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Project Summary

Field Testing and Evaluation of Zerpol® Technology at Pioneer Metal Finishing

Hanna J. Saqa, Daniel J. Watts, Mohammed Elsaady, and Johnny Springer

The U.S. Environmental Protection Agency's Waste Reduction Innovative Technology Evaluation (WRITE) Program has an objective of evaluating technologies that have potential for waste reduction or pollution prevention as compared with other currently used approaches. The Zerpol[1] process, as used in metal plating operations, captures all aqueous effluent from the manufacturing operations, conditions the effluent to remove any metal or cyanide that may be present, and permits the reuse of the conditioned water in rinsing operations. About 30% of the recovered water is fed into the plant boiler to generate distilled water for critical rinsing. The goals of this study were to confirm that the quality of the water derived from the Zerpol process is appropriate for the intended reuse, and that the process is safe, and to estimate the economics of the installation and use of the process as compared to other alternatives.

The evaluation was carried out at Pioneer Metal Finishing in Franklinville, NJ. Field observations and sample collection were carried out over a 1-mo period. Based on the observations, which included determination of the content of metals and solids at selected sampling points throughout the system, it is concluded that for facilities similar to those where the evaluation was conducted, the Zerpol system provides significant advantages and is insensitive to fluctuations caused by acidic or basic bath dumps into the system. At Pioneer, approximately 80% of the process water is reclaimed and recirculated. Estimation of the economics suggests that the incremental cost of about $120,000 for a 2000 gal/day Zerpol system results in savings in chemical usage, labor and maintenance, and waste disposal costs providing a payback period of 5.3 yr. While the system eliminates effluent discharges at the site, it does produce a metal sludge stream that facilitates metal recovery through smelting, and a high solids content stream from boiler blowdown. The system eliminates the use of chlorine for cyanide destruction, eliminating that source of chlororganic materials emitted from the site.

This Project Summary was developed by EPA's National Risk Management Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Waste Reduction Innovative Technology Evaluation (WRITE) program had an objective of identifying and evaluating technologies with potential for waste reduction or pollution prevention as compared with other currently used technologies. The Zerpol process, as applied to waste waters from metal finishing operations, has that potential based upon

[1] Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

claims and reports of its performance. The process involves the capture of all aqueous effluent from the manufacturing operation, conditioning of this effluent to remove any metals or cyanide that may be present from rinsing procedures, and the reuse of the recovered water for rinsing. About 30% of the recovered water is fed into a boiler to produce distilled water for critical rinsing. Boiler blowdown maintains the salt level in the recirculated water at a level acceptable to the metal finishing process. Thus, the use of the Zerpol process has the objective of permitting continued recycling and reuse of water in the manufacturing process. System water loss due to boiler blowdown and evaporation from the process tanks is made up by fresh water supply.

The Zerpol process does produce at least two waste streams, a metal hydroxide concentrate that results from the conditioning of the process effluent (suitable as a resource for metal recovery by smelting or similar operations) and blowdown from the boiler (a concentrated solution of soluble salts). In some instances, waste oil may accumulate at the surface of the effluent storage tanks. This oil is skimmed and disposed of as waste.

A previous EPA-supported study by researchers at the University of Central Florida [2] evaluated the effectiveness of the Zerpol process as a waste management technique for the metal finishing industry. That study concluded that there were potential applications for the process in certain segments of the metal finishing industry. However, the report raised some questions that could not be answered based on the evaluation that was carried out then. These questions included uncertainties regarding rinse water quality, boiler economics and operation, product quality, and safety.

The purpose of this project was to confirm and extend the previous study of the Zerpol process to provide information about its waste reduction potential, operational implications, safety issues, and economics.

The evaluation was carried out at Pioneer Metal Finishing, Inc. in Franklinville. At the time of the study the facility operated one shift per day, five days per week. Pioneer Metal plates a variety of metal objects, emphasizing copper, nickel, and chromium plating operations. All parts are rack plated. All parts are cleaned, acid dipped, copper plated and nickel plated. Forty percent receive chrome. The base metals that are plated are steel, brass or zinc diecast. Components for electric equipment, automobile parts, and refrigeration and plumbing parts make up 80% of the work load.

During the field evaluation period of about one month, the shop was producing approximately 3,000ft^2 of plated surface per shift. The parts varied from small screws up to items with 0.8ft^2 of surface each. The plating lines and the Zerpol system are shown schematically in Figures 1 and 2.

The Zerpol system has been in place at the facility since 1981. This technology allows the conditioning and reuse of process water. The Zerpol technology could be useful not only for the metal finishing industry, but also for many types of water-using industrial operations. In this system, aqueous effluent is accumulated in processing tanks to allow conditioning in a batch mode. In the metal finishing application, conditioning is a step-wise process.

Initially, an active oxygen compound, reported to be hydrogen peroxide [1], is added, as needed, to oxidize cyanide ions. (Although possible compositions of the active oxygen compound and the reducing agent are reported in the literature, Zerpol Corporation indicates that the nature of these formulations is proprietary information. Therefore, during this investigation, no effort was made to determine their exact compositions). This step is followed by the addition of a reducing agent, reported to be sodium hydrosulfide [1], to reduce chromium, if present. Sodium hydroxide is added for pH adjustment to induce precipitation of metals.

After a 2- to 3-day settling period, the clarified water is transferred to a storage tank and used in the shop process as needed. Approximately two-thirds of the recovered water is used in the process for non-critical rinsing and about one-third is directed to the boiler. The steam generated is used for heating process baths. The condensate is used in the plating process for critical rinsing and partially for boiler feed to reduce solids build up in the boiler. The net effect is the near total reuse of the effluent stream, thus attaining a zero discharge condition at the location.

The dissolved solids in the clarified recycled water are kept within acceptable limits by controlling the boiler blowdown. The residual solids streams generated from the precipitation process and from the boiler blowdown are sent off site for reuse or disposal. The metal contents are reclaimed by smelting.

Because effluent conditioning is done in a batch mode, one tank at a time, adequate tank volumes are required for collection of the raw wastewater and for storage of the clarified effluent prior to reuse. The frequency of batch conditioning at Pioneer is dependent upon production schedules; initially it averaged about once every five days or approximately five times per month. The capacity of each of the two effluent processing tanks is 25,000 gal compared to a reported design process usage rate of about 5,000 gal/day. The (clarified) water storage tank holds 50,000 gal. Over the last few years, the process flow rate has been greatly reduced. At the time of the study, it was less than 2,000 gal/day.

Due to the large holding capacities of the tanks, the Zerpol system can handle process dumps such as caustic, acid, and other cleaners without noticeable detrimental effects. Some processes may need de-ionized water for the most critical rinsing, in addition to the use of the condensate produced from the boiler. This condensate is controlled to have a TDS of less than 1000 mg/l. Condensates with higher dissolved solids contents are automatically switched over to the clarified water storage tank.

Two principal concerns associated with the process relate to the successful operation of a boiler with an input TDS of over 5000 mg/l, and whether the produced condensate is satisfactory for critical rinsing requirements and for acceptable product quality in the plating operation. A sufficient demand for steam will help justify the energy input for the operation of the boiler. Water conservation and flow reduction are also key factors in the success of the system.

System Performance Evaluation Data

Several specific sets of field data were collected at the facility to measure and describe the performance of the Zerpol process and to define more closely its areas of applicability. Analysis of the collected data addresses the following five topics: 1) Whether the quality of the recirculated water is appropriate to maintain the plating process effectively and efficiently; 2) Whether the Zerpol process yields a metal concentrate that can be used for metal recovery through smelting or other standard metal recovery technology; 3) Whether unsafe levels of hydrogen cyanide form within the Zerpol system; 4) Whether the use of a boiler to maintain an acceptable TDS level in the recirculated water is a sound, practical and economically feasible alternative; 5) Whether the economics of the installation and operation of the Zerpol system are favor-

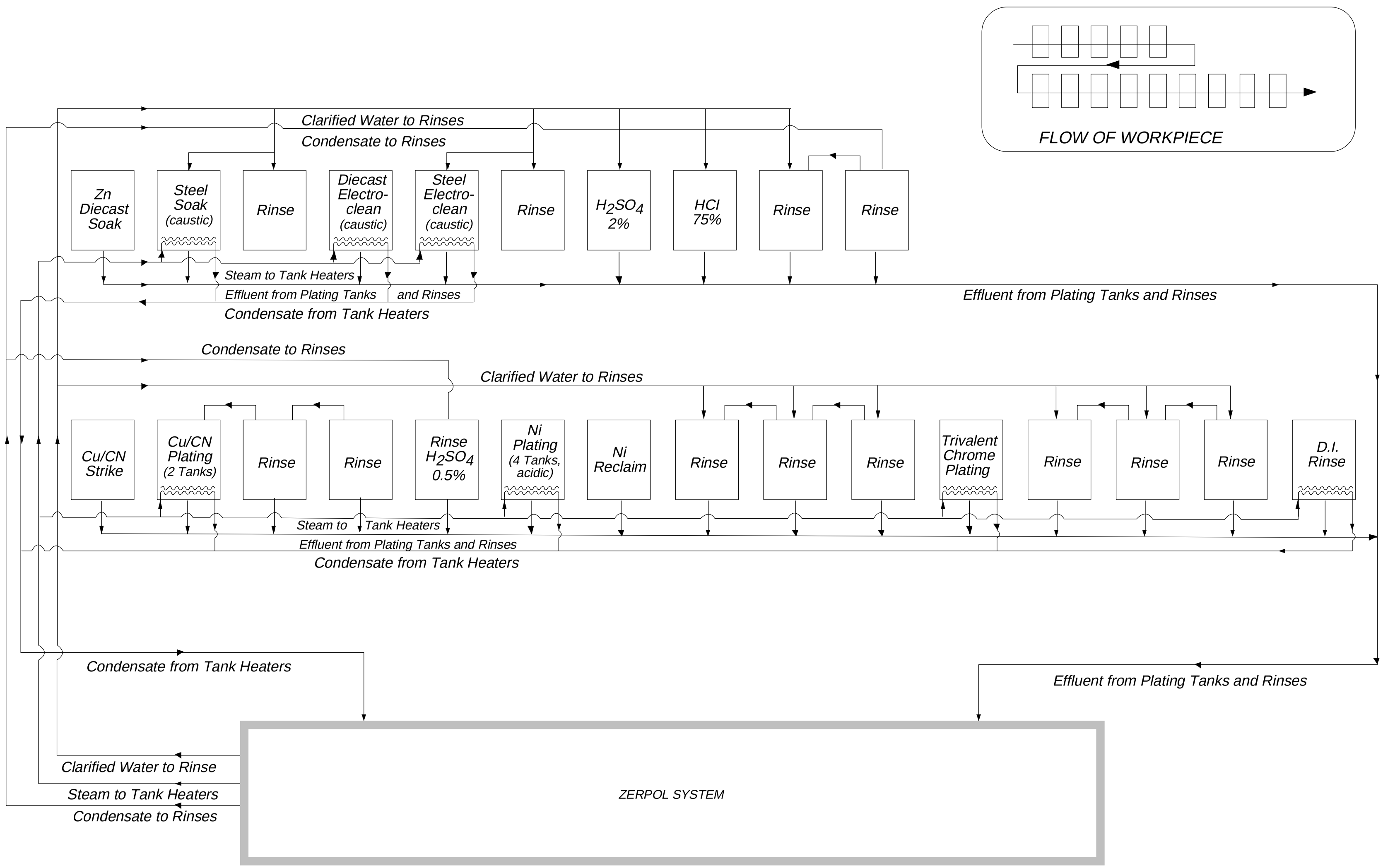

Figure 1. *Schematic of plating system.*

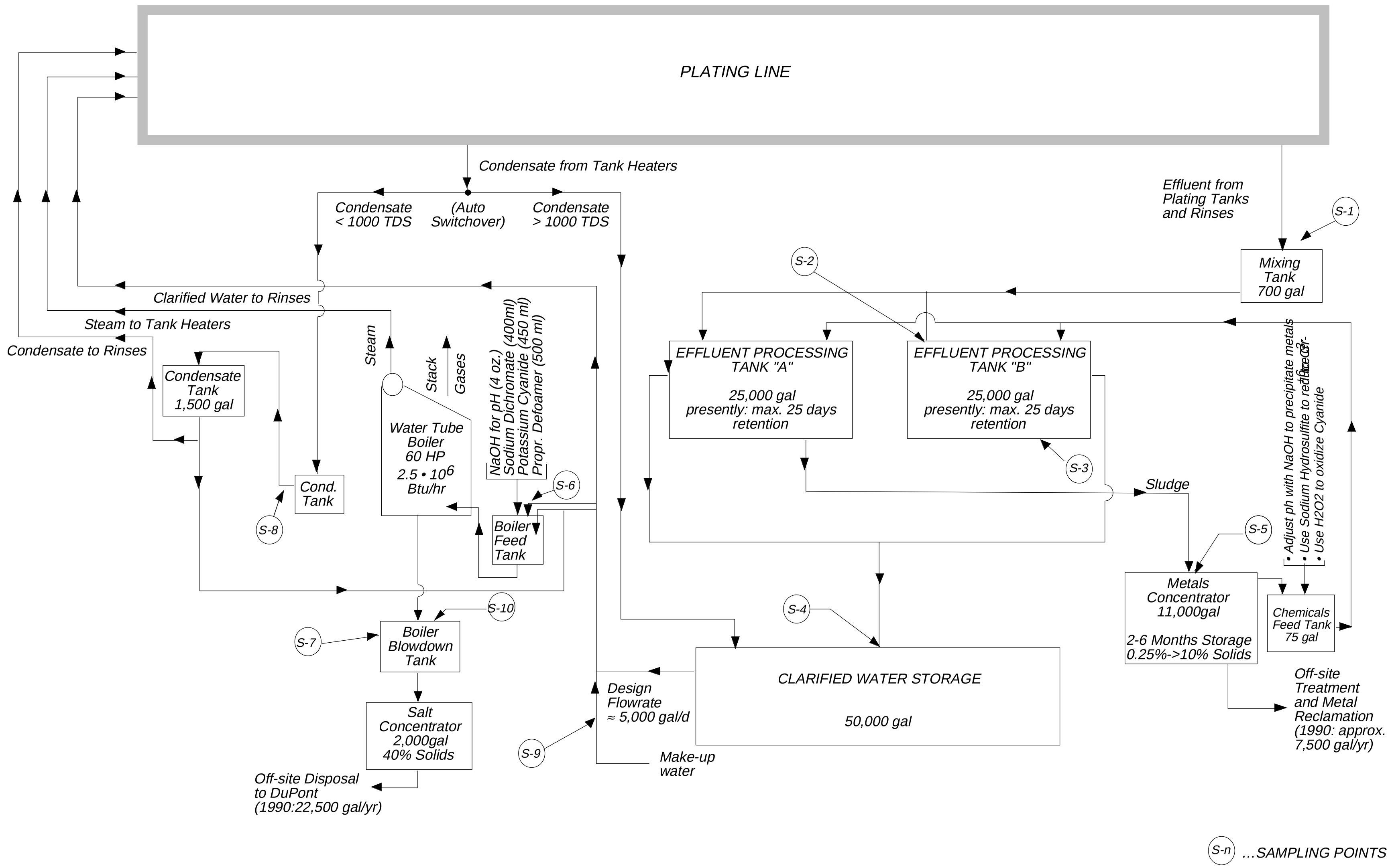

Figure 2. *Schematic of Zerpol system - basic process flow diagram.*

able, particularly in comparison with the costs of using other waste management options.

Field Sampling and Operating Data Gathering

Three types of data were gathered during six-day tests conducted over a 32-day period: 1) Composite stream samples for chemical analysis; 2) Actual flow rate measurements of the generated effluent, recirculated water, steam condensate and boiler fuel gas; 3) Historical operating and maintenance data on the present Zerpol System and the system that preceded it, a system that involved precipitation of metal sludges and discharge of the treated aqueous effluent.

For each test, composite samples of the process and of the Zerpol streams were taken. System flow rates, namely process effluent flow, and the pumping rates of clarified water and of the sludge were measured by capturing the flow in a container and by timing the flow with a stop watch. The boiler feed was measured by an actual water meter.

Samples were taken from ten sampling points and analyzed for cyanide ions, calcium, magnesium, copper, nickel, chromium, iron, zinc, cadmium, phosphorus, total solids, total suspended solids, total dissolved solids, and pH.

The analytical data and volume flow measurements are used to determine mass loading entering and leaving the Zerpol system, and by difference, the amount captured by the Zerpol system.

Similarly, the quality of the condensate was determined, as well as the composition of the boiler blowdown. The boiler operation was monitored during five working shifts. The total volume of water fed into the boiler was metered. The volume of boiler blowdown was determined by metering and by calculations. Composite samples were analyzed.

Because concern was expressed in the previous study about levels of hydrogen cyanide potentially produced in the Zerpol process, air samples were taken, using OSHA standard procedures, at the first point open to the atmosphere after mixing of acid streams and cyanide ion bearing streams. These air samples were taken at the mixing tank ahead of the first holding tank, where analytical measurements of the pH and cyanide content of the water have also been made. Air samples were analyzed for hydrogen cyanide.

Because Pioneer claims that the Zerpol process continues to operate well even when process baths are dumped, samples and measurements were taken before and after the occurrence of these extreme conditions to demonstrate whether heavier inorganic loadings interfere with the quality of the recirculating water.

To address the issue of potential problems with foaming in the boiler that were raised in the previous report on the process, the feed water to the boiler was sampled before and after addition of the defoaming agent and evaluated according to the Standard Test Method for Foam in Aqueous Media (Bottle Test), ASTM D3601-88.

It should be noted that Pioneer frequently reported discharge violations while the former continuous discharge treatment system was in operation from 1975 to 1981. These violations were a primary reason the previous treatment system was replaced and there have been no such incidents since the Zerpol system became operational.

Since the mid-eighties, shop management has substantially reduced the total use of water from the previous 5,000 gal/day to less than 2,000 gal/day. Waste minimization initiatives such as the reuse of dragouts, have been very effective. While the previous system required relatively large volumes of water for most effective operation, the Zerpol system uses substantially reduced water volumes and has encouraged and justified additional pollution prevention efforts. In 1989, the shop operation switched from two per day to one shift starting at 6:00 AM and ending at 2:30 P.M.

The operation of the Zerpol system and the boiler were fine tuned to match the requirements of the plating process. The 25,000-gal effluent processing tank that used to hold the effluent for five work days now holds effluent for about 18-20 work days. This means that the quantity of chemicals used to precipitate the metal hydroxides in the effluent processing tanks has been greatly reduced.

The boiler serves two purposes: It provides 10-psig steam to heat the plating baths. The condensate is used as a source for rinsing and for boiler feed water whenever excess condensate is available. It is also a means of controlling the level of solids in the recirculated process water. The solids are removed from the system through boiler blowdown. For this applica-

Table 1. *Summary of Process Streams Chemical Analyses for Metals and Solids*

Sample Point / Material Analyzed	S-2 Effluent Tank Inlet [mg/l]	S-3 Effluent Processing Tanks [mg/l]	S-4 Clarified Water Tank Inlet [mg/l]	S-5 Sludge Tank Inlet [mg/l]	Boiler Feed (S-6) Clarified Water [mg/l]	Boiler Feed (S-6) Condensate [mg/l]	S-7 Boiler Blowdown [mg/l]	S-8 Steam Condensate Return [mg/l]	S-9 Make Up [mg/l]	Waste Mtl. In Sludge 1,000 Sq. Ft. Plated Area [lb/1000ft^2]
CN	16.63	36.1	2.69	245	2.18	3.21	18.53	0.814	< 0.01	—-
TDS	9820	7820	8380	8620	8329	725	85146	57.2	60	—-
Ca	19.24	13.94	22.9	137	16.94	<8.81	74.1	<8.09	<8.09	0.058
Mg	0.99	0.57	0.73	11.2	0.9	<0.095	1.25	<0.08	0.982	0.0047
Cd	0.26	<0.003	<0.003	<0.235	<0.003	<0.008	<0.008	<0.008	<0.003	0.000099
Cr	22.23	42.14	2	538	1.7	23.36	236	0.12	<0.046	0.23
Cu	11.17	27.89	2.9	445	1.32	0.24	10.08	0.16	<0.02	0.19
Fe	22.22	48.68	2.01	723	2.05	0.47	5.65	0.28	4.99	0.30
Ni	71.86	201	10.1	3628	28.26	3.73	52.57	<1.25	<1.25	1.53
Zn	27.83	84.35	0.92	1434	0.76	0.16	2.3	0.12	0.08	0.60
P	24.91	19.19	<4.69	189	<4.86	<4.69	9.62	<5.98	<4.69	—-

CN in air at Process Effluent Tank: 0.058 mg/m^3.
CN in air at Boiler Blowdown Sump Surface: 0.101 mg/m^3.

tion, the boiler capacity and blowdown frequency are sufficient to keep the total dissolved solids in the recirculated water at less than 10,000 ppm.

Summary of the Results

Table 1 shows that the average TDS of the clarified recirculated process water is about 10,000 ppm; of the steam condensate is about 500 ppm; of the boiler blowdown is 100,000 ppm. This table also shows that the metals concentration of the recirculated water is higher than what is allowed for discharge into a typical POTW, e.g. Ni is 10.1 ppm compared with an allowable limit of 3.98 ppm. The cyanide concentration is 2.69 ppm compared with the limit of 1.20 ppm. Treatment to levels within the allowable limit may be possible, but at much higher cost, may not be economically attractive. The observed levels are routinely maintained by Pioneer because they are economically achievable and do not negatively affect their processes.

Table 2 shows that the clarified water recirculation rate is about 1,700 gal/day. This is much lower than the initial system design rate of 5,000 gal/day. Effluent flow rate is in the range of 3.36-3.82 gpm. About 37% of the recirculated water is diverted through the boiler. Boiler blowdown averages about 0.20 gpm. The boiler generates steam to the process at an average condensate equivalent rate of 1.35 gpm. Average heat delivery to the process from the steam is about 6.55 x 10^5 Btu/hr. Boiler thermal efficiency based upon heat delivered to process compared to heat energy input to boiler is about 39-40%. The daily energy cost to run the boiler is in the range of $104-127/day.

Table 3 shows that the operating cost of the Zerpol system is about 1/3 that of the previous system, however; the installed cost of the Zerpol is nearly two times that of the previous system.

Conclusions

The Zerpol zero discharge system can be used successfully at metal finishing

Table 2. *Operating Data of the Zerpol Effluent Processing System*

Test Series Date Test Number	*1 4/14/92 1*	*1 4/15/92 2*	*1 4/16/92 3*	*2 5/14/92 1*	*2 5/15/92 2*	*Five Day Average*
Clarified Water						
Total Flow/24 hr:	*1747.4 gal*	*1592 gal*	*1705 gal*	*1686 gal*	*1721 gal*	*1690.3 gal*
Flow During Daytime to Process:	*1079.4 gal*	*949.2 gal*	*1058 gal*	*1096 gal*	*1088 gal*	*1054.1 gal*
(Average Flowrate)	*(2.57 gal/min)*	*(2.26 gal/min)*	*(2.52 gal/min)*	*(2.61 gal/min)*	*(2.59 gal/min)*	*(2.51 gal/min)*
** Flow During Night to Boiler:*	*668 gal*	*642.6 gal*	*647 gal*	*590 gal*	*633 gal*	*636.1 gal*
(Average Flowrate)	*(1.59 gal/min)*	*(1.53 gal/min)*	*(1.54 gal/min)*	*(1.40 gal/min)*	*(1.51 gal/min)*	*(1.51 gal/min)*
% of Clarified Water Passing through Boiler:	*38%*	*40%*	*38%*	*35%*	*36.8%*	*37.6%*
Boiler Blowdowns						
Average Flowrate:	*0.28 gal/min*	*0.14 gal/min*	*0.13 gal/min*	*0.19 gal/min*	*0.28 gal/min*	*0.20 gal/min*
Nº Blwdns.-Minutes Ea.-Gal Ea. During Daytime:	*3/1min/39.2gal*	*2/1min/29.4gal*	*2/1min/27gal*	*2/1min/40gal*	*3/1min/40gal*	*2.4/1min/35gal*
During Nighttime:0	*0/0/0*	*0/0/0*	*0/0/0*	*0/0/0*	*0/0/0*	*0/0/0*
Steam from Boiler (as Condensate)						
During Daytime to Process:	*1.18 gal/min*	*1.26 gal/min*	*1.28 gal/min*	*1.16 gal/min*	*1.04 gal/min*	*1.18 gal/min*
Nighttime to Storage Tank:	*1.59 gal/min*	*1.53 gal/min*	*1.54 gal/min*	*1.40 gal/min*	*1.51 gal/min*	*1.51 gal/min*
Average Flowrate (24 hr.):	*1.385 gal/min*	*1.395 gal/min*	*1.41 gal/min*	*1.28 gal/min*	*1.275 gal/min*	*1.35 gal/min*
Average Heat in Steam Flow to the Process:	*6.72 *10^5 Btu/hr*	*6.77 *10^5 Btu/hr*	*6.84 *10^5 Btu/hr*	*6.22 *10^5 Btu/hr*	*6.19 *10^5 Btu/hr*	*6.55 *10^5 Btu/hr*
Condensate						
Flow During Daytime to Process as Rinse Water:	*549.9 gal*	*586.8 gal*	*593 gal*	*509 gal*	*515 gal*	*550.7 gal*
(Average Flowrate)	*(1.31 gal/min)*	*(1.40gal/min)*	*(1.41 gal/min)*	*(1.21 gal/min)*	*(1.23 gal/min)*	*(1.30 gal/min)*
**Flow During Daytime to Boiler:*	*614.1 gal*	*584.8 gal*	*592 gal*	*566 gal*	*556 gal*	*582.6 gal*
(Average Flowrate)	*(1.46 gal/min)*	*(1.40 gal/min)*	*(1.41 gal/min)*	*(1.35 gal/min)*	*(1.32 gal/min)*	*(1.40 gal/min)*
Boiler Data						
Type-yr in Service-Measured Eff.:	*Columbia WL 180 - 3 yr in service - 67% to 68%*					

(continued)

Table 2. *Continued*

Test Series Date Test Number	1 4/14/92 1	1 4/15/92 2	1 4/16/92 3	2 5/14/92 1	2 5/15/92 2	Five Day Average
Boiler Thermal Efficiency: (Btu/hr to Process Btu/hr to Boiler)	39%-41%	38%-40%	38%-40%	42%-44%	42%-44%	40%-42%
Average Energy Input to Boiler:(Btu/hr)	$17.1*10^5$	$17.7*10^5$	$17.7*10^5$	$14.6*10^5$	$14.6*10^5$	$16.3*10^5$
Daily Boiler Energy Costbased upon $0.53 / 10^5 Btu:	$127	$127	$127	$104.7	$104.7	$118.1

Average Effluent Flowrate During Single Tank Filling Period of 25 Days Containing 18 Workdays @ 7 Hours: 3.00 gal/min.
Average Effluent Flowrate During First 3 Test Days (Excluding Bath Dumps): 3.36 gal/min.
Average Effluent Flowrate During First 3 Test Days (Including Bath Dumps): 3.32 gal/min.
Total Effluent Flow During Single Tank Filling Period of 25 Days Containing 18 Workdays @ 7 Hours: 22,700 gal.
*Clarified Water Produced During the 25-Day Period: 19,700 gal Sludge Produced During the 25-Day Period: **3,000 gal.*
** Boiler feed: during daytime - condensate; during nighttime - clarified water Boiler Feed Water Treatment Done Once a Day at 2 p.m.*
*** 99% Water. Water Removed after Settling.*

Table 3. *Comparison of Installation and Operating Cost Data of the Past and Present Treatment Systems at Pioneer*

Equipment	Previous System Individual Treatment Tanks	Present Zerpol System(1) Storage Tanks and Boiler
Chemicals, $/yr2)	12,300 - 15,300	2,700 - 3,300
Labor, Repair, Maintenance & Monitoring3)	35,140	1,890
Sludge + Salts Disposal, $/yr	not available	8,800
Total Operating Costs4), $/yr	47,440 - 50,440	13,390 - 13,9905)
Installed Costs, $	65,000 (1975)	170,000 (1981)
D.I. system, Installed Cost, $	30,000	30,000
Flow, gal/day	16,000 - 40,000	1,500 - 5,000
Operation, day/yr	250	250
Years in service	1975 - 1981	1981 to present
Original flow, gal/day	40,0006)	5,000
Boiler energy cost	(not included)	(not included)

1) Requires Deionized (D.I.) Water System.
2) Includes Chemicals for Boiler and D.I. Water System.
3) Based on Labor Costs of $17.5/hr Includes labor for D.I. Columns Backwash.
4) Costs of Chemicals, Operating Labor, Repair, Maintenance, and Monitoring.
5) Includes Disposal of Sludge and Salts.
6) The Previous System Could Only Function With Diluted Flow, Requiring Large Volumes of Water.

shops where the treated effluent and the generated condensate can be recirculated and reused for rinsing without impairing product quality.

The Zerpol system works well for the Pioneer metal finishing process which was the subject of the one- month field evaluation. During that period, acid and caustic baths were intentionally dumped into the system as part of the normal operation of the facility. This did not result in any noticeable product quality impairment. This system should perform just as well for shops with similar production and quality requirements.

Because the entire effluent is captured and collected in large capacity tanks prior to recycling; 1) risk of accidental release is reduced; 2) special operating permits are not required, although local agencies should also be consulted; 3) compliance with effluent pretreatment standards is not required; 4) timing of chemical addition and processing is flexible; and 5) maintenance emergencies are less frequent and more easily managed than with other waste management options. Also, there seem to be no acute safety concerns. Measured levels of hydrogen cyanide at the effluent mixing tank and at the boiler blowdown sump were extremely low, well within the OSHA standards.

When the required equipment for the zero discharge system is identified, its economics and pollution reduction potential should be compared with those of other systems, such as:

- Zero discharge, low temperature evaporative recovery and treatment systems.
- Non-chemical wastewater treatment system.
- Carbon absorption.
- Microfiltration, Ultrafiltration, Reverse Osmosis.
- Ion Exchange.
- Electrowinning by itself or in combination with other treatment systems.

It should be noted that while it is true that the Zerpol zero discharge system does not contribute to pollution at the site, this does not mean that its recovered materials do not contribute pollution to the environment at the smelting facility. Identifying and quantifying this pollution could not be accomplished in this study because of the reluctance of the smelting operation to provide information, but should be considered in any life-cycle analysis of this and related processes.

The results of this investigation demonstrate that, at this facility, the Zerpol zero discharge system eliminates the discharge of an aqueous wastestream by allowing recycling of most of the process water. The system facilitates the removal of metals in a form that is suitable for metal recovery. Salts from the boiler blowdown are treated as wastes in a standard water treatment facility. These positive factors represent a reduction in the volume of waste generated at the facility through a series of process modifications and have encouraged and facilitated source reduction initiatives at the facility.

The full report was submitted in fulfillment of Assistance Agreement No. CR-816142 by New Jersey Department of Environmental Protection under the sponsorship of the U.S. Environmental Protection Agency.

Hanna J. Saqa and Daniel J. Watts are with New Jersey Institute of Technology, Newark, NJ 07102; Mohammed Elsaady is with the New Jersey Department of Environmental Protection and Energy, Trenton, NJ 08625; and the EPA author, ***Johnny Springer*** *(also the EPA Project Officer, see below) is with the National Risk Management Research Laboratory, Cincinnati, OH 45268.*

The complete report, entitled "Field Testing and Evaluation of Zerpol® Technology at Pioneer Metal Finishing," (Order No. PB95-260 238; Cost: $19.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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