# ON A HIGH-SPEED HALOGEN TINPLATING LINE



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# COUNTERCURRENT RINSING ON A HIGH-SPEED HALOGEN TINPLATING LINE

by

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#### ABSTRACT

Countercurrent rinsing, as applied to high speed strip plating lines, involves the use of a compartmentized rinsing tank. The objective of the use of this method of rinsing is to reduce the amount of water required so as to have a volume of liquid more easily handled to recover the chemicals.

This report covers the first use of this type of rinsing on a high speed plating line. The first unknown to be studied was the operating performance of the multistage rinse system to determine whether or not the basic principles of countercurrent rinsing would hold for a high speed strip plating operation. Secondly, the best manner for recovering the chemicals in the concentrated stream from this rinse system had to be determined.

Efforts to recycle the concentrated rinse back into the main plating system and the problems which were encountered are also described in this report. New technology for solving these problems is described as well as an alternate method involving indirect recycling by means of the Detinning Plant.

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#### I-INTRODUCTION

Weirton Steel Division of National Steel Corporation has completed research on the project "Demonstration and Evaluation of Countercurrent Rinsing for Reducing Pollution from a Halogen Tin Plating Line". This research was sponsored in part by the U.S. Environmental Protection Agency.

This project was designed to demonstrate that the use of countercurrent rinsing is a viable approach to reducing pollution from this type of plating operation and to conserving valuable materials. This demonstration according to Environmental Protection Agency is an essential prerequisite to the industry-wide acceptance of this process because of the complexity of the electrolytic solutions used and the high speed at which the plating lines are operated. Any increase in the concentration of either the ionic constituents of the plating bath or the solid (sludge) material contained therein caused by the return of the concentrated effluent from the first rinse tank to the main electrolyte could result in either the production of poor quality or unsaleable timplate or the frequent disposal of the expensive plating solution or both.

The demonstration and eventual application of countercurrent rinsing systems on halogen tin plating operations could have a significant impact on the amount of pollutants discharged from tin plating operations as approximately fifty percent of the tinplate in the United States is produced by the halogen process. In view of the above the project was initiated and completed in 36 months.

#### Technical Background

In the halogen timplating process, a steel strip is cleaned in an alkaline solution, pickled and passed through a series of electrolytic cells containing a tim bearing solution. Following the actual plating operation the strip must be rinsed before being processed further. Typically the rinsing takes place in three stages; the dragout recovery, the spray wash and the hot rinse. In the dragout recovery tank the strip is dipped into the rinsing solution (water contaminated with plating solution) and is further rinsed by a set of sprays followed by wringer or squeegee rolls. The solution which is sprayed onto and wiped off of the strip flows into the recovery tank. Solution not fed back into the main system is discharged to the sewer. This discharge is the most contaminated effluent from the halogen plating process and is made up of the same constituents as the plating solution but is in a form too dilute to reuse. The major pollutants in this stream are tin, cyanides, fluorides and suspended solids.

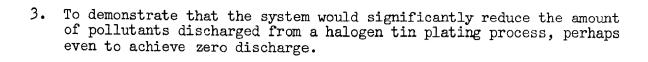
Several concepts for treating this primary dragout rinse had been proposed. These processes included ozonation and alkaline chlorination for destruction of cyanide wastes, calcium precipitation for the removal of fluorides, tin hydroxide formation and ion exchange for the removal of tin and thickening for removal of suspended solids. It appears that these processes may be workable; however, in most cases, the capital and operating costs for these systems are high and the space requirements for these processes preclude their installation in existing plating shops. Also, none of these processes is easily adaptable to the concept of zero waste discharge.

The use of countercurrent rinsing was suggested by personnel at National Steel Corporation as being a process which could achieve a zero discharge at minimal capital and operating expense as well as being a system which would not require excessive space. The process involves the use of countercurrent rinsing to concentrate the dragout wastes sufficiently so that they may be returned to the plating solution storage tank and reused. Computer simulations were run on the system and it was found that the number of countercurrent rinsing tanks required to achieve the necessary concentration in the first rinse tank was not excessive and could be retrofitted into an existing plating line. The main problem anticipated with the system was the buildup of sludge at an excessive rate in the plating solution. It was felt that this sludge buildup could be controlled via a chemical identified as AAAO. This chemical, developed by National Steel Corporation in conjunction with E.I. DuPont DeNemours and Company, Inc., minimizes the formation of this sludge in the plating process.

#### General Objective

The general objective of this project was threefold:

- 1. To successfully design and to install a countercurrent rinsing system on an existing halogen timplating line,
- 2. To demonstrate that over a long period of time the recycle of the primary dragout rinse could be achieved without loss of product quality or frequent solution changes,



### II-CONCLUSIONS

A countercurrent rinse system was designed and installed on the Weirton Steel Division No. 6 Electrotin Line. A four stage system was designed for the recovery of the dragout electrolyte.

No design problems were encountered mechanically in the four stage rinse unit. Equivalent or improved rinsing of the strip resulted from the use of this new system. No problems with sludge buildup were encountered.

Problems resulted due to buildup of chlorides in the main electrolyte upon recycle of the concentrated rinse stream containing the recovered dragout. Methods to solve this problem are being investigated to enable recycle of the rinse water back to the main plating system. An alternate method for recovering the chemical values of the recovered dragout is also a definite possibility.

#### III-RECOMMENDATIONS

It is recommended that a second phase be instigated to evaluate both the recycle of the concentrated rinse into the main (on line) bath and indirect recycle involving the Detinning Plant.

The problems uncovered in the direct recycle of the concentrated rinse from countercurrent rinse system may be solved by a new technique in removing sodium ions from the rinse stream or the main bath. Another system was also investigated.

Plans are under way to recover immediately the tin values from the dragout recovery system by sending the rinse solution to the Detinning Plant. Full recovery of the fluorides and other constituents at the Detinning Plant is also under investigation. This method for recovery may be the most desirable after all the test results are evaluated.

#### IV-DESCRIPTION OF PLATING PROCESS

The Halogen Tin Process is designed to plate tin at high current densities and to produce high-quality tin deposits required for continuous electrotinning of strip steel. The process was introduced commercially in 1942.

The halogen tin bath, as the name implies, is formulated with halogen salts. The bath is operated with a relatively high chloride concentration to obtain maximum conductivity. Fluoride functions largely as a complexing ion in stabilizing the stannous tin. It combines with the tin to form a sodium fluostannite complex salt, the composition of which may be expressed as Na<sub>4</sub>SnF<sub>6</sub>. In the absence of fluoride, stannous chloride hydrolyzes in the pH range 2-4 to form precipitated hydroxy salts.

The halogen bath is subject to oxidation when operated under highly aerated conditions such as are encountered in high speed strip plating lines. The presence of small emounts of iron or copper salts in the halogen bath acts as an accelerator in promoting the oxidation. Without an inhibitor, substantial amounts of stannic tin are formed in the bath through oxidation. In addition to depleting the stannous tin, oxidation causes a significant fluoride loss from the electrolyte since each mole of stannic tin combines with six moles of fluoride to form sodium fluostannate (Na2SnF6). In contrast to the high solubility of the sodium fluostannite salt (Na4SnF6) the sodium fluostannate is relatively insoluble in the electrolyte and separates as a sludge. Addition agents are added to the bath in order to deposit the fine grain type of tin required for continuous electrotinning of strip steel. Without additives, the tin deposit is nonadherent and spongy.

With the high cost of tin and tin salts along with the costs of the fluoride and addition agents, each gallon of electrolyte represents over one dollar in value.

The halogen bath is used in a horizontal type process configuration (see Figure 1). This design comprises a succession of small horizontal cells. The plating solution is circulated continuously through each cell. Electrical contact is made to the strip by the rolls at each end of the cell. The tin anodes are positioned close to the strip travel path, which is just under the solution level, and rest on a center contact support and end support within each cell.

After passing through the plating cell, the strip is passed through a reclaim rinse (see Figure 2) in which the residual plating solution may be removed. The bright, lustrous finish of electrolytic timplate is obtained by fusing and quenching the matte tin coating resulting from the plating process.

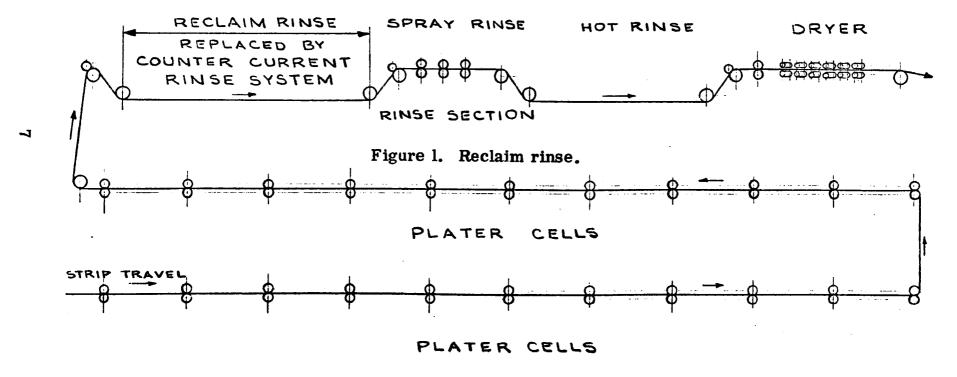


Figure 2. Horizontal pass acid electrotinning configuration (halogen process).

#### V-THEORY AND DESCRIPTION OF COUNTERCURRENT RINSE PROCESS

In the production of timplate, it is essential that after the strip leaves the last plating cell the electrolyte be rinsed completely from the surface of the tin-plated strip. It has been the practice in the mill to employ ample quantities of rinse water to effect this removal and to insure the cleanliness of the final product. However, with this practice only a small amount of the electrolyte removed from the last plating cell on the surface of the strip can be recovered and reused in the plating system. Rinse water that is put into the plating system is limited to only the amount needed to maintain volume. The bulk of the rinse water goes into the sewer and is a contributor to stream pollution. In order to effect a higher percentage of recovery of dragout, the volume of rinse water must be decreased and the concentration of electrolyte increased. A method that can do this is countercurrent rinsing.

As its name implies, the flow of rinse water is counter to the flow of the strip. The main advantage of this type of rinsing is the ability of a much smaller quantity of water to effect the same degree of dragout removal from the strip. This insures the same cleanliness of the strip after rinsing and results in a smaller volume of rinse water that can all be used as makeup back in the main system. This volume has a high concentration of electrolyte salts and effects almost total recovery of dragout.

#### ADAPTATION TO MILL USE

Figure 2 shows the outline of a typical reclaim rinse tank into which the strip passes immediately after the last plating cell. The dotted line shows the present path of the strip through the reclaim tank. The strip is deflected down into the rinse water around sink roll (J<sub>0</sub>) from the wringer rolls (K<sub>0</sub> and K<sub>1</sub>). The strip emerges from the tank from sink roll "J<sub>1</sub>" into wringers "I<sub>1</sub>" and "I<sub>2</sub>." From this set of wringer rolls, the strip is further washed in the hot rinse tank.

To employ the principles of countercurrent rinsing, the tank now in place, or a new tank to replace the existing tank, must be divided into compartments. A four-stage system is shown in Figure 3. The flow of rinse water must be opposite to the direction of strip travel. The flow proceeds through each compartment by the proper positioning of overflow weirs. The level of rinse water is lower in each succeeding compartment or stage. The same rinse water flows through each stage. There are two ways in which the strip may be contacted with the water in each compartment. Sink rolls could be placed below the solution level in each compartment. The strip would thus be diverted down into each compartment and would exit through wringer rolls located between compartments. The second method, would be to pass the strip directly across the top of the compartments as shown in the sketch. The solution in each compartment would be sprayed onto the strip from pumps as indicated. The solution would drain back into each individual compartment at the entrances of the wringer rolls, such as  $(F_0-F_1)$ ,  $(G_0-G_1)$ ,  $(H_0-H_1)$  and  $(I_0-I_1)$ . In the opinion of the operating

people, this method would have advantages. All sink rolls would be eliminated. These rolls are sources of trouble since their positions make them difficult to clean. Also strip breaks at these locations would entail more down time.

It is believed that with the proper size pumps and good spraying practice, the mixing of solution in each stage with the drag through films can be as good, or better, than with the design involving sink rolls. One control is required on the feed water at point A. When the line is not running this valve must be closed to prevent dilution of the system. The flow of the rinse water is A to B to C to D to E.

With a three or four stage system the mathematics indicate the possibility of recovering over 90 percent of the dragout electrolyte. Good mixing of the solution in each stage with the film on the strip is required in approaching the theoretical performance. Cost savings should be considerable especially when all the electrotin lines are considered on a yearly basis.

Using the math model shown in Figure 3, the equilibrium concentrations in each rinse tank of a countercurrent system having "M" tanks can be found by solving "M" simultaneous material balance equations. One equation is written for each tank. A typical equation for the nth tank is:

$$DX_{n-1} - (D + R) X_n + RX_{n+1} = 0$$

where

Xn = the equilibrium concentration in the nth rinse
 tank - ounces/gal

D = dragout flow rate - GPM

R = countercurrent flow rate - GPM

 $X_O = K_O =$ the cell concentration (a constant) ounces/gal

If  $K = \frac{R}{D}$ , the countercurrent flow ratio, is substituted, the typical n<sup>th</sup> equation becomes:

$$X_{n-1}$$
 (1 + K)  $X_n + K X_{n+1} = 0$ 

After solving sets of these equations for 2, 3 and 4 tank systems, it was found that the solution for the equilibrium concentration in the nth tank of a system of "M" tanks could be generalized as follows:

$$i = M - n$$

$$\Sigma \qquad (Ki)$$

$$i = 0$$

$$i = M$$

$$\Sigma \qquad (Ki)$$

$$i = 0$$

Ko = PLATING CELL CONCENTRATION, ml/l (oz/gal.)

D = DRAG OUT RATE, I/min (gpm)

R = COUNTERCURRENT FLOW RATE, I/min (gpm)

K = R/D COUNTERCURRENT FLOW RATIO

X<sub>1</sub>, X<sub>2</sub>, ..... X<sub>M</sub> = EQUILIBRIUM RINSE TANK CONCENTRATIONS, ml/I (oz/gal.)

M = NUMBER OF RINSE TANKS

n = NUMBER OF RINSE TANK BEING

CONSIDERED

Figure 3. Math model.

As an example, the equilibrium concentration of the  $2^{nd}$  tank in a 4 tank system with a countercurrent flow ratio of 2, may be found by setting n = 2, M - 4, and K = 2.

$$X_{2} = \sum_{0}^{2} (2^{1}) \quad K_{0}$$

$$X_{2} = \sum_{0}^{2} (2^{1})$$

$$X_{2} = \frac{2^{0} + 2^{1} + 2^{2}}{2^{0} + 2^{1} + 2^{2} + 2^{3} + 2^{4}} \quad K_{0}$$

$$X_{2} = \frac{1 + 2 + 4}{1 + 2 + 4 + 8 + 16} \quad K_{0} = \frac{7}{31} \quad K_{0}$$

$$X_{2} = .2258 \quad K_{0}$$

The results for 2, 3 and 4 tank systems are given in Figures 4 to 6. As an example, in a two stage system the concentrations of the rinse water in either tank can be found from the graph in Figure 3. If the ratio of water flow to dragout from the last plating cell into the rinse system is two, the equilibrium concentration in stage #1 is 44 percent of the concentration of the electrolyte in the cells. The equilibrium concentration in the second or last stage is 14 percent of the bath composition. If the ratio of rinse water to dragout increases the equilibrium compositions will decrease according to the graph.

A four stage system was chosen for this installation for several reasons. Space was a primary consideration. The graph for a four stage system, Figure 6, indicated low concentrations could be obtained for the final rinse and high concentrations in the first rinse. Thus product quality could be maintained or improved plus a concentrated stream would be generated for closed loop recycling or use in a recovery system. A five stage system would be harder to maintain and no big advantage over a four stage system. A three stage system would not give enough difference between the first and last tanks.

Figure 4. Rinse tank equilibrium concentration as percent of cell concentration (two tank system).

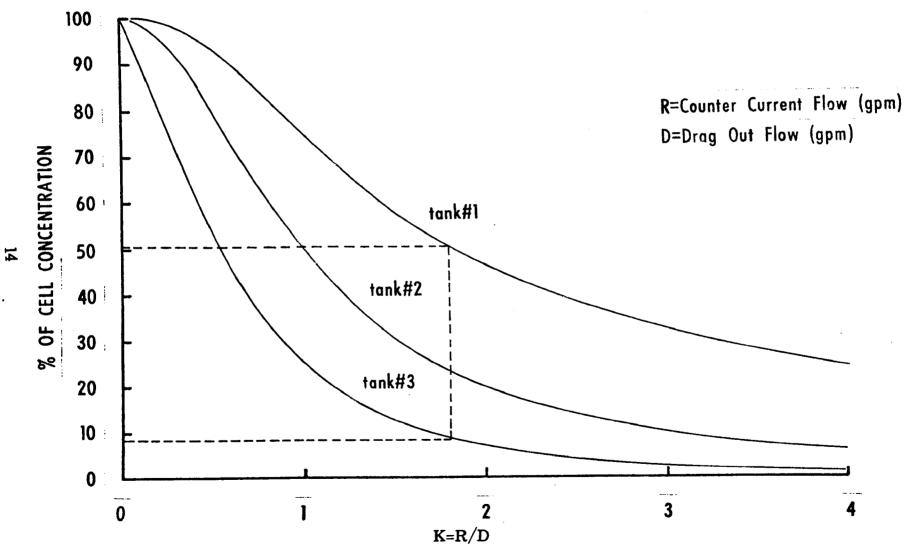


Figure 5. Rinse tank equilibrium concentrations as percent of plating cell concentration (three tank system).

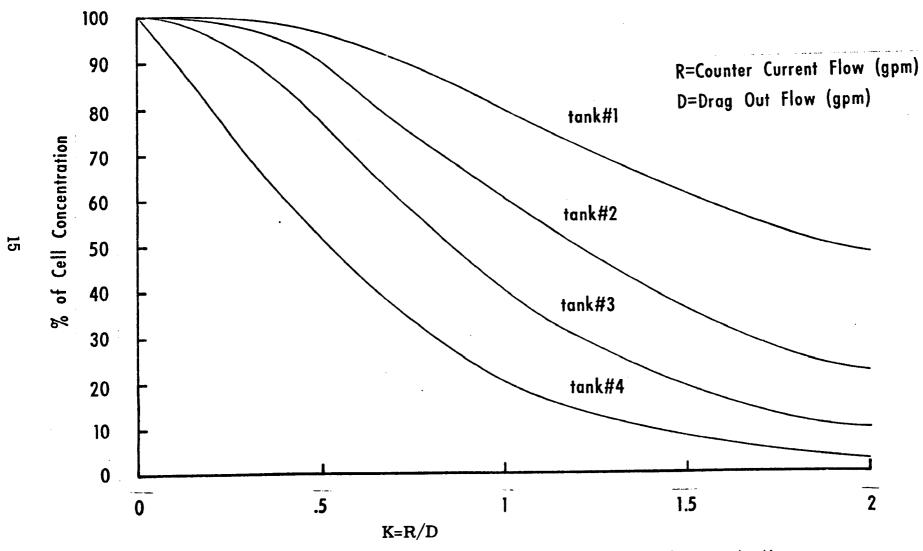


Figure 6. Rinse tank equilibrium concentrations as a percentage of cell concentration (four tank system).

#### VI-DESIGN AND INSTALLATION OF COUNTERCURRENT RINSE EQUIPMENT

The No. 6 Electrolytic Tinning Line was designed in 1964. The line was built to produce tin plate coils as follows:

LINE SPECIFICATIONS	
Maximum Coil Weight	60,000 lb.
Minimum Strip Thickness	0.003 in.
Maximum Strip Thickness	0.036 in.
Minimum Strip Width	16 in.
Maximum Strip Width	45 in.
LINE SPEED	
Entry End	1600 fpm at 240 volts
·	2400 fpm at over voltage
Center Section	1600 fpm at 240 volts
	2000 fpm at over voltage
Exit End	1600 fpm at 240 volts
	2400 fpm at over voltage

The line is 492'-6" long. The plater cells are located in the center section. The reclaim tank is located immediately after the last plater cell on the third deck of the plater structure. The original tank was equipped with an entry end and exit dunk roll to submerge the strip for 25'-0" in the reclaim water rinse.

Specifications were drafted for the replacement of the existing dunk-type replaim tank section with a cascade, wringer roll type rinse tank. The scope of work included removal of the reclaim tank, modifying the adjacent tanks, alterations to the structural supports and installation of the new equipment.

The new reclaim rinse tank has four compartments for circulating rinse solution. Fresh demineralized water is added to the No. 4 or last compartment. Each compartment overflows in a countercurrent direction from compartment No. 4 to compartment No. 1. The individual compartments have a pump suction line for the spray pumps. The No. 1 compartment is furnished with an overflow line.

The spray pumps take solution from the individual tank compartments and pump to the spray headers in the same tank compartment. Each compartment is also furnished with a hopper for addition of chemicals.

#### NEW EQUIPMENT SPECIFICATIONS:

- Fabricated of 5/8" thick mild steel, Tank 1/4" rubber lined and 3/16" rubber covered. Cover - Fabricated 1/4" thick mild, steel 14" rubber lined. Drive Bases - Fabricated 5/8" thick mild steel. Pump Bases - Fabricated 5/8" thick mild steel. Rolls - Nine (9)-10" diameter and 54" face steel, rubber covered. One (1)-15-1/2" diameter by 54" face steel. rubber covered. - Ten (10)-single reduction gear type Roll Drives with steel housing. - Nine (9)-3 Horsepower, 1150/2300 rpm Roll Drive Motors One (1)-5 Horsepower, 1150/2300 rpm Couplings - Gear Type Bearings - Pillow Block Roller Bearing Type Pumps - Four (4)-100 gpm at 50 psi Pump Motors - Four (4)-15 Horsepower, 1750 rpm Spray Headers - Eight (8)-316L Stainless Steel

The tank, drive bases, and pump bases were mounted to a common drip pan. The rinse tank being on the third level of the structure, the drip pan was installed to prevent any spillage from dropping on the structure and/or equipment on the two levels below. The drip pan also served as a unitized sub-base for the equipment. After all equipment was mounted to the pan it was then possible to fabricate and install all piping and apparatus at an off-site location.

The plating line operation was shut down for four (4) days to install the countercurrent rinse tank. The installation was possible in such a short time because of the pre-assembly of equipment and piping. The old reclaim tank was removed, and the new rinse section dropped into place in two (2) lifts of an overhead crane. The balance of the installation time was used to join the new tank section to the existing equipment and connect the piping and electrical terminations.

A schematic of the piping system is shown in Figure 7. The incoming water flows through a rotometer, rated 0 to 5 gpm. This water flows in compartment No. 4. The overflow from compartment No. 1 flows through a rotometer on the way to the main plating system.

The value on the incoming water line is controlled by a solenoid which closes the valve whenever the speed of the line reaches zero. This protects against dilution of the equilibrium concentrations during shut down periods.

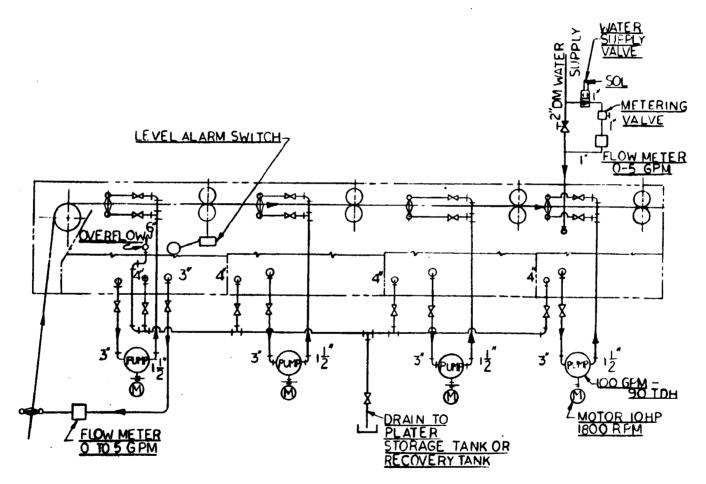


Figure 7. Multistage spray rinse tank piping system.

#### VII-OPERATIONAL RESULTS

#### A. OPERATING PRACTICES AND EXPERIENCE

Production with this new unit began on November 26, 1974. Problems that were anticipated during start-up such as buildup on the rolls and drying out of salts on the strip did not occur.

Sodium bifluoride was added in the No. 4 compartment. This chemical maintains an acid rinse so that the tin in the solution does not hydrolyze and stain the strip. It was found that one pound per hour maintains a pH of 3.5 to 3.8 which is about the same as the plating solution.

After the initial week, the spray nozzles were found to be corroding. These were replaced with stainless steel nozzles and no major problems have occurred with the spray nozzles as long as they were cleaned on a weekly basis.

The rolls need only occasional sanding to remove salt buildup. The solution of the No. 1 compartment has a pH of 3.5 to 3.8 and the total tin concentration ranges from 0.5 to 1.0 ounces per gallon. The No. 4 compartment ranges from 0.10 to 0.15 ounces per gallon. The demineralized water is put into the No. 4 compartment at a rate of 3 to 3.5 gallons per minute.

On start-up of the countercurrent rinse tank, it was found that the quality of the timplate was as good as, or better than, before. The timplate strip is brighter because the countercurrent rinse tank affords better rinsing of the strip. It is only natural that a cleaner water is used to rinse the strip with the countercurrent rinse system versus the old method of immersion rinsing. Since the strip is rinsed better before it goes into the scrubber and the hot rinse tank, there are less salts left on the strip which allow for a brighter strip when tin is melted in the reflow

Eight sets of spray headers are used, two sets in each tank. Each header has eight stainless steel V-jet sprays. The sprays are located five inches apart.

#### B. RINSING PERFORMANCE

In Table 1 the results of the chemical analyses for stannous tin are given. It required three days or 72 hours to reach equilibrium concentrations. Calculations had indicated at least 48 hours would be required. Once equilibrium was reached, the differences in concentrations of the four stages were as expected.

Because of the high flow required to maintain volume in the main plating system, the concentrations in the various stages have not reached the higher levels expected. This, however, is a big advantage because the concentration of the last stage (No. 4) can be kept at a very low level. This means minimum loss of chemicals to the spray and hot rinse sections. It was somewhat surprising to find that a flow rate of 4 to 5 gpm into the countercurrent rinse could be used without a buildup of volume in the main plating system. Apparently the evaporation losses are considerable.

The concentration of the tin in the last stage is about one tenth of the concentration found in the reclaim tank during the base period investigation. Therefore losses to the spray rinse and hot rinse sections have been reduced by around 90 percent. This figure will be checked in future repeat testing by Environmental Control of the effluents from these rinses. This reduction is in addition to the elimination of the losses which occurred from the flow which used to enter the sewer from the reclaim tank.

Sodium bifluoride is being added to the last stage of the countercurrent rinse system to control pH and prevent hydrolysis of tin salts on the strip. Operators have noted that the strip looks cleaner than it did when the old system was in use.

Table 1. Concentrations of Stannous Tin in Each Stage

STAGE(oz/gal (SN++ TIN)\*)

<u>Date</u>	No. 1	No. 2	<u>No. 3</u>	No. 4
11-26-74	0.18	0.09	0.06	-
11-27-74	0.118	0.09	0.06	-
11-28-74	0.37	0.22	0.12	0.03
11-29-74	0.49	0.30	0.12	0.06
11-30-74	0.46	NR	NR	0.06
12-2-74	0.43	0.22	0.09	0.03
12-4-74	0.49	0.24	0.12	0.06
12-6-74	0.49	0.15	0.12	0.06
12-9-74	0.31	0.15	0.09	0.03
12-11-74	0.59	0.31	0.15	0.09
12-13-74	0.46	0.21	0.12	0.06
12-20-74	0.43	0.21	0.12	0.06
12-27-74	0.46	0.24	0.12	.06
1-31-75	0.65	0.34	0.15	0.09
2-38-75	1.08	0.55	0.27	0.15
3-14-75	0.65	0.30	0.15	0.09
4 <b>-10-75</b>	0.62	0.31	0.15	0.06
9-8-75	0.92	0.33	0.12	.04
9-19-75	0.86	0.37	0.15	.05
9-25-75	0.68	0.31	0.12	0.06

<sup>\*</sup> Values should be multiplied by factor 1.2 for total tin.

#### C. FIRST PROBLEM OF CHLORIDE BUILDUP

Throughout December of 1974 a rise in the chloride content of the electrolyte was noted. A plot of the chloride content is shown in Figure 8. As can be seen by the graph the chloride level prior to the start-up of the countercurrent rinse system was between 4.0 and 4.6 ounces per gallon. After the start-up of the new rinse system on November 26, the chloride content started to rise. A level of 5 ounces per gallon was reached on December 13; a level of 6 ounces per gallon was reached on December 22 and finally a level of 7 ounces per gallon was reached shortly after the first of the new year.

The levels of tin and fluoride did not increase. The reasons for the increase in chloride have become obvious. Chemical additions were reduced for several components which normally supply hydrogen ions to the plating bath. Both stannous chloride and sodium bifluoride are acid salts. With a cut back in the additions of these chemicals more hydrochloric acid was added to control pH.

The desired pH range is 3.3 to 3.5. The pH will gradually rise due to the electrode reactions at the cathode (strip) and also due to the formation of sludge. According to the DuPont Manual, one of the major causes for change in pH during operations is the difference in anode and cathode efficiency. Hydrogen ions are consumed in the formation of hydrogen at the cathode. Another cause for increase in pH according to the DuPont Manual is the oxidation reaction. This can be expressed as follows:

$$2Sn+2 + O_2 + 4H^+ \rightarrow 2Sn+4$$
 and  $2H_2O$ 

Since the reaction removes hydrogen ions, the pH increases.

To counteract this rise in pH, hydrochloric acid was added. During the rise of chlorides in December, it was hoped that an equilibrium concentration would be reached before salting out occurred. This is a condition which occurs when the total salt content rises too high and crystallization develops in the plating system, especially on rolls, causing denting of the surface of the strip. When the chloride content exceeded 7.0 oz/gal, the dent problem developed and corrective action had to be taken. Steps were taken which included running part of the effluent from the countercurrent rinsing system to the sewer rather than back into the plating system.

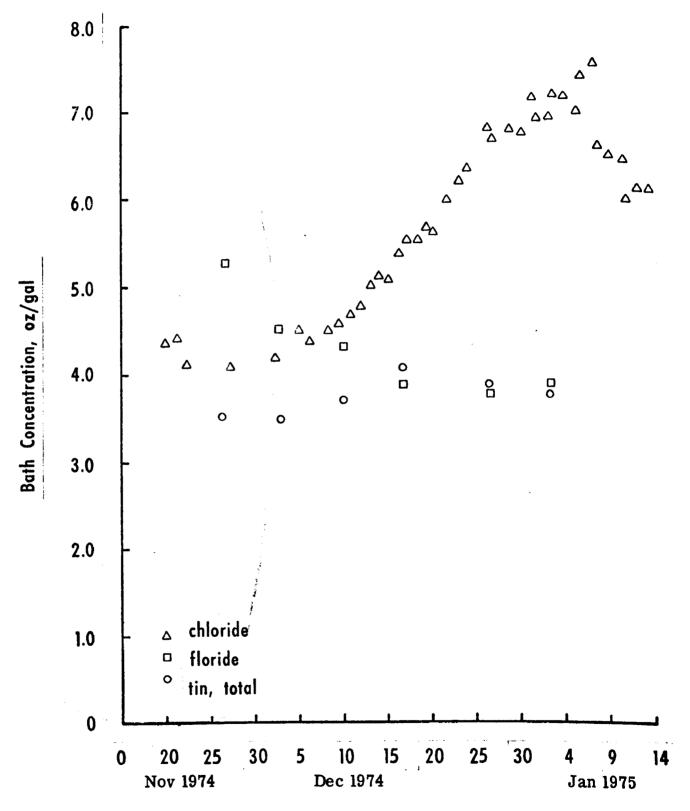


Figure 8. Bath concentration vs. time.

#### D. ECONOMIC STUDY FOR ONE YEAR OF OPERATION

In Figure 9 a graph shows the consumption of stannous chloride and hydrochloric acid for the year (1974) prior to the installation of countercurrent rinsing and the first year of its use (1975). The amounts are given as the chlorides of each of the two chemicals. Taking an average for each twelve month period, see Figure 8, the amounts used per month were -

	<u>1974</u>	<u> 1975</u>
SnCl <sub>2</sub> (Cl)	6,000 lbs	3,000 lbs.
HCl (Cl)	1,000 lbs	2,200 lbs

As the consumption of stannous chloride was reduced the use of hydrochloric acid had to be increased to obtain the acidity required to maintain the pH within the desired range (3.4 to 3.7).

The line was operated at a slightly higher pH in order to control the level of chlorides below a level where salting out would occur. This will be discussed in more detail later. However, with certain slight changes in operation the tin plating line was able to operate without denting problems at least until November 1975.

The 3,000 pound difference in chlorides from the reduction in the rate of consumption of stannous chloride is equivalent to  $\frac{3000}{0.63}$  or

4,762 pounds per month of stannous chloride. Taking a cost of stannous chloride at \$2.60 per pound this represented a savings of \$12,380 per month. From this must be subtracted the increased cost in the use of hydrochloric acid. The 1,200 pounds per month increase amounted to \$60 per month based on a cost of \$32 per ton of 32% acid. The net savings was thus \$12,380 - \$60 or \$12,320 per month or \$147,840 per year. There were other changes made during the year by Operations which may have assisted in this cost reduction. Additions were made more often which insured more complete dissolution of the chemicals. This change was made in the summer of 1975.

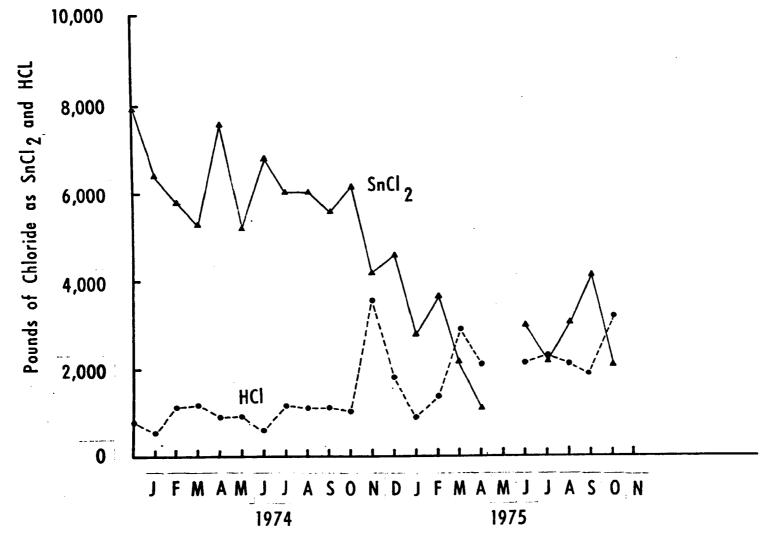


Figure 9. Rate of monthly consumption--No. 6 electro-line.

#### E. PROBLEMS GENERATED

After one year of operation an evaluation has been made of the new rinse system. Some problems have developed not due to the mechanical performance of the equipment but due to the pecularities of the Halogen Tin Plating Process. It was anticipated prior to the installation that this might be the case and some modification of the process or operation would be required to obtain maximum benefit from dragout recovery.

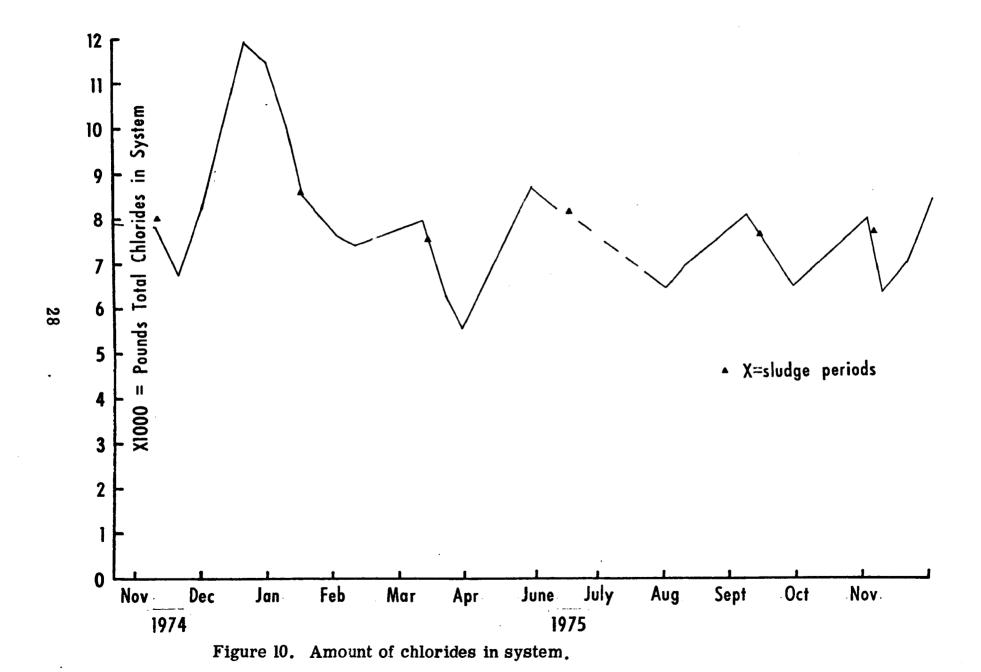
Since oxidation of tin in the halogen electrolyte occurs continuously, sludge is produced also continuously. Sludge contains sodium, tin and fluoride but very little chloride. There is, therefore, a continuous need for additions of sodium, fluoride and tin to replace the amounts lost in sludge formation. While part of the tin may be supplied by the differences in electrode efficiencies the other elements must be added by periodic chemical additions.

The electrolyte also becomes more basic with coulombic input due to the generation of hydroxide ions at the cathode and with the consumption of hydrogen ions in sludge formation. Therefore, regular additions of either stannous chloride or hydrochloric acid must be made for control of the pH at a fixed value.

Another pecularity of the halogen electrolyte is the need to keep the sodium chloride content below the level where salting out, or saturation occurs. Sodium chloride formation within the bath will lead to denting of the strip due to buildup on rolls. The anions, particularly fluorides and chlorides, must be held within a certain range to avoid this problem.

In Figure 10, the amount of chlorides in the system is shown. After the initial surge of buildup in January the levels were reduced by operating the electrolyte at a slightly high pH thus reducing the additions of hydrochloric acid. Operating personnel have contended that the denting problem has been greater than normal even during the best periods. In November 1975, the denting problem became severe. The blame was given to countercurrent rinsing and the flow was diverted to the sewer from the first stage.

It has been found that the use of countercurrent rinsing along with dragout recovery and reuse has affected to some extent two aspects of the halogen process; (1) the control of pH and (2) the level of chlorides.



# VIII-SOLUTIONS TO PROBLEMS GENERATED

#### A. USE OF HYDROFLUORIC ACID

As previously mentioned the problem of chloride buildup resulted because additions of hydrochloric acid were still required for pH control after recovery of dragout was instituted. Since chlorides are not removed from the system in the formation of sludge, the elimination of losses due to dragout results in an increasing concentration of chlorides in the electrolyte. A solution to this problem, as suggested by Dr. D. A. Swalheim of DuPont, is to substitute hydrofluoric acid (HF) in place of hydrochloric. Fluorides are removed from the system in sludge formation.

This possibility has been studied and is still under consideration. However, the problem with using hydrofluoric acid is the hazardous nature of this chemical. Burns due to hydrofluoric acid are extremely serious. Nevertheless this acid is used in many plants where proper safety precautions are employed.

In efforts to counter the reluctance of operating personnel to consider the use of hydrofluoric acid, the Environmental Department of R & D has designed a system for minimizing the hazards involved in unloading, transporting, and emptying containers of HF. This system consists of a portable heavy steel tank with a double valve control. A sketch of this system is shown in Figure 11. All the employee in charge of adding the HF has to do is open the air vent and turn the long stemmed valve on or off. When the container is empty, as indicated by a floating ball type, liquid level instrument, the nozzle is rinsed out via a special water connection and removed.

Another method for handling HF is shown in Figure 12. This method appeared in the January 17, 1977 issue of <u>Chemical Engineering</u>. Air pressure is used to fill and transport to the user tank a predetermined amount of the acid. No pumps or carboys are required. With the storage tank located outside the building, the time that the acid is in the plant at full strength is limited to just a few minutes.

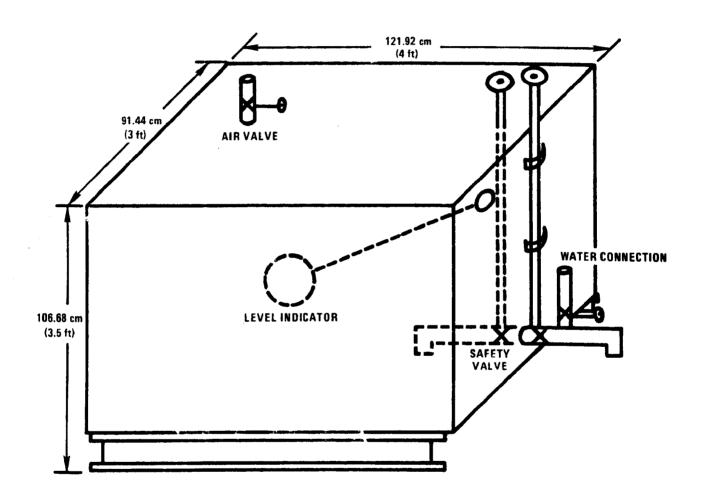


Figure 11. Proposed HF tank.

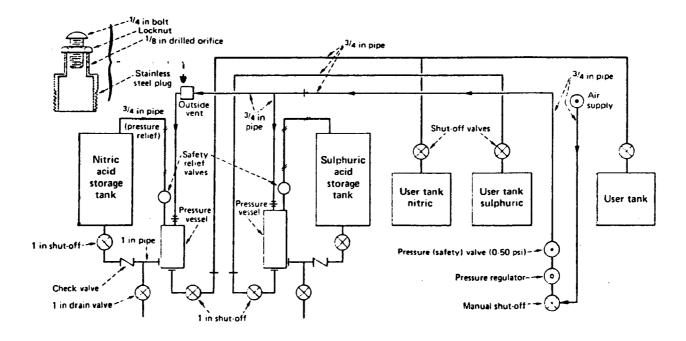
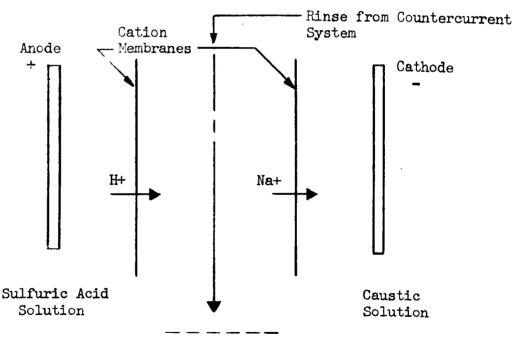


Figure 12. Distribution system for strong acid using neither pumps nor carboy. (© Chemical Engineering, 1/17/77, page 150; used with permission.)

#### B. USE OF AN ALKALINITY REMOVAL UNIT

Recent advances in technology has extended the use of electrodialysis cells from laboratory curiosities to commercial use. These cells employ perm-selective membranes, which have ion exchange properties. New fields for use of these cells include continuous ion exchange. In this process, one ion is exchanged for another, in the same manner as an ion exchanger, with the exception that in this process the resin (the membrane) is regenerated continuously by electrical energy, rather than cyclical, by chemical regeneration.

In the halogen bath there is a continued need to add acid to counter the buildup of sodium ions due to the oxidation of the tin and to the generation of hydroxyl ions at the cathode. As a result sodium hydroxide is produced. The concentrated rinse from the countercurrent rinse system can be made to pass between two cationic membranes wherein the sodium is migrated from the bath through the cation membrane to the cathode compartment forming sodium hydroxide. At the same time hydrogen is passed from the acid in the anode compartment into the concentrated rinse water. A diagram of the process follows:



Acidified Rinse to Plater System

Alkalinity is removed from the stream and acid is generated thus reducing or eliminating the acid requirements. In this manner, an alkalinity removal unit might permit operation of a closed loop system. If more removal of alkalinity is required to balance the system, electrolyte from the plating cells could be passed through the unit.

The only by-product from the unit is a solution of caustic soda. This material has wide usage for acid neutralization. The purity should be sufficient to permit use in processes requiring solutions of caustic soda.

#### C. INDIRECT RECYCLE VIA DETINNING PLANT

Located at the Weirton Steel Division is a Detinning Plant, which was designed primarily for the recovery of tin from scrap tinplate. However, this plant also processes sludge from the plating lines. A flow sheet of the process is shown in Figure 12A. The sludge enters the system at the point where sodium stannate filter cake is fed to the dissolving tank. When sludge is being processed the sludge replaces the filter cake in the system. The concentrated rinse from the countercurrent rinse system is now being sent to this plant for recovery of the tin values. The rinse solution replaces part of the water used to dissolve the sludge.

The chemical principles on which the entire operation is based are generally well known. Metallic tin will dissolve in a hot solution of sodium hydroxide to form soluble hydrated sodium stannate. Once the alkaline solution has become saturated with sodium stannate, precipitation occurs and the crystalline solid is periodically removed and separated from the detinning solution. It is then dissolved in water in a suitable tank. This is the same tank or point in the process where sludge or concentrated rinse solution is added. The stannate solution is transferred to a second tank where it is converted to stannic hydroxide by controlled additions of sulfuric acid. The tin hydroxide thus formed appears as a white insoluble compound. Sodium sulfate. the other product of the conversion, remains dissolved in solution as well as the fluorides from the sludge and recovered rinse. The tin hydroxide is next filtered and washed. The wet filter cake is then dried and mixed with anthracite coal. When this mixture of hydrated tin oxide and carbon is heated to about 2200°F, the oxide is reduced to metallic tin.

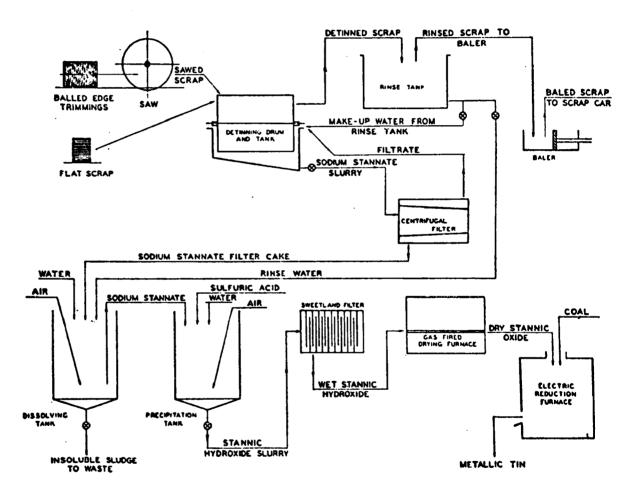


Figure 12A. Flow chart of the detinning and tin recovery process. (© Iron and Steel Engineer Year Book, 1953, page 207; used with permission.)

# IX-ENVIRONMENTAL ASPECTS

## A. GENERAL INFORMATION

The most important environmental aspect of countercurrent rinsing is that the effluent from the countercurrent rinse tank has been concentrated to such an extent that direct or indirect recovery methods can be employed. Recovery of the effluent from the countercurrent rinse tanks can permit significant reductions in the loadings of the key pollutants such as tin, chlorides, fluorides, syanides, suspended solids, etc., to the receiving stream. Since the most convenient method of recovery was the re-use of this offluent in the electrolytic process, this environmental study was accomplished with the effluent from the countercurrent rinse tanks recycled to the electrolytic plating solution tank.

It was the expressed intent of Weirton Steel Division to gather sufficient environmental background data on the original rinse system (see Figure 13) as to have a solid basis for comparison with the countercurrent rinse system (see Figure 14). In this regard, the environmental survey was designed to establish the existing average background loadings of key pollutants prior to the installation of the countercurrent rinsing system. These averages were then compared with the average loadings of the same parameters which were being diverted to the sewer after the installation of the countercurrent rinsing system. The background survey and the subsequent installation of the system shall be referred to as Phase I of the project in this report. The start-up and optimization of the system shall be referred to as Phase II and the evaluation of the system shall be referred to as Phase Il: of this project. During Phase I of the project, effluents from the recovery tank (Figures 13 and 15), spray wash (Figures 13 and 16), and hot rinse (Figures 13 and 17), were diverted to the sewer. During Phase III of the project only the effluents from the spray wash and the hot rinse were diverted to the sewer since the effluent from the countercurrent rinse tank was recycled to the plating solution tark.

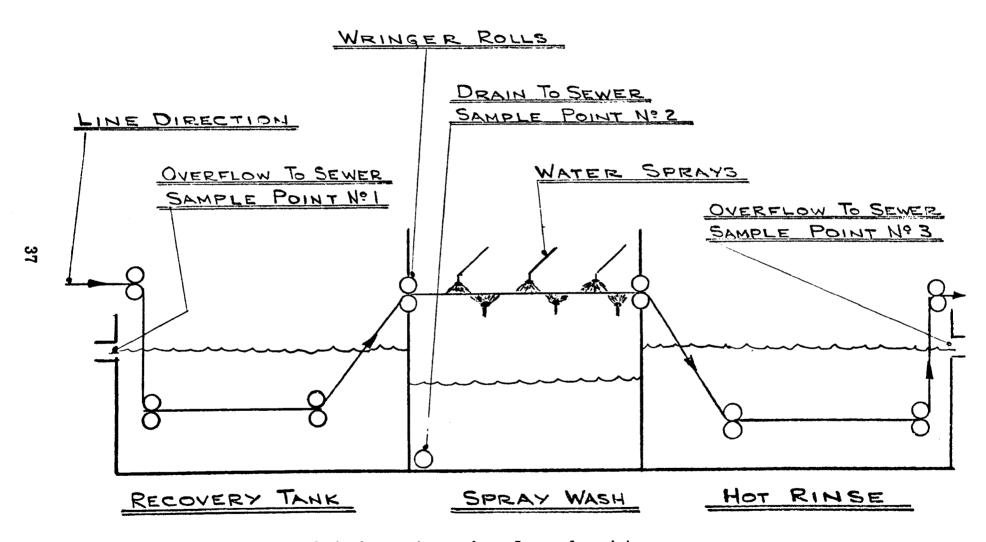


Figure 13. Background rinsing system, phase I sample points.

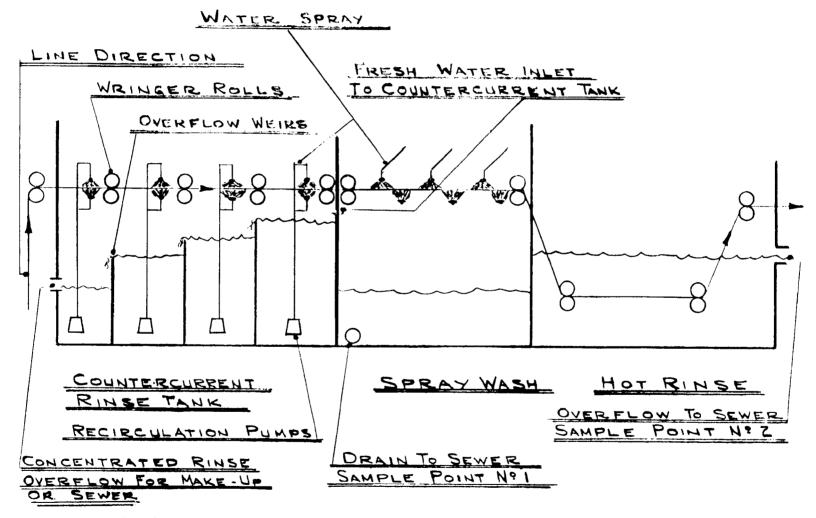


Figure 14. Countercurrent rinsing system, phase III sample points.

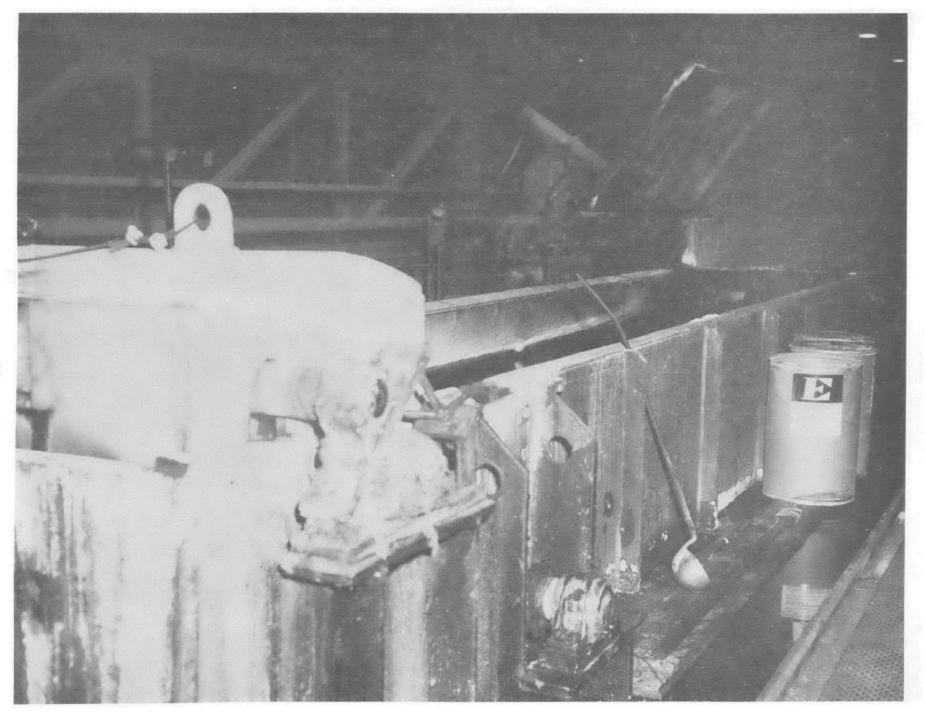


Figure 15. Recovery tank.

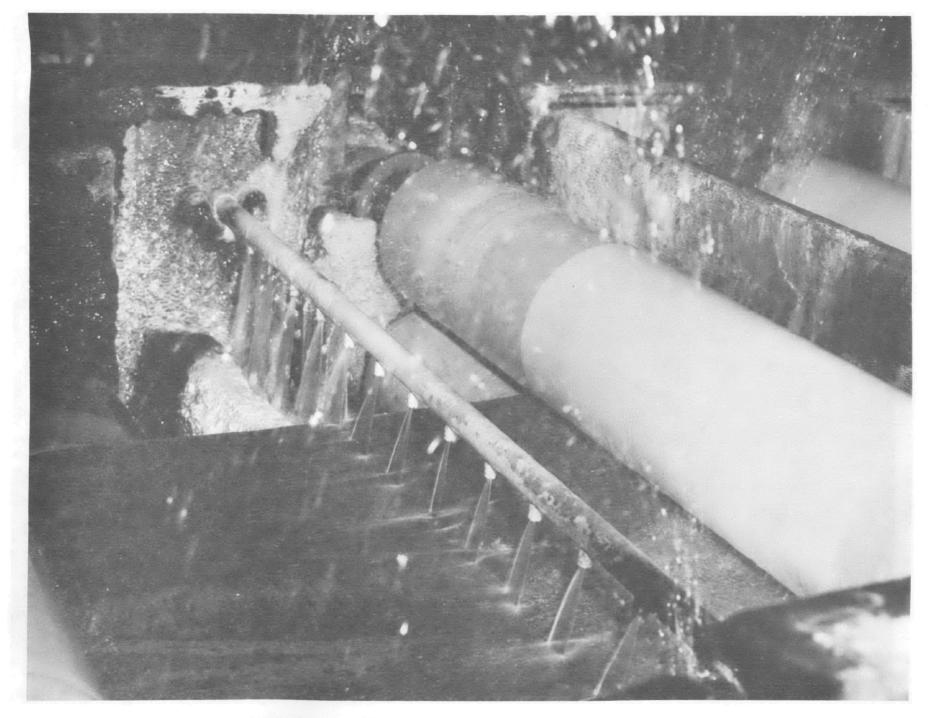


Figure 16. Spray wash.

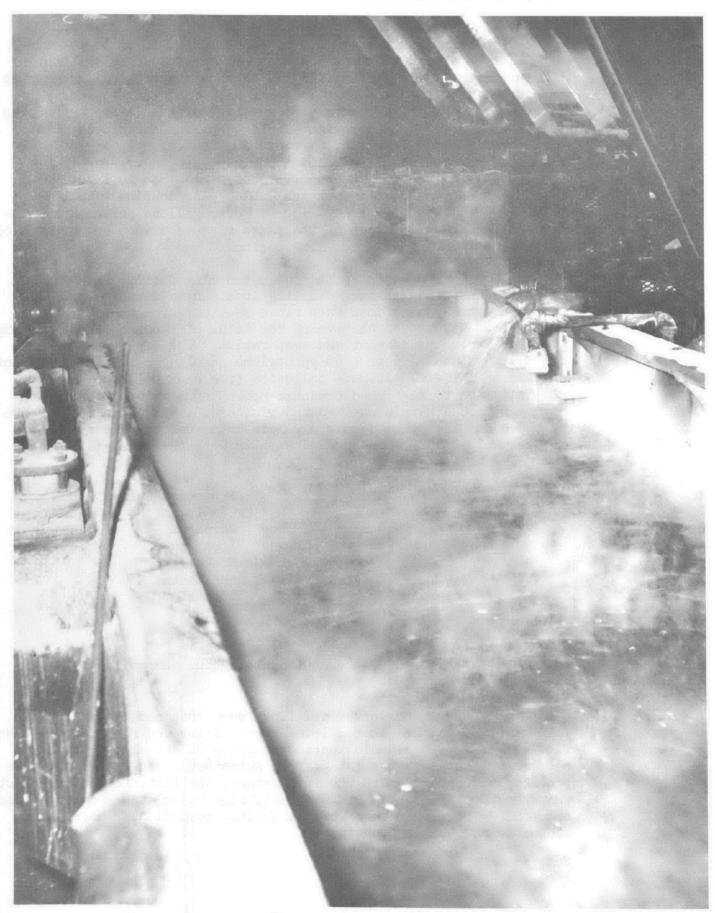


Figure 17. Hot rinse.

# B. BACKGROUND SURVEY (PHASE I) General Description

A total of seventeen samples was taken during the period of approximately one month (August 5 to September 6, 1974) to provide base line data with which to compare data obtained from the ensuing countercurrent rinse system. Figure 13 shows the basic rinse system and identifies the three sample locations. The recovery tank (Sample Point No. 1) was merely a dunk tank with an average incoming fresh water supply of approximately five gallons per minute. The spray wash (Sample Point No. 2) rinse section was composed of a series of sprays above and below the strip with an average flow of about fifty gallons per minute. The hot rinse (Sample Point No. 3) section was composed of a dunk tank which was occupied with hot water (180°F.) with a make-up flow of forty gallons per minute. The overflow or drains of each of the three rinse sections were channeled to the sewer during the base line period.

Figure 18 is a schematic of the basic sampling facilities. A flow meter was installed at each sampling location to measure the amount of fresh water coming into each rinse section. The summation of these flows was representative of the total effluent from the plating process, including dragout and evaporation. The effluent from each rinse was channeled into a polypropylene sampling box. Two representative samples of the effluent were collected from each polypropylene box utilizing the refrigerated pressure operating sampler described in Figure 19. One sample was treated with sodium hydroxide to preserve cyanides and the other sample was left untreated for the remainder of the analyses. The background samples were then analyzed for the following parameters:

Suspended Solids Temperature Cadmium Ηg Chromium Acidity or Alkalinity Iron Chlorides Chemical Oxygen Demand Nickel Phosphates Free Cyanides Total Cyanides Potassium Fluorides Sodium Sulfates Tin

All samples analyzed were collected as 24-hour composites.

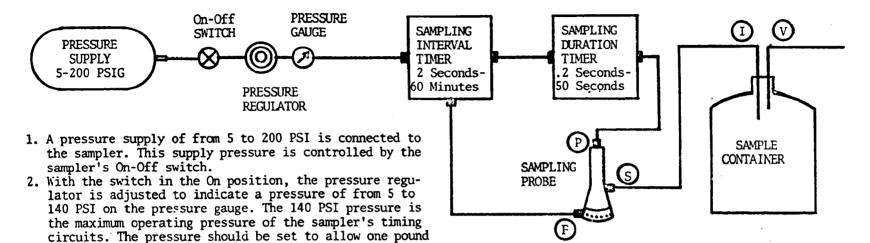
## Flow Rates

During the background survey all flows were obtained by setting the make-up water to the desired level using calibrated flow meters. These flow meters provided an instantaneous read-out and also provided an electronic signal to the integrators which totalized the flows. Due to problems encountered with the integrators, the instantaneous read-out was checked periodically and the daily flow calculated from the direct read-out. The flow meters were calibrated periodically using the stopwatch and bucket technique.

Figure 18. Sampling diagram (essentially the same for: recovery tank, spray wash, hot rinse).

UNTREATED

SAMPLE



- of pressure for every two feet of vertical lift.

  3. Pressure is now applied to the sampling interval timer. This timer controls the length of time between samples. The interval timer is continuously adjustable from 2 seconds to 60 minutes between samples.
- 4. When the interval timer completes its time cycle it applies pressure to the sampling duration timer. This timer controls the length of time that the sampler releases pressure to the sampling probe. The greater the vertical lift or the longer the horizontal run, the longer the period of time that is required to purge the sample from the sample tubing.
- 5. Upon completion of the duration timer's time cycle, the applied pressure is released and enters connection "P" on the sampling probe. The sampling probe is a gravity-fill unit and holds a sample of 50 ml. Pressure is exerted upon the liquid contained in the probe and forces it to exit through the fitting "S" located on the side of the probe. The liquid travels through the connecting tubing and into the sample container. The sample container may be located at any point from several feet to over 200 feet from the sampling probe. Normally the container is located in the sampler's case or refrigerator.

  NOTE: Only the sampling probe is submerged in the liquid to be sampled. The liquid never enters the sampler's control circuits.
- 6. When the sample is deposited in the sample container, the pressure in the lines is vented through the 'V' connection on the sample container. In the event that the total composite sample taken over a period of time should exceed the container's capacity, it will be discharged through the 'V' connection on the container.
- 7. After the sampling lines are purged of all sample, the timing circuits must reset themselves automatically. During this reset period which occurs immediately after the sample is taken, the timers must vent their timing valves. The vent pressure from the timing valve on the interval timer is connected to the sampling probe through connection "F". This vent pressure is used to purge the probe's inlet screen of any foreign matter.
- 8. The sampler requires a pressure supply of from 5 to 200 PSI. R-12, nitrogen or compressed air can be used to power the sampler. Since the sampler is operated on pressure only, it is explosion-proof.

Figure 19. Schematic, pressure operated sampler.

## Chemical Analysis

The analyses were performed using procedures found in one of these three sources:

- 1. Standard Methods for the Examination of Water and Wastewater, 13th Edition.
- 2. ASTM Standards, Part 23, Water; Atmospheric Analysis.
- 3. E.P.A. Manual of <u>Methods for Chemical Analysis of Water and</u> Wastes.

The only exception of the above statement pertains to the analysis of free cyanides. Since an approved method has not been published, an American Iron and Steel Institute's method was used. A summary of each procedure used for each parameter is listed in Appendix I (4, 5. 6). All metals were analyzed on a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer.

### Results

Table 2 indicates the average daily loading in bounds for each rinse rank over the seventeen-day sampling duration. A daily tabulation of the results can be found in Appendix II.

TABLE II

PHASE I - BACKGROUND EFFLUENT LOADINGS

	RECOVERY Avera Effluent L	ge	SPRAY W Avera <u>Effluent L</u>	ge	HOT RINSE Average <u>Effluent Loadin</u>	g S
Flow	5 gpm - 720	O gpd	53.53 gpm	- 77,082 gpd	40 gpm - 57,600	gpd
Temperature	112 <b>°F</b> •		93	°F.	182°F.	
Нф	4.46		4.14		5.31	
Acidity/ Alkalinity	Acidity/7.9	9 Lbs/Day	Acidity/22	.l Lbs/Day	Alkalinity/1.93	Lbs/Day
Chlorides	153	Lbs/Day	82.9	Lbs/Day	35.7	Lbs/Day
C.O.D.	121	Lbs/Day	27.2	Lbs/Day	17.7	Lbs/Day
Free Cyanide	s .032	Lbs/Day	0.16	Lbs/Day	.045	Lbs/Day
Total Cyanid	es 2.35	Lbs/Day	0.66	Lbs/Day	-14	Lbs/Day
Fluorides	281	Lbs/Day	59.6	Lbs/Day	10.0	Lbs/Day
Sulfates	17.5	Lbs/Day	110	Lbs/Day	75.3	Lbs/Day
Suspended So	lids 21.6	Lbs/Day	56.9	Lbs/Day	15.0	Lbs/Day
Chromium	0.051	Lbs/Day	0.01	5 Lbs/Day	Detectable Lim	it
Iron	3.86	Lbs/Day	1.40	Lbs/Day	0.27	Lbs/Day
Nickel	0.044	Lbs/Day	< Detectal	ole L <b>imit</b>	←Detectable Lim	it
Potassium	0.47	Lbs/Day	3.09	Lbs/Day	1.97	Lbs/Day
Sodium	260	Lbs/Day	94.4	Lbs/Day	16.9	Lbs/Da <b>y</b>
Tin	203	Lbs/Day	58.6	Lbs/Day	3.25	Lbs/Day

# C. EVALUATION OF COUNTERCURRENT RINSING (PHASE III)

#### General Description

After the start-up and optimization of the system (Phase II), a series of eleven samples were taken over a period of six weeks August 26 to October 3, 1973) to evaluate the improvement in pollutant loadings coming from the new rinse system featuring a countercurrent rinse tank as the primary rinse. (See Figure 14 for a schematic of the countercurrent rinsing system.) As can be seen from Figure 14, the spray wash and the hot rinse were being used as make-up for the plating solution. The identical sample points (Figure 14) and sampling facilities (Figure 18) were used for both Phase I (Background) and Phase III (Countercurrent Evaluation) sampling programs. Sampling of the countercurrent system was delayed several times due to equilibrium problems in the plating process.

## Flow Rates

Due to problems which developed with the flow meters, the flows which were obtained during the countercurrent rinsing system evaluation were arrived at by the stopwatch and bucket technique. The flows were set before each test interval and re-checked at the end of the 24-nour testing period to insure their reliability.

#### Chemical Analysis

The chemical analyses of the effluents from the spray wash and the hot rinse were analyzed by the same procedures as previously outlined. Summaries of the analytical methods may be found in Appendix I.

#### Results

Table III indicates the average daily loading, in pounds, of the eleven samples taken for the countercurrent rinse system evaluation. A complete day-by-day tabulation of the analysis may be found in Appendix III.

TABLE III

PHASE III - COUNTERCURRENT RINSING EFFLUENT LOADING

	SPRAY WASH Average Effluent Loading	HOT RINSE Average Effluent Loading
Flow	27,027 g.p.d.	46,172 g.p.d.
Temperature	88.3 Deg. F.	172.2 Deg. F.
pН	5.3	7.5
Acidity/Alkalinity	1.28 Lbs. Alkalinity	7.41 Lbs. Alkalinity
Chlorides	10.7 Lbs	22.3 Lbs.
C.O.D.	3.81 Lbs.	2.38 Lbs.
Free Cyanides	0.034 Lbs.	0.035 Lbs.
Total Cyanides	0.040 Lbs.	0.065 Lbs.
Fluorides	7.45 Lbs.	0.99 Lbs.
Sulfates	27.0 Lbs.	42.8 Lbs.
Suspended Solids	10.1 Lbs.	7.80 Lbs.
Chromium	∠Detectable Limit	≺Detectable Limit
Iron	0.16 Lbs.	0.33 Lbs.
Nickel	∠Detectable Limit	∠ Detectable Limit
Potassium	1.05 Lbs.	1.64 Lbs.
Sodium	11.6 Lbs.	5.81 Lbs.
Tin	11.0 Lbs.	2.52 Lbs.

## D. DISCUSSION OF RESULTS

Table IV illustrates the magnitude of reduction of the major pollutants that can be achieved by one hundred percent recycle of the effluent from a countercurrent rinsing system on a high speed electrolytic tin plating operation. Total recovery of the countercurrent rinsing effluent occurred during the two months preceeding the evaluation until approximately six weeks after the termination of the evaluation.

An analysis of the analytical results from this survey indicates the following reduction in daily loadings of key pollutant from an electrolytic tin plating operation when a countercurrent rinsing recovery system is employed:

Tin	95% Reduction
Total Cyanides	97% Reduction
Fluorides	98% Reduction
Chlorides	88% Reduction
Sodium	95% Reduction

During this period in which the effluent from the countercurrent rinse tank was completely re-used as make-up for the plating solution the possible environmental improvements were demonstrated. However, as indicated in Section VII of this report, product quality problems prevented the continued operation of the electrolytic plating line utilizing this concept. In this regard, three alternatives have been proposed in Section VIII of this report, which could eliminate the product quality problems previously described. The environmental aspects of each alternative is discussed below:

1. <u>Use of Hydrofluoric Acid</u> - Section VIII-A describes the mechanism by which this alternative should eliminate product quality problems. The utilization of hydrofluoric acid as a source for fluoride and to control pH should permit the continuous recycle of one hundred percent of the countercurrent rinsing effluent into the plating solution tank, thus achieving the reductions in pollutant discharges indicated above. However, a potential safety hazard exists in the handling of hydrofluoric acid, and the acceptance of this alternative is questionable even if the safety precautions described in Section VIII-A are adopted.

- 2. Use of an Alkalinity Removal Unit A description of the operating principles of an alkalinity removal unit and its ability to eliminate the product quality problems associated with this project is documented in Section VIII-B. This unit would treat the countercurrent rinse tank effluent, utilizing electrodinalysis principles, and it should permit the recycle of one hundred percent of the countercurrent rinsing effluent into the plating solution tank, thus achieving the pollutant reductions previously cited. A small quantity of sodium hydroxide would be produced as a by-product from the alkalinity removal treatment process. This material would be utilized in a wastewater neutralization treatment system serving the Tin Mill operations.
  - 3. Indirect Recycle Via Detinning Plant As stated in Section VIII-C, Weirton Steel Division has a unique advantage in that the company operates a Detinning Plant which has the capability to remove the tin from the countercurrent tank effluent. By storing the effluent which cannot be directly re-used and transporting it to the Detinning Plant, a significant amount of the pollutants from the tin plating operations can be recovered and thus preventing their return to the environment. If zero discharge from the tin plating system cannot be achieved, then tests should be conducted to find out exactly how much blowdown must be removed from the system to prevent the accumulation of materials in untenable amounts. If, for example, it can be demonstrated that the system will work satisfactorily with a 70 percent recycle, the remaining 30 percent could be transported to the Detinning Plant for recovery. This alternative should also achieve the reduction in pollutant loadings previously documented.

This project has shown that significant environmental benefits can be derived by the direct or indirect recovery of the countercurrent rinsing effluent. The adoption of any one of the three proposed alternative solutions for the product quality problem should accomplish the desired environmental benefits. The selection of the alternative to be utilized, therefore, becomes one of economic, process, and safety considerations.

TABLE IV

COMPARISON OF BACKGROUND VS COUNTERCURRENT RINSING EFFLUENT LOADINGS

	Background Evaluation Total Average Effluent Loading	Countercurrent Rinsing Evaluation Total Average Effluent Loading	% Reduction
Flow	-	-	_
Temperature	-	-	-
рН	-	-	-
Acidity/Alkalinity	28.2 Lbs. Acidity	8.69 Lbs Alkalinity	-
Chlorides	271.6 Lbs.	33.0 Lbs.	87.8
C.O.D.	165.9 Lbs.	6.19 Lbs.	96.3
Free Cyanides	0.237 Lbs.	.069 Lbs.	70.9
Total Cyanides	3.15 Lbs.	.105 Lbs.	96.7
Fluorides	350.6 Lbs.	8.44 Lbs.	97.6
Sulfates	202.8 Lbs.	69.8 Lbs.	65.6
Suspended Solids	93.5 Lbs.	17.9 Lbs.	80.9
Chromium	0.066 Lbs.	<pre><detectable limit<="" pre=""></detectable></pre>	-
Iron	5.53 Lbs.	.49 Lbs.	91.1
Nickel	0.044 Lbs.	∠Detectable Limit	-
Potassium	5.53 Lbs.	2.69 Lbs.	51.4
Sodium	371.3 Lbs.	17.41 Lbs.	95.3
Tin	270 Lbs.	13.52 Lbs.	95.0

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- 4. 1974 Manual and Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 239.
- 5. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 495, Method 220 (1971).
- 6. ASTM Standards, Part 28, Water; Atmospheric Analysis, p. 273, Method 512-67, Reteree Method A (1973).

#### ANALYTICAL METHODS

#### Hq

- All pH measurements were made on a Beckman Zeromatic II using glass electrode with a saturated calomel electrode used as the reference potential as specified in the 1974 Manual of Methods for Chemical Analysis of Water and Wastes, U.S Environmental Protection Agency; Page 239. The instrument was calibrated daily with buffer solutions.

### ACIDITY

- All acidity analyses were performed as outlined by the procedure listed in Standard Methods for the Examination of Water and Wastewater, 13th Edition, Page 50, Method 101 (1071).

All acidity analyses were performed by titrating an unaltered sample to a pH of 4.5 using standardized sodium hydroxide as the titrant.

## ALKALINITY

- All alkalinity analyses were performed as outlined by procedure listed in Standard Methods for the Examination of Water and Wastewater, 13th Edition, Page 52, Method 102 (1971).

All alkalinity analyses were performed by titrating an unaltered sample to a determined end point of pH 4.5 using standardized sulfuric acid as a titrant.

# DEMAND (C.O.D.)

CHEMICAL OXYGEN - All C.O.D. analyses were performed as outlined by the procedure listed in Standard Methods for the Examination of Water and Wastewater, 13th Edition, Page 495, Method 220 (1971). A proper aliquot of sample is mixed with sulfuric acid, mercuric sulfate, silver sulfate, and standard potassium dichromate and the excess potassium dichromate in the cooled mixture is titrated with standard ferrous ammonium sulfate to the endpoint indicated by ferroin.

#### CHLORIDES

- 1 For the Spray Wash and Hot Rinse Locations all chloride analyses for the above locations were performed according to the procedure outlined in the ASTM Standards, Part 23, Water; Atmospheric Analysis, Page 273, Method 512-67, Referee Method A (1973). According to this method, an acidified sample is titrated with a dilute mercuric nitrate solution to a blue-violet endpoint shown by a mixed diphenylcarbazone-bromophenol blue indicator.
- 2 For the Recovery Tank and the Countercurrent Tank Locations because of interferences shown when using the above method, pre-treatment steps, as outlined in Standard Methods for the Examination of Water and Wastewater,

# (cont'd)

- 13th Edition, Page 379, Method 2030, 4B (1971) were followed. This pre-treatment involves boiling the acidified sample to remove volatile compounds and then oxidizing the sample with hydrogen peroxide. After the pre-treatment, the standard mercuric nitrate procedure (as outlined in the preceding paragraph) is followed.

#### CYANIDES

1 - Total - all total cyanide analyses were performed as outlined in Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Page 40 (1974). All samples were collected by a refrigerated sampler and split into a treated and untreated plastic bottles. The treated bottles contained sodium hydroxide to prevent significant losses in cyanide.

The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux system of mineral acid in the presence of mercuric chloride and magnesium chloride and a distillation operation where the HCN is then collected in a scrubber containing sodium hydroxide solution. The pH of the scrubber solution is adjusted to a pH of 7.0 and reacted with chloramine - T. Proper sample aliquots were used in order that all samples could be determined colorimetrically at a wave length of 620 nm.

2 - Free - all free cyanide analyses were performed by the same procedure as that listed for total cyanides except that the catalysts (mercuric and magnesium chlorides) were not added, thus preventing the breakdown of the iron-cyanide complexes. The samples were also preserved by both refrigeration and by the addition of sodium hydroxide.

#### FLUORIDES

- all the fluoride analyses were determined potentiometrically using a selective ion fluoride electrode in
conjunction with a standard single junction sleeve-type
reference electrode and a pH meter having an expanded
millivolt scale. The procedure used is contained in
manual of Methods for Chemical Analysis of Water and
Wastes, Page 65 (1974), published by the Environmental
Protection Agency. The method involves adjusting the
pH of the sample by means of a buffer solution and
chelating the polyvalent cations which could interfere.

#### PHOSPHORUS

- all phosphorus analyses were performed according to the method outlined in a manual of Methods for Chemical Analysis of Water and Wastes, U.S Environmental Protection Agency, Page 249. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

#### SULFATES

- all sulfate analyses were performed as outlined in Standard Methods for the Examination of Water and Wastewater, 13th Edition, Page 334, Method 156C 1971). Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a spectrophotometer and compared to a curve prepared from standard sulfate solutions.

#### METALS

- (Cadmium, chromium, iron, nickel, potassium, sodium and tin) all the metals were treated and analyzed as outlined in the manual of Methods for Chemical Analysis of Water and Wastes, Environmental Protection Agency Metals (Atomic Absorption), Page 78. All metal samples were preserved with HNO3. All analyses were performed on a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer. The samples were prepared by taking an appropriate aliquot to which HNO3 had been added and evaporating carefully to dryness. Repeated HNO3 additions were made until the removal of organic material was completed. The samples were then redissolved and analyzed using the atomic absorption spectrophotometer equipped with hollow cathode lamps.

COUNTERCURRENT RINSING
PHASE I - CHEMICAL ANALYSES

ALLEMDIA II	PHASE I - CHEM.	IOAD ANADIOED	DATE 0/ / 00 8/0/74
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5gpm - 7,200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	110° F	93°F	181°F
ηd	4.5	4.0	3.8
ACIDITY/ALKALINITY	Oppm - 0 1bs	Acidity 42 ppm - 17.7 lbs	Acidity 8.0 ppm - 3.84 lbs
CHLORIDES	1800 ppm - 108. lbs/Day	140 ppm - 58.4 lbs/Day	114 ppm - 54.8 lbs/Day
COD	892 ppm - 53.6 lbs/Day	33 ppm - 139. lbs/Day	41 ppm - 19.7 lbs/Day
FREE CYANIDES	1.44 ppm09 lbs/Day		
TOTAL CYANIDES	54 ppm - 3.24 lbs/Day	.54 ppm23 lbs/Day	.038 ppm018 1bs/Day
FLUORIDES	4,200 ppm - 252 lbs/Day	86 ppm - 36.1 Ins/Day	46 ppm - 22. lbs/Day
SULFATES	250 ppm - 15.0 lbs/Day	166 ppm - 69.8 lbs/Day	166 ppm - 79.7 lbs/Day
SUSPENDED SOLIDS	694 ppm - 41.7 lbs/Day	138 ppm - 580.0 lbs/Day	18 ppm - 8.65 lbs/Day
CHROMIUM	0.80 ppm048 lbs/Day	0.03 ppm013 lbs/ <b>Da</b>	у*
IRON	144.5 ppm - 8.68 lbs/Day	2.4 ppm - 1.01 lbs/Day	.40 ppm19 lbs/Day
NICKEL	1.25 ppm075 lbs/Day	*	*
POTASSIUM	7.0 ppm - 0.42 lbs/Day	4.78 ppm - 2.01 lbs/Da	y4.0 ppm - 1.92 lbs/Day
SODIUM	3517 ppm - 211 lbs/Day	132 ppm - 55.5 lbs/De	23.3 ppm - 11.2 lbs/Day
TIN	3180 ppm - 191 1bs/Day	'94 ppm - 39.5 lbs/Day	18.0 ppm - 8.6 lbs/Day

<sup>\* &</sup>lt;Detectable Limit

----- - Analysis Not Performed

	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERATURE	120 <sup>0</sup> F	92 <sup>0</sup> F	185 <sup>0</sup> F
pH	4.4	4.2	4.6
	Acidity 20 ppm - 1.20 lbs/Day	Acidity 12 ppm - 5.04 lbs/Day	Alkalinity 2.0 ppm - 0.96 lbs/Day
CHLORIDES	2250 ppm - 135 lbs/Day	85 ppm - 35.7 lbs/Day	72 ppm - 34.6 lbs/Day
COD	1235 ppm - 74.2 lbs/Day	27 ppm - 11.3 lbs/Day	46 ppm - 22.1 lbs/Day
FREE CYANIDES	0.40 ppm024 lbs/Day	0.84 ppm35 lbs/Day	
TOTAL CYANIDES	137 ppm - 8.23 lbs/Day	3.52 ppm - 1.48 lbs/Dey	.16 ppm077 lbs/Day
FLUCRIDES	5500 ppm - 330 lbs/Day	56.0 ppm - 23.5 lbs/Da	y 56 ppm - 26.9 lbs/Day
SULFATES	312 ppm - 18.7 lbs/Day	166 ppm - 69.8 lbs/Da	158 ppm - 75.9 lbs/Day
SUSPENDED SOLIDS	625 ppm - 37.5 lbs/Day	98 ppm - 41.2 lbs/Day	11 ppm - 5.28 lbs/Day
CHROMIUM	0.95 ppm057 lbs/Day	*	*
IRON	89.5 ppm - 5.37 lbs/Day	1.6 ppm - 0.67 lbs/Day	0.40 ppm19 lbs/Day
NICKEL	0.80 ppm048 lbs /Day	*	*
POTASSIUM	7.25 ppm44 lbs/Day	4.26 ppm - 1.79 lbs/ba	3.71 ppm - 1.78 lbs/Day
SODIUM	4350 ppm - 261 lbs/Day	86 ppm - 36. 1 lbs/Day	, 24.4 ppm - 11.7 lbs/Day
TIN	3775 ppm - 227 lbs/Day	52 ppm - 21.9 lbs/Day	9 ppm - 4.32 lbs./Day

<sup>\* &</sup>lt; Detectable Limit

<sup>---- -</sup> Analysis Not Performed

	PHASE 1 - CHEM	ICAL ANALYSES	DATE 8/7 to 8/8/74
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	111°F	930 F	182° F
рН	4.65	4.2	4.15
ACIDITY/ALKALINITY	Alkalinity 296 ppm - 17.8 lbs/Day	Acidity 12.0 ppm -5.04 lbs/Day	Acidity 4.0 ppm - 1.92 lbs/Day
CHLORIDES	2200 ppm - 132 1bs/Day	185 ppm - 77.8 lbs/Day	154ppm - 74.0 lbs/Day
COD	1390 ppm - 83.5 lbs/Day	42.5 ppm -17.9 lbs/Day	39 ppm - 18.7 lbs
FREE CYANIDES	0.41 ppm025 lbs/Day	0.94 ppm40lbs/Day	
TOTAL CYANIDES	120 ppm - 7.21 lbs/Day	2.4 ppm - 1.01 lbs/Da	70.21 ppm - 0.10 lbs/Day
FLUORIDES	5000 ppm - 300 los/Day		750 ppm - 24.0 lbs/Day
SULFATES	287 ppm - 17.2 lbs/Day	170 ppm - 71.5 lbs/Day	146 ppm - 70.14 lbs/Day
SUSPENDED SOLIDS	649 ppm - 39.0 lbs/Day	181 ppm - 76.1 lbs/Da	714 ppm - 6.73 lbs/Day
CHROMIUM	0.85 ppm - 0.05 lbs/Day	.02 ppm01 lbs/Day	*
IRON	74.5 ppm - 4.47 lbs/Day	2.5 ppm - 1.05 lbs/Dev	0.39 ppm19 lbs/Day
NICKEL	0.65 ppm039 lbs/Day	*	*
POTASSIUM	7.7 ppm - 0.46 lbs/Day	4.5 ppm - 1.89 lbs/Day	3.72 ppm - 1.75 lbs/Day
SODIUM	4150 ppm - 249 lbs/Day	161 ppm - 67.7 lbs/Day	24.4 ppm - 11.7 lbs /Day
TIN	3785 ppm - 227 lbs/Day	'83 ppm - 34.9 lbs/Day	11 ppm - 5.28 lbs/Day

<sup>\* &</sup>lt; Detectable Limit
---- Analysis Not Performed

	PRASE I - CHEM	IOAL ANALIS ES	DATE 8/12 to 8/13/74
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	107 <sup>0</sup> F	95°F	176°F
pH	4.5	4.0	4.1
ACIDITY/ALKALINITY	Oppm - O lbs/Day	Acidity 18 ppm - 7.57 lbs/Day	Acidity 4.0 ppm - 1.92 lbs/Day
CHLORIDES	1540 ppm - 92.5 lbs/Day	165 ppm -69.4 lbs/Day	94 ppm - 45.2 lbs/Day
COD	10,108 ppm - 607 lbs/Day	49 ppm - 20.6 lbs/Day	64 ppm - 30.7 lbs/Day
FREE CYANIDES	.84 ppm05 lbs/Day		.100 ppm05 lbs/Day
TOTAL CYANIDES	5.32 ppm32 lbs/Day	.566 ppm24 lbs/Dec	.277 ppm13 lbs/Day
FLUCRIDES	3500 ppm - 210 lbs/Day	88 ppm - 37.0 lbs/Day	14 ppm - 6.73 lbs/Day
SULFATES	233 ppm - 14.0 lbs/Day	180 ppm -75,71bs/Day	154 ppm - 74.0 lbs/Day
SUSPENDED SOLIDS	1238 ppm - 74.3 lbs/Day	178 ppm -52.1 1bs/Bay	31 ppm - 14.9 lbs/Day
CHROMIUM	0.90 ppm054 lbs/Day	.05 ppm013 lbs/Day	*
IRON	100 ppm - 6.00 lbs/Day	3.7 ppm -1.35 lbs/Day	0.33 ppm16 lbs/Day
NICKEL	0.95 ppm057 lbs/Day	*	*
POTASSIUM	6.5 ppm - 0.39 lbs/Day	4.84 ppm -1.98 lbs/De	y4.09 ppm - 1.96 lbs/Day
SODIUM	3150 ppm - 189 lbs/Day	147 ppm -87.9 lbs/Day	32.2 lbs - 15.5 lbs/Day
TIN	2500 ppm - 150 lbs/Day	87 ppm -39.1 1bs/Day	15 lbs - 7.21 lbs/Day

<sup>\* &</sup>lt;Detectable Limit

<sup>---- -</sup> Analysis Not Performed

	TIMOD I - OIDII		
	RECOVERY TANK	SPRAY WASH .	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	113°F	91°F	180°F
Hq	4.5	4.2	5•4
ACIDITY/ALKALINITY	0.0 ppm - 0 lbs/Day	Acidity 96 ppm - 40.4 lbs/Day	Alkalinity 4.0 ppm - 1.92 lbs/Day
CHLORIDES	2900 ppm - 174 lbs/Day	240 ppm - 101 lbs/Day	72 ppm - 34.6 lbs/Day
COD	1588 ppm - 95.4 lbs/Day	93 ppm - 39.1 lbs/Day	32 ppm - 15.4 lbs/Day
FREE CYANIDES	.54 ppm032 lbs/Day		.06 ppm029 lbs/Day
TOTAL CYANIDES	2.48 ppm15 lbs/Day	.42 ppm18 lbs/Day	.099 ppm048 lbs/Day
FLUORIDES	7000 ppm - 420 lbs/Day	155 ppm -65.2 lbs/Day	15 ppm - 7.21 lbs/Day
SULFATES		180 ppm - 75.7 lbs/ <b>Day</b>	150 ppm - 72.1 lbs/Day
SUSPENDED SOLIDS	238 ppm - 14.29 lbs/Day	124 ppm - 52.1 1bs/Day	21 ppm - 10. 1 lbs /Day
CHROMIUM	1.0 ppm06 lbs/Day	.03 ppm013 lbs/bay	*
IRON	72 ppm - 4.32 lbs/Day	3.2 ppm - 1.35 lbs/bay	.37 ppm - 0.18 lbs/Day
NICKEL	.95 ppm057 lbs/Day	*	*
POTASSIUM	8.65 ppm52 lbs/Day	4.71ppm- 1.98 lbs/Day	3.93 ppm - 1.89 lbs/Day
SODIUM	5900 ppm - 354 lbs/Day	209 ppm - 87.9 lbs/120	36.7 ppm - 17.6 lbs/Day
TIN	4345 ppm - 261 lbs/Day	93 ppm - 39.1 lbs/bay	13 ppm - 6.24 lbs/Day

<sup>\* \*</sup> Cetectable Limit

----- - Analysis Not Performed

	FRACE 1 = UNDM.	TOVE VINTERS	DATE 0/14 00 0/1///4
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	111°F	90°F	186°F
Hq	4.6	3.7	4.2
ACIDITY/ALKALINITY	Alkalinity 142 ppm - 8.53 lbs/Day	Acidity 84 ppm - 35.3 lbs	Acidity 4.0 ppm - 1.92 lbs/Day
CHLORIDES	3180 ppm - 191 lbs/Day	20 oppm - 35.3 lbs/Day	79 ppm - 38.0 lbs/Day
COD	1445 ppm - 86.8 lbs/Day	80 ppm - 33.6 lbs/Day	19 ppm - 9.13 lbs/Day
FREE CYANIDES	1.34 ppm08 lbs/Day	<del></del>	.113 ppm05 lbs/Day
TOTAL CYANIDES	7.0 ppm42 lbs/Day		.413 ppm20 lbs/Day
FLUORIDES	9400 ppm - 564 lbs/Day	155 ppm -65.2 lbs/Day	28 ppm - 13.5 lbs/Day
SULFATES	184 ppm - 11.0 lbs/Day	166 ppm -69.8 lbs/Day	150 ppm - 72.1 lbs/Day
SUSPENDED SOLIDS	193 ppm - 11.6 lbs/Day	175 ppm -73.6 lbs/Day	26 ppm - 12.5 lbs/Day
CHROMIUM	.75 ppm045 lbs/Day	.05 ppm02 lbs/Day	*
IRON	81.5 ppm - 4.89 lbs/Day	3.5 ppm -1.47 lbs/Day	0.5 ppm24 lbs/Day
NICKEL	1.00 ppm06 lbs/Day	*	*
POTASSIUM	10.45 ppm63 lbs/Day	4.89 ppm -2.06 lbs/Deg	4.12 ppm - 1.98 lbs /Da
SODIUM	4500 ppm - 270 lbs/Day	205 ppm -86.2 lbs/Day	48.9 ppm - 23.5 lbs/Day
TIN	4795 ppm - 288 lbs/Day	150 ppm -63.1 lbs/Day	22 ppm - 10.6 lbs/Day

\* < Detectable Limit

----- - Analysis Not Performed

	PHASE I - UNDMI	0.112	DATE 0/17 00 0/20/14
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERATURE	109 <sup>0</sup> F	91 <sup>0</sup> F	183 <sup>0</sup> F
Hq	4.4	3.6	3.7
ACIDITY/ALKALINITY	Acidity 248 ppm - 14.9 lbs/Day	Acidity 150 ppm -63.1 lbs/Day	Acidity 12 ppm - 5.76 lbs/Day
CHLORIDES	3300 ppm - 198 lbs/Day	80 ppm - 33.6 lbs/Day	78 ppm - 37.5 lbs/Day
COD	1417 ppm - 85.1 lbs/Day	83 ppm - 34.9 lbs/Day	28 ppm -13.5 lbs/Day
FREE CYANIDES	.68 ppm041 lbs/Day	.31 ppm13 1bs/Day	.15 ppm075 lbs/Day
TOTAL CYANIDES	15 ppm90 lbs/Day		.29 ppm14 lbs/Day
FLUORIDES	3800 ppm - 228 lbs/Day	260 ppm <b>-</b> 109 lb <b>s/</b> Day	29 ppm -13.9 lbs/Day
SULFATES	357 ppm - 21.4 lbs/Day	İ	122 ppm - 58. 6 lbs/Day
SUSPENDED SOLIDS	384 ppm - 231.1 lbs/Day	ļ	49 ppm - 23.5 lbs/Day
CHROMIUM	.85 ppm051 lbs/Day	.03 ppm013 lbs/Day	
IRON	75.5 ppm - 4.53 lbs/Day		0.72 ppm35 lbs/Day
NICKEL	.85 ppm051 lbs/Day	*	*
POTASSIUM	8.55 ppm51 lbs/Day	5.36 ppm -2.25 lbs/Da	4.13 ppm - 1.98 lbs/Day
SODIUM	5400 ppm - 324. lbs/Day	372 ppm - 156 lbs/Day	46.7 ppm - 22.4 lbs/Day
TIN	3520 ppm - 211 lbs/Day	,	31 ppm - 14.9 lbs/Day

<sup>\* &</sup>lt; Detectable Limit

<sup>---- -</sup> Analysis Not Performed

CCUNTERCURRENT RINSING PHASE I - CHEMICAL ANALYSES DATE 8/20 to 8/21/74				
	RECOVERY TANK	SPRAY WASH	HOT RINSE	
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd	
<b>TEMP</b> ERA TURE	113°F	93°F	184°F	
Ηg	4.5	3 <b>.</b> 9	4.5	
ACIDITY/ALKALINITY	Oppm - O lbs/Day	Acidity 138 ppm - 58.0 lbs/Daj	Oppm - O lbs/Day	
CHLORIDES	2700 ppm - 162 lbs/Day	384 ppm -161 1bs/Day	59 ppm - 28.3 lbs/Day	
COD	1533 ppm - 92.1 lbs/Day	100 ppm -42.0 lbs/Da	12 ppm - 5.76 lbs/Day	
FREE CYANIDES				
TOTAL CYANIDES	32 ppm - 1.92 lbs/Day	8.0 ppm -3.36 lbs/Da	2.4 ppm - 1.15 lbs/Day	
FLUORIDES	5800 ppm - 348 lbs/Day	245 ppm -103 lbs/Day	29 ppm - 13.9 lbs/Day	
SULFATES	330 ppm - 19.8 lbs/Day	174 ppm -73.1 lbs/Day	154 ppm - 74.0 lbs/Day	
SUSPENDED SOLIDS	227 ppm - 13.6 lbs/Day	119 ppm -50.0 lbs/Day	39 ppm - 18.7 lbs/Day	
CHROMIUM	0.80 ppm048 lbs/Day	.02 ppm008 lbs/Day	*	
IRON	63.5 ppm - 3.81 lbs /Day	3.4 ppm -1.43 lbs/Day	0.68 ppm33 lbs/Daj	
NICKEL	0.85 ppm - 0.051 lbs/Day	*	*	
POTASSTUM	8.7 ppm - 0.52 lbs/Day	5.28 ppm -2.22 lbs/Da	y4.22 ppm - 2.03 lbs/De	
SODIUM	5200 ppm - 312 lbs/Day	321 ppm -135 lbs/Day	48.9 ppm - 23.5 lbs/Da	
TIN	3675 ppm - 221 lbs/Day	228 ppm -95.81bs/Day	25 ppm - 12.0 lbs/Day	

<sup>\* &</sup>lt; Detectable Limit

--- - Analysis not Performed

DATE 8/21 to 8/22/74

	PROBLE - URBIT	10.11	DATE 0/21 00 0/22/14
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	110°F	92°F	183°F
Нд	4.4	3.9	4.3
ACIDITY/ALKALINITY	Acidity 116 ppm - 6.97 lbs/Day	Acidity 132 ppm -55.5 lbs/Day	Acidity 18. ppm = 8.65 lhs/Day
CHLORIDES	4800 ppm - 288 lbs/Day	440 ppm -185 1bs/Day	
COD	6238 ppm - 375 lbs/Day	106 ppm -44.6 lbs/Day	46 ppm - 22.1 lbs/Day
FREE CYANIDES	.633 ppm038 lbs/Day	.273 ppm 1151bs/Day	.087 ppm042 lbs/Day
TOTAL CYANIDES	2.5 ppm15 lbs/Day	.64 ppm27 lbs/Day	.124 ppm060 lbs/Day
FLUORIDES	5000 ppm - 300 lbs/Day		.33 ppm - 15.9 lbs/Day
SULFATES	287 ppm - 17.2 lbs/Day		150 ppm - 72.1 lbs /Day
SUSPENDED SOLIDS	271 ppm - 16.3 lbs/Day	203 ppm -85.3 Lbs/Day	81 ppm - 38.9 lbs/Day
CHROMIUM	.85 ppm051 lbs/Day	*	*
IRON	67 ppm - 4.02 lbs/Day	5.2 ppm -2.19 lbs/Day	.74 ppm36 lbs/Day
NICKEL	.90 ppm054 lbs/Day	*	*
POTASSIUM	8.85 ppm53 lbs/Day	5.39 ppm -2.27 lbs/Da	74.30 ppm - 2.07 lbs/Day
SODIUM	6350 ppm - 381 lbs/Day	331 ppm 139 lbs/Day	55.6 ppm - 26.7 lbs/Day
TIN	4455 ppm - 268 lbs/Day	271 ppm -114 lbs/Day	

<sup>\* &</sup>lt; Detectable Limit

			DATE 9/22 00 0/23/14
	RECOVERY TANK	<u>SPRAY WASH</u>	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	35 gpm - 50,400 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	115 <sup>0</sup> 5	95 <sup>0</sup> F	178 <sup>0</sup> F
рН	4.5	3.65	4.0
ACIDITY/ALKALINITY	0. Oppm - 0 lbs/Day	Acidity 164 ppm -68.9 lbs/Day	Acidity 10 ppm - 4.80 lbs/Day
CHLORIDES	4600 ppm - 276 lbs/Day	544 ppm -229 lbs/Day	96 ppm - 46.1 lbs/Day
COD	1303 ppm - 78.2 lbs/Day	84 ppm -35.3 lbs/Day	54 ppm - 25.9 lbs/Day
WREE CYANIDES		.813 ppm34 lbs/Day	
TOTAL CYANIDES	17.6 ppm - 1.06 lbs/Day	2.3 ppm97 lbs/Day	.167 ppm08 lbs/Day
FLUORIDES	6000 ppm - 360 lbs/Day	320 ppm -135 lbs/Day	33 ppm - 15.9 lbs/Day
SULFATES	384 ppm - 23.1 lbs/Day	166 ppm -69.81bs/Day	150 ppm - 72.1 lbs/Day
SUSPENDED SOLIDS	249 ppm - 15.0 los/Day	170 ppm -71.5 lbs/Day	81 ppm - 38.9 lbs/Day
CHROMIUM	.90 ppm054 lbs/Day	.02 ppm0081bs/Day	*
IRON	71 ppm - 4.26 lbs/Day	5.5 ppm -2.31 lbs/Day	.72 ppm35 lbs/Day
NICKEL	.55 ppm033 lbs/Day	*	*
POTASSIUM	9.1 ppm55 lbs/Day	5.53 ppm -2.32 lbs/Dev	4.17 ppm - 2.00 lbs/Day
SODIUM	6500 ppm - 390 lbs/Day	418 ppm - 176 lbs/Day	62.2 ppm - 29.9 lbs/Day
TIN	4930 ppm - 296 lbs/Day	347 ppm - 146 lbs/Day	37 ppm - 17.8 lbs/Day

<sup>\* &</sup>lt; Detectable Limit

	PHASE I - CHEM.	TOAL ANALISES	DATE 0/20 00 0/21/14
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	80 gpm - 115,200 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	112°F	94 <sup>0</sup> F	180°F
На	4.3	4.2	6.5
ACIDITY/ALKALINITY	Acidity 485 ppm - 29.1 lbs/Day	Acidity 2.0 ppm -1.921bs/Day	Alkalinity 18.0 ppm - 865 lbs/Day
CHLORIDES	2200 ppm - 132 lbs/Day	50 ppm -48.0 lbs/Day	46 ppm - 22.1 lbs/Day
COD	1944 ppm - 117 lbs/Day	19.4 ppm -18.61bs/pev	43 ppm - 20.7 lbs/Day
FREE CYANIDES	cate data and and and and		.10 ppm048 lbs/Day
TOTAL CYANIDES	10.8 ppm65 lbs/Day	.6 ppm58 lbs/Day	.112 ppm054 lbs/Day
FLUORIDES	2850 ppm - 171 lbs/Day	47 ppm -54.2 lbs/Day	5.2 ppm - 2.50 lbs/Day
SULFATES	295 ppm - 17.7 lbs/Day	170 ppm -163 lbs/Day	174 ppm - 83.6 lbs/Day
SUSPENDED SOLIDS	261 ppm - 15.7 lbs/Day	48 ppm -46.1 lbs/Day	36 ppm - 17.3 lbs/Day
CHROMIUM	.75 ppm045 lbs/Day	* 1	*
IRON	32.5 ppm - 1.95 lbs/Day	1.5 ppm -1.44 lbs/Day	.80 ppm38 lbs/Day
NICKEL	.45 ppm027 lbs/Day	*	*
POTASSIUM	6.15 ppm37 lbs/Day	4.91 ppm -4.721bs/Day	4.31 ppm - 2.07 lbs/Day
SODIUM	3150 ppm - 189 lbs/Day	109 ppm -105 lbs/Day	27.8 ppm - 13.4 lbs/Day
TIN	2500 ppm - 150 lbs/Day	62 ppm - 59.6 lbs/Day	14 ppm - 6.73 lbs/Day

<sup>\* &</sup>lt; Detectable Limit

1.2.0 2 2		DATE 0/27 to 0/20/14
RECOVERY TANK	SPRAY WASH	HOT RINSE
5 gpm - 7200 gpd	80 gpm - 11,200 gpd	40 gpm - 57,600 gpd
112°F	95°F	181°F
4.5	5.0	6.3
Oppm - O lbs/Day	1	Alkalinity 28 ppm - 13.5 lbs/Day
2000 ppm - 120 1bs/Day	35 ppm -33.6 lbs/Day	58 ppm - 27.9 lbs/Day
1012 ppm - 60.8 lbs/Day	35 ppm -33.6 lbs/Day	58 ppm - 27.9 lbs/Day
.007 ppm0004 lbs/Day	.0001 ppm0001 lbs/	
4.0 ppm24 lbs/Day		.05 ppm024 lbs/Day
3250 ppm - 195 lbs/Day		2.6 ppm - 1.25 lbs/Day
295 ppm - 17.7 lbs/Day	174 ppm - 167 lbs/Da	, 180 ppm - 86.5 lbs/Day
195 ppm - 11.7 lbs/Day	45 ppm - 43.2 lbs/Da	, 30 ppm - 14.4 lbs/Day
.85 ppm051 lbs/Day	.02 ppm019 lbs/Da	*
35 ppm - 2.10 lbs/Day	1.3 ppm -1.25 lbs/Day	.61 ppm29 lbs/Day
.55 ppm033 lbs/Day	*	*
7.25 ppm44 lbs/Day	4.89 ppm -4.70 lbs/Da	y 4.40 ppm - 2.11 lbs/Day
3250 ppm - 195 lbs/Day	73 ppm -70.1 lbs/Day	27.8 ppm - 13.4 lbs/Day
2480 ppm - 149 lbs/Day	25 ppm -24-0 lbs/Day	9 ppm - 4.32 lbs/Day
	RECOVERY TANK  5 gpm - 7200 gpd  112°F  4.5  Oppm - 0 lbs/Day  2000 ppm - 120 lbs/Day  1012 ppm - 60.8 lbs/Day  .007 ppm0004 lbs/Day  4.0 ppm24 lbs/Day  3250 ppm - 195 lbs/Day  295 ppm - 17.7 lbs/Day  195 ppm - 11.7 lbs/Day  .85 ppm051 lbs/Day  35 ppm - 2.10 lbs/Day  .55 ppm033 lbs/Day  7.25 ppm44 lbs/Day  3250 ppm - 195 lbs/Day	5 gpm - 7200 gpd       80 gpm - 11,200 gpd         112°F       95°F         4.5       5.0         Oppm - 0 lbs/Day       35 ppm - 3.6 lbs/Day         2000 ppm - 120 lbs/Day       35 ppm - 33.6 lbs/Day         1012 ppm - 60.8 lbs/Day       35 ppm - 33.6 lbs/Day         .007 ppm0004 lbs/Day       .0001 ppm0001 lbs/Day         4.0 ppm24 lbs/Day       .45 ppm43 lbs/Day         3250 ppm - 195 lbs/Day       36 ppm - 34.6 lbs/Day         295 ppm - 17.7 lbs/Day       174 ppm - 167 lbs/Day         .85 ppm051 lbs/Day       .02 ppm019 lbs/Day         .55 ppm033 lbs/Day       1.3 ppm - 1.25 lbs/Day         .55 ppm44 lbs/Day       4.89 ppm -4.70 lbs/Day         73 ppm -70.1 lbs/Day       73 ppm -70.1 lbs/Day

<sup>\* \*</sup> Cetectable Limit

	TIMOD 1 - OHDI	1	DAID 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	80 gpm - 115,200 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	112°F	95°F	184°F
Hq	4.5	4.0	8.2
ACIDITY/ALKALINITY	Oppm - O lbs/Day	Acidity 16.0 ppm _15.4 lbs/Bay	Alkalinity 18.0 ppm - 8.65 lbs/Day
CHLORIDES	2100 ppm - 126 lbs/Day	50 ppm -48.0 lbs/Day	36 ppm - 17.3 lbs/Day
COD	1166 ppm - 70.0 lbs/Day	31 ppm -29.8 lbs/Day	12 ppm - 5.76 lbs/Day
FREE CYANIDES	.0001 ppm - 0 lbs/Day	.028 ppm027 lbs/Day	.0002 ppm - 0 lbs/Day
TOTAL CYANIDES	24 ppm - 1.44 lbs/Day	.38 ppm37 lbs/Day	.10 ppm05 lbs/Day
FLUORIDES	4300 ppm - 258 lbs/Day	51 ppm 49.0 lbs/Day	3.6 ppm - 1.73 lbs/Day
SULFATES	295 ppm - 17.7 lbs/Day	166 ppm - 159 lbs/Dey	170 ppm - 81.7 lbs/Day
SUSPENDED SOLIDS	74 ppm - 4.44 lbs/Day	40 ppm -38.4 lbs/Day	5.0 ppm - 2.40 lbs/Day
CHROMIUM	.90 ppm054 lbs/.Day	*	*
IRON	39. ppm - 2.34 lbs/Day	1.10 ppm 1.06 lbs/	.53 ppm25 lbs/Day
NICKEL	.50 ppm03 lbs/Day	*	*
POTASSIUM	9.1 ppm55 lbs/Day	4.95 ppm -4.76 Du:	4.34 ppm - 2.08 lbs/Day
SODIUM	4150 ppm - 249 lbs/Day	96 ppm -92.2 lbs/Day	
TIN	2780 ppm - 167 lbs/Day	42 ppm -40.4 lbs/Day	10 ppm - 4.80 lbs/Day

<sup>\* &</sup>lt; Detectable Limit

<sup>---- -</sup> Analysis Not Performed

			DRIH 9, 47 00 0/ JC/ 14
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	80 gpm - 115,200 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	115 <sup>0</sup> F	95 <sup>0</sup> F	184 <sup>0 p</sup>
pH	4.5	4.2	8.3
ACIDITY/ALKALINITY	0.0 ppm - 0 lbs/Day	Acidity 8.0 ppm -7.691bs/Day	Alkalinity 22.0 ppm - 10.6 lbs/Day
CHLORIDES	2400 ppm - 144 lbs/Day	80 ppm -76.9 lbs/Day	
COD	933 ppm - 56.0 lbs/Day	47 ppm - 45.2 1bs/Day	16 ppm - 7.69 lbs/Day
FREE CYANIDES	.02 ppm001 lbs/Day		.02 ppm01 lbs/Day
TOTAL CYANIDES	4.8 ppm29 lbs/Day	.126 ppm12 lbs/Da	.172 ppm083 lbs/Day
FLUORIDES	3800 ppm - 228 lbs/Day	5300m -50.9 lbs/Day	2.1 ppm - 1.01 lbs/Day
SULFATES	287 ppm - 17.2 lbs/Day	158 ppm =152 lbs/Day	158 ppm - 75.9 lbs/Day
SUSPENDED SOLIDS	180 ppm - 10.8 lbs/Day	50 ppm -48.0 lbs/Day	19 ppm - 9.13 1hs/Day
CHROMIUM	.80 ppm048 lbs/Day	.03 ppm029 lbs/Day	*
IRON	37 ppm - 2.22 lbs/Day	1.4 ppm -1.35 lbs/Day	
NICKEL	.65 ppm039 lbs/Day	*	*
POTASSIUM	8.6 ppm52 lbs/Day	5.25 ppm -5.041bs/hay	4.68 ppm - 2.25 lbs/Day
SODIUM	3600 ppm - 216 lbs/Day	92 ppm -88.4 1bs/Day	27.8 ppm - 13.4 lbs/Day
TIN	2865 ppm - 172 lbs/Day	' 47 ppm -45.2 lbs/Day	7 ppm - 3.36 lbs/Day

\* \* CDetectable Limit

	PHASE I - CHEMICAL ANALYSES		DATE 9/3/ 60 9/4/14
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	80 gpm - 115,200 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	112°F	92 <b>°</b> F	178 <sup>0</sup> F
Hq	4.3	4.3	7.0
ACIDITY/ALKALINITY	Acidity 812 ppm - 48.8 lbs/Day	Acidity 6.0 ppm _5.76 lbs/Day	Alkalinity 8.0 ppm - 3.84 lbs/Day
CHLORIDES	1620 ppm - 97.3 lbs/Day	50 ppm _ 48.0 lbs/Day	24 ppm - 11.5 lbs/Day
COD	894 ppm - 53.7 lbs/Day	20 ppm - 19.2 1bs/Day	41 ppm - 19.7 lbs/Day
FREE CYANIDES		.175 ppm17 lbs/Day	
TOTAL CYANIDES	16.5 ppm99 lbs/Day	.183 ppm176 lbs/Day	.12 ppm058 lbs/Day
FLUORIDES	3250 ppm - 195 lbs/Day	39 ppm - 33.5 lbs/Day	3.2 ppm - 1.54 lbs/Day
SULFATES	303 ppm - 18.2 lbs/Day	180 ppm -173 lbs/Day	162 ppm - 77.8 lbs/Day
SUSPENDED SOLIDS	195 ppm - 11.7 lbs/Day	18 ppm - 17.3 lbs/Day	20 ppm - 9.61 lbs/Day
CHROMIUM	.95 ppm057 lbs/Day	.04 ppm038 lbs/Day	*
IRON	31 ppm - 1.86 lbs/Day	1.0 ppm96 lbs/Day	.59 ppm - 028 lbs/Day
NICKEL .	.65 ppm039 lbs/Day	*	*
POTASSIUM	6.7 ppm40 lbs/Day	4.34 ppm -4.171bs/Bey	3.97 ppm - 1.91 lbs/Day
SODIUM	3400 ppm - 204 lbs/Day	69 ppm - 66.3 lbs/Day	27.8 ppm - 13.6 lbs/Day
TIN	2435 ppm - 146 lbs/Day	26 ppm - 25.0 lbs/Day	13 ppm - 6.24 lbs/Day

<sup>\* &</sup>lt; Detectable Limit

· · · · · · · · · · · · · · · · · · ·		TOTAL TRAINING ED	DATE 9/4/ to 9/5/74
	<u>RECOVERY TANK</u>	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	80 gpm - 115,200 gpd	40 gpm - 57,600 gpd
TEMPERATURE	114°F	89°F	186°F
Hq	4.4	4.8	5.3
ACIDITY/ALKALINITY	Acidity 360 ppm - 21.6 lbs/Day	Alkalinity   2.0 ppm _1.92 lbs/Day	Alkalinity 12.0 ppm - 5.76 lbs/Day
CHLORIDES	1860 ppm - 112 lbs/Day	60 ppm -57.6 lbs/Day	36 ppm - 17.3 lbs/Day
COD	884 ppm - 53.1 lbs/Day	16 ppm -15.4 lbs/Day	32 ppm - 15.4 lbs/Day
FREE CYANIDES	****	.002 ppm002 Day	
'rotal cyanides	152 ppm - 9.13 lbs/Day	.88 ppm85 lbs/Day	.25 ppm12 lbs/Day
FLUORIDES	3400 ppm - 204 lbs/Day	j	2.46 ppm - 1.18 lbs/Day
SULFATES	295 ppm - 17.7 lbs/Day	186 ppm - 179 lbs/Day	166 ppm - 79.7 lbs/Day
SUSPENDED SOLIDS	210 ppm - 12.6 lbs/Day	45 ppm - 43.2 lbs/Day	25 ppm - 12.0 lbs/Day
CHROMIUM	.80 ppm048 lbs/Day	.03 ppm03 lbs/Day	*
IRON	35 ppm - 2.10 lbs/Day	1.2 ppm -1.15 lbs/Day	.57 ppm27 lbs/Day
NICKEL	.50 ppm03 lbs/Day	*	*
POTASSIUM	6.45 ppm39 lbs/Day	4.27 ppm -4.101bs/Day	3.77 ppm - 1.81 lbs/Day
SODIUM	3400 ppm - 204 lbs/Day	72 ppm - 69.2 lbs/Day	25.6 ppm - 12.3 lbs/Day
TIN	2735 ppm - 164 lbs/Day	30 ppm - 28.8 lbs/Day	11 ppm - 5.28 lbs/Day

<sup>. \* &</sup>lt; Detectable Limit

<sup>----- -</sup> Analysis Not Performed

DATE 9/5 to 9/6/74

		TOAL ANALISES	DATE 7/ 3 to 9/ 0/ 74
	RECOVERY TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	5 gpm - 7200 gpd	80 gpm - 115,2 <b>6</b> 0 gpd	40 gpm - 57,600 gpd
TEMPERA TURE	110°F	91°F	135 <sup>0</sup> F
Hg	4.3	4.5	5.9
ACIDITY/ALKALINITY	Acidity 660 ppm - 39.6 lbs/Day	Oppm - O lbs/Day	Alkalinity 16 ppm - 7.69 lbs/Day
CHLORIDES	1900 ppm - 114 lbs/Day	65 ppm -62.4 lbs/Day	26 ppm - 12.5 lbs/Day
COD	160 ppm - 9.61 lbs/Day	8 ppm - 7.69 lbs/Day	44 ppm - 21.1 lbs/Day
FREE CYANIDES	.125 ppm008 lbs/Day	.1 ppm - 096 lbs/Day	
TOTAL CYANIDES	60 ppm - 3.60 lbs/Day	.3 ppm029 lbs/Day	.126 ppm061 lbs/Day
FLUORIDES	3700 ppm - 222 lbs/Day	48 ppm -46.1 lbs/Day	2.56 ppm - 1.23 lbs/Day
SULFATES	272 ppm - 16.3 lbs/Day	166 ppm - 159 lbs/Day	154 ppm - 74.0 lbs/Day
SUSPENDED SOLIDS	245 ppm - 14.7 lbs/Day	90 ppm - 86.5 lbs/Day	25 ppm - 12.0 lbs/Day
CHROMIUM	.60 ppm04 lbs/Day	.03 ppm03 lbs/Day	*
IRON	45 ppm - 2.70 lbs/Day	1.4 ppm -1.35 lbs/Day	.61 ppm29 lbs/Day
NICKEL	.45 ppm027 lbs/Day	*	*
POTASSIUM	6.8 ppm41 lbs/Day	4.43 ppm <b>4.26 lbs/Day</b>	3.72 ppm - 1.79 lbs/Day
SODIUM	3700 ppm - 222 lbs/Day	117 ppm -112 lbs/Day	
TIN	2700 ppm - 162 lbs/Day	64 ppm -61.5 lbs/Day	11 ppm - 5.28 lbs/Day

<sup>\* \*</sup> Cetectable Limits

<sup>----- -</sup> Analysis Not Performed

COUNTERCURRENT RINSING

APPENDIX III	COUNTERCURRENT PHASE III _ CHEMI	RINSING CAL ANALYS[6]	DATE 8/26/75
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLON TO SEWER	0 gal/min - 0 gal/da <b>y</b>	24,000 gal/day	43,200 gal/day
TEMPERA TURE	_	87° F.	175° F.
рН		4.3	7.3
ACIDITY/ALKALINITY		Acidity 6.0 ppm - 1.20 lbs/Day	Alkalinity 14.0 ppm - 5.04 lbs/Day
CHLORIDES	_	80 ppm -16.0 lbs/Day	50 ppm - 18.0 lbs/Day
COD	_		-
FREE CYANIDES	_	lbs/ .176 ppm -0.35 Day	.119 ppm043 lbs/Day
TOTAL CYANIDES	_	lbs/ .251 ppm05 Day	.202 ppm073 lbs/Day
FLUORIDES	-	40 ppm -8.01 Lbs/Day	3.6 ppm - 1.29 lbs√Day
SULFATES	_	1bs/ 153.6 ppm - 30.7 Day	. 149.6 ppm - 53.9 lbs√Day
SUSPENDED SOLIDS	_	1bs/ 6.0 ppm -1.20 Day.	12.0 ppm - 4.32 lbs/Day
CHROMIUM	_	*	*
IRON	_	0.35 ppm07 lbs/Da	y 0.37 ppm13 lbs/Day
NICKEL	-	*	*
POTASSIUM	-	lbs/ 4.73 ppm95 Day	4.31 ppm - 1.55 lbs/Day
SODIUM	-	89 ppm -17.8 lbs/Day	22 ppm - 7.93 lbs/Day
TIN	_	65 ppm -13.0 lbs/Day	9 ppm - 3.24 lbs/Day

<sup>\*</sup>Detectable Limit
\_Analysis not performed.

	THASE III - ON	DILIOND MINITED	DRID O/27/1)
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
flow to sewer	0 gal	24,000 gpd	43,200 gpd
TEMPERA TURE	-	85° F.	177° F.
рH	-	4.1	6.9
ACIDITY/ALKALINITY	_	Acidity lbs./ 10 ppm -2.00 Day	Alkalinity 12.0 ppm - 4.32 lbs./Da
CHLORIDES	_	75 ppm -15.0 lbs/Day	300 ppm - 108 lbs./Day
COD	<u>-</u>		-
FREE CYANIDES	<u>-</u>	lbs/ .170 ppm034 Day	.280 ppm10 lbs./Day
TOTAL CYANIDES		.170 ppm0341bs/Da	7 .345 ppm12 lbs./Day
FLUORIDES	<u>-</u>	44 ppm - 8.81 lbs/Day	8.0 ppm - 2.88 lbs./Day
SULFATES	<u>-</u>	1bs/ 149.6 ppm - 29.9 Day	. 142.8 ppm - 51.5 lbs./D
SUSPENDED SOLIDS	_	lbs/ ll ppm - 2.20 day.	22.0 ppm - 7.93 lbs./Da
CHROMIUM	-	*	*
IRON	-	0.52 ppm10 lbs/Da	v 0.53 ppm19 lbs./Day
NICKEL	-	* .	*
POTASSIUM	-	1bs/ 4.62 ppm92 Day	4.28 ppm - 1.54 lbs./Da
SODIUM	_	87 ppm -17.51bs/Day	
TIN	_	65 ppm -13.0 lbs/Day	

<sup>\*</sup> Detectable Limit.

<sup>- -</sup> Analysis Not Performed

DATE 9/2/75

		TITONII AMADIOAO	DUIT
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 gal	24,000 gpd	43,200 gpd
TEMPERATURE	· -	84° F.	173° F.
pH	-	5.4	8.0
ACIDITY/ALKALINITY	-	Alkalinity Lbs/ 6.0 ppm -1.2 Day	Alkalinity 22 ppm - 7.93 lbs/Day
CHLORIDES	<u>-</u>	1bs/ 32.5 ppm - 6.5 Day	20 ppm - 7.21 lbs/Day
COD	-	1bs/ 10.2 ppm - 2.04 Day	6.8 ppm - 2.45 lbs/Day
FRFE CYANIDES	<u>-</u>	lbs/ .360 ppm072 Day.	.162 ppm058 lbs/Day
TOTAL CYANIDES	<u>-</u>	1bs/ .360 ppm072 Day	.244 ppm088 lbs/Day
FLUORIDES	<u>-</u>	28 ppm - 5.60 lbs/Day	3.4 ppm - 1.22 lbs/Day
SULFATES	<u>-</u>	114.8 ppm - 23.0 Day	, 121 ppm - 43.6 lbs./Day
SUSPENDED SOLIDS	-	lbs/ 47 ppm - 9.41 Day	14 ppm - 5.04 lbs/Day
CHROMIUM	<u>-</u>	*	*
IRON	-	lbs/ 1.49 ppm30 Day	2.35 ppm85 lbs/Day
NICKEL	_	*	*
POTASSIUM	-	4.82 ppm96 lbs/Day	4.32 ppm - 1.56 lbs./Day
SODIUM	-	42 ppm -8.41 lbs/Day	18 ppm - 6.49 lbs./Day
TIN	-	25 ppm -5.00 lbs/Day	4 ppm - 1.44 lbs./Day

<sup>\* \*</sup> Detectable Limit
- Analysis Not Performed

	PRASE III - UHE	MICAL ANALISES	DATE 7/7/17
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 gal	24,000 gpd	43,200 gpd
TEMPERA TURE	<del>-</del>	89° F.	175° F.
Н	-	4.5	8.0
ACIDITY/ALKALINITY	-	0.0 ppm -	Alkalinity 12.0ppm - 4.32 lbs./Day
CHLORIDES	_	80 ppm -16.0 lbs/Day	61 ppm - 22.0 lbs./Day
COD	_	27.2 ppm -5.44 Day	6.8 ppm - 2.45 lbs./Day
FREE CYANIDES	-	1bs/ .176 ppm035 Day	.09 ppm032 lbs./Day
TOTAL CYANIDES	_	lbs/ .330 ppm066 Day .	.148 ppm054 lbs./Day
FLUORIDES		64 ppm -12.8 Lbs/Day	1.7 ppm61 lbs./Day
SULFATES	<u>-</u>	lbs/ 112 ppm -22.4 Day .	100 ppm - 36.0 lbs./Day
SUSPENDED SOLIDS	-	75 ppm -15.0 lbs/Day	17 ppm - 6.12 lbs./Day
CHROMIUM	-	*	*
IRON	-	0.76 ppm -15 lbs/Day	0.66 ppm24 lbs./Day
NICKEL	-	*	*
POTASSIUM	-	4.61 ppm -92 lbs/Day	4.22 ppm - 1.52 lbs./Day
SODIUM	-	74 ppm -14.8 lbs/Day	14 ppm - 5.04 lbs./Day
TIN	-	52 ppm -10.4 lbs/Day	4 ppm - 1.44 lbs./Day

<sup>\*</sup> Detectable Limit

<sup>- -</sup> Analysis Not Performed

DATE 9/11/75

	FRASE III - CHER	TICAL ANALISAS	DATE 9/11/17
·	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	O gal	23,826 gpd	43,200 gpd
TEMPERA TURE	-	91° F.	175° F.
pH Hq	-	4.4	8.1
ACIDITY/ALKALINITY	-	Acidity lbs/ 2.0 ppm40 Day	Alkalinity 22 ppm - 7.93 lbs./Day
CHLORIDES		50 ppm -9.94 lbs/Day	67.5 ppm - 24.3 lbs./Day
COID	••	17 ppm -3.38 lbs/Day	6.8 ppm - 2.45 lbs./Day
FREE CYANIDES	_	lbs/ .176 ppm035 Day .	.032 ppm012 lbs./Day
TOTAL CYANIDES	-	lbs/ .176 ppm035 Day	.191 ppm069 lbs./Day
FLUORIDES	-	1bs/ 56.0 ppm -11.1 Day	2.0 ppm72 lbs./Day
SULFATES	-	1bs/ 142.8 ppm -28.4 Day	121.2 ppm - 43.7 lbs./Day
SUSPENDED SOLIDS	_	1bs/ 47.0 ppm -9.34 Day	20.0 ppm - 7.21 lbs./Day
CHROMIUM	<u>-</u>	*	*
IRON	<b>-</b>	1bs/ 0.26 ppm052 Day	0.59 ppm - 0.21 lbs./Day
NICKEL		*	*
POTASSIUM		1bs/ 4.52 ppm090 Day	4.20 ppm - 1.51 lbs./Day
SODIUM	_	50 ppm -9.94 lbs/Day	13 ppm - 4.68 lbs./Day
TIN	<u> </u>	50 ppm -9.94 lbs/Day	6 ppm - 2.16 lbs./Day

<sup>\* &</sup>lt;Detectable Limit
- - Analysis Not Performed</pre>

	LUNDE III - OUEN	ITUAL ANALISIS	DATE // TZ/ / 3
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 Gal	23 <b>,8</b> 26 gpd	43,200 gpd
TEMPERA TURE	<u>-</u>	90° F.	180° F.
Hg	_	4.6	7.0
ACIDITY/ALKALINITY	_	Alkalinity 2.0 ppm40 lbs/Day	Alkalinity 18.0 ppm - 6.49 lbs./Day
CHLORIDES	-	65 ppm -12.9 lbs/Day	18.5 ppm - 6.67 lbs./Day
COD	_	_	_
FREE CYANIDES	_	1bs/ .162 ppm032 Day .	.082 ppm030 lbs./Day
TOTAL CYANIDES	_	lbs/ .162 ppm032 Day .	.220 ppm079 lbs./Day
FLUORIDES	<u>-</u>	48 ppm -9.54 lbs/Day	1.24 ppm45 lbs./Day
SULFATES		146 ppm -29.0 lbs/Day	135.6 ppm - 48.9 lbs./Day
SUSPENDED SOLIDS	_	55 ppm -10.9 lbs/Day	38 ppm - 13.7 lbs./Day
CHROMIUM	_	*	*
IRON	<del>-</del>	0.50 ppm10 lbs/Day	0.71 ppm26 lbs./Day
NICKEL	<del>-</del>	*	*
POTASSIUM	<u>-</u>	4.70 ppm93 lbs/Day	4.25 ppm - 1.53 lbs./Day
SODIUM	-	53 ppm -10.5 lbs/Day	12 ppm - 4.32 lbs./Day
TIN		125 ppm -24.8 lbs/Day	

		EMICAL ANALYSES	DATE 9/18/75
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 gal	36,000 gpd	25,488 gpd
TEMPERATURE	<u>-</u>	93 <sup>0</sup> F.	178° F.
pH	<u>-</u> ,	6.7	7.5
ACIDITY/ALKALINITY	-	Alkalinity 18 ppm -5.4 lbs/Day	Alkalinity 20 ppm - 4.25 lbs./Day
CHLORIDES		20 ppm-6.0 lbs/Day	54 ppm - 11.5 lbs./Day
COD		11.9 ppm-3.6 lbs/Day	7 5.1 ppm - 1.08 lbs./Day
FREE CYANIDES	_		ay .066 ppm914 lbs./Day
TOTAL CYANIDES		1bs/ .096 ppm029 Day	.066 ppm014 lbs./Day
FLUORIDES		14 ppm -4.20 lbs/Day	7 1.6 ppm34 lbs./Day
SULFATES	-	114.8 ppm-34.5 lbs/Da	97.2 ppm - 20.7 lbs./Day
SUSPENDED SOLIDS	-	32 ppm-9.61 lbs/Day	26 ppm - 5.53 lbs./Day
CHROMIUM	_	*	*
IRON		.72 ppm22 lbs/Da	0.93 ppm - 0.20 lbs./Day
NICKEL	-	*	* .
POTASSIUM	-	4.63 ppm-1.39 lbs/Da	4.27 ppm - 0.91 lbs./Day
SODIUM	-	30 ppm _9.01 lbs/Day	14 ppm - 2.98 lbs./Day
TIN		26 ppm -7.81 lbs/Day	12 ppm - 2.55 lbs./Day

<sup>\* &</sup>lt; Detectable Limit
- - Analysis Not Performed

DATE 9/19/75

	PHASE III - CHEM	ILCAL ANALYSES	DATE 9/19/75
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SWWER	0 gal	36,000 gpd	25,488 gpd
TEMPERA TURE		87° F.	177° F.
Hq	-	6.2	7.3
ACIDITY/ALKALINITY		Alkalinity 10 ppm-3.00 lbs/Day	Alkalinity 20 ppm - 4.25 lbs./Day
CHLORIDES		35 ppm-10.5 lbs/Day	16.0 ppm - 3.4 lbs./Day
COD		10.2 ppm-3.06 lbs/Da	78.5 ppm - 1.81 lbs./Day
FREE CYANIDES	<del>-</del>	.066 ppm020 lbs/Day	.066 ppm014 lbs./Day
TOTAL CYANIDES	_		.238 ppm051 lbs./Day
FLUORIDES	-	1bs/ 22.64 ppm-6.80 Day	3.3 ppm - 0.70 lbs./Day
SULFATES	_	1bs/ 114.8 ppm-34.5 Day	97.2 ppm - 20.7 lbs./Day
SUSPENDED SOLIDS	-	54 ppm-16.2 lbs/Day	33 ppm - 7.01 lbs./Day
CEROMIUM	-	*	*
IRON	_	0.83 ppm25 lbs/Day	1.27 ppm - 0.27 lbs./Day
NICKEL	<u>-</u>	*	*
POTASSIUM	<u>-</u>	4.68 ppm-1.14 lbs/bay	4.33 ppm092 lbs./Day
SODIUM	_	23 ppm-6.91 lbs/Day	15 ppm - 3.19 lbs./Day
TIN	-	16 ppm-4.80 lbs/Day	3 ppm64 lbs./Day

<sup>\* \*</sup> Cetectable Limit

<sup>- -</sup> Analysis Not Performed

DATE 9/26/75

•	PHASE III - CHEM	CAL ANALYSES	DATE 9/20/75
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 gal	22,320 gpd	39,312 gpd
TEMPERATURE		85° F.	175° F.
PH	_	8.1	6.5
ACIDITY/ALKALINITY		Alkalinity 28 ppm-5.21 lbs/Day	Alkalinity 12.00 ppm - 3.93 lbs./Day
CHLORIDES	-	54 ppm-10.1 lbs/Day	30 ppm - 9.84 lbs./Day
COD	_	1bs/ 20.4 ppm_3.80 Day	6.8 ppm - 2.23 lbs./Day
PREE CYANIDES		.104 ppm02 lbs/Day	.046 ppm015 lbs./Day
TOTAL CYANIDES	_	.104 ppm02 lbs/Day	.135 ppm044 lbs./Day
LUCRIDES		35.2 ppm-6.55 lbs/Day	2.0 ppm - 0.66 lbs./Day
SULFATES	-	1bs/ 124.8 ppm_23.2 Day	102.8 ppm - 33.7 lbs./Day
SUSPENDED SOLIDS	_	64 ppm_11.9 lbs/Day	21 ppm - 6.89 lbs./Day
CHRONIUM	-	*	*
IRON	-	0.85 ppm16 lbs/Day	0.93 ppm - 0.30 lbs./Day
NICKEL		*	*
POTASSIUM	_	4.70 ppm_0.87 lbs/De	4.19 ppm - 1.37 lbs./Day
SODIUM	-	41 ppm-7.63 lbs/Day.	14 ppm - 4.59 lbs./Day
TIN	-	40 ppm_7.45 lbs/Day	6 ppm - 1.97 lbs./Day

<sup>\*</sup> Optectable Limit
- Analysis Not Performed

		PRIORE ANALIDED	DATE 7/20/13
	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 Gal	27,792 gpd	72,000 gpd
TEMPERA TURE	·	89° F.	176° F.
Hq	_	4.7	7.8
ACIDITY/ALKALINITY	-	Alkalinity 4.0 ppm -0.93 lbs/Day	Alkalinity 24 ppm - 14.4 lbs./Day
CHLORIDES		32 ppm -7.42 lbs/Dry	22 ppm - 13.2 lbs./Day
COD	_	1bs./ 24.08 ppm-5.58 Day	6.88 ppm - 4.13 lbs./Day
FREE CYANIDES	_	1bs/ .131 ppm030 Day	.054 ppm032 lbs./Day
TOTAL CYANIDES	<u>-</u>	lbs/ .176 ppm041 Day	.122 ppm073 lbs./Day
FLUORIDES	<u>-</u>	22 ppm-5.10 lbs/Day	2.0 ppm - 1.20 lbs./Day
SULFATES		lbs/ 89.2 ppm_20.7 Day .	86.8 ppm - 52.1 lbs./Day
SUSPENDED SOLIDS	<u>-</u>	49 ppm-11.4 lbs/Day	15 ppm - 9.01 lbs./Day
CHROMIUM		*	*
IRON	<u>-</u>	0.83 ppm19 lbs/Day	0.68 ppm41 lbs./Day
NICKEL		*	*
POTASSIUM	_	4.59 ppm-1.06 lbs/Day	4.25 ppm - 2.55 lbs./Day
SODIUM		70 ppm-16.2 lbs/Day	ll ppm - 6.61 lbs./Day
TIN	-	73 ppm_16.9 lbs/Day	7 ppm - 4.20 lbs./Day

<sup>\* &</sup>lt;Detectable Limit
- Analysis Not Performed</pre>

DATE 10/3/75

<u> </u>	FRASE 111 - CHEM	ICAL ANALISES	DATE 10/3/73
₹.0*4	COUNTERCURRENT TANK	SPRAY WASH	HOT RINSE
FLOW TO SEWER	0 gal	31,536 gpd	86,400 gpd
TEMPERATURE	_	91° F.	177° F.
Ha	· .	5.3	8.0
ACIDITY/ALKALINITY	<u>-</u>	Alkalinity 6 ppm-1.58 lbs/day	Alkalinity 26 ppm - 18.7 lbs./Day
CHLOR IDES		28 ppm-7.36 lbs/Day	29 ppm - 20.9 lbs./Day
COD	<u>-</u>	lbs/ 13.6 ppm=3.58 Day	3.4 ppm - 2.45 lbs./Day
FIEE CYANIDES	_	1bs/ .140 ppm037 Day	.050 ppm036 lbs/Day
TOTAL CYANIDES	_	1bs/ .140 ppm037 Dav	.073 ppm053 lbs./Day
FLUORIDES			1.2 ppm - 0.86 lbs./Day
SULFATES		1bs/ 77.2 ppm-20.5 Day	92 ppm - 66.3 lbs./Day
SUSPENDED SOLIDS	<u>-</u>	54 ppm_14.2 lbs/Day	18 ppm - 13.0 lbs./Day
CHROMIUM	-	*	* /
IRON	_	0.58 ppm15 lbs/Day	0.84 ppm61 lbs./Day
NICKEL	<u> </u>	*	*
POTASSIUM	<u>-</u>	1bs/ 4.63 ppm-1.22 Day	4.20 ppm - 3.03 lbs./Day
SODIUM	-	35 ppm9.21 lbs/Day	11 ppm - 7.93 lbs./Day
TIN	-	31 ppm_8.15 lbs/Day	5 ppm - 3.60 lbs./Day

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)				
3. RECIPIENT'S ACCESSION NO.				
5. REPORT DATE September 1977				
6. PERFORMING ORGANIZATION CODE				
8. PERFORMING ORGANIZATION REPORT NO.				
10. PROGRAM ELEMENT NO.				
1BB610; ROAP 21ADT-003				
11. CONTRACT/GRANT NO.				
Grant S801989				
13. TYPE OF REPORT AND PERIOD COVERED Final; 2/73-5/76				
14. SPONSORING AGENCY CODE				
EPA/600/13				

Mail Drop 62, 919/541-2733.

16. ABSTRACT The report describes the results of the first use of countercurrent rinsing (involving the use of a compartmentized rinse tank) in high-speed strip plating lines. The objective of using this rinse method is to reduce the amount of water required so as to have a volume of liquid more easily handled in recovering chemicals. The first unknown studied was the operating performance of the multistage rinse system to determine if the basic principles of countercurrent rinsing would hold for a high-speed strip plating operation. Second was the best way to recover the chemicals in the concentrated stream from this rinse system. The report also describes problems encountered in recycling the concentrated rinse into the main plating system. It also describes new technology for solving these problems and an alternate method involving indirect recycling using the detinning plant.

17. KEY WO	ORDS AND DOCUMENT ANALYSIS	
a. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Rinsing	Stationary Sources	13H,07A
Plating	Countercurrent Rinsing	
Tin Coatings	Tinplating	11C
Halogens	Chemical Recovery	07B
Circulation	Detinning	
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