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FINAL REPORT FOR POLLUTION PREVENTION CHALLENGE GRANT

Prepared by: Dann Dettman, Project Coordinator

CAROLINA GALVANIZING CORPORATION

I. Project Scope and Pollution areas addressed:

During the galvanizing process metal is pickled in hydrochloric acid to remove metal scale and rust prior to applying a zinc coating. A fresh pickling bath starts out at 15% hydrochloric acid with little or no dissolved metals present. As the work is processed, iron is dissolved into the bath and the metal level rises. Zinc is also introduced into the bath by means of stripping reject work or from zinc left on racks and fixtures from previous galvanizing runs. As the metals rise, the free hydrochloric acid level drops and more must be added to maintain the pickling rate. Eventually a dissolved metal level will be reached where pickling action will cease and the bath must be discarded. Due to the low pH and high metal content, this material must be handled as a hazardous waste. Present state and federal regulations require the waste to be solidified and stabilized prior to landfilling, or the material may be deep well injected until November 1990.

In lieu of land disposing as a waste, a method to separate the 3 major components was investigated. If successful, this would allow the recovered acid to be reused in the pickle process. Iron chloride recovered from the waste could be used as a water conditioner for waste treatment operations and the zinc chloride recovered could be used in the pretreatment operation called fluxing prior to galvanizing or sold to other industries needing zinc chloride.

Chemical analysis shows the main components in the pickle liquor waste vary in strength. Typically the range is:

5-8% Hydrochloric Acid  
5-10% Iron chloride (Ferrous and Ferric)  
4-11% Zinc chloride  
0.5% Misc. metals  
Balance water  
pH 0-1

Separation methods investigated included ion exchange, selective chemical precipitation, metal encapsulation, and spray roasting.

## II. Assessment of Technology

### 1. Ion Exchange

Two sources of ion exchange technology were investigated. The first source was manufactured by Eco-Tec Limited located in Pickering, Ontario. The unit they manufacture is called Acid Purification Unit (APU) and is designed to continually remove mixed heavy metals from acids by absorbing free acid on the ion exchange resin beads and allowing the metals to pass through. This stream containing the metals is removed from the system and discarded as a byproduct which is normally chemically treated by conventional metal precipitation methods which result in a mixed metal sludge that must be landfilled. The application we were seeking would take this mixed metal stream and remove the zinc resulting in a zinc chloride solution and a iron chloride solution with a small amount of various metals remaining in the iron solution. By coupling another metal selective ion exchange unit with the APU unit, this separation was attempted.

The initial step was to conduct a performance analysis. A 2.5 GPM size was selected in order to process all of the waste pickle liquor generated by Carolina Galvanizing Corporation in one month by operating the system one shift daily throughout the month. An average waste feed stream was characterized at:

8% free HCl  
10% iron  
6% zinc

Although this "typical" stream would not remain constant from batch to batch, it would give us a point on which to analyze the performance.

The results of the performance analysis were not favorable, even using the lowered metal values. The recovered streams are as follows:

Recovered HCl	6% HCl	2% Iron	2.3 GPM
Recovered Iron	1.3% Iron	0.3% HCl	1.7 GPM
Recovered zinc	0.5% Zinc	0.6% Iron	0.2% HCl 31 GPM

The recovered streams were unacceptable for the following reasons:

1. Recovered HCl values too low in strength to effectively pickle steel
2. Recovered zinc solution has too low of a zinc value and too high of an iron level (actually higher than the zinc).
3. Recovered iron solution too weak to be of any commercial value or use as a water conditioner.
4. High water consumption to process waste (35 GPM).
5. Weak solutions resulting in large volumes - would require excessive storage capacity and additional equipment to re-concentrate to usable levels.

Costs for equipment to produce the above results are \$200,000. With the resulting streams being of no usable or commercial value, additional equipment would have to be purchased to strengthen the solutions. Estimated costs for this equipment would exceed \$300,000 as one unit would be required for each stream. In addition, added auxiliary equipment and tanks would be required and additional labor requirements make this process unattractive. Furthermore, once the excess water is removed during the concentration operations, treatment would be required to meet discharge limitations for POTW use.

Even considering these disadvantages, the greatest one is the high iron level in the zinc stream, which produces the largest volume. Even after concentration, the iron level would be too great for reusing in the galvanizing process and would be of no commercial value for any known process requiring zinc chloride solutions.

A second source of ion exchange resin was tested to improve the zinc removal efficiency and system performance. A sample of a zinc selective ion exchange resin, trade name Amberlite IRA-400, was obtained from Rohm and Haas Company of Philadelphia, PA. Bench scale tests were performed on the

resin using an acid adjusted to similar values. In addition, a worst case acid bench test was performed using an acid with 11% zinc. These results were even less favorable.

It has been determined that the acid contains iron dissolved as ferrous and ferric ions. As a result, the ion exchange resin cannot differentiate between the zinc ions and the ferric ions, thus separation by ion exchange is not possible with the mixed iron ions.

In conclusion, the ion exchange equipment available today can effectively remove metals from a pickling bath in low concentrations, but are not efficient if the metal levels exceed 2%. In order to utilize ion exchange equipment to recover free acid, CGC would need a unit on each of its twelve pickle tanks at a cost of over 1.5 million dollars. Even with this equipment, effective metal separation would not be possible in order to recover the zinc.

## 2. Selective Chemical Precipitation

Methods for selective precipitation investigated included using lime and trisodium phosphate to drop out iron and leave zinc in solution. Both methods would require using a conventional metal removal waste treatment system (neutralization, clarification filtration) and produces an iron rich sludge of no marketable value which must be landfilled. No free acid recovery would be possible as the acid would be neutralized prior to metal precipitation. The resulting zinc solution still contained an appreciable amount of iron due to the mixed iron ions. Oxidizing the iron effectively reduced the iron level in the zinc solution. Although this method was investigated knowing full recovery was not possible, the results were unacceptable due to:

1. No free acid recovery
2. Iron rich sludge must be landfilled, although it could be considered non-hazardous under RCRA.
3. Time and labor consuming process.
4. Poor quality zinc solution recovered due to presence of iron and other metals.

5. Conventional waste treatment system required.

3. Metal Encapsulation

This method involved using a proprietary product available from Wagnerite systems Inc. of Gulfport, MS. This product, named SIOCH Acid Extender, uses a sodium silicate based catalyst to encapsulate metals dissolved in the acid and drops them out of solution as a sludge. Periodic tank cleanouts are necessary to remove the sludge from the tank bottom. A pickle tank can be extended up to four times the normal period of effective use. This system cannot recover any metals. The sludge must be landfilled, and according to the producer, is considered non-hazardous although we did not test to verify this claim.

A special waste treatment system is used to process this sludge to landfillable quality (no free liquids). This system is not desirable due to:

1. Special waste treatment system required.
2. No metal recovery - sludge must be landfilled.
3. Sludge volume increased over conventional treatment.

4. Spray Roasting

The spray roasting method investigated is built by Perox Inc. of Pittsburgh, PA. Spray roasting involves spraying concentrated waste acid into a refractory furnace to be heated. The gases exit the top of the roasting chamber and pass to an absorbing chamber to be converted back to liquid acid. The iron is converted to iron oxide and settles to the bottom of the roaster as granular solids. This system actually regenerates acid by converting the iron chloride to hydrochloric acid and iron oxide. High quality iron oxide is marketable and in high demand. A 20% hydrochloric acid solution can be produced with a 99% regeneration efficiency. The problem is it cannot convert high levels of zinc chloride. At 1% zinc the resulting iron oxide will be too contaminated to be of any commercial value and the zinc chloride will carry over as a gas and crystallize out in the scrubber unit and piping plugging up the system. This

method, although promising for regenerating acid and iron chloride, cannot handle zinc in excess of 0.5%, thus it would not be acceptable for galvanizing waste acid.

# GENERAL APU<sup>®</sup> PROCESS

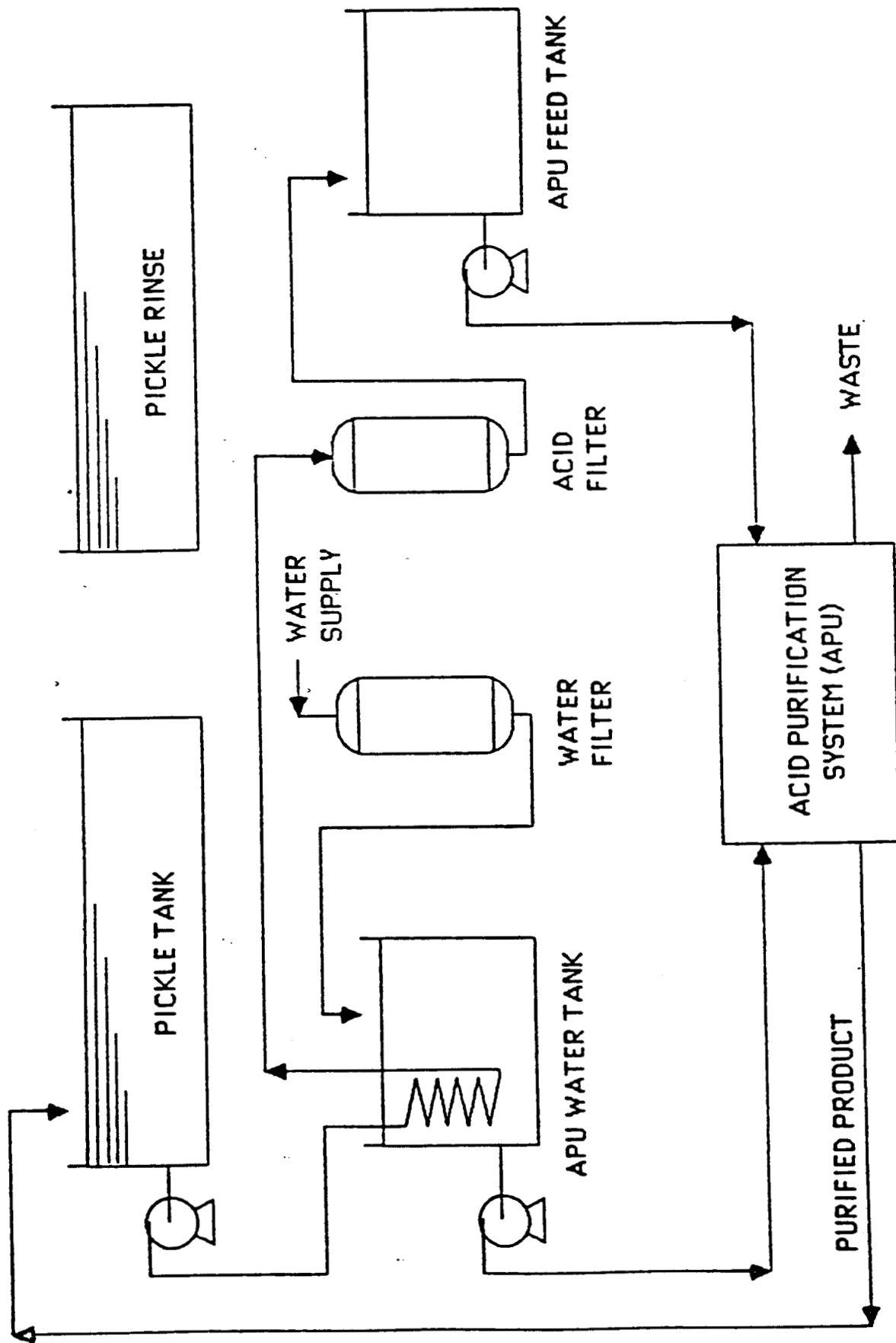
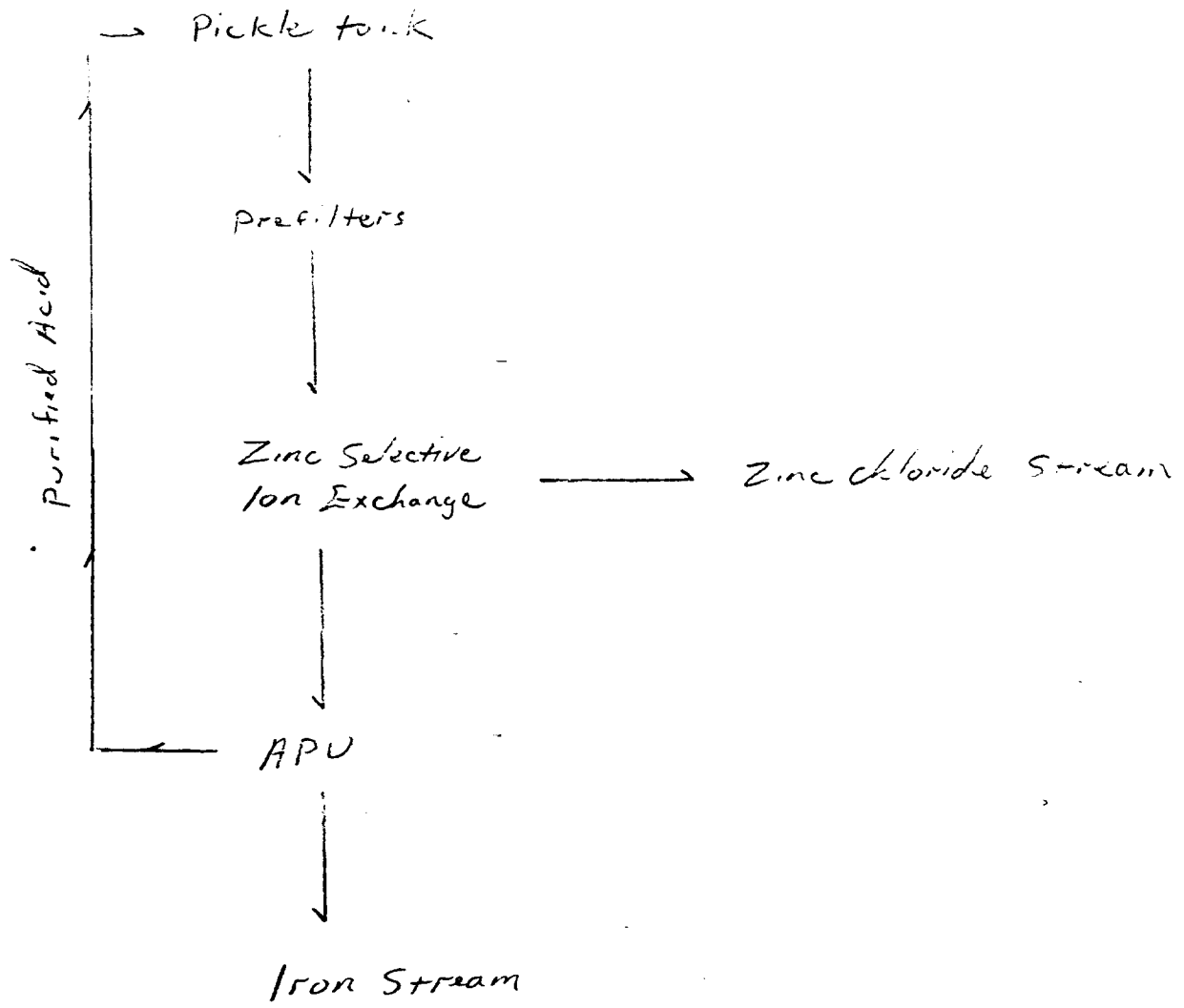


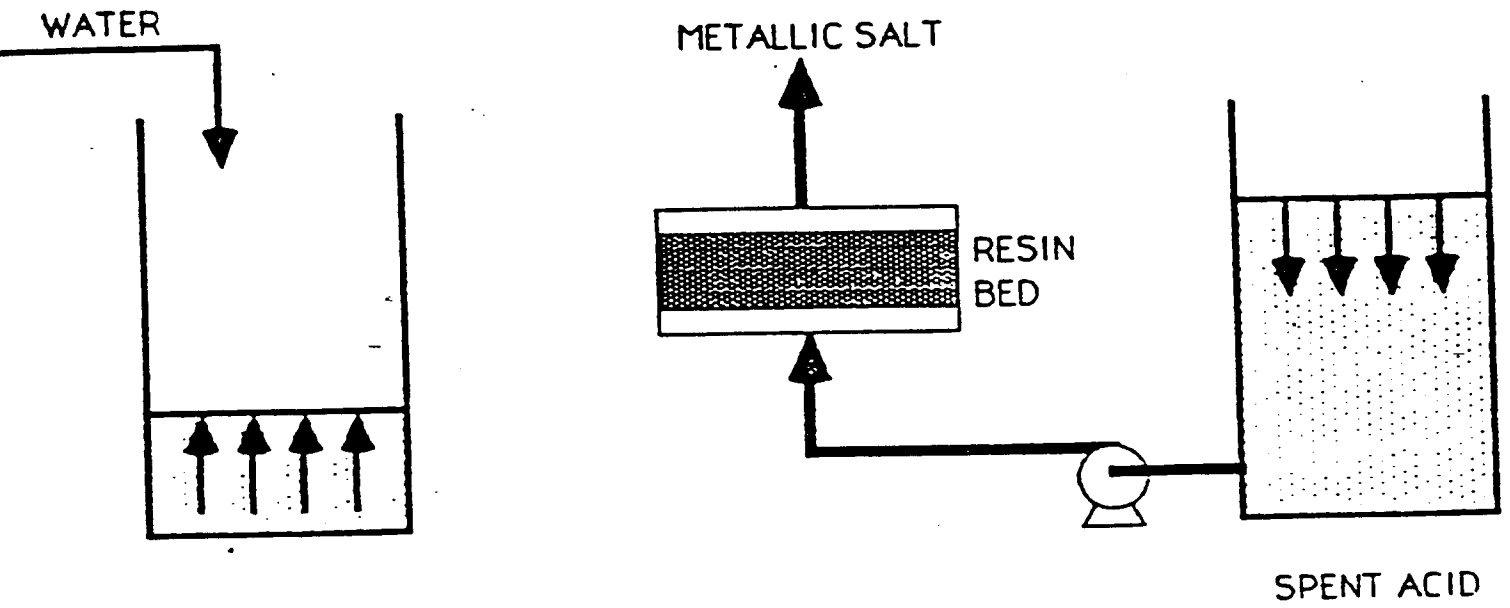
FIGURE 1: TYPICAL ACID PURIFICATION (APU) SYSTEM PROCESS



# Modified System



# UPSTROKE



# DOWNSTROKE

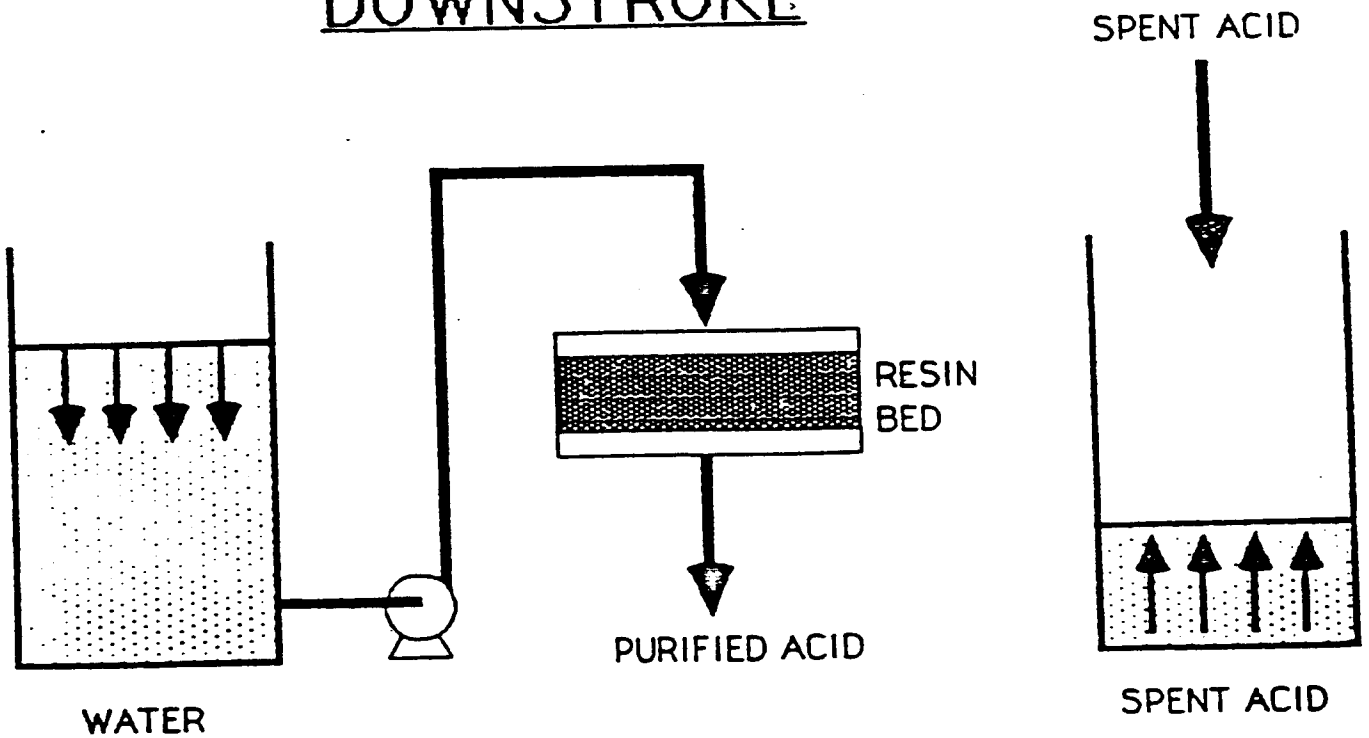


FIGURE 3: STEPS IN THE APU<sup>®</sup> PROCESS

Carolina Galvanizing - APU performance

<u>Stream</u>	Composition (g/L)			Flow (l/h)	G/m	G/hour
	Zn	Fe	HCl			
Feed	60	100	80	566	2.5	150
Zn free Product	-	21	60	566	2.5	150
Zn waste	4.8	6.4	1.6	7018	31	1860
Fe free Product	-	13	62	530	2.3	140
Fe waste	-	12.6	2.8	395	1.7	100

- % free acid recovery = 73%

Budgetary cost - \$200,000.00

Mr Dan Dettman  
Carolina Galvanizing Corp  
PO Box 487  
Aberdeen, NC 28315



Independence Mall West

**From:**  
Charlie Dickert  
Technical Support Manager  
Fluid Process Chemicals

**Date:** 9-1-88

**Comments:**

Dan: We spoke about using this resin to pull Zn from the pickle liquor as the anionic complex. Iron should not be removed by the resin if it is in the ferrous form. Zn can then be recovered from the resin simply by rinsing with water. The only hitch to the separation is the high concentration of the metals. If so, then we should consider this approach very early in the life of the bath when metal concentrations are lower.

**Your Local Contact is: Ed Nace**

**Telephone: 609-488-9713**

<u>Sample(s) Sent</u>	<u>Ionic Form</u>	<u>Literature Enclosed</u>
Amberlite IRA-400	Cl	IRA-400

**Ready to use as supplied?**

**Yes X**

**No**

**If not, suggested pretreatment:**

The following test conditions are suggested for the initial trials. Depending upon the results other conditions should be explored especially with respect to economizing the system if a commercial installation is planned.

**Adsorption flow rate 0.5 gpm/CF**

**Other: Same as 4 BV/hr**

**Regenerant: Water**

**Regeneration flow rate: 0.25 gpm/CF**

## Amberlite Resin Test Procedure

A column to hold the ion exchange resin was constructed from pvc pipe which allowed stream to be fed through resin. Exit stream was checked for zinc metal every 20 mls. Test was stopped when metal level started to rise. The stream was then fully analyzed for zinc, iron and acid.

Resin regeneration was accomplished by passing DI water through the column. A conductivity probe measured the exit stream and regeneration was stopped when conductivity levels dropped. Exit stream was analyzed for zinc, iron and acid.

Amberlite Resin Test Results

Feed Acid "Typical"

6% Zinc      60,000 ppm  
10% Iron      100,000 ppm  
8% Hydrochloric Acid

Run 1

Zinc Free Product (iron stream)

42 ppm Zn      3800 ppm Fe      7% Acid      200 ml

Zinc Stream

3200 ppm Zn      6100 ppm Fe      1% Acid      2800 ml

Run 2

Iron Stream

220 ppm Zn      3900 ppm Fe      5% Acid      220 ml

Zinc Stream

3900 ppm Zn      6990 ppm Fe      1% Acid      2600 ml

Run 3

Iron Stream

190 ppm Zn      3400 ppm Fe      7% Acid      200 ml

Zinc Stream

3100 ppm Zn      5200 ppm Fe      1% Acid      3100 ml

Run 4

Iron Stream

57 ppm Zinc      3700 ppm Fe      7% Acid      180 ml

Zinc Stream

4100 ppm Zinc      5100 ppm Fe      1% Acid      2800 ml

Amberlite Resin Test Results  
Feed Acid "Worst Case"

5% Iron 50,000 ppm  
11% Zinc 110,000 ppm  
6% Acid

Run 1

Iron Stream

290 ppm Zinc 4400 ppm Fe 4% Acid 60m

Zinc Stream

270 ppm Zn 120 ppm Fe 0 Acid 18,600 m

Run 2

Iron Stream

240 ppm Zn 3900 ppm Fe 5% Acid 40m

Zinc Stream

210 ppm Zn 140 ppm Fe 0 Acid 19500 m

## Selective Metal Precipitation

### Phosphate Method

1. Add Trisodium Phosphate slurry to acid waste until pH is 2.6
2. Allow solids to settle - Add polymer to aid precipitation
3. Decant liquid and Analyze for Zinc, Iron and Acid

### Lime Method

1. Add lime slurry (high calcium hydrated lime) to acid waste until pH is 4.0
2. Allow solids to settle - Add polymer to aid precipitation
3. Decant liquid and analyze for Zinc, Iron, and acid.

Analysis of pilot scale testing expanded to include Iron, Zinc, Acid, Nickel, Copper, Chromium, Cadmium, and Lead.



## Selective Metal Precipitation Test Results

### Phosphate Method on Typical Acid

Bench Test Iron 1% Zinc 5% Acid 1%

Pilot Test Fe 9400 ppm  
Zn 47000 ppm  
Acid 1%  
Pd 76 ppm  
Cu 140 ppm  
Ni 1500 ppm  
Cd 10 ppm  
Cr 600 ppm

### Lime Method on Typical Acid

Bench Test Iron < 1% Zinc 5% Acid 0

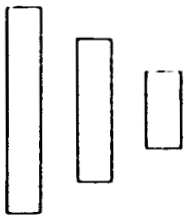
Pilot Test Fe 6000 ppm  
Zn 48000 ppm  
Acid None Detected  
Pd 50 ppm  
Cu 120 ppm  
Ni 1100 ppm  
Cd 10 ppm  
Cr 520 ppm

### Moisture Content of Sludges

Lime sludge 75%

Phosphate sludge 70%

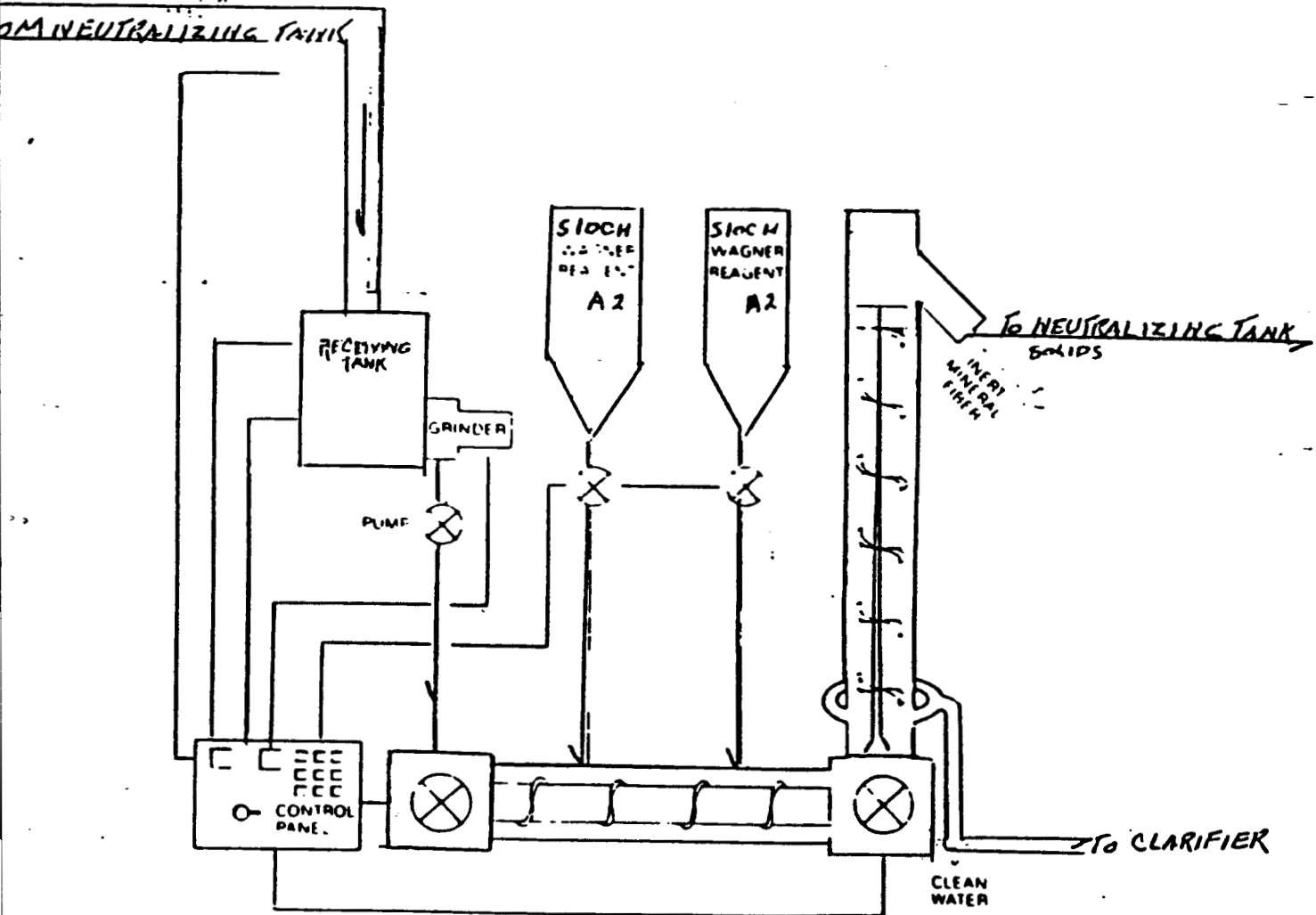
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# WAGNERITE SYSTEMS, INC.

4422 West Beach • Gulfport, MS 39501 USA  
(601) 868-1162

## Liquid Treatment Process



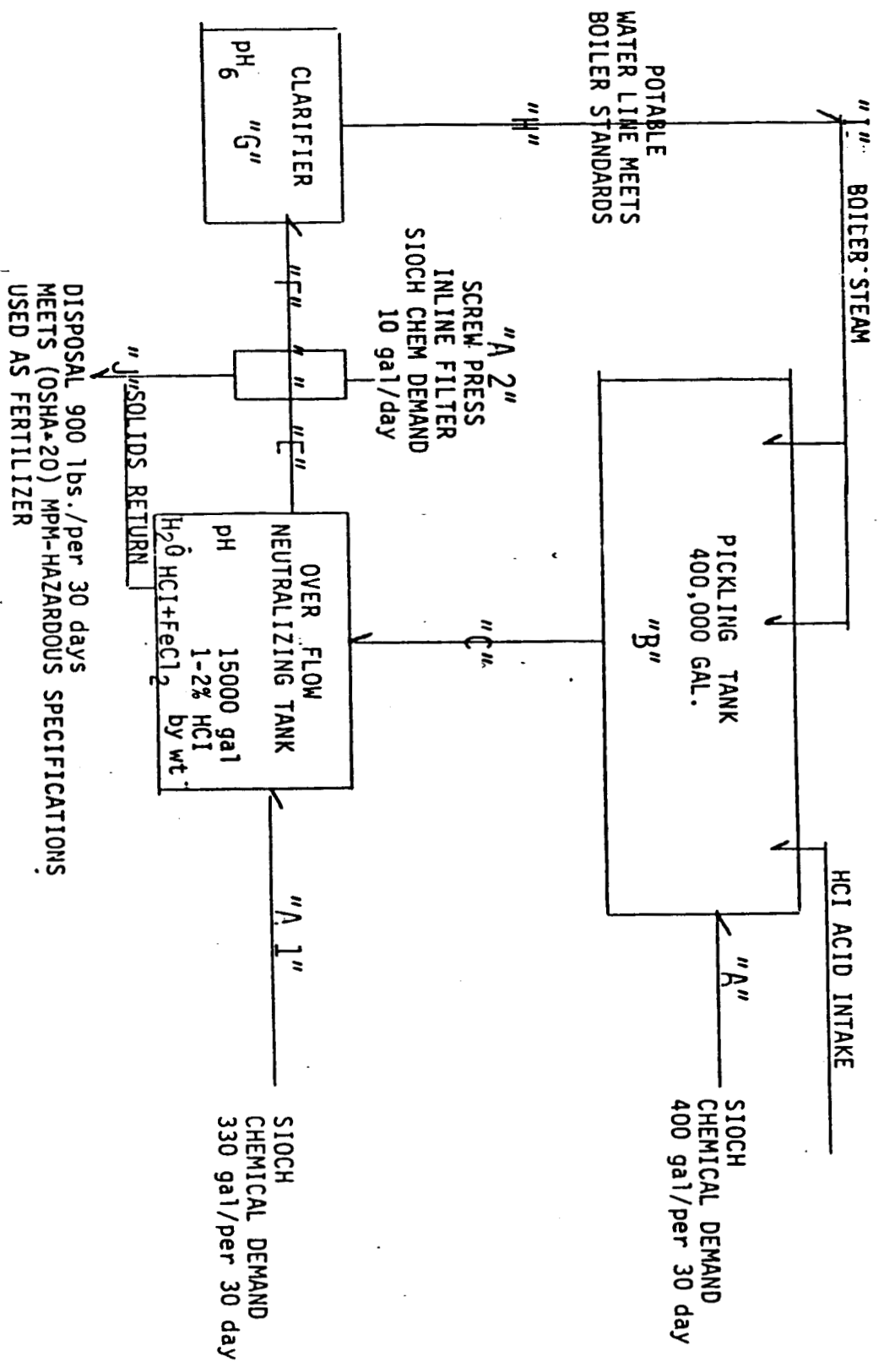
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SCREW PRESS

# WAGNERITE SYSTEMS, INC.

4422 West Beach • Gulfport, MS 39501 USA  
(601) 868-1162

## CLOSED LOOP FLOW SYSTEM



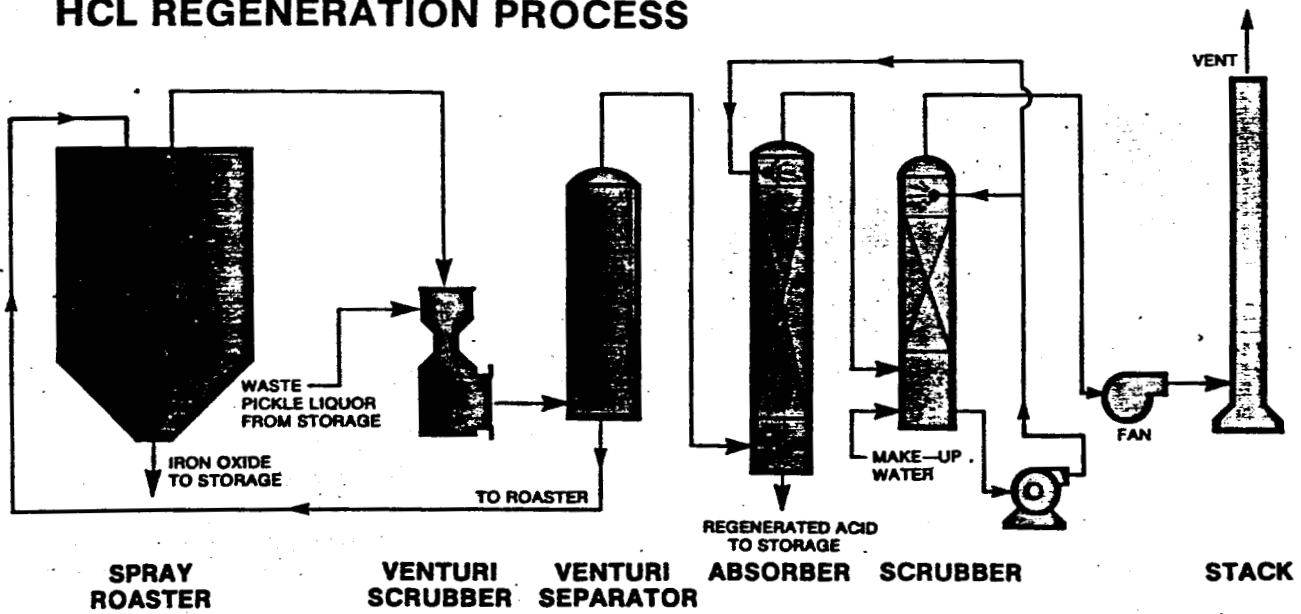
Test results Metal Encapsulation  
SIOCH Acid Extender

Procedure

1. To 3 gal Acid add SIOCH slurry
2. Circulate for 3 Hours
3. Test for Iron and Acid

Run		<u>Before</u>	<u>AFTER Treatment</u>
Run 1	Acid	11 %	11 %
	Iron	6 %	4 %
Run 2	Acid	9 %	9 %
	Iron	5 %	4 %
Run 3	Acid	9 %	8 %
	Iron	6 %	5 %
Run 4	Acid	11 %	9 %
	Iron	6 %	3 %
Run 5	Acid	4 %	2 %
	Iron	5 %	5 %

# SPRAY ROASTER HCL REGENERATION PROCESS



## LAB testing

Three waste samples characterized by Heritage Environmental Services for Zinc and Iron content. In House testing performed using Hach DR/2000 spectrophotometer and Hach test kits and reagents, or "pickle pill" titration capsules manufactured by

Foremost Supply Co., Inc

Henderson, Ky

Ion exchange performance analysis was provided by Eco-Tec Lmtd.

**SERVICE LOCATION**  
INDIANAPOLIS, IN



**QUOTATION NUMBER**  
08-05-19  
**HES WASTESTREAM NO.**  
08-05-19

HERITAGE ENVIRONMENTAL SERVICES, INC  
CORPORATE HEADQUARTERS  
7901 WEST MORRIS STREET  
INDIANAPOLIS, INDIANA 46221  
317/243-0811

**WASTESTREAM PROFILE**

**WASTE DESCRIPTION / COMMON NAME**

SPENT PICKLE LIQUOR

**DOT SHIPPING / HAZARD CLASS**

RQ, WASTE ACID LIQUID, CORROSIIVE LIQUID, UN1760 (K062)

UPON LABORATORY ANALYSIS OF A REPRESENTATIVE SAMPLE, THE FOLLOWING MAJOR CONSTITUENTS WERE EVALUATED:

ANALYTE	ACTUAL VALUES	UNIT	ALLOWABLE RANGE
001 SOLIDS	10	%	
002 PH	<1		
003 IRON	49,600		
004 ZN	111,000		

Any oils, oily wastes or other materials shipped to HES, Inc. which contain detectable levels of PCB's (Polychlorinated Biphenyls) will subject the generator (or other responsible party) to all reasonable costs for proper transport, disposal and or decontamination of all contaminated materials and equipment.

Generators of oils, or oily wastes must provide a certification to HES that the waste is not contaminated with any constituents other than those incidental to normal use.

GENERATOR WARRANTY: To the best of my knowledge the above is a true, accurate and complete description of the waste material offered for disposal and/or reclamation.

(Signature)

**SERVICE LOCATION**  
INDIANAPOLIS, IN



**QUOTATION NUMBER**  
08534  
**HES WASTESTREAM NO.**  
09052512

**HERITAGE ENVIRONMENTAL SERVICES, INC.**  
CORPORATE HEADQUARTERS  
7901 WEST MORRIS STREET  
INDIANAPOLIS, INDIANA 46231  
317/243-0811

**WASTESTREAM PROFILE**

**WASTE DESCRIPTION / COMMON NAME**  
SPENT PICKLE LIQUOR  
**DOT SHIPPING / HAZARD CLASS**  
RQ, WASTE ACID LIQUID, CORROSIVE LIQUID, UN1760 (K062)

UPON LABORATORY ANALYSIS OF A REPRESENTATIVE SAMPLE, THE FOLLOWING MAJOR CONSTITUENTS WERE EVALUATED:

ANALYTE	ACTUAL VALUES	UNIT	ALLOWABLE RANGE
001 SOLIDS	10	%	
002 PH	1		
003 IRON	58,400		
004 ZN	26,500		

Any oils, oily wastes or other materials shipped to HES, Inc. which contain detectable levels of PCB's (Polychlorinated Biphenyls) will subject the generator (or other responsible party) to all reasonable costs for proper transport, disposal and or decontamination of all contaminated materials and equipment.

Generators of oils, or oily wastes must provide a certification to HES that the waste is not contaminated with any constituents other than those incidental to normal use.

**GENERATOR WARRANTY:** To the best of my knowledge the above is a true, accurate and complete description of the waste material offered for disposal and/or reclamation.

(Signature)



**SERVICE LOCATION**  
**INDIANAPOLIS, IN**



**QUOTATION NUMBER**  
 09552

**HES WASTESTREAM NO.**  
 09052511

HERITAGE ENVIRONMENTAL SERVICES, INC.

CORPORATE HEADQUARTERS  
 7901 WEST MORRIS STREET  
 INDIANAPOLIS, INDIANA 46231  
 317/243-0811

**WASTESTREAM PROFILE**

**WASTE DESCRIPTION / COMMON NAME**  
 SPENT PICKLE LIQUOR

**DOT SHIPPING / HAZARD CLASS**  
 RQ, WASTE ACID LIQUID, CORROSIVE LIQUID, UN1760 (K062)

UPON LABORATORY ANALYSIS OF A REPRESENTATIVE SAMPLE, THE FOLLOWING MAJOR CONSTITUENTS WERE EVALUATED:

ANALYTE	ACTUAL VALUES	UNIT	ALLOWABLE RANGE
001 SOLIDS	.50	%	
002 PH	<1		
003 IRON	49,900		
004 ZN	91,500		

Any oils, oily wastes or other materials shipped to HES, Inc. which contain detectable levels of PCB's (Polychlorinated Biphenyls) will subject the generator (or other responsible party) to all reasonable costs for proper transport, disposal and or decontamination of all contaminated materials and equipment.

Generators of oils, or oily wastes must provide a certification to HES that the waste is not contaminated with any constituents other than those incidental to normal use.

**GENERATOR WARRANTY:** To the best of my knowledge the above is a true, accurate and complete description of the waste material offered for disposal and/or reclamation.

(Signature)

# DR/2000 and DR/3000 Spectrophotometers: Parameters, Methods, Ranges and Reagent Sets

The table below lists test ranges, methods of analysis and corresponding reagent sets for DR/2000 and DR/3000 Spectrophotometers. The complete procedure for each test is included in the respective manual.

higher ranges can be analyzed by sample dilution. Parameters marked with an (EPA) are EPA-approved for reporting purposes; sample pretreatment may be required on some procedures. DR/2000 test ranges marked with an \* are included in the DREL/2000 Portable Laboratory. If no reagent set is listed for a parameter, order needed reagents and supplies separately.

The ranges are given for the precalibrated instrument readout;

Test	Method	DR/2000 Range	DR/3000 Range
Aluminum	Aluminon	0-0.80 mg/L	0-1.000 mg/L
Arsenic (EPA)	Silver Diethyldithiocarbamate	0-0.200 mg/L	0-0.200 mg/L
Barium	Turbidimetric	0-100 mg/L	—
Barium (AccuVac)	Turbidimetric	0-100 mg/L	—
Benzotriazole	UV Photolysis	0-16.0 mg/L	0-15.0 mg/L
Boron	Carminc	0-14.0 mg/L	0-20.0 mg/L
Bromine	DPD	0-4.50 mg/L*	0-4.00 mg/L
Bromine (AccuVac)	DPD	0-4.50 mg/L	0-4.00 mg/L
Cadmium	Dithizone	0-80 µg/L	0-180 µg/L
Chloride	Mercuric Thiocyanate	0-20.0 mg/L	0-25.00 mg/L
Chlorine, free (EPA)	DPD	0-2.00 mg/L*	0-1.70 mg/L
Chlorine, free (AccuVac) (EPA)	DPD	0-2.00 mg/L	0-1.70 mg/L
Chlorine, free (EPA)	DPD2	0-2.00 mg/L	0-1.70 mg/L
High Hardness			
Chlorine, total (EPA)	DPD	0-2.00 mg/L*	0-1.70 mg/L
Chlorine, total (AccuVac) (EPA)	DPD	0-2.00 mg/L	0-1.70 mg/L
Chlorine, total (EPA)	DPD2	0-2.00 mg/L	0-1.70 mg/L
High Hardness			
Chlorine dioxide (LR)	Chlorophenol Red	0-1.00 mg/L	0-1.00 mg/L
Chlorine dioxide (MR)	Direct Reading	—	0-50.0 mg/L
Chlorine dioxide (HR)	Direct Reading	0-700 mg/L	0-700 mg/L
Chromium, hexavalent (EPA)	1,5-Diphenylcarbohydrazide	0-0.60 mg/L*	0-1.00 mg/L
Chromium, hexavalent (AccuVac) (EPA)	1,5-Diphenylcarbohydrazide	0-0.60 mg/L	0-1.00 mg/L
Chromium, total (EPA)	Alkaline Hypobromite Oxidation	0-0.60 mg/L	0-0.70 mg/L
Chromium, trivalent	Direct Reading	0-20.0 g/L	0-20.0 g/L
Cobalt	P.A.N.	0-2.00 mg/L	0-2.00 mg/L
Color, True	APHA Pt-Co	0-500 units	0-500 units
Copper (EPA)	Bicinchoninate	0-5.00 mg/L*	0-5.00 mg/L
Copper (AccuVac) (EPA)	Bicinchoninate	0-5.00 mg/L	0-5.00 mg/L
Copper	Porphyrin	0-210.0 µg/L	0-250.0 µg/L
Copper, autocatalytic	Colorimetric	0-3.00 g/L	0-3.00 g/L
Cyanide (EPA)	Pyridine-Pyrazalone	0-0.200 mg/L	0-0.240 mg/L
Cyanuric acid	Turbidimetric	0-50 mg/L	—
Detergents	See Surfactants		
Diethylhydroxylamine (DEHA)	Iron Reduction	0-450 µg/L	0-600 µg/L
Erythorbic Acid	Iron Reduction	0-1575 µg/L	0-2100 µg/L
Fluoride (EPA)	SPADNS	0-2.00 mg/L*	0-1.50 mg/L
Fluoride (Ampules) (EPA)	SPADNS	0-2.00 mg/L	0-1.50 mg/L
Formaldehyde	MBTH	0-350 µg/L	0-500 µg/L, 0-1300 µg/L
Hardness, calcium as CaCO <sub>3</sub>	Calmagite, Colorimetric	0-4.00 mg/L	0-2.50 mg/L
Hardness, magnesium as CaCO <sub>3</sub>	Calmagite, Colorimetric	0-4.00 mg/L	0-2.00 mg/L
Hydrazine	p-Dimethylamino-benzaldehyde	0-500 µg/L	0-600.0 µg/L
Iodine	DPD	0-7.00 mg/L*	0-6.00 mg/L
Iodine (AccuVac)	DPD	0-7.00 mg/L	0-6.00 mg/L
Iron, ferrous	1,10-Phenanthroline	0-3.00 mg/L	0-3.000 mg/L
Iron, ferrous (AccuVac)	1,10-Phenanthroline	0-3.00 mg/L	0-3.000 mg/L
Iron, total (EPA)	FerroVer	0-3.00 mg/L*	0-3.000 mg/L
Iron, total (AccuVac) (EPA)	FerroVer	0-3.00 mg/L	0-3.000 mg/L
Iron, total	FerroZinc	0-1.300 mg/L	0-1.400 mg/L
Iron, total	TPTZ	0-1.80 mg/L	0-1.000 mg/L
Iron, total (AccuVac)	TPTZ	0-1.80 mg/L	0-1.000 mg/L
Lead (EPA)	Dithizone	0-160 µg/L	0-300 µg/L
Manganese (LR)	P.A.N.	0-0.700 mg/L	0-0.800 mg/L
Manganese (HR) (EPA)	Periodate Oxidation	0-20.0 mg/L*	0-20.0 mg/L
Molybdenum, Molybdate	Mercaptoacetic Acid	0-35.0 mg/L	0-20.0 mg/L
Molybdenum, Molybdate (LR)	Ternary Complex	0-3.00 mg/L	0-3.00 mg/L

Test	Method	DR/2000 Range	DR/3000 Ran
Nickel (EPA)	Heptoxime	0-1.80 mg/L	0-1.80 mg/L
Nickel	P.A.N.	0-1.000 mg/L	0-1.000 mg/L
Nickel, autocatalytic	Photometric	0-8.00 g/L	0-8.00 g/L
Nitrogen, ammonia (EPA)	Nessler	0-2.50 mg/L*	0-3.00 mg/L
Nitrogen, ammonia	Salicylate	0-0.50 mg/L	0-0.80 mg/L
Nitrogen, Nitrate (LR)	Cadmium Reduction	0-0.40 mg/L	0-0.50 mg/L
Nitrate (MR)	Cadmium Reduction	0-4.5 mg/L*	0-5.0 mg/L
Nitrate (MR) (AccuVac)	Cadmium Reduction	0-4.5 mg/L	0-5.0 mg/L
Nitrate (HR)	Cadmium Reduction	0-30.0 mg/L*	0-30.0 mg/L
Nitrate (HR) (AccuVac)	Cadmium Reduction	0-30.0 mg/L	0-30.0 mg/L
Nitrite (LR) (EPA)	Diazotization	0-0.300 mg/L*	0-0.350 mg/L
Nitrite (LR) (AccuVac) (EPA)	Diazotization	0-0.300 mg/L	0-0.350 mg/L
Nitrite (HR)	Ferrous Sulfate	0-150 mg/L	0-250 mg/L
Nitrogen, total Kjeldahl	Nessler	0-150 mg/L	0-200 mg/L
Oil in water	Colorimetric	0-85 ppm	0-100 mg/L
Oxygen, dissolved	Rhodazine D, Colorimetric	—	0-500 µg/L
Oxygen, dissolved	HRDO	0-13.0 mg/L	0-15.0 mg/L
Oxygen demand, chemical, (COD)	Reactor Digestion	0-150 mg/L	0-150 mg/L
Oxygen demand, chemical, (COD)	Reactor Digestion	0-1500 mg/L	0-1500 mg/L
Oxygen demand, chemical (EPA) (HR) (AccuVac)	Dichromate Reflux	0-800 mg/L	0-800 mg/L
Ozone	DPD	0-1.40 mg/L	0-1.20 mg/L
Ozone (AccuVac)	DPD	0-1.40 mg/L	0-1.20 mg/L
Palladium	N,N'-Dimethyldithiooxamide	0-250 mg/L	—
Phenols (EPA)	4-Aminoantipyrine	0-0.200 mg/L	0-0.200 mg/L
Phosphorus, Acid Hydrolyzable	Hydrolysis to Orthophosphate	Pretreatment steps, see Phosphorus, below, for ranges	
Phosphorus, Organic & Acid Hydrolyzable (EPA)	Oxidation to Orthophosphate		
Phosphorus, reactive	Molybdovanadate	0-45.0 mg/L	0-20.00 mg/L
Phosphorus, reactive	Amino Acid	0-30.00 mg/L	0-20.00 mg/L
Phosphorus, reactive (EPA)	Ascorbic Acid	0-2.50 mg/L*	0-2.000 mg/L
Phosphorus, reactive (AccuVac) (EPA)	Ascorbic Acid	0-2.50 mg/L	0-2.000 mg/L
Phosphonates	Persulfate UV Oxidation	0-2.5 to 0-125 mg/L	0-2.0 to 0-100 mg/L
Polyacrylic acid	Absorption, Colorimetric	0-20.0 mg/L	0-20.0 mg/L
Potassium	Tetraphenylborate	0-7.0 mg/L	—
Residue, nonfilterable	Photometric	0-750 mg/L*	0-1000 mg/L
Selenium	Diaminobenzidine	0-1.00 mg/L	0-1.00 mg/L
Silica (LR)	Heteropoly Blue	—	0-2.000 mg/L
Silica (LR)	Heteropoly Blue	0-1.600 mg/L*	—
Silica (HR)	Silicomolybdate	0-100.0 mg/L	0-30.0 mg/L
Silver	Colorimetric	0-0.60 mg/L	0-0.70 mg/L
Sodium Chromate Sulfate (EPA)	Direct Colorimetric	0-1,100 mg/L*	0-1000 mg/L
Sulfate (AccuVac) (EPA)	SulfaVer 4	0-65 mg/L*	0-50 mg/L
Sulfide	SulfaVer 4	0-65 mg/L	—
Surfactants, Anionic	Methylene Blue	0-0.600 mg/L*	0-0.800 mg/L
Annin & Lignin	Crystal Violet	0-0.275 mg/L	0-0.320 mg/L
Glyltriazole	Tyrosine	0-9.0 mg/L	0-9.00 mg/L
Turbidity	UV/Photolysis	0-16.0 mg/L	0-20.0 mg/L
Volatile Acid	Absorptometric	0-450 FTU*	0-600 FTU
Zinc (EPA)	Esterification	0-2800 mg/L	0-2800 mg/L
	Zincon	0-2.00 mg/L	0-2.500 mg/L

EPA-approved means the procedure meets all requirements of the applicable USEPA-approved method or has been approved as an alternate digestion or distillation may be required.

LR indicates low range, MR indicates mid range, and HR indicates high range.

\*Order COD Reactor separately.

## WASTE EXCHANGE SOURCES

### Iron Chloride Solution

1. Gulbrandson Co.  
Millford, N.J.

Use solution as water treatment conditioner. Will not accept solutions with zinc in excess of 1% and lead levels greater than 50 ppm and chrome levels greater than 100 ppm.

2. ThermalKem  
Rock Hill, S.C.

Use solution as a water treatment conditioner. Cannot accept over 2% zinc. No other restrictions stated.

3. Diamond Shamrock  
Wilmington, N.C.

Will not accept greater than 500 ppm zinc.

4. Industrial and Agricultural Chemicals, Inc.  
Red Springs, N.C.

Will not accept zinc greater than 2%.

### Zinc Chloride Solution

1. DuPont Co.  
Wilmington, DE

No metals in excess of 100 ppm. Zinc level greater than 10%.

2. Mineral Research, Inc.  
Freeport TX.

Iron less than 1%. Zinc greater than 10%.

3. Ind. and Ag. Chem., Inc

Zinc greater than 10%.

Project Costs

1. Labor		
Dann Dettman	135 hours @ \$15.50	\$2092.50
Steve Albanese	25 hours @ \$8.30	\$207.50
Secretary	6 hours	\$50.00
Cary Peterson	6 hours @ \$30.00	\$180.00
		<hr/>
	Total labor	\$2530.00
2. Chemicals		
Lime and Trisodium phosphate for pilot testing		\$65.00
3. Lab supplies and testing costs		\$1910.00
4. Telephone and mail		\$200.00
	Total Project	<u>\$4795.00</u>

CGC contribution (labor)	\$2530.00
Grant contribution	\$2175.00
Amount received	\$3000.00
Refund due	\$825.00 *

\* A check for \$825.00 will be forwarded.

Grant total was to be \$4000.00 and project total was estimated at \$8000.00. Due to the unacceptable ion exchange performance the costs for ion exchange pilot testing were not incurred.

## V. Summary

Metal separation by ion exchange does not work when using concentrated solutions. The resulting streams are too dilute to be of any benefit. Iron present in the ferric ion state interferes with zinc ion selective resins and produce a stream too high in iron to market or use as a zinc chloride solution.

Metal selective precipitation can produce a low iron solution but other metal contaminants remain in solution making it unacceptable for use or marketing. A landfillable sludge is also produced by this method. Metal encapsulation can lower metal values in the pickle bath and extend the life, but the solution must eventually be disposed of as a hazardous waste, and the process of encapsulation produces a sludge of no marketable value which must be landfilled.

Spray roasting can regenerate acid to a usable value and produce a marketable iron oxide product but cannot separate zinc once it gets into the acid solution. A maximum level of zinc this system could handle is 1%.

No acceptable method of separating the zinc, iron and acid components of the spent pickle liquor was achieved from this study. Only by developing methods to prevent zinc from ever entering the bath will we be able to successfully recover the acid by regenerating methods. This would involve stripping rejects in a separate bath, stripping all racks and fixtures in a separate bath prior to using them a second time, and improving housekeeping methods to prevent zinc or zinc coated articles from entering the pickle baths. These steps may hold the zinc levels of the pickle bath low enough to use the spray roasting regenerating method for acid recovery of the pickle liquor, however the stripping solution would have to be disposed of as a hazardous waste due to the high levels of zinc.