

ZERO DISCHARGE DECORATIVE NICKEL CHROMIUM PLATING

By Jaime J. Maliszewski, B.S.  
Reliable Plating Works, Inc.  
Milwaukee, Wisconsin

Pollution restrictions are a major focus in today's finishing industry. Unlike the year 1929, when Reliable Plating Works, Inc. ( R.P.W. ) was founded., today's business has to answer to the E.P.A. Even in 1967 and 1972 when R.P.W. installed its first two (2) fully automated plating lines, there was little concern as to how all the increased waste would be disposed of. The system most shops used was dilution. Unfortunately, the only solution to pollution is no longer dilution.

In this paper, Reliable Plating Works would like to share with you their award winning process which earned them Wisconsin's Governor's Award for Hazardous Waste Treatment. This award was given to R.P.W. for its ability to surpass Wisconsin's strict pollution regulations, while at the same time increasing their efficiency and their profitability.

R.P.W. had to face this challenge in 1984 when they were installing a new manufacturing plant that would house Wisconsin's largest fully automated, job shop, plating line for decorative Nickel and Chrome. This hoist line stretched 120' D.O.T. by 1.8' in height and 12' in width. The hoist would have the capability to plate 1,000 square feet of plating per hour. In other words, not only would this hoist generate a large volume of finished goods, it would also generate an enormous amount of waste to be treated. Treatment of this waste began by treating the cleaner solutions.

#### Extending the life of cleaners

John Maliszewski, President of R.P.W., should be credited with selecting the system that not only helped R.P.W. meet full compliance, but also tripled the life of the cleaners.

The system he chose began with a series of sprays and counterflows installed in its cleaning cycle. John knew that the easiest way to extend cleaner life would be to increase rinsing above the cleaner tanks, not allowing the wetters and caustics to drag out of solution. By using rinse water to spray the parts as they exited the cleaner tanks, R.P.W. was not only able to decrease the amount of material dragged out of solution, they were able to pump some of the material back into the cleaner tanks from the rinse tanks. ( See Diagram I )

The caustic that is left in the rinse water is then used to lower the pH of the acid rinse' water. R.P.W. was able to do this with the help of counterflows. These counterflows traveled from the acid rinse tank, into the caustic rinse tank and finally into a limestone holding tank which leads into the sewer. The flow into the Limestone holding tank should be monitored in order to assure acceptable pH levels ( See Diagram II ) .

Diagram I.  
How to hook up your spray system.

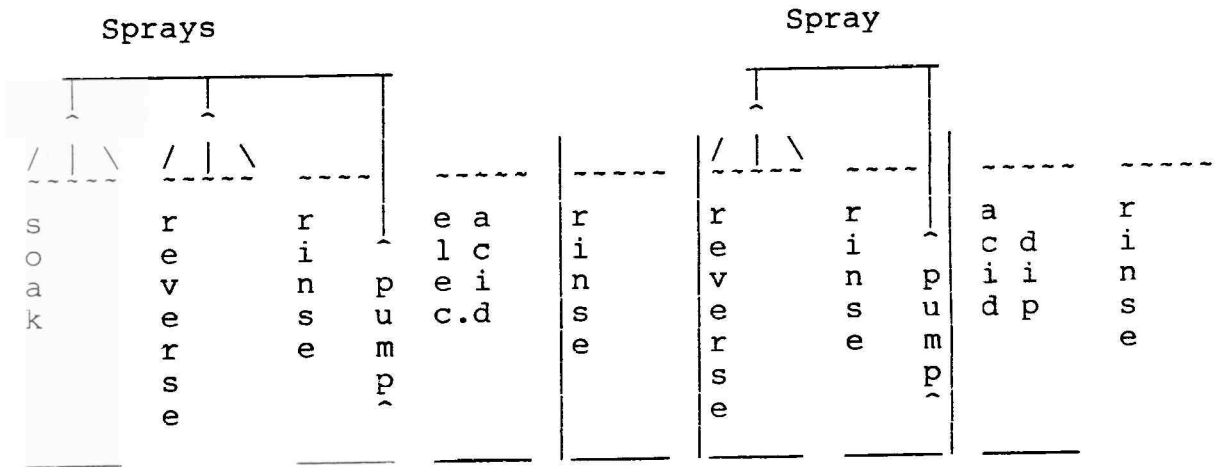
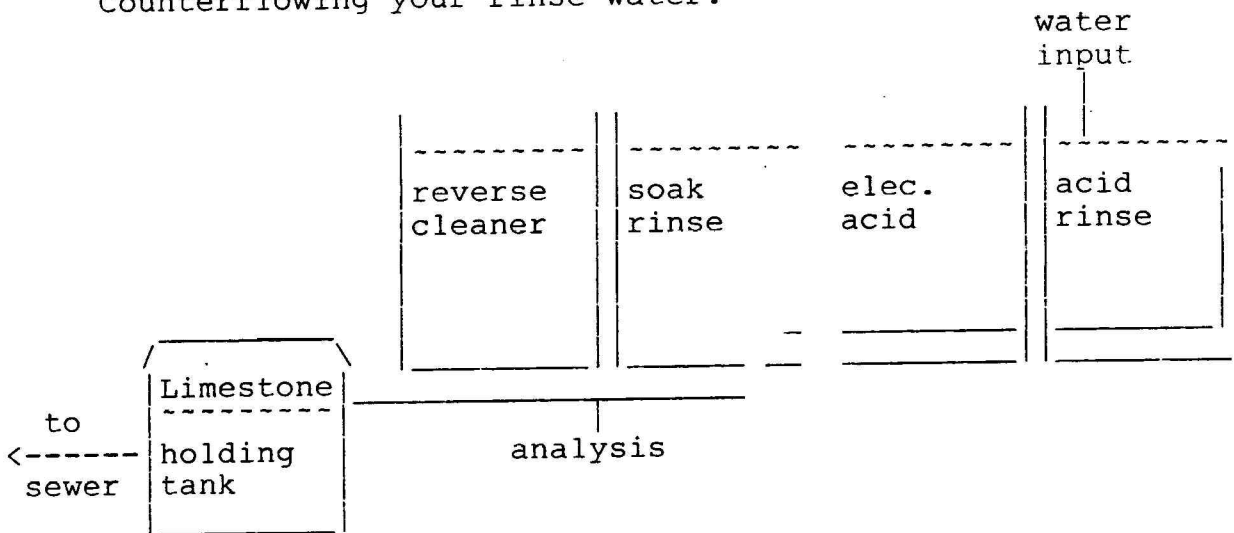


Diagram II.  
Counterflowing your rinse water.



With the addition of sprays, R.P.W. avoided increased up dwell times, longer, more costly cycle times, higher material costs and greater chances of plating problems such as dry on.

The sprays that were used accounted for about 75 percent of the total life extension of the cleaners. The last 25 percent was attained when Jack Maliszewski, C.E.F., Exec. V.P., started a de-sludging and skimming program. This program began by mixing the caustic rinses with the acid rinses" to achieve proper pH so that the rinse water can be let down the sewer. Once these tanks are emptied, the cleaner solutions can be pumped into one of the empty rinse tanks for storage, while employees remove the sludge that is left at the bottom of the cleaner tanks. This sludge is then placed in one of three large holding tanks until it will be hauled off sight when the storage tank becomes full. The sludge-free cleaners are then returned to their appropriate tank and the rinse tanks are filled with fresh water. This process is done after the cleaner has run three months and allows it to run " another three months before it has to be moved into one of the storage tanks and made up new.

The second part of this program, the skimming, is done once every week and takes about 15 minutes per tank on a Saturday. In this process, the cleaner tank must first be cooled and left to settle overnight so that the oils and grease are allowed to separate from solution and float to the top where an employee is able to skim it off into an overflow trough. The trough is then pumped directly into one of the holding tanks.

The Acid bathes, however; were not sprayed, skimmed or de-sludged. In order to increase the life of the Acid bathes, R.P.W. decided to use filtration and bath rotation. The filtration is done by carbon filters that are attached to both the Electrified Acid bath and the Acid Dip bath. The filters remove all the grease from solution. Bath life was further increased by rotating the Acid Dip bath into the spent Electrified Acid tank. By doing this, the cost of making this bath up from scratch is saved. The Acid Dip bath still has to be made up new. Through filtration and bath rotation, Acid bathes are able to last for one month in each tank. This extended the bath life at R.P.W. from two weeks to two months.

Not only did R.P.W. save money on the cost of material, they were also able to decrease the grease related rejects by 90 percent. The only cost other than the cost of hooking up the filters, was the cost of 1 manhour every week that is used to clean the filter and change the cartridges. The cost savings of all the above mentioned recovery systems are noted in the summary.

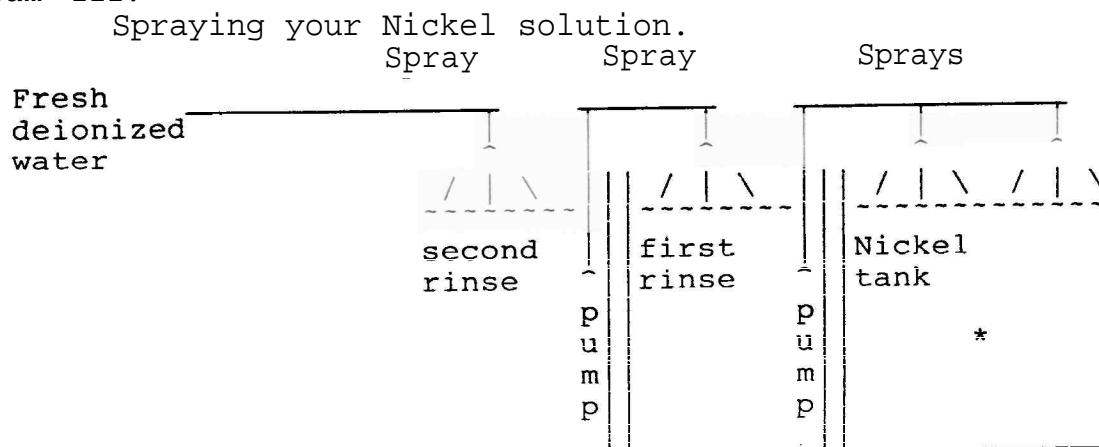
## Evaporating to recover your Nickel Solutions

During these days of skyrocketing Nickel prices no-one wants to see Nickel solution, which contains precious Nickel metal ,

being hauled away as waste. It would be a much better sight to see one of your workers pumping the saturated Nickel solution back into your Nickel tanks that have been concentrated by evaporating the water out of solution.

The first step to recovering Nickel solution is to install sprays above the Nickel tanks. These sprays will spray the parts as they exit the Nickel tank, using water from the first rinse after Nickel. The first rinse after Nickel is then sprayed with water from the second rinse after Nickel ( See Diagram III ). By

Diagram III.



\* These Nickel tanks are heavily filtered in order to keep impurity levels down.

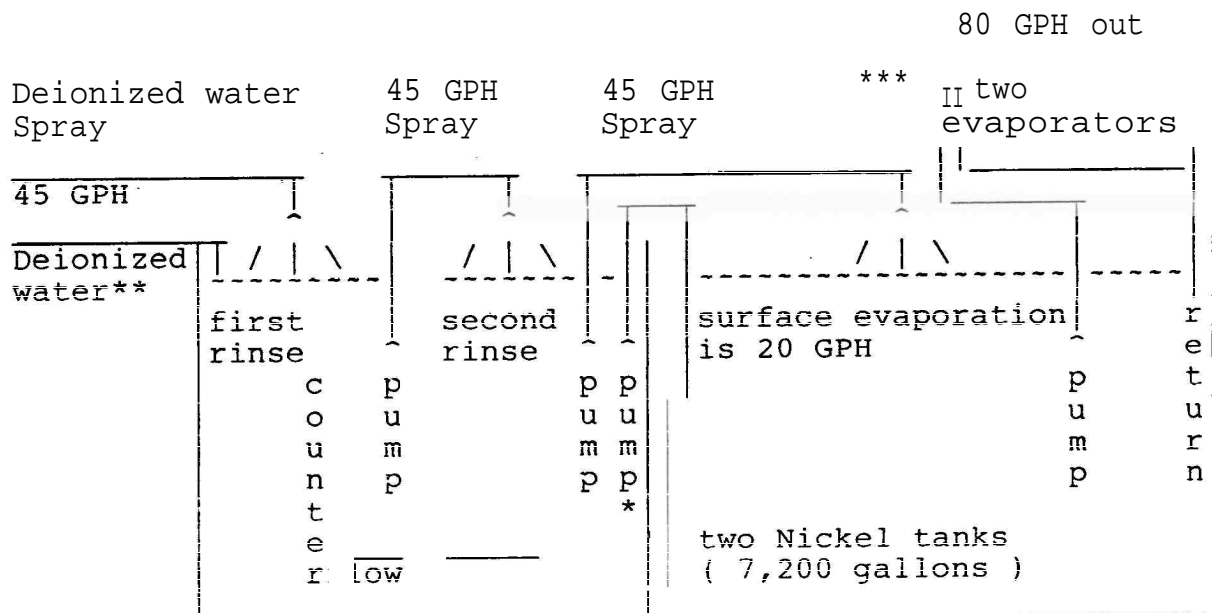
spraying these tanks back into the Nickel, the solution which is dragged out of the Nickel tank will be sprayed back into the Nickel tank through the sprays. Although these sprays reclaim some of the Nickel solution, there was still a need to reclaim more of the dragged out Nickel solution in order to reach 100 percent recovery.

Since the flow of solution was flowing back into the Nickel tank in order to reclaim the dragout, it was necessary to make room in the Nickel tank so that the reclaimed solution would have a place to go. Two atmospheric evaporates were attached to the system, one per 3,600 gallon Nickel tank, in order to make room for the recovered solution. The evaporators were able to work at a rate of 100 gallons per hour with the help of surface evaporation from the two 145 degrees Fahrenheit Nickel tanks. At this rate they were able to empty the first Nickel rinse once every 22 hours by pumping the solution from the first rinse back into the Nickel tanks.

To insure that no Nickel would escape down line, a counterflow was added which moved the water from the second rinse into the first rinse tank. Reliable Plating was able to recover all of its Nickel solution ( this includes brighteners, Nickel salts, Nickel chloride, etc... ) that was dragged out of the Nickel tank and return it to the Nickel tank by using sprays, evaporators, counterflows and pumps. ( See Diagram IV )

Diagram IV

Two evaporator set up for two Nickel tanks.



\* pump is used as needed to fill Nickel tank.

\*\* valve to add fresh deionized water as needed.

\*\*\* evaporators which spray out the side work best since they don't clog up as fast as the evaporators which discharge on top.

Although R.P.W. was able to hold its nickel discharge in compliance, other areas such as of Zinc, Lead and Calcium began to climb, causing plating problems. It seems that the evaporators were doing too much recovery. Even though R.P.W. had no Zinc in house, Zinc levels were rising. The source was found to be the city water, which after recovery, increased in impurity levels. The solution to this problem was the installation of a deionize water unit. This unit eliminated the impurity problems not only in the recovery of the Nickel solution, but also in the recovery of Chromium. Deionized water is used to fill all tanks leading into the recovery tanks to avoid this build up of impurities.

## How to recover low temperature Chromium

Evaporating your Chromium solution may sound difficult to do since the temperature of the bath is generally about 112 degrees Fahrenheit. At R.P.W. it was found that only 12 gallons of solution could be evaporated per hour, by use of an atmospheric evaporator and surface evaporation from the Chromium tank. This evaporation rate was unable to make up for the solution that was being dragged out and counterflowed back into the Chromium tank. There was still a need to increase the evaporation of solution so that more rinse water could be counterflowed back into the Chromium tank.

To increase the evaporation rate, R.P.W. had to change its Drag out tank into a Recovery tank. This change was done by running a heating coil into the new recovery tank that would heat the solution to 140 degrees fahrenheit ( a suitable temperature for evaporation ) . This solution was then pumped through a second evaporator which increased total evaporation from both tanks ( evaporation includes both tanks surface evaporation and evaporation from the evaporators ) to 45 gallons per hour.

By evaporating the Chromium solution, a Chromium mist is produced that must be piped into your fume scrubber. This must be done so that in gaining your waste water compliance you don't go out of compliance by polluting your air. By doing this you are also able to reclaim the Chromium that is pulled out of the air by your fume scrubber and put it back into your Chromium tank.

Counterflows were also used to move the dragged out Chromium solution back through their rinse tanks and back into their Chromium tank ( See Diagram V ) . This left no rinse water going into the sewer.

In order to complete the system, R.P-W. had to add a series of sprays to all the Chromium rinses, the Recovery tank, and the Chromium tank ( See Diagram V ) . The sprays not only doubled the amount of rinsing on the parts, they also helped the flow of concentrated solution back into the Chromium tank. By doing t-his you are able to add fresh deionized water to the last rinse keeping it cleaner which causes your parts to come out with only minor water spotting.

By solving our waste problems we increase our impurity levels in our chrome. To eliminate this we added a Clay Pot Reverse Osmosis System that pulled out our unwanted Chlorides, Tri-valent Chromium, and other Metals. This system works so good that we added one to all of our lines in less than six months. The sludge from this system can be dried and sold to metal smelters as Nickel and Chromium.

As you all know, Murphy's Law states that if it can happen it will happen, and so RPW, Inc. added its safety catch. The safety catch consists of a Rapid Sand Pressure Filtration System, Activated Carbon Cartridge Filtration, and a Metal Selective Ion Exchange Unit. This system was installed just so RPW, Inc. could get past burps in the system ( parts with no drain holes, etc...)

The Rapid Sand Pressure Filtration System protects the Ion Exchange Unit from iron oxide fouling. This system will collect dirt and iron oxide and will not affect the downstream concentration of regulated metals ( Nickel and Chromium ) . A stand by filter is needed for times when backwashing is needed on the primary filter. This secondary filter will now run until it requires a backwash. All backwash material from these filters is clear for direct sewer discharge.

The Activated Carbon Cartridge Filtration System which follows Rapid Sand unit, protects the Ion Exchange unit from oil and grease fouling of the resin. This is necessary even though our waste stream consists of only 5 mg/l of oil.. The carbon cartridges are replaced weekly ( or as needed ) and do not generate any hazardous waste for treatment.

The Metal Selective Ion Exchange Unit, which is the final step in our treatment system, will remove the regulated soluble metals through utilization of selective ion exchange. Selective ion exchange will be accomplished by employing a chelating cation exchange resin in the sodium form that is preferential for heavy metal cations in the following order of selectivity as compared to calcium. MURCURY 2800:1, COPPER 2300:1, LEAD 1.200:1., NICKEL 57:1, TRI-CHROME 20:1., ZINC 17:1, CADMIUM 15:1, COLBALT 6.7:1, IRON (FERROUS) 4:1, MAGANESE 1.2:1, and CALCIUM 1:1. In order to recover hexavalent chromium ( which acts as a anion ) the chelating cationic resin will be capped with an anionic resin operating in the hydroxide form.

We use two 100 percent capacity ion exchange columns that are charged with three cubic feet of resin each. These units will run for approximately three weeks before they will have to be recharged. When recharged the resin must first be regenerated with sodium hydroxide to remove the hexavelant Chromium from the anionic resin. It then has to be regenerated with hydrochloric acid to remove the metal from the chelating resin followed again by regeneration with sodium hydroxide to both clean the resin and return it to the sodium form. All the regenerated waste waters are directed to an evaporation tank were it is dried and resold as metal salt.



Table I

Total cost of installation of a recovery system.

Installation Costs:	\$ 7,000.00
(2) Nickel evaporators	8,000.00
(2) Chromium evaporators	
Sprays:	2,860.00
(1.1) Pumps	1,672.00
(88) Spray heads	650.00
PVC Piping	
Counterflows:	1,100.00
PVC Piping	480.00
(2) Transfer pumps	7,000.00
(2) Acid filters	6,900.00
(3) Holding tanks 4'x8'x8'	30,000.00
(1) Deionized water unit	
(1) Metal Selective Ion Exchange	
includes Rapid Sand Pressure Filter	23,000.00
and Carbon Filter	15,000.00
(1) Clay Pot Chrome Clarifier	11,200.00
Labor ( 4 wks. / 2 men at \$35.00/hr.)	
	\$114,862.00
Total installation cost. =	

Table II

Running cost of a recovery system for one year.

Waste hauled offsite twice a year	\$ 2,000.00
Deionized water treatment	7,200.00
Labor:	
12 hours overtime/ week (@ \$31.50/hr.)	19,656.00
3 hours per day (@ \$21.00/hr.)	16,380.00
Electricity & Gas	19,410.00
Total yearly running cost =	\$64,646.00

Table III

Yearly cost savings attained by recovering their materials at R.P.W.

Material Name	Cost/Unit	Amount. of \$'s Saved
Nickel sulfate	\$ 1.20/lb.	\$ 37,440.00
Nickel chloride	1.28/lb.	13,312.00
Nickel metal ("87")	2.20/lb.	45,760.00
( Nickel metal "90")	(4.75/lb.)	* (98,800.00)
Boric acid	0.38/lb.	
Brighteners	20.00/gal.	20,800.00

Table III

Yearly cost savings attained by recovering their materials at R.P.W.

Material Name	Cost/Unit	Amount of \$'s Saved
Nickel sulfate	\$ 1.20/lb.	\$ 37,440.00
Nickel chloride	1.28/lb.	13,312.00
Nickel metal ("87")	2.20/lb.	45,760.00
( Nickel met-al "90")	(4.75/lb.)	* (98,800.00)
Boric acid	0.38/lb.	
Brighteners	20.00/gal.	20,800.00
Chromium	2.15/lb.	54,180.00
Soak:		
make-up cost saved	0.68/lb.	1,500.00
additions saved		4,420.00
Reverse:		
make-up cost saved	0.59/lb.	2,880.00
additions saved		7,700.00
Acids:		
Make-up cost saved	0.29/lb.	8,640.00
additions saved		- o -
Total yearly savings =		\$ 198,456.00
( Total yearly savings 1990 ) =		( \$ 251,496.00 )
<p>** The above numbers were calculated from chemical usages of other machines that. were not recovered prior to 1980. Records of material usage were not available for this Hoist line, since it. was never run without. the recovery unit. running.</p> <p>* Note how much more the savings would be worth in 1990 with \$ 4.75 /lb. Nickel</p>		

Table IV

Installation cost of a destruct system.

Installation costs:	PVC piping	
	Electrical wiring	
	Labor	
	Total	\$ 21,000.00
Equipment costs:	Chrome destruct tank	
	Neutralizing tank	
	Flucuant tank	
	Clarifier	
	Sludge press	
	Solid state controls	
	Miscellaneous:	
	Sump pumps	
	Support frame	
	Reagent feeds & tanks	
	Total	\$104,500.00
	Total Initial Cost:	\$125,500.00
Individual prices of above mentioned parts and labor unavailable. Total costs were exact cost. quoted t-o R.P.W. for a destruct system for their Hoist line t-hat. is hooked up to their total recovery system.		

This Hoist line was never run without its recovery system working so in order to make any comparisons, flow rates and sludge production had to be calculated through estimations. R.P.W.'s system has recovered over 140,000 pounds of combined metals and cleaners per year that. would have had to be hauled away if they were not recovered. Table V will show what the calculated cost. of running a destruct. system on R.P.W.'s line would cost for one year.

Table V

Operating costs of a destruct system for one year.

Cost of shipping sludge:	
67 drums - 4 times per year	
( \$125.00 per 55 gal. drum )	\$33,500.00
Cost of 55 gal. drums ( 268 drums per yr. )	4,020.00
Labor for maintenance and operation:	
@ 2 hours per day labor ( \$21.00 per hour )	5,460.00
Total cost of running for one year	<u>\$42,980.00</u>

As this short summary has shown, recovery systems are a very cost. efficient way to handle your waste. Without recovery you are literally throwing money down the drain. The system at R.P.W. has been able to surpass Wisconsin's strict regulations on waste water emissions since it started product-ion at our new plant in 1984. If your regulations are more strict than Wisconsin's ( See Table VI for Wisconsin's regulations ) it may be necessary to add a down sized destruct system at the end your line.

Table VI

Wisconsin's waste water pollution regulations.

Outfall 001 beginning on the date of first discharge, all wastewaters discharged to the Milwaukee Metropolitan Sewage District through outfall 001 shall not exceed the following effluent limitations:

Pollutant	Maximum (mg/l)	Average (mg/l)
<sup>2</sup>		
Cyanide (T)	1.06	0.57
Copper	2.97	1.82
Nickel	3.50	2.09
Chromium	2.44	1.50
Zinc	2.30	1.30
Lead	0.61	0.38
Cadmium	0.10	0.06
Silver	0.38	0.21
<sup>3</sup>		
Total toxic Organics	1.87	----
Oil and Grease		
Mineral Origin	----	100
Animal/Vegetable	----	200
pH	see footnote 4	see footnote 4

- 1) Outfall 001 consists of the total discharge from the facility, including domestic wastewaters. The discharge limitation in this section have been adjusted based upon the discharge consisting of 88% regulated process waste and 12% dilutional wastes as indicated on the permittees baseline monitoring report.
- 2) Monitoring for cyanide must be conducted after cyanide treatment, if such treatment is present, and before dilution with any other wastestream.
- 3) Total toxic organics is equal to the sum of all concentrations over 0.01 mg/l for the compounds listed in 40 CFR Part 433.11 (e).
- 4) The permittee shall not discharge any wastewater having a pH of less than 5.5.