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RECYCLING EFFLUENT OF CONVENTIONAL WASTE WATER PRECIPITATION TREATMENT VIA ION EXCHANGE AND EVAPORATION

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WORK HISTORY/OBJECTIVE

Vacuum tubes have been used in the electronics industry since the 1880's. More recent evolutions of these devices have seen the movement to higher power and frequencies ranges.(1-500 Kw) They are made of a mixture of metal parts, usually in a glass or ceramic envelope. Many parts are brazed together using silver or a variety of alloys in high temperature furnaces. Before the parts are brazed and exhausted to vacuum, they must be as clean as possible. Chemical cleaning processes such as acid pickling and bright dipping are routinely employed.

My experience with the manufacture of these devices started in 1987 with Amperex Electronics, a division of North American Philips established in the 1940's. In 1989, Richardson Electronics, Ltd. of LaFox, Illinois, acquired this division. The idea was to relocate the manufacturing to their LaFox facility. At this point it was realized that some of the equipment and the processes themselves could be moved easily, but the installed equipment, such as the waste treatment system, was immovable and would have to be constructed as new.

The cleaning process for vacuum tubes and their parts is primarily acid cleaning. Engineering and decorative deposits are copper, nickel and silver.(Fig 1) Due to the nature of the mixture of parts and the fact that most of waste is generated through acid cleaning, segregation of these waste lines was deemed very difficult. Because the processes involved had a long work history, the effluent from this manufacture was well known and well documented. An engineering study completed in 1972 was used as an estimate of the expected pollutants.(Fig 2) The problems were copper, nickel, and of course pH and cyanides.

FIGURE 1

Current Processes

Type	Name	Pollutant
Acids, Pickles, Cleaners, Conversion Coat	HNO_3, H_2SO_4, HCL, HF, H_2CrO_3	Copper, Silver, Nickel, Chrome, Cadmium, Lead, Iron, Fluorides, pH
Base Electro-Cleaners	NaOH, Na_2CO_3	Copper, pH
Plating (Acid Based)	Watts Nickel, Bright Nickel, Woods nickel, Acid Copper, Tri-valent Chrome	Nickel, Copper, Chrome
Plating (Cyanide)	Silver, Copper, Gold	Silver, Copper, Cyanides

THE PROBLEM

At Amperex a conventional waste treatment system was in place since 1969. The technology featured destruction of cyanides via alkaline chlorination and acid neutralization and precipitation. That was sufficient for it's existing permit, being that the discharge to a POTW had relatively, by today's standards, easy limits. Relocation to Richardson was another story, however. The site is located approximately 40 miles west of Chicago in the middle of a corn field. The existing waste streams were being treated by a series of shallow aerobic digestion lagoons, which degenerated the sanitary wastes, but would not be adequate for discharges from these type of processes. Limits here were ten times more stringent than at the old facility.(Fig 2) Concerns regarding this situation were:

1. Prevent any direct discharge into a food chain source.
2. The technology necessary to polish our conventional treatment to meet these more stringent standards.
3. If the future dictated different processes or pollutants, would they be compatible with the treatment?
4. If future limits became more strict, would our discharge comply?

Also there was a question of logic. If we polished our effluent to a quality as good as drinking water standards, a quality much better than the water supply currently obtained from our well, then, why not reuse the water?

FIGURE 2

Water and Waste Parameters

	Typical concen. before treatment	Typical concen. after treatment	Limits to POTW Nassau County, NY	Limits to Enviro. La Fox, IL
Cadmium	-	-	-	0.021
Chromium, Hex	16	0.045	0.1	-
Chromium, Total	18	0.060	2.0	0.143
Copper	25	0.310	2.0	0.020
Iron	-	0.080	4.0	0.286
Lead	-	-	-	0.029
Nickel	15	0.950	2.0	0.143
Cyanide Total	4	0.060	1.0	0.014
Silver	4	0.080	0.1	0.005
Zinc	-	0.005	5.0	0.143
Fluorides	-	0.800	3.0	-
pH	2.3	9.30	5.5-9.5	6.0-9.0

*Above data is in PPM as recorded in May, 1986

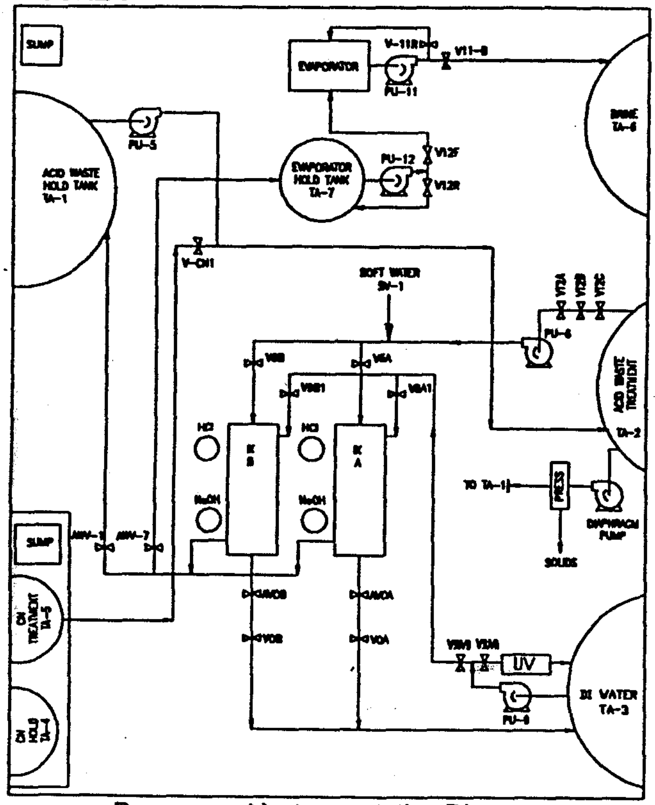
SOLUTION

Various engineering solutions were evaluated at the time of relocation. None seemed to fit the rather difficult situation that we had at Richardson. It was decided to conventionally treat the waste to a point where we would understand the effluent, then take the effluent and

recycle it via ion exchange into DI water, which was needed in the plating and cleaning facility.(Fig 3)

An overall view of the system shows that the metal and acid wastes of a low pH are segregated from the cyanide waste. All processes are contained in vinyl coated concrete areas, which are sloped to their respective transfer sumps and pumped into storage tanks. In the main precipitation system, when the acid collection tank is full it is transferred to an equal volume precipitation tank. The tank is agitated and pH adjusted

FIGURE 3



Process and instrumentation Diagram

to pH 9 and allowed to settle. The cyanide system has a similar reservoir, but it's precipitation tank undergoes chemical oxidation as well. Once an analysis establishes that all the cyanide is destroyed, the cyanide treatment tank can be added to the main precipitation system.

Once the system is allowed to settle, the effluent (what would normally be the effluent) is pumped through a series of ion exchange tanks. These ion exchange tanks consist of, first a sand filter to block any particles, second a carbon filter to screen out any unwanted organics and then a set of strong cationic and anionic ion exchangers. Once the effluent passes through this system it is stored in the DI holding tank. The quality of the water passed once through the ion exchange system normally does not meet the criteria for reuse, therefore, a second system is hooked up in parallel with the DI holding tank and polishes the water to the desired quality before reuse.

Once the ion exchange system has reached its capacity it is eluted or regenerated. Acid and caustic are fed through the respective exchangers, with the effluents mixed and directed to the evaporator holding tank. The solution is pH adjusted and fed to the evaporator. The solution is evaporated to approximately Specific Gravity 1.2 , at which time it is discharged to the brine holding tank. The tanks contents are periodically hauled off-site for disposal.

The solids that are generated through precipitation are removed via conventional filter press and any water filtered out is routed back to the beginning of the treatment cycle. The tank farm and press system all sit in a vinyl coated, depressed area. Any spills or rupture of vessels, plumbing or associated hardware will be contained.

The controls for this system are located in two main panels atop the mezzanine. Indicator lights of the system status can be monitored from the shop floor at all times. The main pH adjustment is made with a remote sensor and an automatic feed control system. Similarly the cyanide system features a pH and ORP control to adjust the hypo-chlorite and caustic injections.

DI WATER

The water budget for this system is a 7000 gallon batch capacity, with an ancillary 3500 gallon cyanide destruction system. The combined capacity is bottlenecked to a 7000 gallon precipitation tank. The turnover and polishing process is accomplished daily/overnight, giving extended polishing time for maximum water quality. Maximum flow rate for water usage is 14.6 GPM for a sustained 8 hours. This is allocated over 12 sets of counter-current rinses, 4 sinks and 8 hoses. For every tank de-ionized, 1000 gallons is lost in the regeneration process. (Fig 4)

FIGURE 4

WATER BUDGET

TANK CAPACITIES

Waste Water Holding Tanks Gallons	Treatment Tank Precipitation Gallons	DI Water Service Tank Gallons
7000 - Acid 3500 - CN	7000	7000

ION-EXCHANGER CAPACITIES

IX Capture	IX Polish	Polish Rate - 16 Hrs.
30 GPM	30 GPM	4.1 Turnovers

WASTE TREATMENT - WATER ALLOCATION

Loss From Regeneration Gallons	Make-up Water Through IX Polish Gallons	Required Evaporation Rate Gallons / Hr.
1000	1000	42

SHOP - WATER ALLOCATION

Water Usage Rate Total - 8 Hr.	12 Sets Double C/C Rinses	4 - Sinks 8 - Hoses
14.6 GPM Continuous	1.0 GPM Continuous	1250 Gallons/ Day Intermittent

The salt budget is limited by the ion exchange capacity. If the rinse contains too much dissolved solids, it will

/erwhelm the ion exchange system. Maximum eoretical capacity for both exchangers is 130 pounds ; $CaCO_3$. Actual maximum capacity as measured on x trials is somewhat extended at 158 pounds. Raw ata is accumulated by reading a simple conductivity ieter, units in PPM and multiplying by the total number ' gallons processed. Raw units are in PPM-gallons, hich of course converts to weight in grams or pounds ; required. This gives a maximum TDS of 2694 PPM ır 7000 gallons processed. Typical effluents are in the ınge of 1,500 to 2,000 PPM. This allows extra resin ıpacity for polishing of the final product. Actual /erage tank volumes and salt concentrations are listed. ig. 5)

IGURE 5

SALT BUDGET

THEORETICAL

Resin Type	Ammt. per Exchanger	Total Exchange Capacity	Total Capacity as CaCO3
Strong Cation IR-120 plus	15 cu.ft.	41.4Kgr/cu. ft.	88 lbs
Strong Anion IRA-410	15 cu.ft.	30.5 Kgr/cu. ft.	65 lbs

Final Theoretical Capacity (Least Capacity x 2 sets of exchangers)=135 lbs

ACTUAL

vg. capacity of 6 full loadings	Avg. capacity converted weight	Extended capacity for 2 sets of exchangers
9,432,000 ppm-gallons	79 lbs	158 lbs

Capacity Loading	Tank Volume	Maximum T.D.S. of Waste Water
9,432,000 ppm-gallons	7000 gallons	1347 ppm
Per double Set of Exchangers		
9,432,000 ppm-gallons	7000 gallons	2694 ppm

Regeneration Waste Breakdown
(one exchanger)

bs on Resin	lbs NaOH (as Na)	lbs HCl (as Cl)	Total lbs	Gal of Regen	Gal. at 1.2 S.G.
80	52	95	227	1000	135

The average quality of the DI water generated from ıis system is 5.0 microseimens, given an overnight olishing sequence. Quality improves to 1.0 µS if water emand is low enough to allow another overnight polish. Fig. 6) Through improved rinsing techniques and ngineering controls, our new shop averaged 7500 allons a week water consumption. This figure can be eferenced against a 7000 gallons per day usage for a imilar parts production rate in 1972 (estimate).

Quality of the water is the best I've ever had for ılating rinse applications. Analysis of the DI water shows only a minor trace (.008 PPM) of silver while other metals were all below detection limits. I did however detect a relatively high total organic carbon level (1-4 PPM). This is presumed to be from the breakdown of the resin associated with the treatment process. This characteristic precludes its use in the manufacture of our semiconductor devices. However, for plating and other cleaning processes of a more rugged nature, the water is excellent. (Fig 6a)

FIGURE 6

D.I. Water Quantity Data
Jan./91-Sep./92

Gallons Processed	Salt Content
80 Tanks	80 Tanks
4933 Gal. / Tank (avg.) (5000)	1988 ppm T.D.S. (avg.) (2000)
394,647 Gal. Total (400,000)	6589 lbs. (6600)

D.I. Water Quality Data
Jan./91-Sep./92

Avg. Water Quality after 15 hrs polishing 5.0 µS (200,000 Ohm-cm)	Av. Water Quality after 15+24 hrs polishing 1.0 µS (1 meg Ohm-cm)

FIGURE 6A

Trace Metal Analysis

Test Parameter	
Cadmium	<0.02
Chromium	<0.05
COD	<20
Copper	<0.02
Cyanide (total)	<0.01
Iron	<0.05
Lead	<0.01
Nickel	<0.05
pH	6.2
Silver	0.008
TOC Range (Tot. Organic Carbon)	1.0-4.0
Zinc	<0.05

REGULATORY ANALYSIS

This system required construction and operating permits for air pollution, water pollution, and for solid waste. In spite of the fact that there is not a discharge, nor a requirement for a NPDES permit per se, it is still controlled by a state operating permit for water pollution control. (Fig. 7)

Analyses of the RCRA wastes that are generated from this facility are broken down into five items. 1. DI water. This is exempt as recycled material. It is a commercial product and it is reused in the process that has generated it. 2. Evaporated water. Water that is expelled through evaporation is a gas and not a solid waste, and not subject to RCRA. 3. Sludge. The sludge that is pressed from the bottom of the precipitation tank is of course your standard F006 waste water treatment sludge. 4. Pickling solutions. Acid pickling and cleaning solutions are discarded and hauled off site rather then being put into the system. Their high TDS level precludes their de-ionization. These are classified as D002. In the rare event of disposal of a plating bath, characterization would be F006. 5. Brine. The brine solution is the trickiest, because it has come in contact with the F006 sludge. Under the "mixture and derived from" rules, it is to be labeled F006. However, it is two processes removed from that sludge and did pass a TCLP analysis for characteristics. This would make it non-hazardous, if it was evaluated on only a characteristic basis. We are currently having it hauled away as an F006 waste-water. However, as most of you are aware the "mixture and derived from" rules will be changed in the future(?) and at that point we may decide to try to delist the waste. (Fig. 7a)

FIGURE 7

	Permits Federal	State	Current Constituants	Requirements
AIR	Delegated	Construction Operating (ISIP) State ID#	NOx SO2	Scrubbers
WATER	Delegated	Construction Operating State ID # (NPDES)	No Discharge	Operator certification. Secondary containment.
LAND	US EPA ID# Delegated	State ID# Generator (RCRA)	F006, D002	90 Day Limits, Manifest, Etc.

FIGURE 7A

RCRA Wastes

Stream	Status	Statute	Comment
D.I. Water	Exempt Recycled Material	40CFR 261.2 (e)(1)(ii)	Water Permit Conditions
Evaporated Water	Exempt Gaseous Not a Solid Waste	40CFR 260 App1	Air Permit Jurisdiction
Solid Sludge	F006	40CFR261.31 (Subpart D)	Standard Sludge
Acids & Pickling Solutions	D002, D007, D008, D011	40CFR261.22 40CFR261.24	NOT A PLATING SOLUTION
Brine	F006 (When Hauled Away)	40CFR261.2 (a)(2) 40CFR261.3 (a)(2)(iv) 40CFR261.3 (c)(2)(I)	"IN TREATMENT" Subject to Clean Water Act Passes TCLP Test

COST ANALYSIS

Capital cost for the construction of this system was approximately $550,000. A breakdown by major units is provided. (Fig. 8) Our biggest expense was associated with the physical building construction itself. This was compounded by the extra care necessary in secondary containment considerations. A breakout of the equipment expenditures found $45,000 spent on the shop, $81,000 spent on the precipitation treatment, and $112,000 spent on the recycling treatment. (It must be remembered that most of the plating equipment was moved from our prior facility.)

FIGURE 8

CAPITOL COSTS

Building-Pit, Shop, Deck	$267,000.00
Pumps & Elevator	$15,000.00
Scrubbers, Vent System	$7,000.00
Tanks	$37,000.00
Ion Exchange Columns	$50,000.00
Evaporator	$15,000.00
Filter Press	$10,000.00
Controls, Levels, pH-ORP	$29,000.00
Electrical & Plumbing Installation	$75,000.00
Floor Coating	$35,000.00
Consultation	$12,000.00
TOTAL	$552,00.00

Operating costs were figured over a span of 21 months. Items considered are normal, correct operations. Expenses incurred in extra training, repairs and mistakes are excluded. Cost is per gallon on an average load of 5000 gallons. (Fig. 9)

FIGURE 9

OPERATING COSTS
(One Treatment 5000 gal)

Category	Item	Unit	Price	Total
Chemical Cost	NaOH	60 lbs	$0.30/lb	$17.96
	HCl	95 lbs	$0.171/lb	$16.15
	Na_2SO_3	0.1 lbs	$0.651/lb	$0.06
	NaClO	5 gal	$1.85/gal	$9.25
			Sub Total:	$43.42
Energy Cost	Gas	10,800 ft^3	$0.0037/$ft^3$	$39.96
	Electricity	267 KWhrs	7.04¢/KWHr	$18.58
			Sub Total:	$58.54
Waste Cost	Sludge	.69 gal	$16.19/gal	$11.14
	Brine	95 gal	$0.6778/gal	$64.38
			Sub Total:	$75.52
Labor Cost	Labor	20 min	$80.00/hr	$26.67
			TOTAL	204.15

Cost per gallon=$0.041

As depreciation costs for equipment follow a standard accounting formula data will be limited to depreciating of the ion exchange resin. In this application the resin is subjected to harsh chemical environments, beyond it's intended use. Accelerated breakdown is expected as the addition of harmful pollutants into the waste stream is difficult to control. To monitor this, a sample of the resin was pulled from the exchangers and analyzed for remaining ion exchange capacity. The volume of resin was also measured to estimate attrition loss. These two factors were multiplied to give an overall resin loss. Factored over the number of gallons processed and the initial cost, I estimate a depreciation loss of $.005 per gallon. (Fig. 10)

FIGURE 10

RESIN DEPRECIATION
DEPLETION through 400,000 GALLONS PROCESSED

	% Remaining Chemically	% Remaining Physically	% Remaining overall
Anion	87%	97%	84%
Cation	86%	97%	83%

ASSUME LINEAR DEPLETION
TOTAL POSSIBLE GALLONS PROCESSED=2,500,000

	cu.ft required	cost per cu. ft	total cost
Anion	30	$225.00	$1,080.00
Cation	30	$130.00	$663.00

Cost per gallon processed= $0.005

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BIOGRAPHY

For the last three years Mr. Zapisek has been the Chemical Engineer and Supervisor of Chemical Processing for Richardson Electronics, Ltd. LaFox, IL. He held a similar position with Amperex, Division of North American Philips for two years prior to their acquisition. He has three years of experience in ion-exchange synthesis and system design with RAI Research, Inc. Hauppague, NY and five years experience in printed circuit manufacturing with Photocircuits, Glen Cove, NY.

Mr Zapisek holds a Masters Certificate in the Environmental Geo-Sciences from Northern Illinois University and a Bachelors Degree in Chemistry from the State College of New Paltz, NY. He has two patents in the field of ion exchange applications.