ZINC RECOVERED DURING 3 PLATING RUNS

Run Number	Zinc Concentration*		Zinc Recovered %
	Input Mean (SD) mg/L	Output Mean (SD) mg/L	
1	68 (± 59)	17 (± 20)	75
2	248 (± 48)	33 (± 26)	87
3	38 (± 15)	4 (± 2)	89

* Means were calculated from 4 samples

Zinc Hydroxide and Recovered Water Reuse

As stated previously, the precipitated zinc hydroxide is collected from the settling tanks and scraped off the filters, then placed in a filter press for dewatering. The zinc hydroxide is then stored until needed in the plating line. During this storage additional drying of the precipitate occurs as the result of evaporation of precipitate moisture to the air. All of the precipitate obtained from the R/R system could eventually be recycled into the plating operation. The company estimates 30% of the zinc hydroxide recovered from the ANC line is recycled.

Recovered water is also collected until needed. Because of the cooling system for the rinsing baths, fresh water is being added to the rinsing tanks. As a result of this input, all of the recovered water was not needed. The water storage system was designed so that overflow from the storage tank was directed to the wastewater treatment unit for the facility where it was pooled with other wastewaters from the plant, treated, and discharged. The company estimates 70% of the water recovered is reused.

PLATING QUALITY COMPARISON

While the reasons for plating are sometimes purely ornamental, more frequently the plate provides protection. Finishes may be bright or dull and it may not always be possible to achieve the desired luster with the ANC system, although advances in the last decade have provided less toxic bath alternatives that produce parts more like the bright, shiny objects that result from a cyanide-based operation (Cushnie 1985). Ultimately, whether the plate is satisfactory or not is up to the customer, but there are two standard tests that can be performed to check quality. The first is to measure thickness. The desired thickness of the plate is generally determined by the use that will be made of the item being plated. There are industry standards for specific items as well as those required to meet customer specification. While the ANC process may not always be the most suitable to the customer needs, the current generation of ANC baths offer better coverage than and color comparable to CN systems (Kansupada 1985). To test the ability of each process to meet the thickness standards metal washers were plated on both lines and thickness measured. Both systems produced acceptable levels of thickness. The CN plated parts measured 0.0004 inches for the zinc plate and the ANC plated parts, 0.0005 inches of zinc.

To assess the corrosion resistance imparted to the object as the result of the zinc plating, these washers were subjected to salt spray testing, following ASTM method B 117 (ASTM 1990). The test objects are suspended in a chamber and sprayed with a salt solution and then checked at designated intervals for signs of corrosion. Washers plated by the CN process showed white (zinc oxide) corrosion after 10 hours and rust after 500 hours of exposure. The washers from the ANC line also show white corrosion after 10 hours but the rust did not appear until 700 hours exposure. This difference is most likely due to the thicker zinc plate on the ANC plated parts, and is probably not significant.

A second salt spray test had similar results. Three sets of washers (50 in each set) were subjected to salt spray testing. The three sets were washers plated on a CN zinc line, washers from the ANC line before any chemical recycling took place, and washers from the ANC line using recycled chemicals and water. In each set approximately 6% (2-4 washers) of the parts showed white corrosion after 10 hours with rust appearing between 700 and 1,000 hours, generally on 50% or more of the pieces. The corrosion protection from each of the three plating lines was essentially the same. The variation among the three test sets of washers was 2% (1/50 parts), i.e. the number of washers showing signs of corrosion in each set was the same at almost every time recorded. Additionally, the protective quality of the plate is deemed acceptable when parts are subjected to the salt spray for periods longer than 24 hours before rusting begins. Using this criterion both the CN and ANC baths provided acceptable corrosion protection.

TOXICITY COMPARISON

Had there been no economic benefit from the change to ANC plating the reduction in health and environmental risk resulting from the elimination of cyanide from the process would have been sufficient to warrant its adoption. CN zinc plating does require extensive treatment before disposal and uses chemicals hazardous to human health. Chemical substitution to achieve source reduction, as was done for this project, not only reduced process costs but also the company's liability because of the reduction in the toxicity of the chemicals being handled and disposed (CDHS 1990).

The exposure of shop workers to toxic chemicals presents the most serious health and safety problems for the electroplating industry. Although no occupational illness has been documented for electroplating operators, they are routinely exposed to hazardous substances which are known to cause serious health problems. Cyanide is generally considered the most potentially dangerous of the electroplating chemicals. It is highly toxic when adsorbed through the skin or ingested, and may be fatal if absorbed in quantities as low as 50-100 mg. Despite this fact, deaths are rare, generally occurring from inhalation of hydrogen cyanide gas that results from acidification of CN plating baths that have spilled on the shop floor or into floor drains. Because cyanide is so toxic, its use in most shops is carefully monitored and employees are trained to use it properly. Training is essential to worker safety in all plating operations. Combining employee education with substitution of less toxic chemicals may provide the least costly and most productive control of workplace hazards. Replacing cyanide plating solutions with noncyanide baths is strongly recommended (Winter and Facciolo 1985).

Not only is there risk to the health of the workers in the facility, but there are potentially greater risks to the environment resulting from the discharge of cyanide to waterways or the land. Slow bleeding of very dilute cyanide wastewaters and even spent plating baths into the sewer system was not an unusual practice in the 1970s when environmental regulations were just starting to address toxic chemicals and their release to the environment. The slow discharge diluted the cyanide so it was not dangerous. But even at low concentrations, cyanide may be toxic to fish and other inhabitants of the waterways into which the waste stream was discharged after processing at the local publicly owned water treatment works. A dramatic example of what could happen from this sort of practice occurred in 1989 in Chicago. A spent plating bath (4,000 gallons) containing cyanide was being slowly discharged into the sewer. This illegal discharge probably would have gone unnoticed had it occurred over two weeks as intended, but someone did not adjust the discharge valve properly and the entire spent bath solution was discharged overnight. The result was a major (20,000) fish kill in the Chicago River, the closing of the city's northwest side treatment facility, and fines and imprisonment for the company and its owner (Krukowski 1992). Removal of cyanide from the process does not totally eliminate the health or environmental risk associated with plating operations. Their wastes are still quite toxic. But this chemical substitution does reduce the risk and some potential liability, for it removes a potentially lethal constituent from both the process and the waste.

A somewhat quantitative evaluation of toxicity using a computer program that rates waste streams as non-toxic, toxic, or highly toxic was originally proposed. This analysis was not possible because cyanide in the waste stream causes it to be classified as lethal at all concentrations. The program is aborted and no rating can be obtained to compare to the "toxic" rating given to the ANC wastes. Modifications to that program are being considered to enable this kind of comparison to be made on cyanide containing samples in the future.

SECTION 5

ECONOMIC ANALYSIS

CAPITAL COSTS

The total costs for the equipment, design, and labor associated with the R/R system was $51,822. Table 6 provides a breakdown of the actual costs. Costs for the make-up materials for the CN and ANC plating baths were $1,771 and $1,860 respectively (see Table 1 for breakdown by chemical). Depletion of plating bath chemicals results from the deposition of the metal on the part and dragout of the plating solution into the rinsing tanks. Weekly costs associated with maintaining the plating baths are $446.50 for the CN bath and $424.50 for the ANC bath. The breakdown of these weekly maintenance costs is provided in Table 7. As mentioned earlier, the bath quality of the CN plating line is not as critical to achieving good plating quality as it is in the ANC plating operation; therefore, fewer analyses of the CN bath are required. Additionally, the analytical parameters of the two plating baths differ. Analysis for cyanide content in the ANC bath is not necessary, thus the cost for 5 analyses/week for the ANC bath is less than 2.5 times that of the 2 analyses/week for the CN bath.

TABLE 6. BREAKDOWN OF COSTS FOR DESIGN, PURCHASE, AND INSTALLATION OF CNT RECOVERY/RECYCLE SYSTEM

Initial Investment	Cost $
Equipment (includes pumps, tanks, pipes, valves, pH controller, and filter press)	14910
Design and Start-up Labor	
CNT	15612
P&H	13300
Bath Conversion Labor (P&H)	8000
Disposal of CN Bath	36000
Total	87822

TABLE 7. COMPARISON OF WEEKLY CHEMICAL MAINTENANCE COSTS FOR CN AND ANC LINES

CN Bath		ANC Bath	
Component	Cost $	Component	Cost $
NaCN	34.00		
NaOH	22.50	NaOH	105.00
Zn Anodes	120.00	Zn Anodes	120.00
Brightener	220.00	Brightener	129.50
Analysis (2x / week)	50.00	Analysis (5x / week)	70.00
Total	446.50	Total	424.50

WASTE PRODUCED AND DISPOSAL COSTS

The primary wastes from any plating operation are the rinsewater, spent or dirty plating baths that must be discarded, metal sludges from routine removal of plating bath contaminants (which may be done either electrically or mechanically), and unacceptable plated products. For the CN and the ANC plating lines, we assumed the amount of unacceptable products to be the same. Total replacement of the plating baths is not normally needed. Plating baths are maintained by routine cleaning and addition of depleted chemicals as needed. The cleaning operations for both the CN and ANC baths result in a mixed metal sludge that must be disposed (following pretreatment to oxidize cyanide for the sludge from the CN operation). The amount of mixed metal sludge resulting from the cleaning of each of these plating systems is essentially the same, so it is not considered as a variable in the operating costs calculation. The annual cost for the cyanide oxidation for this mixed metal sludge is included in the cost comparison of the two systems.

The rinsewater from the CN and ANC lines also have different treatment needs and associated costs. For the CN line, the wastewater is first sent to the cyanide destruct unit of the facilities wastewater treatment area. Once the cyanide is oxidized, the wastewater is mixed with wastewater from the rest of the facility's plating operation and metals are precipitated as mixed sludges and disposed. For the ANC line, there is no cyanide to treat, so the wastewater goes directly to the R/R system where it is precipitated as reasonably pure zinc hydroxide. This precipitate can be used to replenish the ANC bath being studied and any others that might exist in the facility. It might also be sold for other uses. The R/R system keeps the ANC line waste segregated thus facilitating recycling options. At present P&H Plating Co. is recycling only a portion of the recovered materials. Since there are no longer any CN zinc lines at P&H Plating, the potential uses for the R/R system precipitate have increased and the company is now considering using the excess from that line to replenish other ANC lines.

Because this test plating line is one of many generating the waste the plant produces, and because there is an efficient waste treatment unit operating in the facility, the economic benefits of the recycling effort made possible by the installation of the R/R system are not obvious when examining the annual waste disposal costs for the company. This would not be the case if the R/R system were being used throughout the facility on all appropriate lines or even on all ANC lines. With additional waste stream segregation leading to recovery of useable products and their recycling even more, substantial savings would be realized.

Treatment and disposal costs at P&H for a single zinc plating line typically amount to >$100,000/year. The annual disposal costs for metal sludges during the period the R/R system was being tested, were slightly above $52,000. Approximately 50% of this sludge resulted from zinc plating operations at the company thus zinc disposal costs were $26,000. This amount includes transportation costs. The unused zinc hydroxide precipitate being disposed accounts for 5% of the total sludge being produced at P&H and costs $2,600 annually for disposal. Annual treatment costs for the wastewater from the CN line during the project were $14,000 for cyanide oxidation and $69,000 for metal removal and collection resulting in a total treatment cost of $83,000. These costs include chemicals but not the labor required for wastewater treatment. Labor is assumed to be comparable to that needed for the operation of the recovery system (10 hours/week). These treatment costs are reduced by the removal of cyanide from the process. Even greater reductions in these costs are achieved with the use of the R/R system which has an annual operational costs of $10,900 ($7,500 for labor, $400 for chemicals, $1,000 for utilities, and $2,000 for parts).

OPERATIONAL COST COMPARISONS

Because the company does not have electrical and water metering on each line, it is difficult to assess the differences in these areas that have resulted from the installation of the system. We will assume that the annual output from each line (calculated as the number of parts plated) is the same and look at the different power and water needs of the two operations required to produce that output. There are some general differences in water and power consumption between the CN and ANC systems that can be compared and used in the calculation of operational costs.

The rectifier for the CN line is air cooled, but the one for the ANC system is water cooled. The air cooling is accomplished by a fan which will use electricity that is estimated to increase the power needs of the line <5% per plating run. The water cooled unit does not require this added electrical need. Furthermore, the water used to cool the rectifier is cycled into the rinsing tanks and constantly replenishes the rinsewater. This steady source of new water means only 70% of the recovered rinsewater is recycled.

Although the operating voltage/amperage for the plating line varies with the items being plated and the type of plate required, for comparable runs the CN line routinely operates at lower voltage and amperage. The duration for a similar run on each line also varies for the plating efficiency is better when using the ANC process meaning that a thicker plate can be achieved in a shorter period of time. While there may be problems associated with obtaining plating thicknesses >0.0008 inches with the ANC process, the parts plated at P&H with both the CN and ANC lines require thicknesses $\leq$0.0005 inches which is easily achieved. The efficiency of the ANC plating process is particularly good in the 0.0003 - 0.0005 inch thickness range, which is the range required for the parts generally plated at P&H. Although the ANC consumes more power while it is operating, it is operated for a shorter period to achieve a plate of similar thickness and quality to that produced by the CN line. At a rate of $0.10/kilowatt hour (the cost to Commonwealth Edison customers in Chicago) the additional power consumption for the CN operation required for rectifier cooling would be a very small portion of the overall operating costs for the plating line. Because the power usage is not directly measured and will be very similar for the two systems, power consumption is not used for the calculations in the economic assessment that follows.

Labor costs for the operation of the plating portion of the lines are assumed to be the same; however, there are new costs associated with the operation of the R/R system. There are weekly labor costs of ~$150 (10 hours at $15.00/hour). Sulfuric acid is used to adjust the pH and promote the precipitation process at an annual cost of $400. Finally, annual power costs to keep the recovery system in operation are ~$1000 (estimated by P&H).

While the reduction in risks may be sufficient to justify the change from CN to ANC, the economic benefits that can result from such a change most certainly encourage its adoption. When a R/R system is installed on the ANC line, the economic benefits become too significant to dismiss. A comparison of the costs for the first year's operation of the ANC line, and then to the ANC line with the R/R unit to the annual costs of the CN operation is summarized in Table 8. Most of these costs have already been discussed. Although there will be down times for all of the plating lines because of maintenance and the number of jobs the company is processing, it was suggested by the company that calculations be made for eight hours a day, five days a week, and 50 weeks per year. This should provide a reasonable estimate of the annual work load for each plating line as the lines frequently operate during two eight hour shifts, six days a week for 52 weeks.

Bath component costs were listed in Table 1 (p. 17). Weekly maintenance costs for each plating bath were provided in Table 7 (p. 26). For the CN and ANC lines the annual costs were derived by simply multiplying these weekly costs by 50 weeks. For the ANC with R/R line, 30% of the zinc hydroxide was used to replenish the zinc in the plating bath. To account for this recycling effort, the weekly costs of the zinc portion of the maintenance costs was reduced by 30% making the weekly costs $388.50 instead of $424.50 for an annual cost of $19,425 rather than $21,225.

TABLE 8. COMPARISON OF ANNUAL OPERATIONAL COSTS FOR CN PROCESS, ANC PROCESS WITHOUT R/R UNIT, AND ANC PROCESS WITH R/R UNIT AT P&H PLATING CO.

Process Operation	CN Costs ($)	ANC Costs ($)	ANC + R/R* Costs ($)
Bath makeup	1771	1860	1860
Bath maintenance	22325	21225	19425
Water usage (Flow rate 10gpm) 1. Use @ $7.56/7480g	1213	1213	364
2. Sewering @ $5.59/7480g	897	897	269
Wastewater treatment 1. Cyanide oxidation	14000	0	0
2. Metal precipitation	69000	69000	20700
3. Labor	7500	7500	2250
Sludge disposal	2600	2600	1820
Total	119306	104295	46688

* Assumes 70% water and 30% zinc hydroxide recycled

For the city of Chicago, the water usage charge includes costs for the amount of water actually used and the amount sewered. The flow into the recovery unit is 10 gallons per minute (gpm) and the same flow rate was assumed for the CN line and the ANC line without the recovery unit. The total number of gallons used on each plating line is then calculated as:

Total gallons used = 10 gallons/minute x 60 minutes/hour x
8 hours/day x 5 days/week x 50 weeks/year.

The total water needed by the CN and ACN lines using this calculation is 1,200,000 gallons/year. Because of the recycling effort on the ANC with the R/R system, only 30% of that amount (360,000 gallons) of fresh water is required. The amounts sewered for each line will be the same as water needed. The rates provided by the City of Chicago Water Operations group are based on $13.15/1,000 ft^3 (1,000 ft^3 = 7480 gallons) broken down as indicated in Table 8. Total water costs for the CN and ANC lines where no recycling takes place are the same, $2,110. If the R/R system is used, 70% of the water can be recycled, thus reducing both the amount needed and the amount sewered for a total cost of $633 which saves the company $1477 in annual water charges per plating line.

Wastewater treatment costs are reduced by the change from CN to ANC and then are even further reduced by installing the R/R system. To determine treatment costs, P&H Plating Co. personnel used the total costs of the all treatment steps divided by the percentage of the waste stream coming from each line. These costs include chemicals and power usage. Treatment for the CN line requires pretreatment (cyanide oxidation) followed by metal precipitation and collection for a total cost of $83,000. Once cyanide is no longer used in the operation, the only treatment needed is metal precipitation and collection which saves the company $14,000, the costs that would have been needed for cyanide oxidation. Adding the R/R system to the ANC line results in even greater savings. Because 70% of the wastewater is passed through the R/R system and reused, only 30% is sent to the facility treatment unit. Although this water should be essentially metal free, it is treated as if zinc were present; however, the volume has been reduced by 70% resulting in a 70% reduction in treatment costs for ANC with R/R, making those costs $20,700.

Labor is presented as a separate item because it must be calculated for both the facility treatment unit and the R/R system. The R/R system requires 10 hours of labor per week with an average rate of $15.00. Because the volume of wastes are the same and the types of process used to treat and recover/recycle the wastes are so similar, 10 hours a week at $15.00/hour to process the CN and ANC wastewaters in the facility treatment unit are assumed. Table 8 does not include the R/R system operational costs in its comparison. While labor for CN and ANC wastewater processing would indeed be the same, adding the R/R water recycle to the ANC line would reduce the labor cost because the volume of water was reduced. The company estimates the cost treating the unused R/R processed water to be $2250 rather than $7500 to treat the wastewater through the standard treatment process.

The final cost listed on Table 8 is for the disposal of the sludge (metal precipitate). Again this was determined by the company to be a percentage of the total costs for sludge disposal. The fact that this is the same for the two lines without recycling options is expected. There are two reasons why it is less when the recycling option is employed. The company is only recycling 30% of the zinc hydroxide it recovers. The remaining 70% is disposed with the sludges resulting from the facility treatment unit. Although 30% of the water recovered from the R/R system is sent to the treatment unit, it is essentially clean. The metal content of that recovered water is too low to add an appreciable quantity to the company's waste sludge; therefore, the calculated cost for sludge disposal of the unused precipitate from the R/R system is 70% of that for the sludge that would result from treatment of the ANC line without the R/R option.

Table 8 shows an annual cost savings of $15,011 for switching from a CN to an ANC process and >$70,000 when the R/R system is also added to the line; however, this is not a totally accurate portrayal of operational costs. There are costs associated with the operation of the R/R system. These costs are calculated to be $10,900 annually (see p. 27). Incorporating these added costs into the overall operational costs reduces the company's saving to $61,718 or approximately half of the normal operating expenses for the line.

Two other factors must be considered in this calculation and those are the costs associated with the disposal of the CN bath when conversion to ANC occurs and the cost of the design, parts, assembly, and installation of the R/R unit. These costs were provided in

Table 6 (p. 25). Taking the worse case, the cost of disposal of 1,800 gallons of CN plating bath at $20/gallon would be $36,000. This amount for disposal and the cost of the design and installation of the R/R system are considered the capital expenses for the project.

TOTAL SYSTEM COMPARISONS

The capital costs and the annual operational expenses were entered into a spreadsheet program (General Electric 1987) that calculates a number of economic indices. The program also uses other economic factors, such as inflation rate, in its calculations. These factors are assumed to remain constant over the 10 year life of the project. The factors used in the calculations for the assessment are provided in Table 9.

TABLE 9. ASSUMPTIONS FOR ECONOMIC CALCULATIONS

Item	Factor	Source
Inflation Rate	4%	Consumer Price Index
Discount Rate	7.72%	10 year treasury bill rate +0.5%
Federal Tax Rate	34%	General Electric, (1987)
Depreciation Schedule	7 years	General Electric, (1987)
Project Life	10 years	P&H Plating Co.
Labor Costs	$15/hour	P&H Plating Co.
Sludge Disposal Costs	$209/cubic yd	P&H Plating Co.
Water Costs		
Water Usage	$7.56/7480 gallons	Metropolitan Water
Water Sewering	$5.59/7480 gallons	Reclamation District of Greater Chicago

The assumptions from Table 9 combined with the first year's operational expenses, including the capital costs, were used to estimate the annual expenses for the operation of the CN line, the ANC line, and the ANC line with an active R/R system, over the course of the project life of 10 years. The comparisons were between the existing operation (CN) and the modification by chemical substitution (ANC), CN and ANC with recovery and recycling of chemicals and water (R/R), and ANC and ANC with R/R.

Table 10 presents the 10 year annual breakdown for the CN line. Because these tables were intended to show the areas of difference between the three possible plating line configurations, costs that were essentially the same for all three systems (power and labor for the plating operation) are not included in the calcluations. Annual expenses for the ANC line are provided in Table 11. Except for the first year of operation, when there are capital costs, the ANC operating expenses run $15,000-$20,000 less than those for the CN line. The

TABLE 10. ANNUAL OPERATING EXPENSES FOR ZINC CYANIDE PLATING LINE OVER 10 YEARS (DOLLAR AMOUNT BEFORE TAXES AND DEPRECIATION)

Process Operation	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Bath makeup	1771									
Bath maintenance	22325	23218	24147	25113	26117	27162	28248	29378	30553	31775
Water usage										
1. Use @ $7.56/7480 gallons	1213	1262	1312	1364	1419	1476	1535	1596	1660	1726
2. Sewering @ $5.59/7480 gallons	897	933	970	1009	1049	1091	1135	1180	1228	1277
Wastewater treatment										
1. Cyanide oxidation	14000	14560	15142	15748	16378	17033	17714	18423	19160	19926
2. Metal precipitation	69000	71760	74630	77616	80720	83949	87307	90799	94431	98209
3. Labor @ $15/hour	7500	7800	8112	8436	8774	9125	9490	9869	10264	10675
Sludge disposal @ $209/cubic yard	2600	2704	2812	2925	3042	3163	3290	3421	3558	3701
Total	119306	122236	127126	132211	137499	142999	148719	154668	160854	167289

TABLE 11. ANNUAL OPERATING EXPENSES FOR ALKALINE-NONCYANIDE PLATING LINE OVER 10 YEARS (DOLLAR AMOUNT BEFORE TAXES AND DEPRECIATION)

Process Operation	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Capital expenditures										
Disposal of cyanide bath	36000									
Bath makeup	1860									
Bath maintenance	21225	22074	22957	23875	24830	25823	26856	27931	29048	30210
Water usage										
1. Use @ $7.56/7480g	1213	1262	1312	1364	1419	1476	1535	1596	1660	1726
2. Sewering @ $5.59/7480g	897	933	970	1009	1049	1091	1135	1180	1228	1277
Wastewater treatment										
1. Cyanide oxidation	0	0	0	0	0	0	0	0	0	0
2. Metal precipitation	69000	71760	74630	77616	80720	83949	87307	90799	94431	98209
3. Labor @ $15/hour	7500	7800	8112	8436	8774	9125	9490	9869	10264	10675
Sludge disposal @ $209/cubic yard	2600	2704	2812	2925	3042	3163	3290	3421	3558	3701
Total	140295	106532	110794	115225	119834	124628	129613	134797	140189	145797

expenses listed in Table 12 show that the savings to the company increase by more than a factor of 4 ($60,000-$80,000) when the R/R unit is made operational on the ANC line.

The spreadsheet used the assumptions in Table 9 and the first year's operating expenses, including the capital costs, for each of the three plating operations to calculate the implied rate of return, the net present value, and the payback period for the line modifications. The results of this calculation are presented in Table 13 (Table 2 in summary).

While the replacement of CN by ANC is economically advantageous to the company, making the change and including the recovery/recycle option results in even greater economic benefits. Capital expenses for the system would be recovered in 18 months of operation. The implied rate of return for the ANC + R/R option is approximately 72% with a net present value of $281,122.

The goal of the project was to develop a closed-loop system that would achieve zero discharge of the wastewater and total reuse of the recovered chemicals. That was not achieved. The system that was installed, however, is simple, has substantially reduced water usage and will have paid for itself within 1.5 years of operation. Once the initial outlay has been recovered, operational costs can be reduced by 50% or more depending on the recycling effort desired by the plating operation. Because verification of recovered water and precipitate quality are necessary before recycling becomes an option, a truly closed loop system is not possible, but a R/R unit such as the one currently in operation at P&H Plating could be easily and inexpensively installed on ANC lines at other plating facilities with similar or even greater economic benefit resulting from the recycling of the recovered materials.

TABLE 12. ANNUAL OPERATING EXPENSES FOR ALKALINE-NONCYANIDE PLATING LINE WITH OPERATIONAL RECOVERY/RECYCLE UNIT (DOLLAR AMOUNT BEFORE TAXES AND DEPRECIATION)

Process Operation	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Capital expenditures										
Recovery/recycle unit	51822									
Disposal of cyanide bath	3600									
Bath makeup	1860									
Bath maintenance	19425	20202	21010	21850	22725	23633	24579	25562	26584	27648
Water usage										
1. Use @ $7.56/7480 gallons	364	379	394	409	426	443	461	479	498	518
2. Sewering @ $5.59/7480 gallons	269	280	291	303	315	327	340	354	368	383
Wastewater treatment										
1. Cyanide oxidation	0	0	0	0	0	0	0	0	0	0
2. Metal precipitation	20700	21528	22389	23285	24216	25185	26192	27240	28329	29463
3. Labor @ $15/hour	2250	2340	2434	2531	2632	2737	2847	2961	3079	3202
Sludge disposal @ $209/cubic yard	1820	1893	1969	2047	2129	2214	2303	2395	2491	2590
Equipment maintenance recirculation pump			755			850			956	
General maintenance	300	312	324	337	351	365	380	395	411	427
Recovery/recycle unit operation	10900	11336	11789	12261	12751	13262	13792	14344	14917	15514
Total	113310	58269	61355	63024	65545	69017	70893	73729	77634	79745

TABLE 13. COMPARISON OF ECONOMIC INDICES FOR THE ALKALINE NONCYANIDE PLATING PROCESS WITH AND WITHOUT THE RECOVERY/RECYCLE SYSTEM

Index	Option	
	ANC	ANC + R/R
Capital Investment	$36,000	$87,822
Payback Period	3 years	1.5 years
Net Present Value	$57,500	$281,122
Implied Rate of Return	27.0%	71.9%

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APPENDIX A

ANALYTICAL QUALITY ASSURANCE

At the outset of this project data quality objectives were set and procedures put into place to ensure that they were met. A project quality assurance plan describing the analytical protocols was prepared and accepted. In general, these objectives were met, although problems were encountered due to the complex nature of the samples being analyzed. Analysis for water content and corrosion were performed by P&H's contract laboratory. These data were never intended for use in the calculations of recovery, so quality assurance information was not obtained.

For the analyses performed at HWRIC's laboratory the protocols established in the quality assurance plan were used. Analytical procedures are described in detail in SW-846 (USEPA 1986). Only brief summaries are included in this report. Calibration curves were determined each day that samples were analyzed using 5 standards (a single standard was used for TOC determinations). Since daily sample runs generally did not exceed 20 samples, a blank and complete calibration curve began and ended each sampling run. Duplicate analyses and spikes were performed every 6 samples. Data from these samples were used to assess precision and accuracy. Two check standards of known concentration were prepared and analyzed every 6 samples to further assess accuracy and as immediate checks on the standard curve. The analyte concentrations of these check samples were chosen to check the accuracy of the data at both the high and low ends of the standard curve.

METAL ANALYSIS

Samples were analyzed by atomic absorption to determine metal content. Data from these analyses are included in Appendix B. (Tables B-2, B-4, B-5, B-7, and B-8). Sludge samples were prepared following method 3050. This method calls for digestion of the sample in nitric acid and hydrogen peroxide. The digestate is reflexed with hydrochloric acid prior to analysis by flame AA according to methods 7950 for zinc analyses, 7380 for iron, 7140 for calcium and 7770 for sodium. Aqueous samples were prepared following 3010. This procedure calls for the digestion of the sample with nitric acid prior to analysis.

These methods suggest the use of a 5-point calibration curve. This recommendation was followed and standards were selected to fit the anticipated concentration ranges of the samples. Because the metal concentrations of the samples go from very high (% quantities) in the sludge to very low (ug/L) quantities in the treated wastewaters, some samples were diluted prior to analysis.

In general, manufacturer's operating procedures were followed during the analyses. Software packages which were included with the instruments were used to generate the standard curve that was then used to calculate the concentrations of the metals in the samples. Check samples were selected to check the upper and lower portions of the calibration curve. Samples were analyzed in groups of 6 or less. Check samples, a reagent blank, at least one duplicate, and one spike were analyzed with each set of 6 samples. Raw data tables are provided in Appendix B. These data are presented as run logs, i.e. the samples (both the unknown and the quality control) are listed as analyzed.

TOTAL ORGANIC CARBON (TOC)

Analysis for TOC was not routinely performed during the project. These analyses were used to simply check for the presence of organic carbon that would result if brightening agents were carried over in the recycling operations. One standard was used to calibrate the instrument, following the manufacturer's directions. Samples were selected at random. Because these analyses were not integral to the determination of the quality of the recovered/recycled materials nor the quality of the plate, quality control procedures were greatly reduced. TOC analysis was included in the original list of analyses that would be performed for there was a possibility organic carbon concentrations could become elevated through the recycling efforts. The analysis of these randomly selected samples showed this was not the case so there was no need to continue to analyze for this parameter.

The TOC determinations followed method 9060. Two different instruments were used, one for solids and the second for aqueous samples. Solid samples were analyzed by combustion. A single known sample was used to check instrument performance. Instrument software calculated TOC concentrations. Liquid samples were analyzed by wet chemical oxidation. Again, a single standard was used to check instrument performance and calculate the TOC content in the test samples.

ACCURACY, PRECISION, AND COMPLETENESS

Accuracy, precision, and completeness were determined for the three sets of data reported by HWRIC's laboratory. The data sets included the analysis of zinc hydroxide precipitate from the R/R system, the input and output samples from the initial testing of the R/R system, and the input and output samples from the final testing of the R/R system.

Accuracy is the agreement of a measurement or average of measurements with an accepted reference or known material. One measure of the accuracy of each data set is presented as the percent recovery of the quality control standards. This is a measure of the agreement between the known or calculated value of the standard and the measured value. The percent recovery is calculated as follows:

$$\%Recovery = (Experimental\ Value) \div (Known\ Value) \times 100\%.$$

The second evaluation of accuracy uses the percent recovery of spiked samples to assess the effect of the matrix on the samples analyses. It is calculated using this formula:

$$\%Recovery = [(Spiked\ Sample) - (Unspiked\ Sample)] \div (Amount\ Spiked) \times 100\%.$$

Precision measures the agreement among individuals measurements of the same sample. Precision is determined in two ways for these data sets. The precision among three or more replicates, in this case the analyses of the quality control standards and/or triplicate sample analyses, is calculated as percent relative standard deviation (%RSD), which is calculated as:

$$\%RSD = s \div \bar{x} \times 100\%,\ where$$

$$\bar{x} = \Sigma x_1 \div n = the\ arithmetic\ mean\ of\ a\ set\ of\ results,\ and$$
$$s = \sqrt{\Sigma}\ (x_1 - \bar{x})^2 \div (n-1) = the\ standard\ deviation\ among\ replicates.$$

When only two values are determined, as in the case of duplicates, precision is defined as the relative percent difference (RPD) and calculated:

$$RPD = (D_1 - D_2) \div [(D_1 + D_2) \div 2] \times 100\%, where$$

$$RPD = Relative\ Percent\ Difference$$
$$D_1 = the\ larger\ of\ the\ two\ observed\ values,\ and$$
$$D_2 = the\ smaller\ of\ the\ two\ observed\ values.$$

The completeness criterion compares the number of measurements taken to the number considered valid. A percent completeness for each of the three data sets is provided with Tables A-1 through A-3. The overall percent completeness for all of the samples analyzed for the project is 94%, which is slightly less than desired, but acceptable for the evaluation of the R/R system.

TABLE A-1. QUALITY ASSURANCE (QA) DATA FOR THE ANALYSIS OF RECOVERED PRECIPITATE OBTAINED DURING THE INITIAL EVALUATION OF THE CNT SYSTEM

Sample Type	N*	Metals Analyzed Zinc	Iron	Calcium	Magnesium
Check Samples					
% Recovery		99	115	100	99
% RSD	4	2	1	10	1
Spikes					
% Recovery	2	121	91	149	110
Duplicates					
RPD	4	6	11	9	5

Completeness for data set = (200 valid) ÷ (204 total) x 100% = 98%

*N=Number of samples analyzed

TABLE A-2. QUALITY ASSURANCE (QA) DATA FOR THE OUTPUT WATER SAMPLES OBTAINED DURING THE INITIAL EVALUATION OF THE CNT SYSTEM

Sample Type	N*	Metals Analyzed Zinc	Iron
Check Samples			
% Recovery		116	100
% RSD	16	7	1
Spikes			
% Recovery	6	105	112
Triplicates			
%RSD	6	2	3

Completeness for data set = (92 valid) ÷ (92 total) x 100% = 100%

*N=Number of samples analyzed

TABLE A-3. QUALITY ASSURANCE (QA) DATA FOR THE INPUT AND OUTPUT WATER SAMPLES OBTAINED DURING THE FINAL EVALUATION OF THE CNT SYSTEM

Sample Type	N*	Metal Analyzed Zinc
Check Samples		
% Recovery		107
% RSD	6	3
Spikes		
% Recovery	4	118
Duplicates		
RPD	4	2

Completeness for data set = (57 valid) ÷ (67 total) x 100% = 85%
*N=Number of samples analyzed

The data summaries presented in Tables A-1 through A-3 show that except for completeness and the percent recovery of zinc for the check samples analyzed with the liquids obtained during the initial tests of the system, all of the quality assurance objectives for the project were met. For the precipitate (solid) samples check samples percent recovery falls within the range 80-120%, check samples %RSD is less than 20%, spike percent recovery falls within the range 60-140%, and duplicates RPD is less than 40%. The objectives for the liquid samples were: percent recovery range of 90-110% for check samples, %RSD less than 10% for check samples, percent recovery range of 75-125% for spikes, and RPD of less than 25% for duplicates. The problem with completeness resulted from a contamination problem in the water and reagent blanks on one of the days that analyses were being performed. The measured zinc content of the blanks was greater than the lowest and second lowest standard and larger than 2 of the 6 samples analyzed in that run. Because the data evaluation occurred some time after the analyses were performed, the cause of the blank contamination could not be determined, these data were not used in the calculations, and it was decided that repeating the analyses was not necessary. The valid data provided all of the needed information. The other problem is with the accuracy of the control samples analyzed with the first set of water samples from the recovery system. Again, the extent of the deviation from the theoretical was not noticed until some time after the analyses were completed. In this case, though, the deviation from the objective was not that great and the accuracy obtained was sufficient to use in the system evaluation, so all of the data were used.

REFERENCE STANDARDS

The laboratory did not participate in performance evaluations (PEs) during the periods that these analyses were performed. The lab does participate in the U.S. Geological Survey's

(USGS) performance assessment for metals on a quarterly basis. Over the course of the project HWRIC's performance on these USGS PE samples was rated satisfactory for zinc, iron, calcium, and magnesium. While these samples are natural waters and soils and not truly comparable to the wastewaters and sludges analyzed for this project, they are prepared and analyzed following the same procedures and offer the best substitute available.

Certified standards were used to prepare the calibration and check sample standards. These were prepared several times over the course of the study from different stock solutions and were consistently within 10% of the theoretical concentration.

DETECTION LIMITS (DL)

Concentration of metals in the samples in most cases were far above the minimum capabilities of the instruments. This was true for all but the blanks and treated rinsewater samples. These samples had concentrations in the ug/L range but generally at or slightly above the DL. For this study, it was not necessary to achieve the lower limits prescribed in the quality assurance plan, for the cleaned water was acceptable for recycle at much higher concentration ranges. The data were verified by duplicate analyses and spikes, in addition to blanks and check standards. All data used in the evaluation are provided in Appendix B.

APPENDIX B

ANALYTICAL DATA

TABLE B-1. WATER CONTENT OF ZINC HYDROXIDE FROM CNT RECOVERY/RECYCLE SYSTEM

Sample No.	% of Water	Sample No.	% of Water
399	87.84	415	86.04
400	89.63	416	88.60
401	91.87	417	88.86
402	91.07	418	88.83
403	89.19	419	90.49
404	89.53	420	89.97
405	91.73	421	92.21
406	89.28	422	88.34
407	89.81	423	87.82
408	88.91	424	89.37
409	89.28	425	92.34
410	87.64	426	92.93
411	91.50	427	93.04
412	89.28	428	89.22
413	87.39	429	86.25
414	91.01	430	64.55

TABLE B-2. ANALYSIS OF DRIED ZINC HYDROXIDE SLUDGE SAMPLES FROM P&H PLATING CO.

	Concentration %			
Sample Number	Zinc (Zn)	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)
P&H399	70.4	0.78	5.47	4.26
P&H400	69.8	0.56	2.58	4.92
P&H401	47.0	0.77	8.14	4.52
P&H402	55.1	1.0	8.50	2.34
P&H402DUP	51.3	1.04		2.38
P&H403	60.3	1.65	5.63	2.23
P&H404	59.0	1.05	5.44	2.57
P&H405	64.9	0.55	2.88	1.06
P&H406	62.4	1.06	5.42	1.04
P&H407	69.0	0.43	0.70	0.97
P&H408	59.7	0.52	4.25	1.23
P&H409	65.2	0.70	4.80	1.95
P&H410	67.2	0.78	3.60	1.66
P&H411	64.7	1.17	3.66	1.74
P&H411DUP	64.6	1.28	3.80	1.73
P&H412	58.3	0.82	3.20	1.48
P&H413	72.7	0.39	0.15	0.14
P&H414	72.4	0.21	0.23	0.26
P&H415	75.7	0.33	0.36	0.58
P&H416	72.4	0.79	2.16	1.20
P&H417	71.3	0.32	0.86	0.92
P&H417SP	60%	65%	258%	340%
P&H418	70.8	0.31	0.93	1.12
P&H419	77.4	0.44	0.80	0.99
P&H419DUP	65.0	0.28	0.60	0.85
P&H420	71.6	0.72	1.00	0.97
P&H421	63.1	0.26	0.74	0.59
P&H422	70.5	0.29	0.86	0.67
P&H423	72.1	0.48	0.65	0.78
P&H423SP	220%	111%	189%	101%
P&H424	64.9	0.62	3.97	2.49
P&H425	61.8	3.32	6.36	2.10
P&H426	51.4	2.80	5.89	0.20
P&H426DUP	52.3	3.79	7.12	1.83
P&H427	54.5	3.05	0.79	0.24
P&H428	58.6	1.59	5.46	2.19
P&H429	62.4	0.91	4.46	2.07
P&H430	45.5	1.10	4.83	1.91

DUP=Duplicate
SP=Spike

TABLE B-3. CARBON ANALYSIS FOR RANDOMLY SELECTED ZINC HYDROXIDE SLUDGES

Sample No.	Total Carbon % (TC)	Total Inorganic Carbon % (TIC)	Total Organic Carbon % (TOC)[a]
$CaCo_3$ (Std.)[b]	11.9	12.1	
399	0.4	0.4	0
406	1.6	1.6	0
413	0.1	0.1	0
420	0.4	0.4	0
427	2.0	2.0	0
430	2.1	0.2	1.9

a TOC=TC-TIC
b Theoretical TIC=12%

TABLE B-4. RUN LOG FOR ANALYSIS OF RINSEWATER SAMPLES (INPUT) TAKEN DURING INITIAL TESTING OF R/R SYSTEM

P&H Sample ID#	Sample No.	pH	Zn (mg/L)	Fe (mg/L)
Reagent Blank	RBlk		0.07	0.28
Check Std.	CS-1		0.25	0.86
Check Std.	CS-2		0.82	7.1
N080PHLD78	1	12.5	180	0.65
N080PHLD63	2	12.6	120	0.37
N080PHLD66	3	12.6	170	0.75
N080PHLD75	4	12.6	160	0.50
N080PHLD70	5	12.8	260	0.60
N080PHLD71	6	12.7	210	0.54
N080PHLD70	5D	12.8	260	0.65
N080PHLD70	5T	12.8	260	0.61
N080PHLD71	6S	12.7	280	0.84
Reagent Blank	RBlk		0.07	0.27
Check Std.	CS-1		0.30	0.85
Check Std.	CS-2		0.83	7.1
N080PHLD74	7	12.6	140	0.35
N080PHLD62	8	12.6	120	0.33
N080PHLD79	9	12.5	170	0.69
N080PHLD67	10	12.6	150	0.77
N070PHLD58	11	12.9	310	0.33
N070PHLD59	12	12.9	330	0.23
N080PHLD67	10D	12.6	160	0.77
N080PHLD67	10T	12.6	140	0.77
N070PHLD59	12S	12.9	380	0.53
Reagent Blank	RBlk		0.08	0.28
Check Std.	CS-1		0.25	0.85
Check Std.	CS-2		0.82	7.1
N070PHLD51	13	12.7	190	0.27
N070PHLD54	14	12.6	170	0.51
N070PHLD50	15	12.7	200	0.29
N070PHLD55	16	12.5	160	0.46
N070PHLD50	15D	12.7	200	0.29
N070PHLD50	15T	12.7	190	0.27
N070PHLD55	16S	12.5	200	0.71
Reagent Blank	RBlk		0.08	0.28
Check Std.	CS-1		0.26	1.0
Check Std.	CS-2		0.82	7.1

CS-1 (Theoretical) = 0.25 mg Zn/L and 0.85 mg Fe/L
CS-2 (Theoretical) = 0.80 mg Zn/L and 7.1 mg Fe/L
D = Duplicate
T = Triplicate
S = Spike

TABLE B-5. RUN LOG FOR ANALYSIS OF TREATED WATER SAMPLES (OUTPUT) TAKEN DURING INITIAL TESTING OF R/R SYSTEM

P&H Sample ID#	Sample No.	pH	Zn (mg/L)	Fe (mg/L)
Reagent Blank	RBlk		0.01	0.01
Check Std.	CS-1		0.30	0.27
Check Std.	CS-2		0.80	0.80
N080FTLD80	1	10.1	53	0.98
N080FTLD81	2	10.2	92	1.4
N080FTLD76	3	10.1	14	0.32
N080FTLD77	4	10.1	15	0.32
N080FTLD73	5	10.1	12	0.21
N080FTLD72	6	10.1	12	0.20
N080FTLD73	5D	10.1	12	0.20
N080FTLD73	5T	10.1	12	0.22
N080FTLD72	6S	10.1	15	0.50
Reagent Blank	RBlk		0.01	0.01
Check Std.	CS-1		0.30	0.27
Check Std.	CS-2		0.80	0.81
N080FTLD69	7	10.2	10	0.13
N080FTLD68	8	10.2	10	0.13
N080FTLD65	9	10.1	2.2	0.24
N080FTLD64	10	10.1	2.3	0.27
N070FTLD61	11	10.1	6.5	0.09
N070FTLD60	12	10.1	6.6	0.11
N080FTLD64	10D	10.1	2.3	0.27
N080FTLD64	10T	10.1	2.3	0.26
N070FTLD60	12S	10.1	8.9	0.36
Reagent Blank	RBlk		0.01	0.02
Check Std.	CS-1		0.30	0.28
Check Std.	CS-2		0.79	0.82
N070FTLD57	13	10.1	37	0.79
N070FTLD56	14	10.1	36	0.71
N070FTLD53	15	10.1	6.2	0.13
N070FTLD52	16	10.0	6.4	0.13
N070FTLD53	15D	10.1	6.5	0.13
N070FTLD53	15T	10.1	6.1	0.13
N070FTLD52	16S	10.0	8.7	0.40
Reagent Blank	RBlk		0.01	0.03
Check Std.	CS-1		N/A	0.28
Check Std.	CS-2		0.79	0.81

CS-1 (Theoretical) = 0.25 mg ZN/L and 0.25 mg FE/L
CS-2 (Theoretical) = 0.80 mg ZN/L and 0.80 mg FE/L
D = Duplicate
T = Triplicate
S = Spike

TABLE B-6. CONTRACT LABORATORY TOC ANALYSIS OF RINSEWATER SAMPLES TAKEN DURING INITIAL TESTING OF R/R SYSTEM

Sample No.	TOC (mg/l)
N070PHLD54	<1.0
N080PHLD67	<1.0
N080PHLD62	<1.0
N080PHLD78	<1.0
N070PHLD50	<1.0

No quality assurance data provided

TABLE B-7. RUN LOG FOR ANALYSIS OF ZINC IN RINSEWATER SAMPLES TAKEN SEPTEMBER 12, 1992 AND SEPTEMBER 19, 1992 FOR THE FINAL EVALUATION OF THE R/R SYSTEM

Sample	Sample Date	Lab #	Anal. Date	Conc. ug/ml
Blank		Blk	Oct. 3	0.0
Standard 1		Std1	Oct. 3	0.1
Standard 2		Std2	Oct. 3	0.3
Standard 3		Std3	Oct. 3	0.5
Standard 4		Std4	Oct. 3	0.7
Standard 5		Std5	Oct. 3	1.0
Reagent Blank		RBlank	Oct. 3	0.00
Low Check Std.		CS-L	Oct. 3	0.26
High Check Std.		CS-H	Oct. 3	0.79
A1 Tank 3 Inlet	Sept. 12	91-1430	Oct. 3	1.2
B1 Tank 7 Inlet	Sept. 12	91-1431	Oct. 3	46
A2 Tank 3 Inlet	Sept. 12	91-1432	Oct. 3	4.8
B2 Tank 7 Inlet	Sept. 12	91-1433	Oct. 3	9.7
A3 Tank 3 Inlet	Sept. 12	91-1434	Oct. 3	150
B3 Tank 7 Inlet	Sept. 12	91-1435	Oct. 3	2.0
A4 Tank 3 Inlet	Sept. 12	91-1436	Oct. 3	22
B4 Tank 7 Inlet	Sept. 12	91-1437	Oct. 3	10
Alkaline Plating Bath	Sept. 12	91-1438	Oct. 3	9900
Rectifier Coolant Water	Sept. 12	91-1439	Oct. 3	0.00
Cyanide Rinse 11:20	Sept. 12	91-1440	Oct. 3	320
Cyanide Rinse 2:00	Sept. 12	91-1441	Oct. 3	250
Cyanide Rinse 2:55	Sept. 12	91-1442	Oct. 3	170
A4 Tank 3 Inlet	Sept. 12	91-14436D	Oct. 3	22
B1 Tank 7 Inlet	Sept. 12	91-14431S	Oct. 3	52
Reagent Blank		RBlank	Oct. 3	0.00
Low Check Std.		CS-L	Oct. 3	0.27
High Check Std.		CS-H	Oct. 3	0.81
A1 Tank 3 Inlet	Sept. 19	91-1463	Oct. 3	250
A2 Tank 3 Inlet	Sept. 19	91-1464	Oct. 3	180
A3 Tank 3 Inlet	Sept. 19	91-1465	Oct. 3	290
A4 Tank 3 Inlet	Sept. 19	91-1466	Oct. 3	270
B1 Tank 7 Inlet	Sept. 19	91-1467	Oct. 3	9.7
B2 Tank 7 Inlet	Sept. 19	91-1468	Oct. 3	21
B3 Tank 7 Inlet	Sept. 19	91-1469	Oct. 3	32
B4 Tank 7 Inlet	Sept. 19	91-1470	Oct. 3	69
Cyanide Rinse AM	Sept. 19	91-1471	Oct. 3	210
Cyanide Rinse PM	Sept. 19	91-1472	Oct. 3	102
A3 Tank 3 Inlet	Sept. 19	91-1465D	Oct. 3	290
B4 Tank 7 Inlet	Sept. 19	91-1470S	Oct. 3	150
Reagent Blank		RBlank	Oct. 3	0.00
Low Check Std.		CS-L	Oct. 3	0.26
High Check Std.		CS-H	Oct. 3	0.79

Tank 3=Untreated Sample
Tank 7=Treated Sample
CS-L (Theoretical)=0.25 mg/L
CS-H (Theoretical)=0.80 mg/L
D=Duplicate
S=Spike

TABLE B-8. RUN LOG FOR ANALYSIS OF ZINC IN RINSEWATER SAMPLES TAKEN SEPTEMBER 7, 1992 AND OCTOBER 10, 1992 FOR THE FINAL EVALUATION OF THE R/R SYSTEM

Sample	Sample Date	Lab #	Anal. Date	Conc. ug/ml
Blank		Blk	Oct. 17	0.0
Standard 1		Std1	Oct. 17	0.1
Standard 2		Std2	Oct. 17	0.3
Standard 3		Std3	Oct. 17	0.5
Standard 4		Std4	Oct. 17	0.7
Standard 5		Std5	Oct. 17	1.0
Reagent Blank		RBlank	Oct. 17	0.30
Low Check Std.		CS-L	Oct. 17	0.29
High Check Std.		CS-H	Oct. 17	0.79
*A1 Tank 3 Inlet	Sept. 27	91-1476	Oct. 17	30
*B1 Tank 7 Inlet	Sept. 27	91-1477	Oct. 17	10
*A2 Tank 3 Inlet	Sept. 27	91-1478	Oct. 17	20
*B2 Tank 7 Inlet	Sept. 27	91-1479	Oct. 17	0.00
*A3 Tank 3 Inlet	Sept. 27	91-1480	Oct. 17	50
*B3 Tank 7 Inlet	Sept. 27	91-1481	Oct. 17	39
*A4 Tank 3 Inlet	Sept. 27	91-1482	Oct. 17	40
*B4 Tank 7 Inlet	Sept. 27	91-1483	Oct. 17	7.0
*A4 Tank 3 Inlet	Sept. 27	91-1482D	Oct. 17	40
*B4 Tank 7 Inlet	Sept. 27	91-1483S	Oct. 17	56
Reagent Blank		RBlank	Oct. 17	0.00
Low Check Std.		CS-L	Oct. 17	0.28
High Check Std.		CS-H	Oct. 17	0.80
A1 Tank 3 Inlet	Oct. 10	91-1486	Oct. 17	25
B1 Tank 7 Inlet	Oct. 10	91-1487	Oct. 17	2.9
A2 Tank 3 Inlet	Oct. 10	91-1488	Oct. 17	30
B2 Tank 7 Inlet	Oct. 10	91-1489	Oct. 17	2.9
A3 Tank 3 Inlet	Oct. 10	91-1490	Oct. 17	37
B3 Tank 7 Inlet	Oct. 10	91-1491	Oct. 17	6.8
A4 Tank 3 Inlet	Oct. 10	91-1492	Oct. 17	58
B4 Tank 7 Inlet	Oct. 10	91-1493	Oct. 17	3.0
B4 Tank 7 Inlet	Oct. 10	91-1493D	Oct. 17	3.3
B1 Tank 7 Inlet	Oct. 10	91-1487S	Oct. 17	71
Reagent Blank		RBlank	Oct. 17	0.10
Low Check Std.		CS-L	Oct. 17	0.28
High Check Std.		CS-H	Oct. 17	0.81

*High blank at start of run-data not used to calculate means in Table 5

Tank 3=Untreated sample
Tank 7=Treated sample
CS-L (Theoretical)=0.25 mg/L
CS-H (Theoretical)=0.80 mg/L
D=Duplicate
S=Spike