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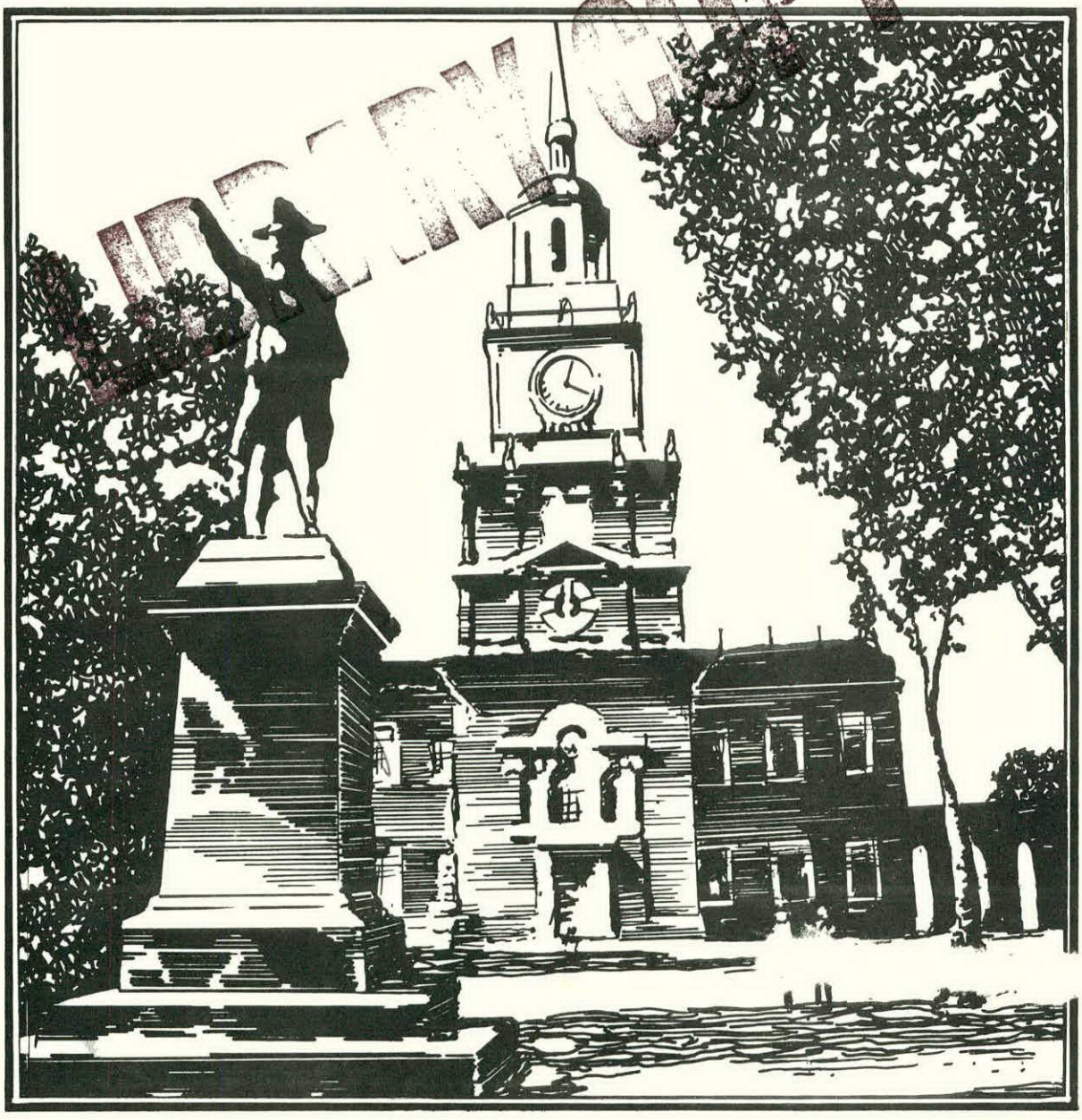

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Session E—Environmental I'

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Environmental II

Session E

E-1

Environmental II
Session E

Waste Treat or Recovery?
An Introduction to Resource Recovery

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WASTE TREAT OR RECOVERY?
AN INTRODUCTION TO RESOURCE RECOVERY

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The first point that we have to accept is that there are no magic solutions to waste treatment problems. We have, however, developed a practical approach that can bring effluent contamination levels down to a point where you will meet local discharge limitations, possibly with no conventional treatment.

Our corporate philosophy in the field of waste treatment is twofold: Recover valuable plating chemicals rather than destroying valuable plating chemicals; and, Complement recovery techniques with non-sludge generating techniques.

We have found that the ion-exchange and the electrolytic processes are the most viable, complementary techniques available. Some inplant changes need to be made in order to allow you to accommodate ion-exchange. The changes we suggest emphasize waste reduction at the tank to reduce the loading on the ion-exchange resin in order to maximize the time between removal or regeneration.

These changes will provide you with additional benefits compared to the use of conventional treatment technologies. First, you will have less floor space taken up with treatment equipment. Second, you will have a much lower capital investment in equipment. Third, you will reduce your water and sewer use bills.

This presentation will outline the process of cleaning up your waste streams. I must preface it by saying that there is really only so much you can do with these techniques. They are not the complete answer to all your problems, but they are simple, inexpensive, and they can be most effective.

The generally accepted approaches to waste treatment (Fig.1 & 2) can be divided into destruct technologies and recovery technologies. I'm sure you are all familiar with them; you have read enough articles on what they can do and what they can't do.

Your waste streams should be segregated. There are three reasons why you should segregate your lines:

1. Efficient treatment -- if you put everything together, you get an average treatment where pH is a factor, and you can't recovery any metal values.

2. You get much more economical recovery.

3. To isolate chelates, which would make treatment processes totally inoperable.

Figure 3 suggests how to segregate waste lines. The point to make about streams that do not require treatment is that regulatory authorities don't like to see you use non-contact water to dilute your process water. So, if you take a sample that includes degreaser, air-conditioning, or other such non-contact water, they expect you to prorate the analysis as though it were not being diluted. One answer, of course, is to reuse cooling water through your rinses. Now it is process water, and you have the advantage of its dilution effect even though it probably is not a significant factor.

You must consider the effect of cooling water flow on waste treatment equipment capabilities.

You can put an ion-exchange system at the end of each plating tank. If you put it at the end-of-the-pipe, you aren't going to get anything back. After regeneration, you will have a mixed waste, and most studies say that mixed wastes are simply not an economical source for recovering metal values.

Figure 4 is an EPA slide showing schematically what a conventional destruct system looks like. You can surmise that:

1. It can be very complicated.
2. It takes up a lot of room.
3. It probably costs a lot of money.
4. It requires some pretty good people to run it.
5. You are losing the chemicals that you are having to destruct.
6. You are adding destruct chemicals.
7. You are generating a sludge.

Destruct technologies are really not the way that you want to go. We are not saying that they don't work, but if nothing more, you are creating a sludge which is hazardous. Who needs it? There soon may be no land fills. Try to avoid sludge if at all possible!

A critical point to emphasize is that when you mix metal-bearing waste solutions and use alkaline precipitation with lime, hydroxide or carbonate, all metals don't precipitate

completely at the same pH. So, if you have a mixed stream, you have a problem. You have to use an average pH. Many times the levels that you can attain by doing this are not quite low enough. You can use Sulfide Precipitation (Fig.5), which results in much lower residual metal ion concentrations. However, notice the top right-hand corner of Figure 5 which shows for comparison the hydroxide performance. How many of you realize that if you raise your pH too high, many precipitated metals go back into solution?

No matter what approach you take to waste treatment, you can at all times implement water-use reduction -- even if only to save the dollar value of wasted water and sewer use charges.

You can minimize your dragout volume. I will go over that very briefly with you a little later to show you the methods that can be used.

You can implement chemical recovery. In the conventional recovery techniques, you either return a concentrated solution to the tank, destruct this concentrate, or recover metals from a concentrate using electrolytic methods.

You can also use integrated treatment (Fig.6). This is a destruct technology where dragout generally goes downstairs where it is treated and the cleaned solution is sent back upstairs for reuse in rinses.

Resource Recovery means you return materials unchanged directly to the tank from which they were dragged out. It is important to consider that while you can plate out metals from dragout solutions, a gallon of dragged out nickel solution, worth approximately $4.70, contains about 10 oz. per gallon of nickel. If nickel metal is selling for $3 a pound, and you can get $3 a pound for recovered nickel, you're only recovering about 60% of the value of that dragged out gallon of solution. The question about returning impurities to the bath is settled by improving bath maintenance or increasing carbon treatment/electrolytic purification frequencies as necessary.

Water-use reduction (Fig.7) is accomplished by common sense approaches. There is only one thing that rinsing does for you -- it reduces the impurities on a plated piece to the point where you can progress to the next step and get a satisfactory product. Why use more water than you have to?

I am sure that you've already implemented a lot of these. for those who haven't thought of every one, let's cover them briefly:

Flow Control Valves -- platers like to open their water valves full. Put a flow control valve on each water line and know your flow.

Aeration of Rinses -- whether you pump the rinses, bring air agitation in, or use a syphon breaker, the more agitation you get, the more effective is your rinsing.

Countercurrent/Counterflow Rinsing is accepted by just about everybody today as the smartest way to go. Figure 8 shows water coming into a single stage overflowing rinse tank. That is the way it was for years and years. Figure 9 shows a double counterflow rinse tank where the same amount of water used in the single rinse tank now feeds two rinse tanks. So, you have two for the price of one.

Figure 10 shows water flows required for each gallon of dragout to attain ten parts per million in the final rinse. The numbers are very striking. You can reduce 60-85% by going to a double counter/current rinse and 90-97% by going to a triple. Most people feel that anything beyond a triple is really not buying you anything. That is up to you whether you can afford the extra labor of going to four. Four is better than three, but can you afford the extra step productionwise?

Conductivity Controllers -- These devices allow water to flow into the rinse tank when the water is dirty, and shut water off when the rinse is clean. That is the only reason you have running rinses -- because the water is dirty. If the water is clean, why have pure water continually flowing. It doesn't make sense at all. If you can reuse cooling water, that's great because it is water you have paid for, and it can do a second job.

Rinse Timers -- When work enters the rinse, the operator just hits a switch, water flows for a fixed time, and that is that. That is not quite as sophisticated as a rinse controller, but it works. You can limit your water usage and get good rinsing.

You can recirculate treated rinses if you have a backlog of treated rinse. You can have this water in a holding tank and pump it back.

Open-ended Hoses -- If any of you have had a tank overflow when somebody is filling it at the end of the day, you know the problem. If you use a spring-loaded hose nozzle, you eliminate potential problem.

Don't wash down spills. Use an absorbent material. Save an awful lot of water. You are still going to have to wash down at the end of the day to remove stagnant water that lays under the floor boards. However, if you have a spill, there is no sense in doing anything except using an absorbent material.

Check your tanks and make sure that they are not leaking; you can lose a lot of solution. In the days of water shortages they used to warn about, "One drop per minute" from dripping faucets. It is the same thing with a plating tank.

Minimizing Dragout Volume (Figure 11)-- If you can keep solution in the tank, it isn't a pollutant, and you don't need waste treatment. What you can't keep in will need to be cleaned up by some conventional technique(s).

If you rack a part properly so that it doesn't drain onto the part below, drainage will be more effective.

Drip Timing -- Figure 12 shows that if you can fit it into your production cycle, a 15 second drip time will remove all your solution that is going to drain off.

You can use non-ionic wetting agents, which will not contribute any foreign ions to your plating bath. This will reduce surface tension and reduce the amount of dragout on every part that is withdrawn from a plating tank.

You can put drain boards between the tanks to keep solution off the floor and returned to tanks.

You can remove your parts slowly and smoothly. If you withdraw them slowly, you'll find that you have much less dragout than when you pull them out quickly.

Fog rinses and airknives generally lend themselves more to automatic plating than to rack plating and recover a good amount of dragout.

Rack maintenance -- Many people lose solution because their racks are falling apart. You can also ruin baths due to cross contamination caused by defective racks.

If you can use a higher bath temperature, you will reduce the viscosity and reduce the dragout. With most nickel tanks it doesn't make much difference if you raise the temperature unless you have big parts that flash dry and stain as you pull them out.

Use lower concentration baths if you can. You have seen the low nickel baths that cut the nickel concentration during the days of the energy shortage when you had to go to lower operating temperatures on your baths.

I have seen some dragout figures published by EPA, typically, 1.5 gallons per 1,000 sq.ft. My experience indicates that the figures can be closer to 4 gallons per 1,000 sq. ft. for rack plating and even higher for barrel.

Figure 13 shows dragout data from a large plating shop at the end of one shift. I think they are impressive because they show graphically the performance of dragout tanks.

On the rack nickel the figures in parentheses mean that the two nickel tanks, each with two dragouts, were followed by a common Dragout #3 and Dragout #4. Contaminent level came down to 1.5 parts per million in the fourth common nickel tank.

From the rack copper data you can see that having four dragouts brought copper contamination down to half a part per million.

Now we are going to cover the final items, namely the recovery techniques that we have found to be successful. We, of course, have addressed the conventional recovery technologies. They are all fine; they all work, but they have a price; whether it be in manpower, energy, space, or sludge.

In addition, some conventional recovery techniques (Electrolytic, Ion-Exchange, and Carbon Adsorption) recover only part of the value of the dragged out solution. Brighteners, wetters, chemical additives, and metal fabrication charges are not recovered.

With Resource Recovery you return all of the material values that you paid for. Implementation of an effective reclamation program requires:

1. Dragout tanks on all contaminating processes. Dragout is returned to the operating tank automatically to replenish evaporation.

2. Warm and/or acidified rinses (or fog spray) to effectively remove contaminants from parts.

3. A closed-loop counterflow rinse to feed back to the dragout tank.

4. The use of some technique to reduce bath volume of room temperature baths. These include: forced evaporation, aeration, or a combination of tank overflow and evaporation.

These techniques reduce and can eliminate the need for conventional waste treatment. In those instances where the above techniques alone cannot keep up with contaminants, electrolytic techniques can be added to the dragout(s), and ion-exchange can be added to the closed loop counterflow rinses.

With attention to dragout from acid processes, it is often possible to avoid pH adjustment of an effluent stream.

FIGURE 1

CONVENTIONAL DESTRUCT TECHNOLOGIES

1. ALKALINE PRECIPITATION
2. SULFIDE PRECIPITATION
3. CYANIDE OXIDATION
4. CHROMIUM REDUCTION
5. BOROHYDRIDE PRECIPITATION
6. STARCH XANTHATE
7. FKJA FORMALDEHYDE PRECIPITATION
8. CHELATE DESTRUCT

FIGURE 2

CONVENTIONAL RECOVERY TECHNOLOGIES

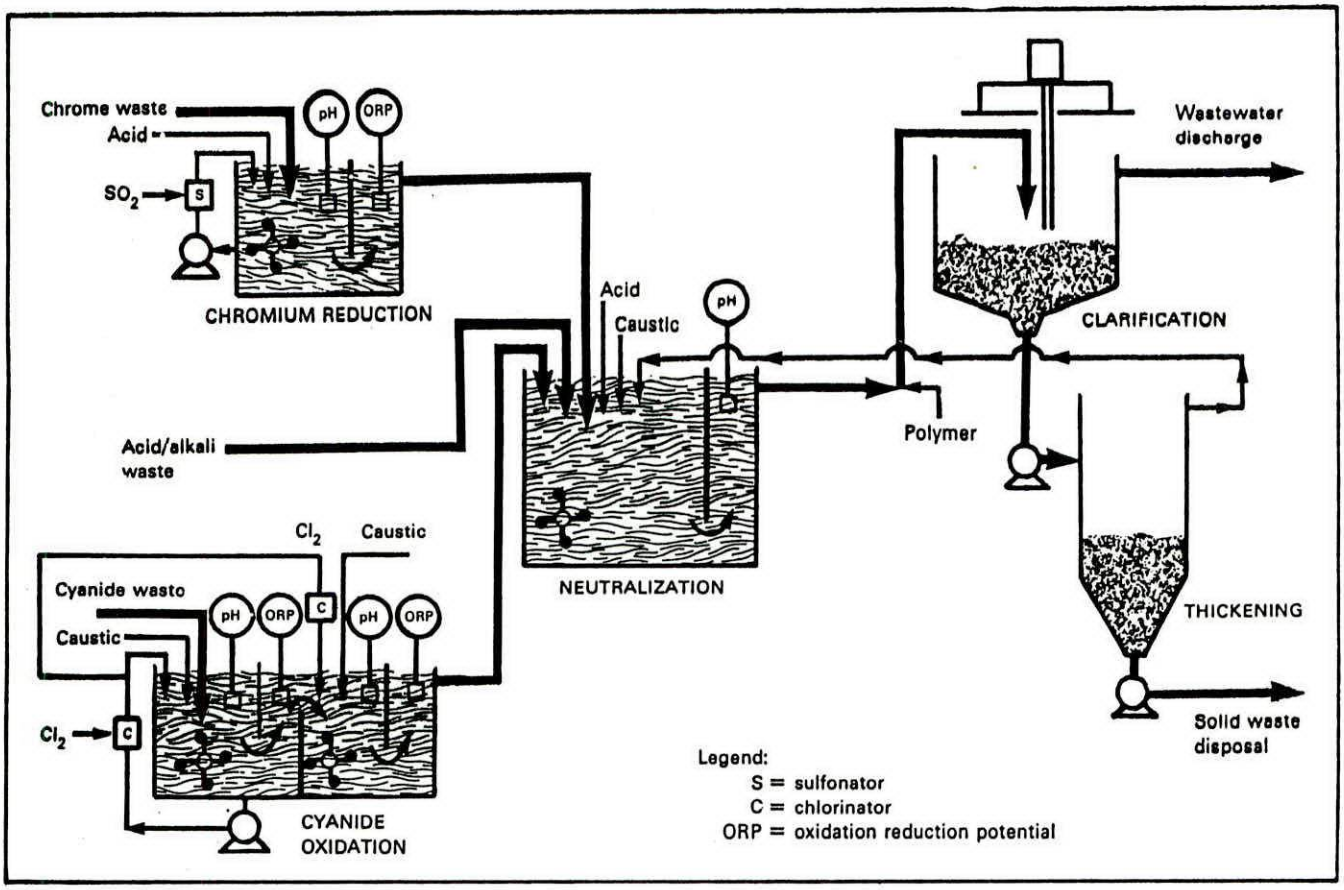
1. ELECTRODIALYSIS
2. REVERSE OSMOSIS
3. EVAPORATIVE RECOVERY
4. ELECTROLYSIS - DC/PULSE PLATE
5. CARBON ABSORPTION
6. ION-EXCHANGE

FIGURE 3

STREAM SEGREGATION

1. CYANIDE-BEARING RINSES
2. CHROMIUM-BEARING RINSES
3. ACID-ALKALI NON-CHELATED RINSES (NON-CYANIDE, NON-CHROME)
4. CHELATED RINSES
5. STRONG DUMPS OF EACH ABOVE
6. STREAMS NOT REQUIRING TREATMENT

FIGURE 4



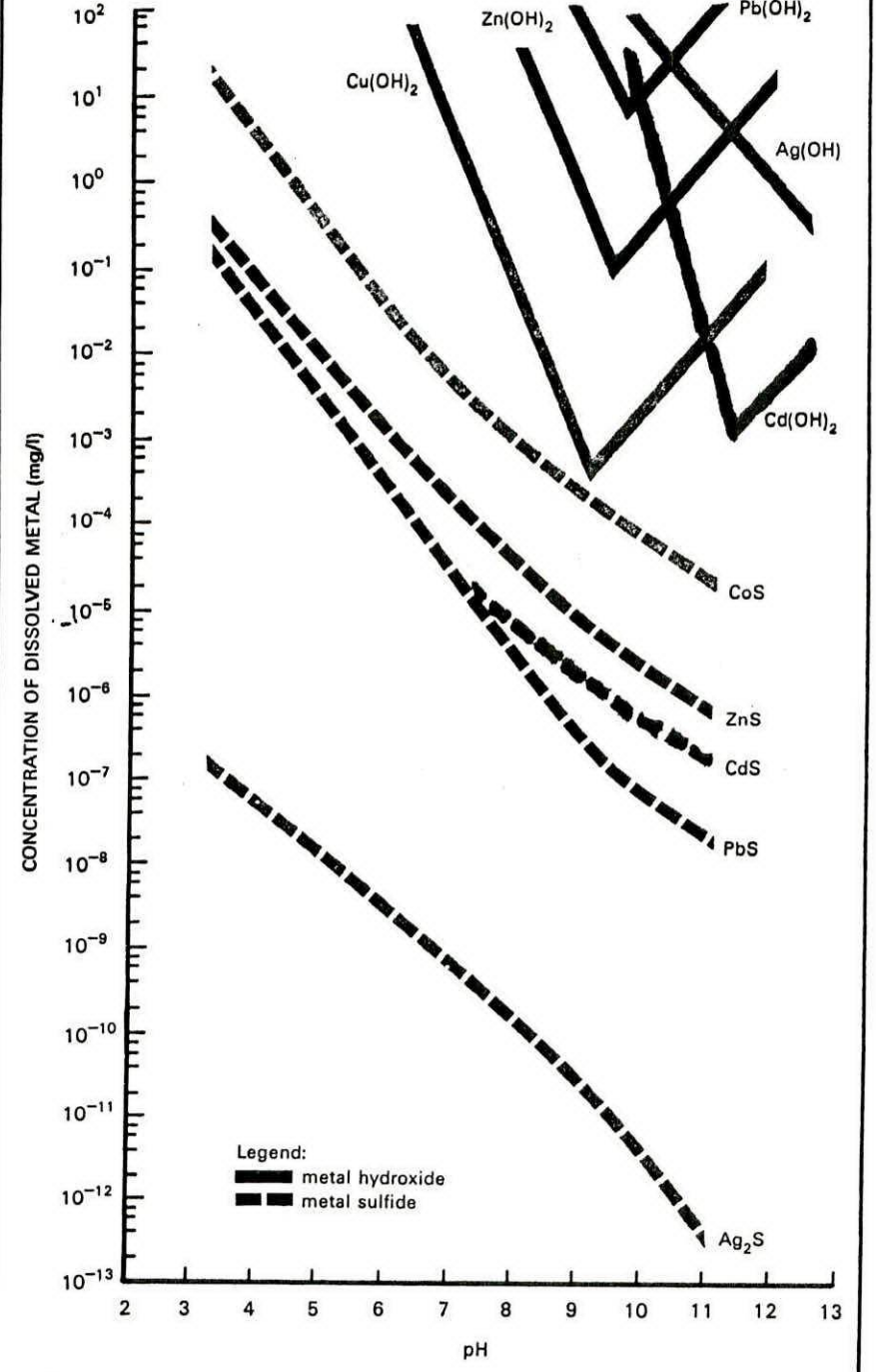
Electroplating Industry Conventional Wastewater Treatment

REPRODUCED FROM
ENVIRONMENTAL REGULATIONS AND TECHNOLOGY

EPA 625/10-80-001, AUGUST 1980, p. 13.

FIGURE 5

Solubilities of Metal Hydroxides and Sulfides as a Function of pH

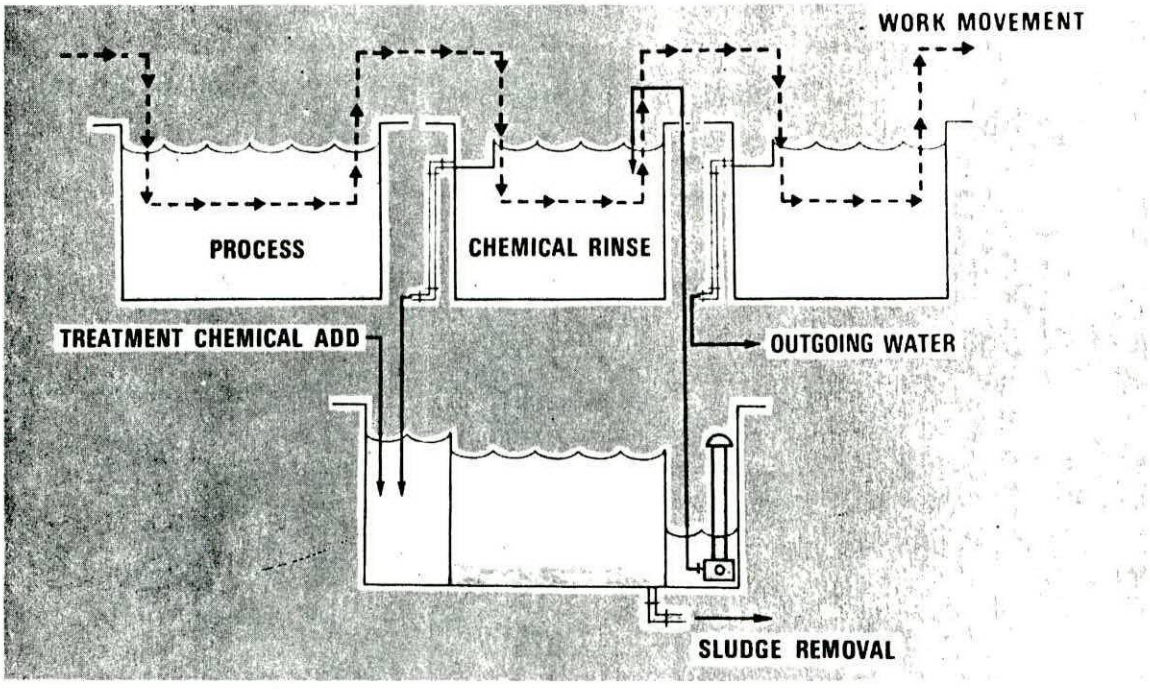


Note.—Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modern Alkaline Cooling Water Treatment," in *Industrial Water Engineering* (p. 31), Jan.-Feb. 1973.

REPRODUCED FROM:
CONTROL AND TREATMENT TECHNOLOGY FOR THE METAL FINISHING INDUSTRY
EPA 625/8-80-003, AUGUST 1980, p. 3

FIGURE 6



Integrated chemical rinse.

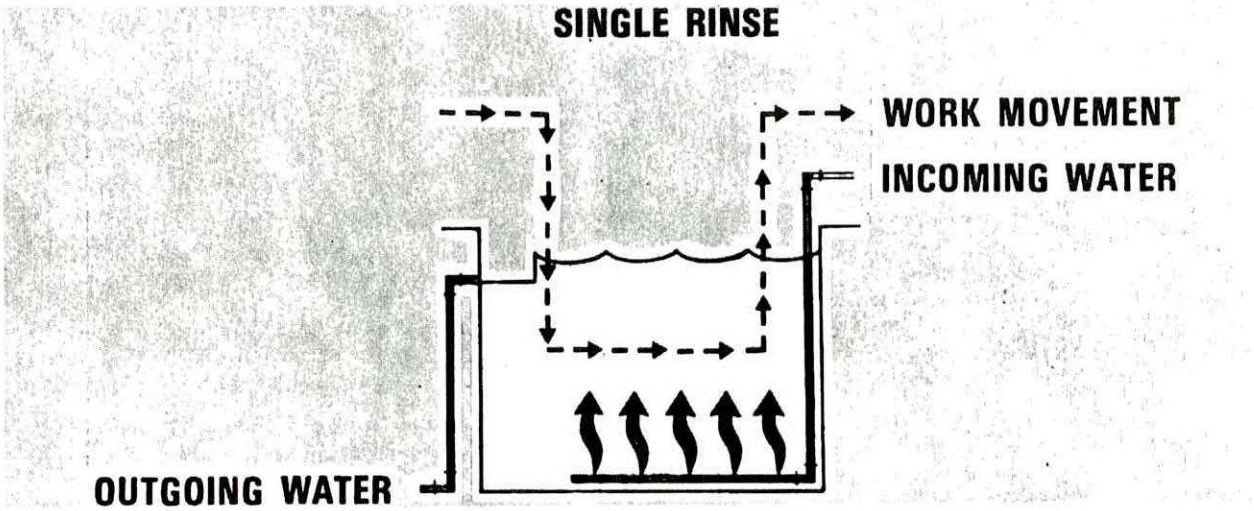
REPRODUCED FROM:
IN PROCESS POLLUTION ABATEMENT -- UPGRADING METAL FINISHING FACILITIES TO REDUCE POLLUTION
EPA 625/3-73-002, JULY 1973, p. 30.

FIGURE 7

WATER USE REDUCTION

- FLOW CONTROL VALVES
- AERATION/AIR AGITATION/PUMPING
- COUNTERCURRENT RINSING
- CONDUCTIVITY CONTROLLERS
- REUSE COOLING WATER
- RINSE TIMER
- RECIRCULATE TREATED EFFLUENT
- REUSE ACID RINSES AFTER ALKALINE CLEANERS
- NO OPEN-ENDED HOSES (SPRING-LOADED HOSE NOZZLES)
- CLEAN UP SPILLS WITH ABSORBENT - NO WASHDOWN
- INSPECT FOR LEAKING TANKS, VALVES, ETC.

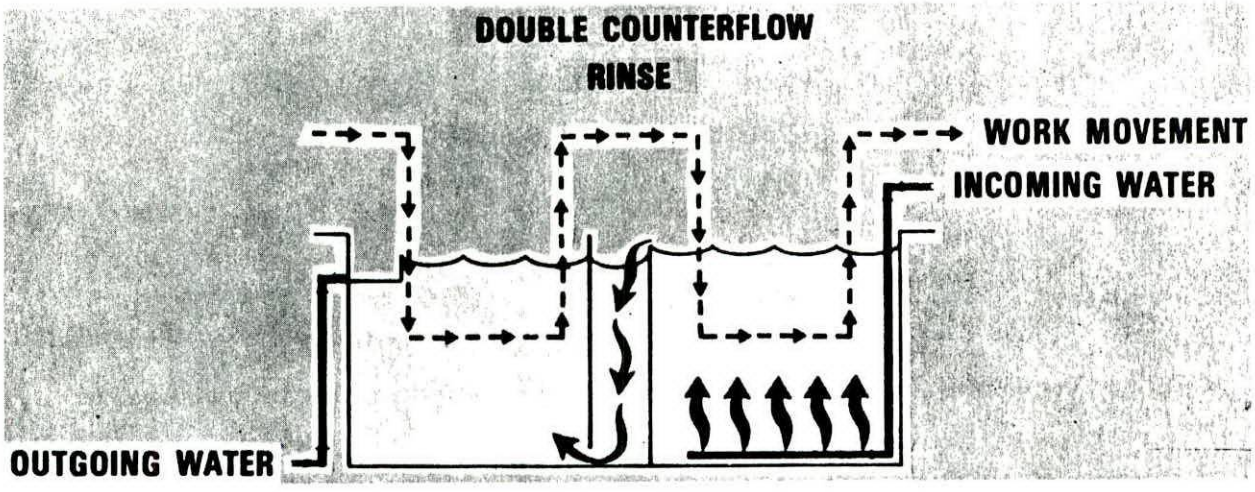
FIGURE 8



REPRODUCED FROM:
IN-PROCESS POLLUTION ABATEMENT, UPGRADING METAL-FINISHING FACILITIES TO REDUCE POLLUTION

EPA 625/3-73-002, JULY 1973, p. 27.

FIGURE 9



REPRODUCED FROM:
IN-PROCESS POLLUTION ABATEMENT, UPGRADING METAL-FINISHING FACILITIES TO REDUCE POLLUTION

EPA 625/3-73-002, JULY 1973, p. 27.

FIGURE 10

REDUCTION OF FLOW

IN MULTIPLE RINSE TANKS

RINSE RATIO	PERCENT REDUCTION OF FLOW NO. OF TANKS		
	1	2	3
10	0	68	80
100	0	90	95
1,000	0	97	99
10,000	0	99	99.8

FIGURE 11

MINIMIZING DRAGOUT VOLUME

- PROPER RACKING
- DRIP TIMERS
- WETTING AGENTS
- DRAIN BOARDS
- REMOVE PARTS SLOWLY
- FOG RINSES
- RACK MAINTENANCE
- INCREASED BATH TEMPERATURES
- LOWER CONCENTRATION BATHS

FIGURE 12

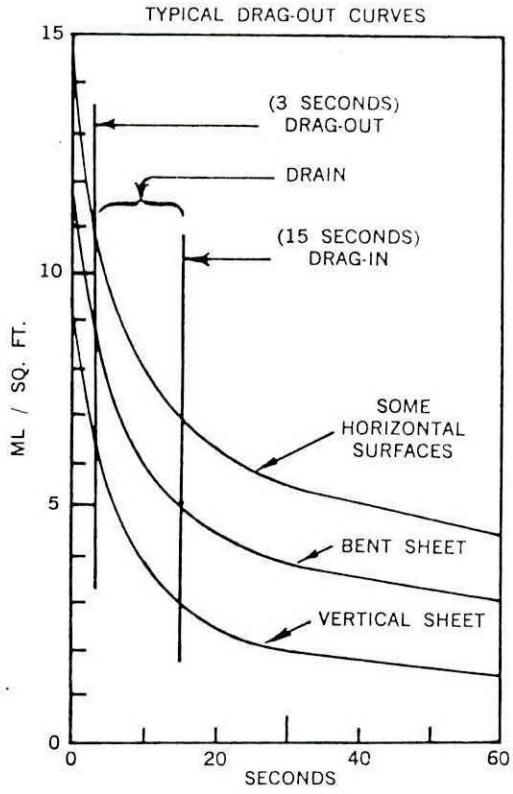

TYPICAL DRAG-OUT CURVES
15
10
5
0
ML / SQ. FT.
(3 SECONDS)
DRAG-OUT
DRAIN
(15 SECONDS)
DRAG-IN
SOME
HORIZONTAL
SURFACES
BENT SHEET
VERTICAL SHEET
0
20
40
60
SECONDS

FIGURE 13

DRAGOUT DATA

BARREL NICKEL

D.O. #1 . . . . . 12,800 mg/l Ni
D.O. #2 . . . . . 4,040 mg/l Ni

RACK NICKEL

D.O. #1
1,100 mg/l Ni . . . . 1,640 mg/l Ni
D.O. #2
220 mg/l Ni . . . . . 368 mg/l Ni
COMMON D.O. #3
70 mg/l Ni
COMMON D.O. #4
1.5 mg/l Ni

BARREL COPPER

D.O. #1 . . . . . 6,100 mg/l Cu
D.O. #2 . . . . . 1,720 mg/l Cu

RACK COPPER

D.O. #1 . . . . . 740 mg/l Cu
D.O. #2 . . . . . 110 mg/l Cu
D.O. #3 . . . . . 18 mg/l Cu
D.O. #4 . . . . . 0.4 mg/l Cu

E-2

Environmental II
Session E

Recovery of Metals from Effluents by High Efficiency Air Agitation Electrowinning

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RECOVERY OF METALS FROM EFFLUENTS BY HIGH EFFICIENCY AIR AGITATION ELECTROWINNING

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INTRODUCTION

Although it has been recognized only relatively recently that the electrowinning process could be employed for the recovery of metals from wastewaters, the basic process is well established. Electrorefining, a process closely related to electrowinning, was introduced about a hundred years ago. Today, practically all of the world's copper (approx. 8,000,000 metric tons/year) is electrorefined. Although copper electrowinning is by far the most common, other metals such as zinc, nickel, cadium are also electrowon to a significant extent.

Electrowinning and electrorefining, have traditionally been carried out on a very large scale. An average copper refinery producing 500 tons per day of copper utilizes approximately 200,000 m^2 of total electrode area. This corresponds to about 50,000 anodes and 50,000 cathodes suspended in about 1500 tanks occupying a total floor area of about 6000 m^2 By way of comparison, a typical effluent stream is very much smaller, perhaps yielding less than 0.01 tons per day of metal.

The primary limitation of electrowinning technology for effluent recovery is that the traditional design does not lend itself to the treatment of low metal concentrations. Solution metal concentrations in conventional electrowinning operations are usually in the order of 30-50 g/L while most effluent streams contain less than 10 g/L and frequently less than 1 g/L.

Because of the large size of commercial electrowinning and electro-refining installations for primary metals production, the depressed market conditions of metals and because of the rather conservative philosophies of the industry, recent developments in cell design, which would improve performance and extend the operating concentration range of the process,

have not been exploited. Because of the smaller size of effluent applications it is feasible to incorporate the latest cell design innovations to alleviate the concentration limitation of the process.

THE ELECTROWINNING PROCESS.

In electrowinning, metal is deposited from solution onto cathode blanks by application of a direct electrical current according to equation (1). In a competing reaction, hydogen ions are reduced to gaseous hydrogen according to (2). As the concentration of metal ions in solution is lowered the potential of (1) approaches that of (2) and the majority of the current is consumed by the hydrogen evolution process.

Oxygen evolves simultaneously from insoluble anodes, according to equation (3).

$$Cu^{++} + 2\,e^{-} \longrightarrow Cu^{0} \qquad (1)$$

$$2\,H^{+} + 2\,e^{-} \longrightarrow H_2 \qquad (2)$$

$$H_2O \longrightarrow 1/2\,O_2 + 2H^{+} + 2e^{-} \qquad (3)$$

For the most part, electrowinning cells utilize a basic design comprising alternating flat sheet cathodes and anodes. As metal is plated onto the cathode, the stagnant liquid film adjacent to the cathode surface tends to become depleted in metal. The current density, which determines the rate of metal deposition, must not exceed the rate at which metal ions diffuse through this film to the cathode. If the current density is too high, the concentration of metal ions in the film will be excessively depleted producing a condition known as "concentration polarization". This results in an adverse effect on the current efficiency as well as the quality of the deposit, as a result of hydrogen evolution.

Concentration polarization tends to promote the growth of minute surface imperfections in the deposit in the following manner. The mass transfer to the tips of these imperfections protruding into or through the diffusion film is greatly improved compared with smooth parts of the cathode (see Fig. 1). The low concentration polarization at these tips compared with the rest of the cathode disturbs the uniformity of the current distribution and

results in increased current density on these imperfections.

The allowable or *critical* current density is determined by two principal factors:

1. the concentration of metal ions in the bulk of the solution
and

2. the thickness of the film.

With conventional electrowinning designs employing flat plate electrodes, the maximum allowable current density for high quality deposits is impracticably low below a concentration of about 10 g/L. The rule of thumb for conventional electrowinning (referred to as the "capability index" is a current density (in amps/ft^2) of about 0.5 to 0.7 times the copper concentration in g/L [1,15]. Meyer [2] for example, reported the efficiency of deposition as a function of Cu concentration and current density. He also described the quality of the deposit.

Table 1 - Copper Electrowinning with no agitation [2]

concentration [Cu](g/L)	current density (A/dm^2)	current efficiency	deposit quality	capability index
10	0.54	99	good	0.50
4	0.52	41	spongy	1.21
4	0.26	99	good	0.61
1	0.54	41	poor	5.00
1	0.08	93	good	0.75

There are basically two different design approaches to extending the operating concentration range of the electrowinning process. The first approach accepts the fact that low current densities must be employed at low concentrations and counteracts this by using cathodes with high effective surface areas such as porous beds of conductive particles or fibres [3,4]. The second approach seeks to increase the allowable current density by reducing the thickness of the diffusion film.

A major practical consideration in the selection of a novel cell design is the form in which the final metallic product is obtained. Designs employing flat plate cathodes produce an easily harvested sheet of metal

which is marketable. High surface area cathode designs usually produce a metal product which must be further processed to achieve marketability. This is a serious limitation to the high surface area approach, particularly where larger quantities of metal are involved. In addition, the complexity of any particular cell design and the anticipated problems associated with its operation must be seriously weighed against its relative advantages in performance.

One way of decreasing the cathode film thickness is to agitate the electrolyte by recirculating the solution at a high velocity past the cathode, parallel to the surface [5,6]. Published data indicates that a capability index of approximately 1.1 can be achieved at copper concentrations below 10 g/L at 21°C with this cell[7](see Figure 3). This is approximately twice that reported by Meyer with no agitation, a significant improvement.

HIGH EFFICIENCY AIR AGITATION

Another well known agitation technique is air agitation. Air agitation is employed extensively in the electroplating industry. Kennocott Copper, at one time the largest U.S. copper producer, sought a means of reducing electrowinning plant costs for processing the relatively dilute leach liquors characteristic of low grade copper ores. A development program that extended through the 1970's yielded a patented electrowinning cell design based upon a new high efficiency air agitation (HEAA) scheme [8]. A uniform curtain of fine air bubbles is directed across the face of the cathode which reduces the thickness of the diffusion layer of liquid adjacent to the cathode and dramatically increases the rate of mass transport to the cathode from the bulk liquid. This reportedly allowed deposition of metal at current densities which are high in relation to the metal concentration, while producing metal of excellent purity and mechanical integrity. Extensive testing on laboratory and pilot plant scale indicated that this cell design could increase the electrowinning capability index to 3-5 ASF/g/L. Most of this work was conducted on copper electrowinning applications at metal concentrations in excess of 10 g/L. Table 2 shows some typical results. These results can be compared to conventional electrowinning cells which operate at concentrations of 30-50 g/L and current densities of 1.96 amps per dm^2 (21 ASF).

Ettel[9] made a detailed comparison of various agitation schemes including the electrolyte recirculation method and a well designed air agitation system. Assuming one wanted a three-fold increase in mass transfer over natural convection, he calculates that the power required for agitation by electrolyte recirculation would be about 10 times higher than for air sparging. He concluded that the most effective approach was air agitation.

Ettel's work at INCO, utilizing a similar air agitation scheme to Kennecott's, yielded comparable results. One experiment conducted at Cu= 2 g/L (see Table 2) obtained a capability index of approximately 4, which is almost *four* times that of the electrolyte recirculation cell!

Based upon this data it is evident that the air agitation technique has a lot of potential in treating dilute solutions. It was felt, however, that more testing was required with the HEAA cell to better determine its utility in treating solutions at metal concentrations of less than 10 g/L.

Table 2 - Published Data: Copper electrowinning with air agitation

	#1 [10]	#2 [9]
Cu concentration (g/L)	32	2
current density (A/dm^2)	15.2	0.806
acid concentration (g/L)	171	5
temperature	63.°C	N/A
voltage	2.8	N/A
capablility index	4.4	4

CELL DESIGN

Although, as discussed above, very few innovations in electrowinning cell design have been exploited in the primary metals industry, this does not mean that there have not been any developments in the field. A number of these improvements were incorporated into the HEAA cell design to supplement and complement the air agitation.

Cathode size

Most commercial electrowinning cells used in the primary metals industry

employ "standard" cathodes measuring approximately 1m x 1m. Given the much smaller size of effluent applications, it was felt that smaller cathodes, which if necessary could be removed by hand without the aid of a crane, would be more appropriate.

Close anode/cathode spacing.

Conventional cells typically employ cathode/anode spacing of about 5 cm (2 inch). This was reduced to about 2.5 cm (1 inch). Closer anode to cathode spacing reduces the "IR" voltage drop across the cell, resulting in lower energy consumption and improves agitation[9]. It also allows for a reduction in the overall size of the cell for a given cathode area requirement.

Non-retentive cathode blanks.

Metal is deposited on permanent stainless steel cathode "blanks" from which it can be easily stripped. The design of the cell is such that non-conductive edge stripping, to prevent the edges of the deposit on each face from joining, is **not** required. Special treatment of the cathode blank surface with parting agents is also **not** required. Removal of metal from cathodes can be done on a individual basis by manually lifting each cathode from the cell, or a crane can be employed to simultaneously remove the entire cathode inventory for more efficient, high production processing.

Lead/calcium alloy anodes.

A patented lead/calcium alloy[11] is employed for the anodes for sulfate systems. This results in the production of a very high purity deposit. The excellent physical characteristics of this alloy extend anode life considerably. Anodes are soldered to the copper crossbars to ensure fault free electrical contact. Since occlusion of anode corrosion products is a major contributor to cathode lead impurities, the use of these more stable anodes results in the production of purer copper[12].

Figure 2 shows a commercial **HEAA** cell designed for treating dilute solutions. This unit contains 22 cathodes each containing 56 dm^2 (6 ft^2) for a total of 1230 dm^2 (132 ft^2) of cathode area.

While the potential increase in performance with air agitation is sub-

stantial, the design remains fairly simple, yields deposits which can be readily harvested and marketed and maintains a basic similarity to the traditional design, upon which a wealth of practical experience and data has been accumulated over many years of commercial scale operation.

EXPERIMENTAL

It was decided to perform testing on full sized cathodes, because of the misleadingly good cathode quality and high current density capability obtained with smaller cells that had been reported in comparison tests[13]. The cell employed for the tests utilizes a single cathode with approximately 56 dm^2 of total area (both sides) and incorporates the above design features. One anode is employed on each side of the cathode. Figure 3 shows the test cell along with a spare cathode.

Electrolyte was circulated continously between the cell and a small reservoir. The total electrolyte volume was approximately 130 L. Cooling coils were installed in the reservoir to maintain the temperature at approximately 25°C. Runs were conducted over periods of time ranging from 2-16 hours to deposit sufficient metal so that deposit quality could be established. Concentrated copper sulfate solution was metered to the cell to maintain the copper concentration as constant as possible over the duration of the run. A sulfuric acid concentration of apporoximately 1M was obtained in the electrolyte at all times.

Table 3 - Test Results: Copper electrowinning with air agitation

	#1	#2	#3	#4	#5
[Cu] (g/L)(avge)	.125	.54	.81.	1.95	10
$[Cu]_i$ (g/L)	.1	.5	1.05	2.0	9.4
$[Cu]_f$ (g/L)	.15	.58	0.55	1.9	10.5
CD (A/dm^2)	.0538	.269	0.321	.936	5.38
CD (ASF)	0.5	2.5	5.11	8.7	50
voltage	NA	1.2	1.2	1.5	NA
avge. cap. index	4.0	4.62	3.7	4.5	5
run time (hr)	4	2	16	4	3
current eff.(%)	56%	>99%	95%	93%	91%
depost quality	smooth	smooth	smooth	rough	rough

DISCUSSION OF RESULTS

Results for five different runs, ranging in copper concentration from 0.1-10 g/L, are summarized in Table 3. These runs correspond to the maximum current density at a given concentration of copper for which an acceptable deposit was obtained. The deposit produced in runs 1-3 was very smooth and adherent. It is possible that the current density could have been increased somewhat and still been acceptable. The deposit produced in runs 4 and 5 was somewhat rough, but adhered firmly to the substrate and although possibly not acceptable for commercial copper production, was considered acceptable as saleable scrap material. Under the latter conditions the current density was probably approaching the upper limit.

The copper concentration fluctuated somewhat during run 3. Considering the extended length of this run (16 hours), the cell operated at the lower range of copper concentration for a considerable length of time towards the end of the run, during which time the deposit was presumably good, since the final deposit was smooth. It could then be stated, with some justification, that the capability index for this run was as high as 5.45 for this run.

The lower current efficiency (56%) for run 1 should be noted. The increased tendency for hydrogen evolution is undoubtedly a result of the increased cathode potential as a result of the very low copper concentration (0.1 g/L) along with the high (1M) hydrogen concentration.

The capability index obtained was approximately 4 throughout the concentration range of 0.1-10 g/L. This compares favorably with the previous published air agitation results summarized in Table 2, at least one of which was conducted under much more favorable, high temperature conditions (63°C). It is almost four times that of the electrolyte circulation system, and eight times that of a cell with no applied agitation!

No attempt was made to study the effect of temperature on capability index although the higher diffusion rates realized at elevated temperatures would undoubtedly have a very significant positive effect. Published data with the electrolyte recirculation cell[7] indicates that increasing the temperature from 21°C (70°F) to 60°C (140°F) allows a four and one

half fold increase in current density. A comparable effect could be experienced with the HEAA cell.

Figure 3 summarizes the results obtained in this study as well as published results with the electrolyte recirculation system and no applied agitation. Note that the temperature for the electrolyte recirculation system was slightly lower (21°C) than for the HEAA tests (25°C). No temperature data is available for the non-agitated data, but it is presumed they were obtained at room temperature.

Under the conditions of run 4 at Cu= 2 g/L, the energy conumption is calculated as 1.37 kwh/kg copper, assuming a 100% rectifier conversion efficiency.

APPLICATION

An excellent application of the HEAA cell is recovery of metal values directly from metal finishing rinsewaters. Normally the cell would be installed in a bypass arrangement on the first rinse tank following the plating bath (i.e. the dragout tank). Spent electrolyte from the cell would overflow back to the rinse tank and be recirculated on a continuous basis through the cell (see Fig. 4). For some applications (e.g. nickel) it is necessary to provide continuous pH adjustment of the rinsewater to counteract the generation of acidity at the anodes. For applications where anions other than sulfate are present, it may be necessary to substitute other anode materials such as precious metal clad titanium for lead alloy, which corrodes in chloride and other media. For cyanide plating rinsewater, as an added benefit, some of the cyanide would be destroyed at the anode by oxidation.

The HEAA cell can be advantageously applied in conjunction with an ion exchange system as shown in Fig. 5. Effluent solution containing a very low concentration of metal (e.g. Cu<1 g/L) is passed through a cation exchange column to yield a barren solution containing less than 1 mg/L. Sulfuric acid elution of the cation exchanger yields a metal sulfate solution containing typically 10-40 g/L of metal. This eluate flows to the electrowinning cell which plates the metal down to a concentration of about 1 g/L or below and simultaneously liberates an equivalent amount of sulfuric acid. The sulfuric acid solution yielded by the electrowinning cell can then be neutralized or in some cases be reused by the cation exchanger

for subsequent regenerations.

Since it is not possible to electrowin nickel below a pH of about 2, it is necessary to continuously neutralize the acid that is generated during electrowinning with sodium hydroxide. As a result, the acid cannot be recycled to the cation exchanger. If a metal selective chelating resin is employed, however, the spent electrolyte can be combined with the dilute effluent stream feeding the ion exchanger to recover the residual nickel. The chelating resin will selectively recover the residual nickel, rejecting the sodium (see Fig. 6).

An important advantage of the combined ion exchange/electrowinning configuration is that by employing sulfuric acid regeneration of the ion exchanger, the cell sees only sulfate solution, despite the fact that the original metal source may contain other anions. This eliminates the need for exotic anode materials when dealing with corrosive anions such as nitrate or chloride. It is possible, for example, to take a bleed from a cupric chloride etch, remove the copper by cation exchange and electrowin copper from the sulfate electrolyte eluted from the ion exchanger.

Metallic salt byproduct solution produced by an acid purification unit (APU) employing a sorption resin operating on a metal etching and pickling operation can also be treated by electrowinning (see Fig. 7)[15]. For example, when operated on sulfuric acid/peroxide baths for brass or copper etches, the APU produces a byproduct containing 20-40 g/L copper. This can be readily reduced to about 1 g/L or below by HEAA electrowinning and then discharged to a conventional precipitation type waste treatment system to obtain compliance.

Further work is now underway investigating performance of the HEAA electrowinning cell for recovery of zinc and other metals from a variety of different types of dilute effluent solutions

ECONOMICS

To evaluate the economics of the HEAA process, consider a simple case of recovering copper from the first rinse following an acid copper plating bath. If this rinse were held at Cu=2g/L, energy consumption would be 1.37 kwh/kg. Considering a rectifier conversion efficiency of 50% this

would represent about 2.74 kwh/kg. Base on a power cost of $0.04/kwh, the operating cost would be $0.11 /kg ($0.05 per lb). The current value of number one grade scrap copper is about $1.21 /kg ($0.55/lb). The direct savings, excluding labor, to run the recovery system would then be about $1.10/kg ($0.50/lb).

The alternative to recovery would be precipitation, and sludge disposal. Assuming the cost of sludge disposal is $400 per ton and that the sludge has been dewatered to 40% $Cu(OH)_2$, there would be an additional savings of $2.27/kg ($1.03/lb) in sludge disposal costs. The labor saved in operating the sludge dewatering equipment would more than compensate for the labor in operating the recovery system. The total savings would then be about $3.37 per kg ($1.53/lb)

The 1230 dm^2 (132 ft^2) cell shown in Figure 2 could recover 869 g/h of copper when operated conservatively at Cu=2 g/L, 0.65 A/dm^2 (6 ASF) and 93% current efficiency. Over 6000 h/y (5 d/w, 24 h/d, 250 d/y) the system would recover 5214 kg of metal, netting a saving of $17,571 annually.

The cost of the recovery system, including cell, rectifier, pump and other accessories, would be approximately $53,000. The payback on the initial capital investment would therefore be 3.0 years, a figure normally considered acceptable. The economics of recovering more concentrated solutions or more valuable metals would obviously be more attractive.

SUMMARY

The **HEAA** electrowinning cell provides an effective means of electrowinning metals from dilute solutions, typical of those associated with effluent streams. High quality deposits are easily harvested in a convenient sheet form which can be readily marketed for a premium price.

The efficient operation of the cell is such that equipment size may be reduced by a factor of approximately eight over conventional non-agitated electrowinning systems, and by a factor of four over competitive electrolyte recirculation systems.

The economics of the process indicates that a rapid return on capital investment may be achieved under certain circumstances.

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Figure 1: Growth of Imperfections

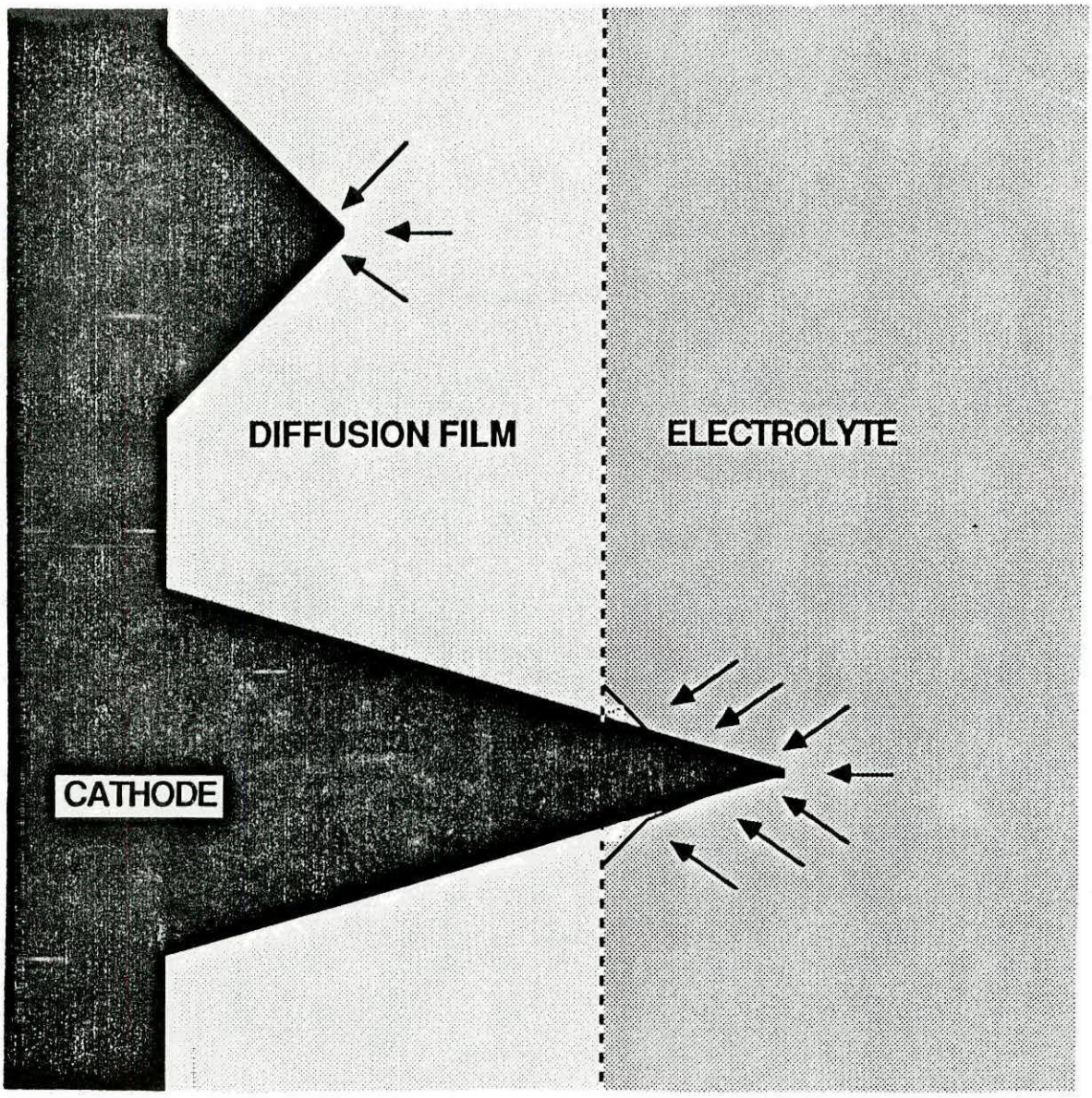


Figure 2: Commercial 1230 dm^2 (132 ft^2) HEAA Electrowinning Cell

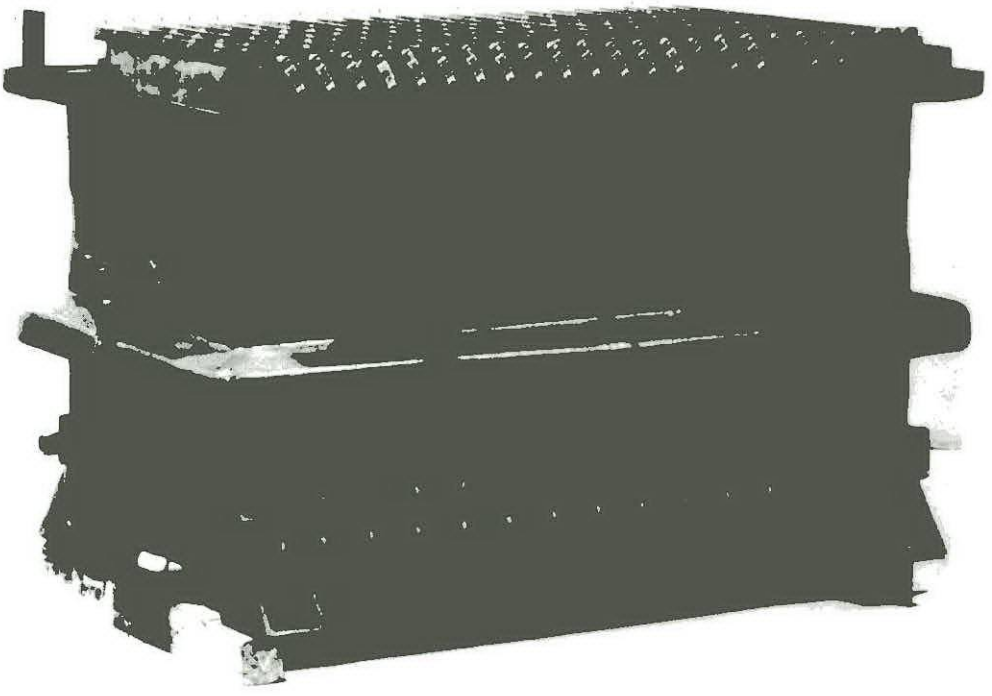


Figure 3: Laboratory HEAA Test Cell

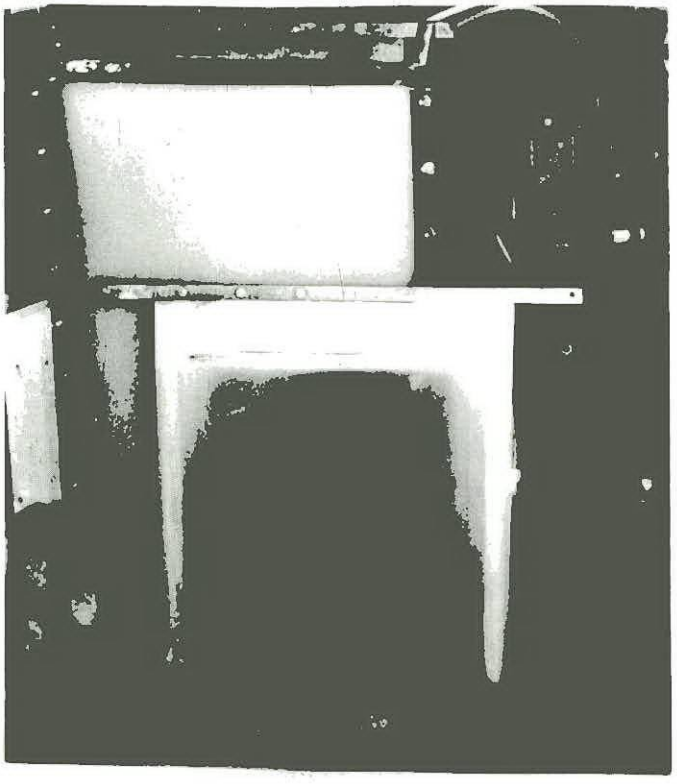


Figure 4: Electrowinning Cell Performance

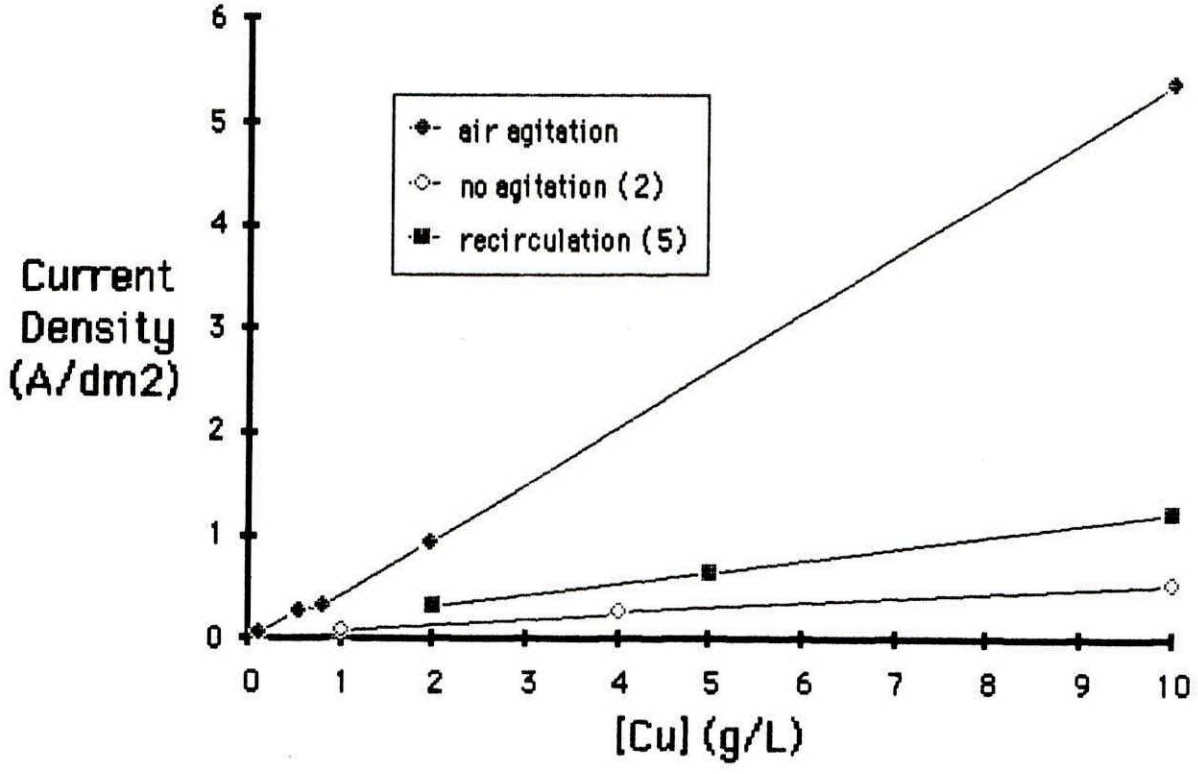


Figure 5: Electrowinning Rinsewater Recovery System

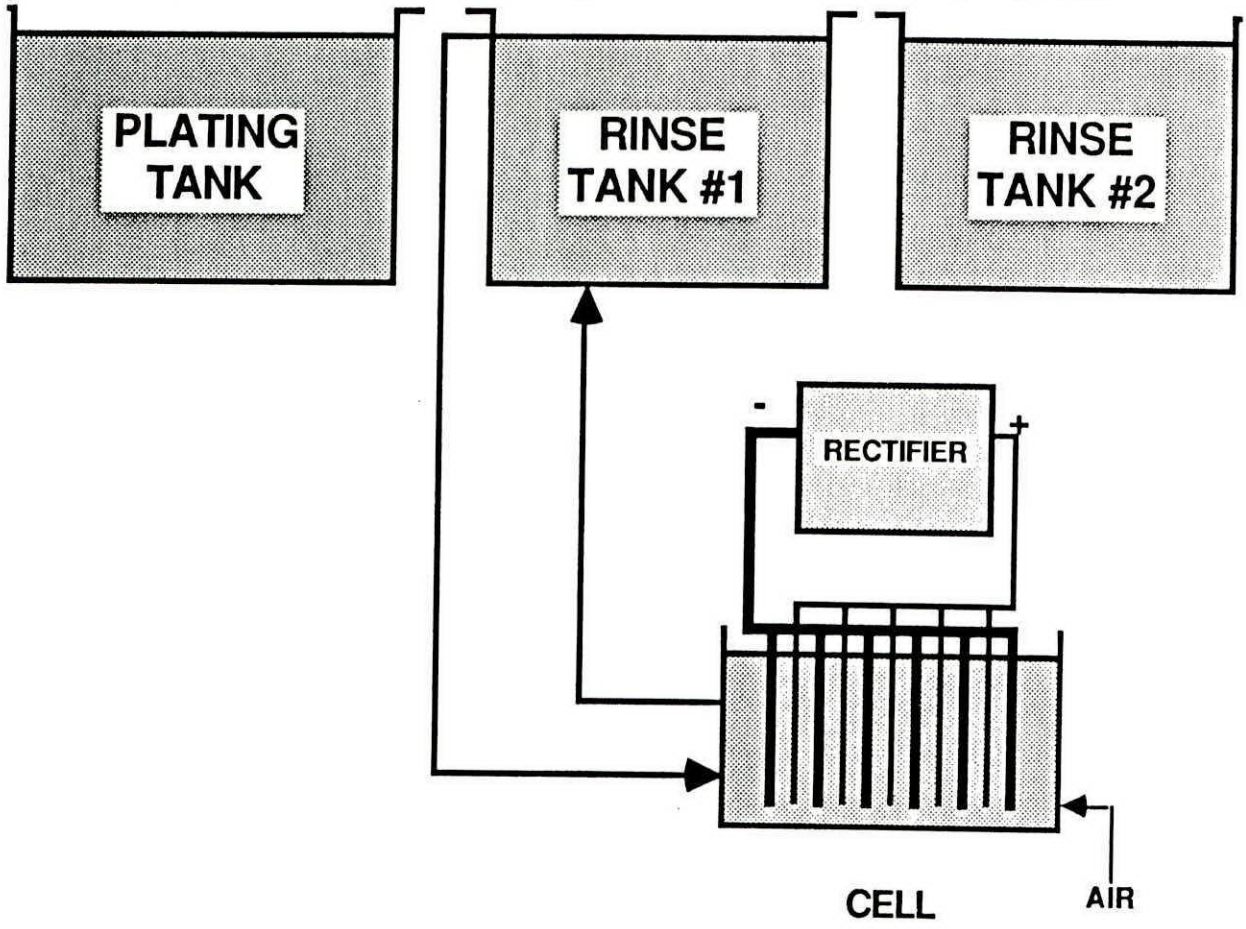


Figure 6: Ion Exchange/Electrowinning Recovery System

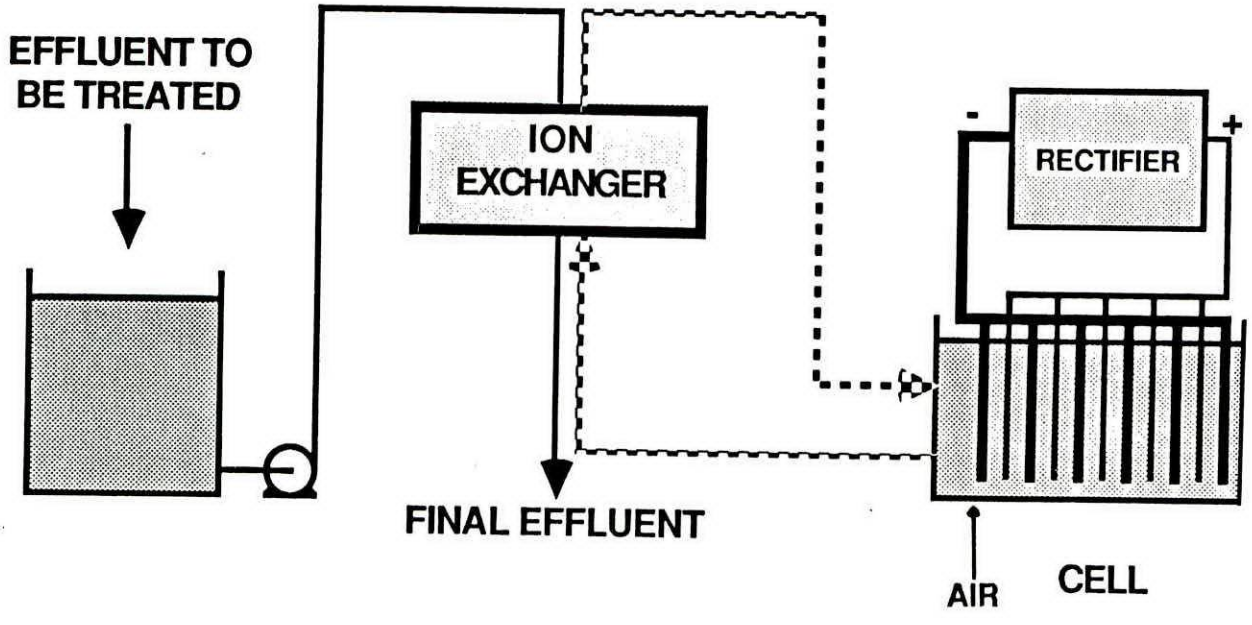


Figure 7: Chelating Ion Exchange/Electrowinning Recovery System

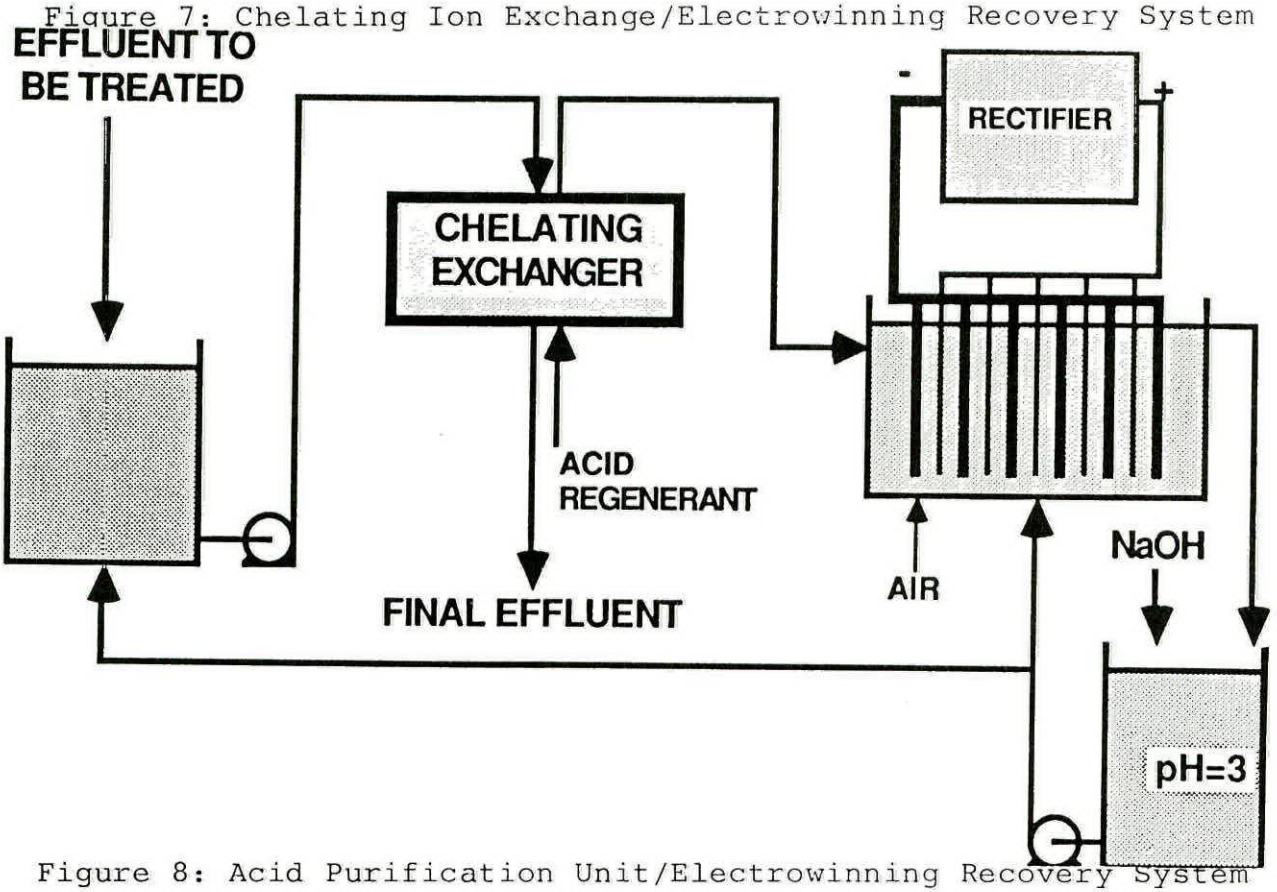
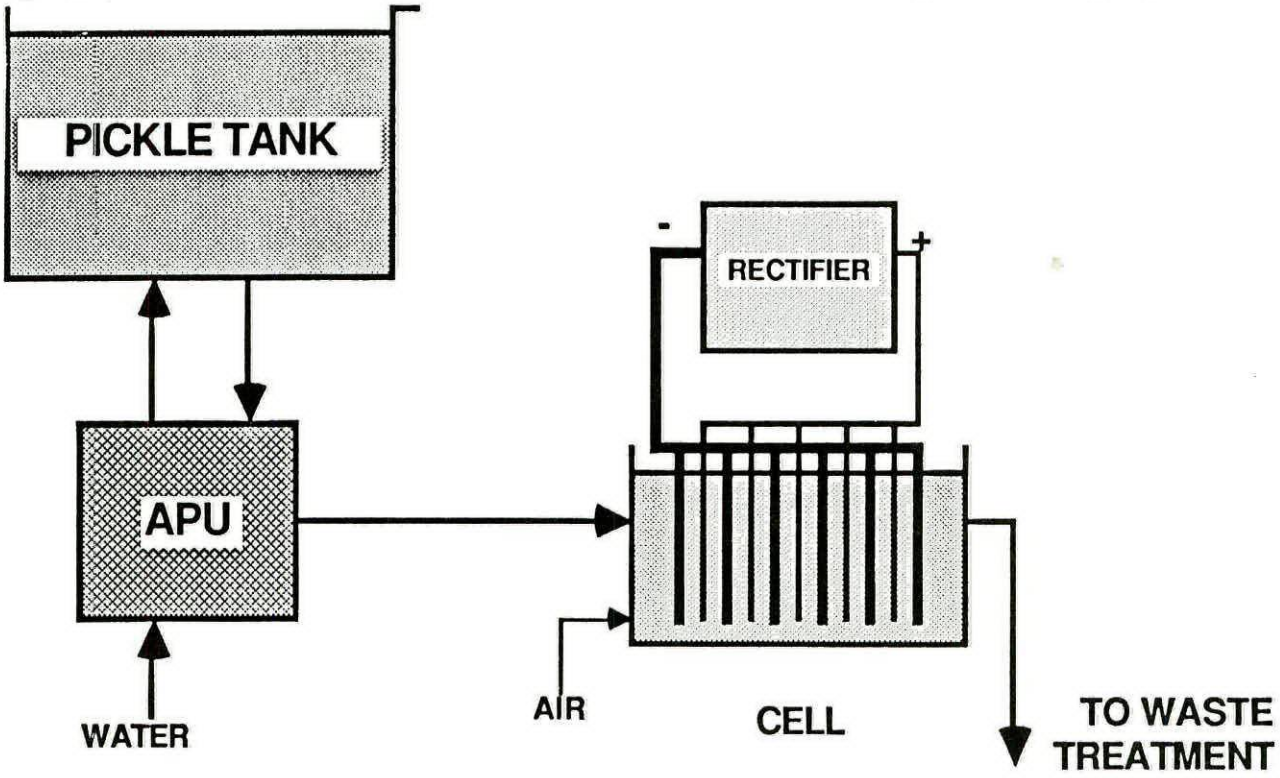


Figure 8: Acid Purification Unit/Electrowinning Recovery System



E-3

Environmental II
Session E

Recovery of Nickel Salts By Electrodialysis Reversal Process

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RECOVERY OF NICKEL SALTS BY ELECTRODIALYSIS REVERSAL PROCESS

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ABSTRACT

Benefits of utilizing Electrodialysis Reversal (EDR) process in recovery of valuable plating chemicals from rinse waters are described in this paper. Expensive metal salts such as nickel sulfamate, chloride, and sulfate are no longer being lost to conventional hydroxide precipitation. The EDR metal recovery system offers a short-time pay-back in capital investment, low operating cost, and minimum operator attention. It also indicates that an efficient recovery process can turn environmental problems into economic opportunities.

INTRODUCTION

The electrodialysis (ED) process was introduced in 1952[1] as a new method of desalting sea water and brackish water based on a physical principle rather than the boiling of water and condensation of steam. The electrodialysis process is an electrochemical seperation process in which ions are transferred through a pair of ion selective membranes from a less concentrated to a more concentrated solution as a result of the flow of direct electric current.

From 1954 to 1970[2], the classical ED systems were operated with the transfer of dissolved ions in one direction only. Problems with membrane fouling such as concentration polarization, scale, slime, and undesirable organic build-up were found to be troublesome. Addition of acids, polyphosphates, or similar agents were used extensively in an attempt to control calcium salts scale. However, the practice of chemical addition was relatively ineffective whenever there was poor flow distribution caused by poor channel design or local blockages from slime, silt, or debris build-up.

The Electrodialysis Reversal (EDR) process is a basic improvement in scale control without continuous addition of descaling or complexing agents. The EDR process achieves cleaning and descaling of electrodialysis membrane surfaces by periodic reversal of the direct current flow through the ED membrane stack, and by a simultaneous interchange of diluting and concentrating streams. Figures 1a and 1b depict the simplified EDR process diagram and schematic respectively.

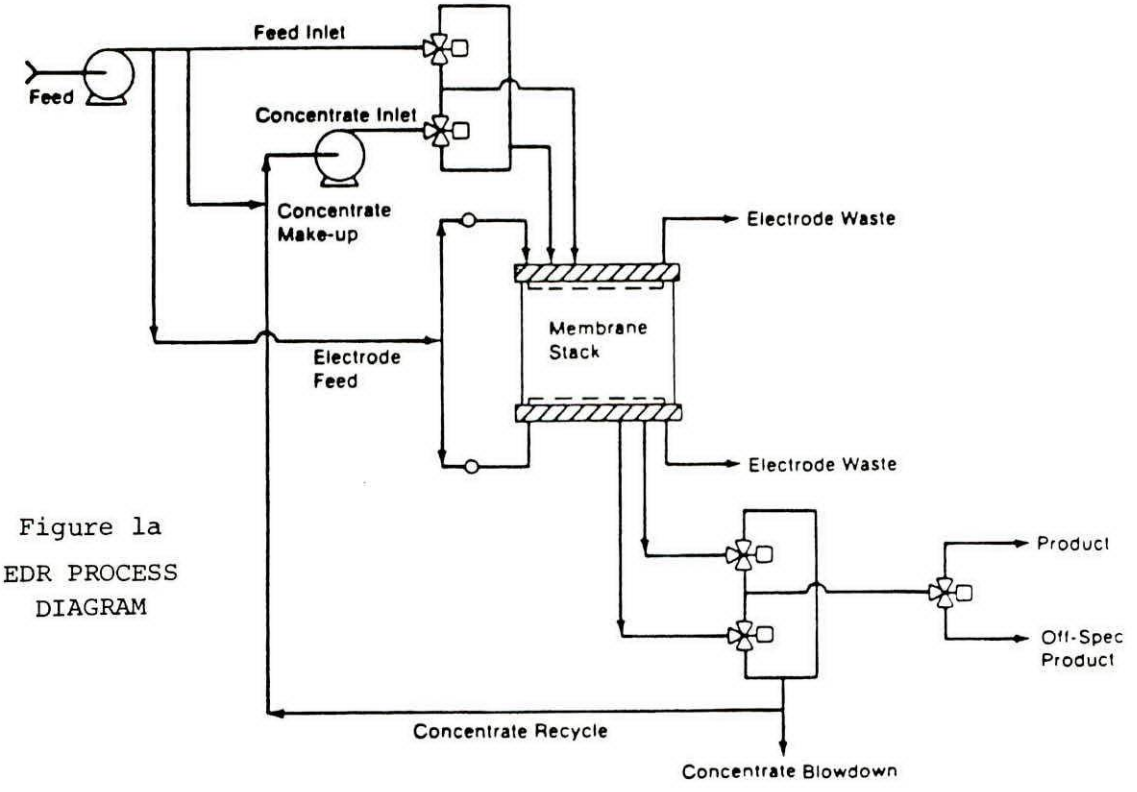


Figure 1a

EDR PROCESS DIAGRAM

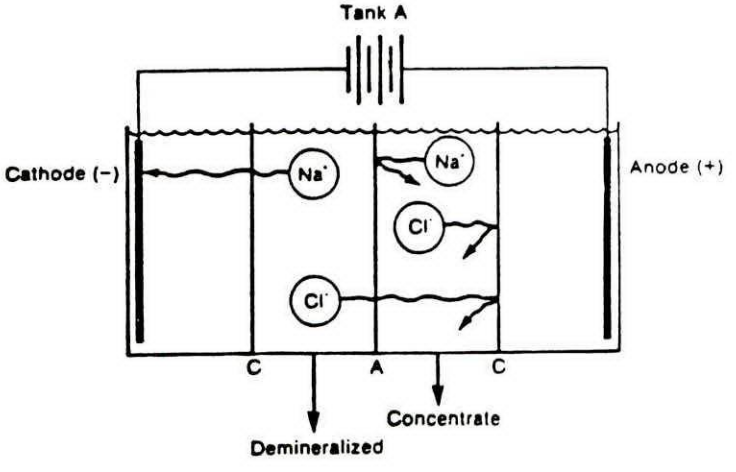
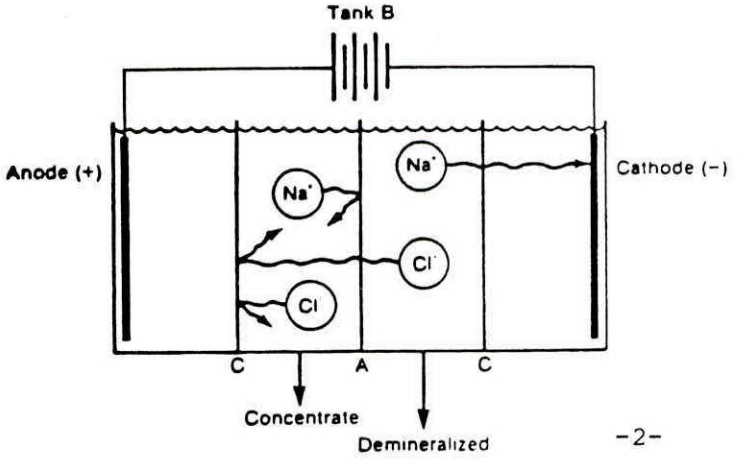


Figure 1b

EDR SCHEMATIC



The polarity reversal principle has been applied successfully in many large commercial units. Today, the largest operating EDR unit is the 6 MGD plant used for demineralizing Tigris River water for a major refinery in Baghdad, Iraq. The success of the EDR process resulted in the design and sale of standard EDR plants ranging in capacity from 500 to 1 million gallons per day. Over 1,400 EDR plants are in use around the world.

Applications of the EDR process range from desalination of brackish water[3] to process water treatment for in situ mining[4], industrial water treatment[5], quality water for safety rest area[6], ponds[7], and deionization of printed wiring board process water[8]. Recently, the EDR process is being used to recover nickel salts from rinse water in nickel plating operation.

EDR NICKEL RECOVERY PROCESS

The early work on unidirectional ED for recovery of nickel salts from rinse water was published in 1972 by Trivedi and Prober[9]. A more comprehensive program conducted by the Ford Motor Company is reported by Marcovac and Heller et. al.[10][11]. Later on, ED is reported in some instances to be used commercially in recovery of nickel salts from rinse water[12]. Today, however, this use of ED is not wide spread due to the following reasons:

- Costs for plating chemicals are considered as raw materials costs and the normal practice has been to pass these costs along to customers.
- Platers have had the impression that electrodialysis systems are less reliable than conventional hydroxide precipitation, evaporation or ion exchange systems.
- Until recently, disposal costs associated with sludge and wastewater effluents have been relatively minor.
- Platers have not been cognizant of the magnitude of cost savings that can be achieved with an effective metal recovery system.

Now having accumulated two years of pilot testing and an additional year of commercial operation with outstanding performance results, EDR systems are available to turn plating waste problems into plating operation profits.

Solving Plating Waste Problems

Consider the case of a large manufacturer of houseware products in the north central area of the U.S. Under environmental pressure to reduce nickel and wastewater effluent discharge levels, the company investigated evaporation, ion exchange, and reverse osmosis prior to selecting an EDR system for its inherent advantages over the other methods. The EDR system was installed to solve a plating shop waste problem.

Based on a reported nickel loss due to dragout of approximately 4,100 lbs per year, the plating operation benefits in four ways as a result of the EDR installation. First, approximately 2,300 gallons of generated nickel hydroxide sludge is eliminated by using the metal recovery system, saving the disposal cost of $6,000 per year. This is based upon an average cost across the nation of $700 per ton of sludge at 35% solids. If long hauling distances are involved, the savings could be greater. Second, there is a reduction of

40,000 gpd in the volume of rinse water waste effluent. By utilizing the metal recovery system, the rinse water requirement for the first running rinse tank is drastically cut. In the involved metropolitan area, basic water and sewerage charges for industry cost $1.17 per thousand gallons. This amounts to over $12,000 per year savings in water charges. Note, however, for an electroplater a surcharge may be involved for the plant effluent arising from its toxicity to anaerobic sewage treatment plants. This cost is not included in these economics. Third, an estimated 4,053 pounds of nickel per year is recovered which, at an average cost of $1.30 per pound for nickel salts, results in a savings of over $21,000 per year. The last benefit is reduced chemical consumption to treat the water , which amounts to a reduced caustic usage of approximately 5,800 pounds per year which, at a cost for caustic in 55 gallon drums of $66 per drum, amounts to an annual savings of $1,100.

The total of these four areas is an annual savings of $40,100. Using a budget price of $50,000 for the EDR Metal Recovery System, the payback on the north central plant is estimated at 2.6 years. Economic calculation are presented in Table 1.

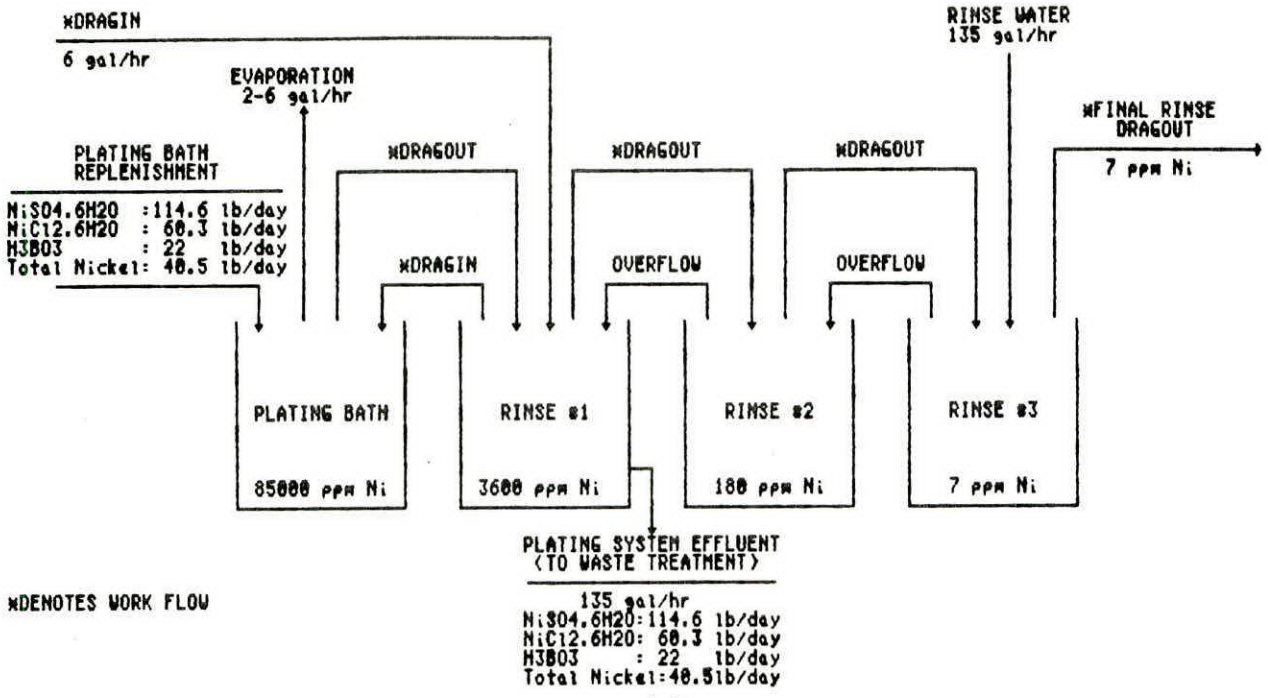
Increasing Plating Operation Profitability

Consider the case of a leading job shop plating operation along the Atlantic Seaboard. The plant, which had been recently modernized, was equipped with a sophisticated waste water treatment system with chrome reduction, cyanide destruction, hydroxide precipitation with clarifier, filter press and cake drier. Although the plant was in conformity with all existing environmental regulations, the owners were aware that total nickel losses due to automatic barrel dragout represented approximately 80 to 100 pounds per day as nickel metal. After investigating recovery options, the owners chose to install an EDR system to recover nickel plating salts that otherwise were being lost via rinse water effluent.

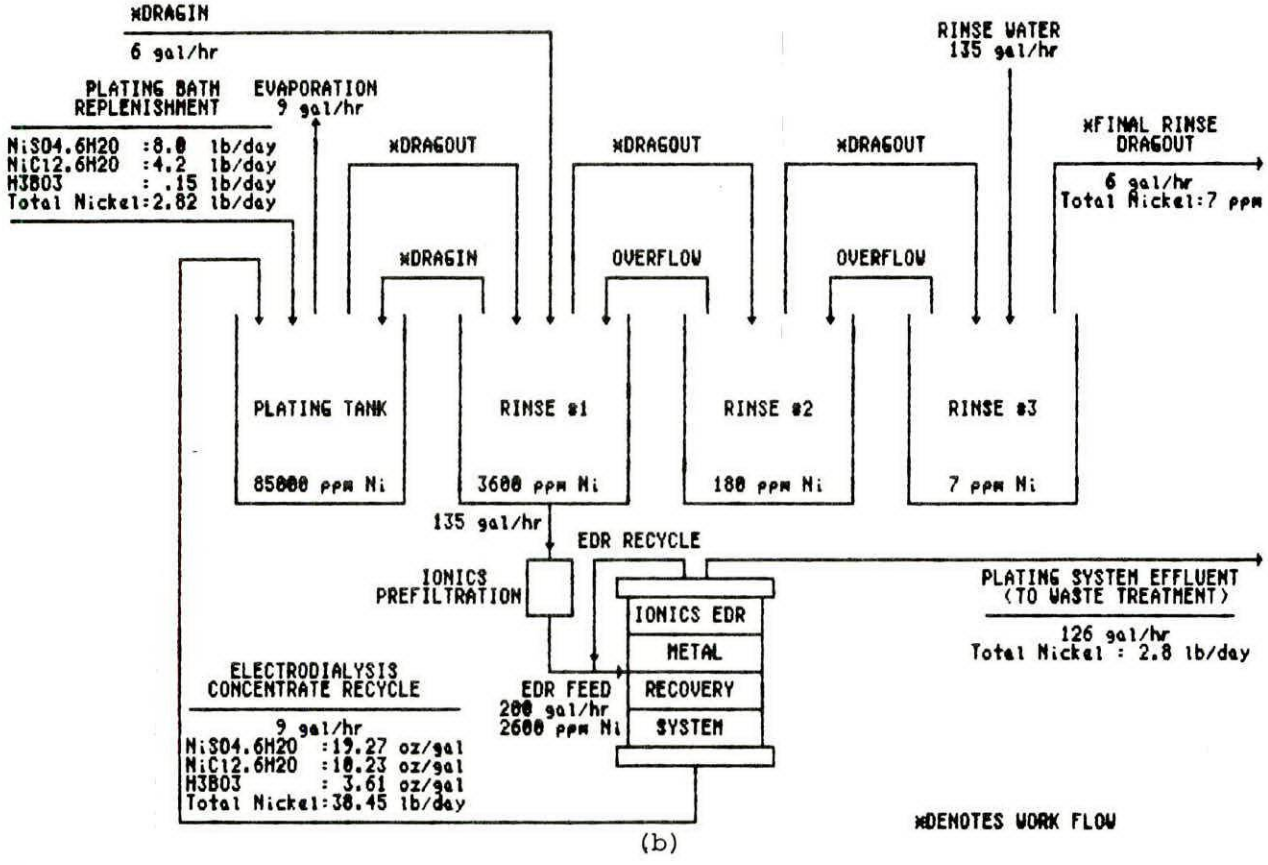
As a result of this installation, the plant profitability improves in three ways. First, annual costs for purchased plating chemicals are reduced by approximately $110,000, based on nickel sulfate at $1.10 per lb., nickel chloride at $1.40 per lb., and boric acid at $0.41 per lb. Second, annual costs for sludge disposal are reduced by $6,600, based on sludge disposal costs of $250 per ton at 95% solids. Third, annual costs for water treatment chemicals are reduced by $2,200, based on 50% sodium hydroxide solution at $0.90 per gallon.

The total of these three areas represents an annual reduction in operating costs of $118,800, a savings which can be used to improve operating profitability or can be passed on to customers to maintain competitive pricing.

Using a budget price of $100,000 for the EDR metal recovery system, the payback on the Atlantic Seaboard plant is estimated at 1.7 years. Details for the plating operation and economic calculations are presented in Figures 2a and 2b and Table 1 respectively.



(a)



(b)

Figure 2: Simplified Flow Schematics of One Nickel Plating Line at a Leading Job Shop on The Eastern Seaboard

TABLE 1

ECONOMICS OF ELECTRODIALYSIS REVERSAL PROCESS FOR NICKEL SALT RECOVERY FROM PLATING RINSE WATER

Items	North Central Plant	Eastern Seaboard Plant
1. Installed Cost		
. Equipment	50,000	100,000
. Installation, labor and materials	1,500	1,500
. Total	51,500	101,500
2. Annual Operating Cost (Estimated)		
. Labor, 100 hours/year @ $10/hour	1,000	1,000
. Maintenance @ 2½% of investment	1,250	2,500
. Raw Materials		
Filter Cartridges	750	1,000
Membrane Replacement (1)	3,000	6,000
. Electricity ($0.05/KWH)	750	1,500
. Total	6,750	12,000
3. Annual Fixed Cost		
. Depreciation, 10% of investment	5,150	10,150
. Tax and Insurance, 1% of investment	515	1,015
. Total Fixed Cost	5,665	11,165
4. Total Cost of Operation	12,415	23,165
5. Annual Savings		
. Plating Chemicals	21,000	110,000
. Sludge Disposal Cost (2)	6,000	6,600
. Water Treatment Chemicals	1,100	2,200
. Water Usage	12,000	--
. Total	40,100	118,800
6. Net Savings (annual savings - (operating + fixed cost))	27,685	95,635
7. Net Savings After Tax 48% Tax Bracket	14,397	49,730
8. Average ROI (%) (net savings after tax/total investment)	27.9	49.0
9. Cash Flow From Investment (net savings after tax + depreciation)	19,547	59,880
10. Payback Period = Total Investment/Cash Flow	2.6	1.7

(1) assuming 2 year membrane life

(2) @ 35% solids for North Central plant and @ 95% solids for Eastern Seaboard plant

IN CONCLUSION

The EDR system is unique in providing the automated self-cleaning process which results in prevention of scale formation on the membrane surfaces. With EDR technology, fouling and frequent cleaning operations associated with classical ED and other membrane systems are virtually eliminated. The EDR system offers the benefits of reliability, low operating cost, minimum operator attention, and short-term payback in capital investment.

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E-4

Environmental II
Session E

Low Cost Recovery

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LOW COST RECOVERY

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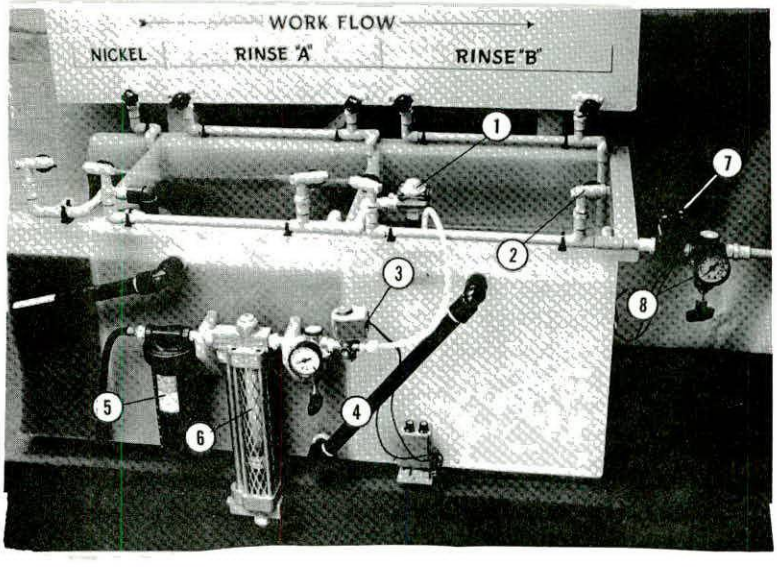
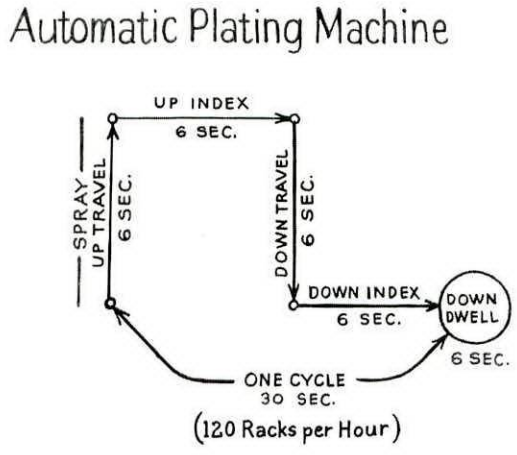
In most plating shops, drag-out is the single greatest cause for expense with regards to chemical consumption and waste treatment cost. Through the years our industry has spent countless thousands of dollars in treating perfectly good chemicals which in turn have to be replenished by newly purchased chemicals. It is paramount that our industry recognize that "a rinse tank is nothing more than a diluted plating tank". It has the same chemicals and in the same proportions as the plating tank. The only difference is a matter of concentration. This paper deals with the concept of returning the dragout back to the plating tank in a cost effective and simple method. We concentrate in two areas:

1. Minimize the amount of rinse water required to adequately rinse plated parts.
2. Maximize the amount of headroom available in the plating tank to accomodate the return of these dragged out chemicals.

MINIMIZE RINSE WATER

To accomplish this first part, we utilize what we call "Pulse Spray Counterflow Rinsing".* Most rinse systems involve adding fresh water to the second rinse tank and allowing this relatively clean water to counterflow through an external pipeline into the first rinse tank where it becomes contaminated in the more contaminated rinse tank. This cleaner rinse water of the second rinse tank can be used far more effectively by counterflowing it through a spray system where it rinses off the more contaminated rinse water of the first rinse, resulting in much less carryover of contamination. This method of rinsing (Fig 1) allows you to accomplish five very distinct rinse operations with only two rinse tanks. You have the spray rinse upon exiting from the nickel tank, spray rinse on exiting from Rinse Tank A and spray rinse upon exiting from Rinse Tank B in addition to the two normal submerged rinses A & B.





For maximum spray rinsing effectiveness, spray must occur only during the vertical exit of the part from the plating or rinse tank. Figure 2 shows the movement sequence of an automatic plating machine. The sprays are triggered only during the 6 sec. up travel and are off during the up index, down travel, down index, and down dwell. The sprays are therefore on for 6 sec. of a 30 sec. cycle or 20% of the time. This allows for a high instantaneous spray flow rate for effective spray rinsing with a low average rinse water flow. All rinse water movement between tanks occurs through the sprays and only during the up motion of the machine. Referring to Fig.1, the movement of water from Rinse Tank B to Rinse Tank A is effected by the air powered pulse pump (1) located in Rinse Tank B. This pulse pump feeds the spray nozzles (2) located over Rinse Tank A. Triggering the pulse pump is an air solenoid valve (3) activated by the control system of the automatic plater. Also required is a pressure regulator (4) to control spray intensity. The system operates on shop air introduced into an oil coalscing filter (5) followed by a MICRO polishing filter (6) which has a colormetric indicating replaceable cartridge. The only fresh water introduced into the rinsing system comes through a water solenoid valve (7) and is also activated by the control system of the automatic plating machine. This fresh water is fed through the spray system located over Rinse Tank B. The water in Rinse Tank B is pumped by the air pump located in Rinse Tank B through the spray nozzles over Rinse Tank A. The water in Rinse Tank A is simultaneously pumped by a second air pulse pump located in Rinse Tank A through the spray nozzles over the plating tank. Therefore all the rinse waters introduced into the rinse system ends up in the plating tank along with the dragged-out chemicals, thereby closing the loop. This method of rinsing has proven to be so effective that it provides the same degree of rinsing with three gallons of water per 100 sq.ft. that with normal counterflow rinsing would require 15.6 gallons per 100 sq.ft. (Figure 3).

PULSE SPRAY COUNTERFLOW RINSING

Water required for comparable rinsing of 100 square feet

Single Rinse "A" only	*500 gal.*
Separate water feed to "A" & "B"	*30.6 gal.*
Water feed to "B" & counterflow to "A"	*15.6 gal.*
Water feed to "B" & pulse spray counterflowed to "A" and to process tank	*3 gal.*

Figure 4 refers to a company located in Tennessee which operates a Full Automatic plating machine 24 hours/day at 120 racks per hour with 6.6 sq.ft. of surface area per rack. This results in 800 sq.ft. of surface area being plated per hour. Operating at 120 racks/hour is a 30 sec. cycle time and in this case they have a 6 sec. lift. The "Pulse Spray Counterflow Rinse" occurs only during this 6 sec. vertical lift. The sprays therefore operate but 1/5 of the time, and therefore allow for an instantaneous spray at five times the average flow rate. They have four 0.5 GPM spray nozzles on each rinse tank. They spray at a 2 GPM rate 20% of the time for an average flow rate of 0.4 GPM. This is but 24 gallons of fresh water per 800 sq. ft. or 24 gallons per hour. This is only 3 gallons/100 sq. ft. of surface area as shown earlier. The three jars shown contain solutions from this automatic plater. The first jar contains the nickel plating solution with a nickel concentration of 11.2 oz/gal. As the work rises

from this tank, it is sprayed down with water from Rinse Tank A where the Nickel content is 0.48 oz/gal. As the work rises from Rinse Tank A, the work is sprayed down with the rinse water from Rinse Tank B which has a nickel metal content of 0.03 oz/gal. Upon exiting from Rinse Tank B, the work is sprayed down with fresh water. This results in near perfect rinsing with only two rinse tanks and using only 24 gal/hr of fresh water.

To accomplish total recovery we must return this 24 gal/hr of rinse water to the Nickel Tank which, under normal conditions, is incapable of accepting this volume due to inadaquate head room.

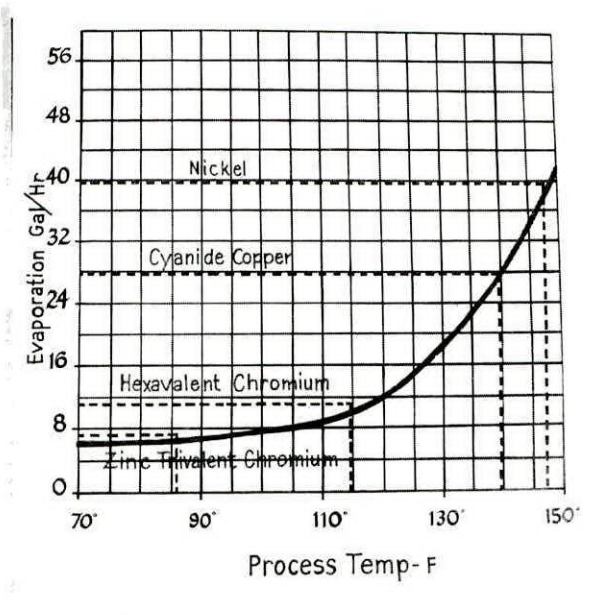
MAXIMIZE HEADROOM

To generate headroom in the process tank, we suggest the use of an atmospheric evaporator because they are inexpensive, effective and simple, requiring very little maintanence.

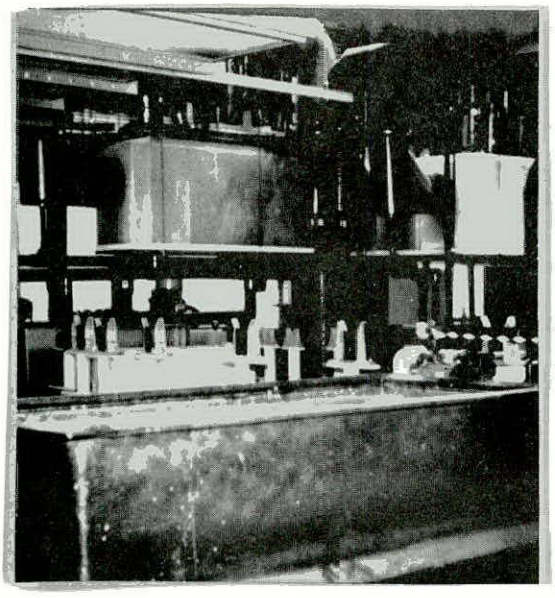
Unsaturated air will absorb moisture from wet surfaces. As the relative humidity drops the rate of evaporation increases. The evaporator creates headroom in the process tank by taking advantage of airs ability to absorb water from the process solution while leaving the valuable salts behind. Depending upon relative temperatures, hot air may warm the process solution and conversely evaporation, which produces a refrigerating effect, cools the solution. Conditions which favor evaporation are: hot air, dry air, hot solution, and high air flow.

Figure 5 shows approximate evaporative rates that can be expected from a fairly small evaporator. Be mindful, however, that this curve is strictly an approximation of evaporative rates to be expected and actual numbers could be less or greater depending upon the atmospheric conditions.

Single effect evaporation requires about 8,000 BTU/gallon of water evaporated. To supply this energy, the evaporator pulls heat from the process solution. In order to make the evaporator more economical to buy and operate, we use equipment the plater already has on hand but is under utilizing. For example when sizing a boiler for a nickel plating line, most of the boiler capacity is to provide energy for a 3 hour heat up. During operation, most of this heat capacity is unused and therefore available for evaporation. By taking advantage of this on hand capacity, the company saves the capitol expense of extra heat generating equipment and actually utilizes his boiler more efficiently with the higher steam demand. With this approach, the evaporator offers a lot of performance with a small price tag.

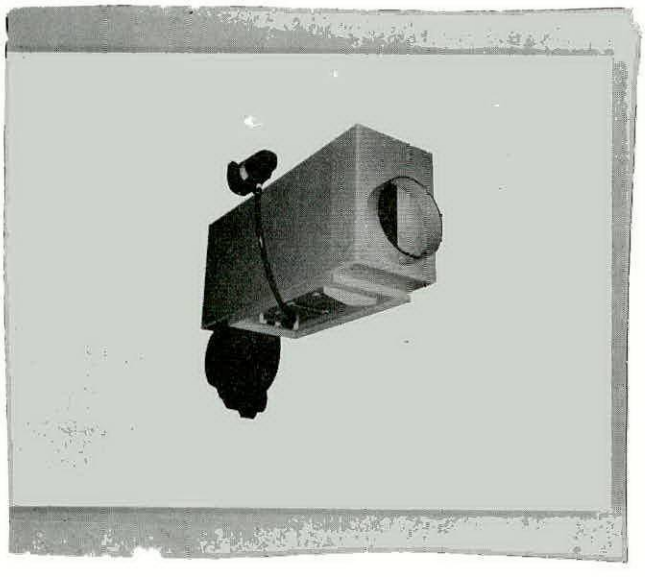


Evaporation of a pure salt solution will produce a pure water vapor while leaving the salts behind in solution. If there are volatile components in the solution, as is sometimes the case in plating processes, these components could enter into the vapor phase, thereby becoming a component of the discharged air. As a general rule of thumb, the air discharged from the evaporator is approximately of the same quality as the air immediately above the plating tank. A toxic tank requiring fume scrubbing may require similiar treatment of the air being discharged from an evaporator. Common practice for tanks with existing ventilation is to use this system to draw air through the evaporator in lieu of using a blower. (Figure 6)



EVAPORATIVE EQUIPMENT

The atmospheric evaporator (Fig.7) is a rather simple flow through device where the process solution is pumped and sprayed over packing to maximize the contact between solution and air. Typically the unit would be located at a higher elevation than the process tank it is servicing to allow for gravity flow return. It is imperative the entire system be chemically compatible with the process solution which it is servicing. Materials of construction such as PVC, polyethylene, and polypropylene are very commonly used in the plating industry.



Other areas of consideration are:

1. Horizontal air discharge to prevent condensation from running back into the evaporator.

2. Randomly oriented packing which continously redistributes the fluid flow to prevent channeling and plugging.

3. Non-atomizing spray nozzles which minimize foaming and provide good fluid distribution.

4. Vertical mist eliminators to provide the best draining of coalesced droplets

5. Easy accessibility to the interior without having to dismantle the ducting.

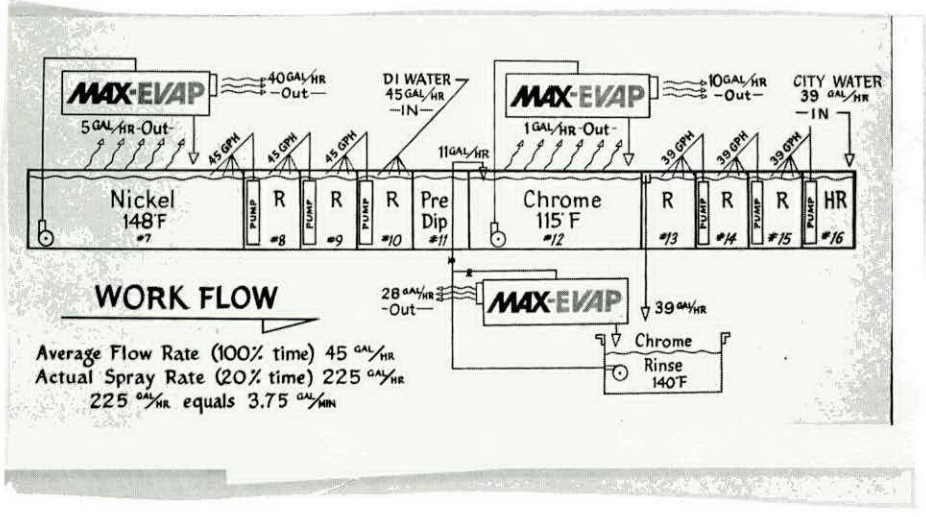
6. Blower separated from the spray compartment to keep corrosive solution away from the blower.

The evaporator allows the plater to recover some or all of his dragged-out plating chemicals. Any degree of recovery, partial or total, will result in reduced waste treatment costs as well as savings on plating chemicals.

CLOSING THE LOOP

Referring to Fig. 8, you can see how easy it is to obtain a closed loop system when dealing with a process that is elevated in temperature such as nickel. At 148°F, the anticipated evaporative rate is approximately 40 gal/hour (Fig. 5). Coupling this with normal tank evaporation of approximately 5 gal/hour results in a total evaporative loss from the nickel tank of 45 gal/hour. This allows for the addition of 45 gal/hour of rinse water to the Nickel Tank. This 45 gal/hour is added at Tank #10 by way of a water solenoid valve actuated by the machine to spray during uplift only. Because the spray occurs only 20% of the time, the instantaneous spray flow rate is 5 times the 45 gal/hr or 225 gal/hr which equals nearly 4 gpm. By locating a spray nozzle at each of the four corners of each rinse tank, each nozzle will spray at approximately 1 gpm for 6 seconds every 30 seconds. This results in excellent rinsing with only 45 gal/hour of fresh water being introduced into the system which when "Pulse Spray Counterflowed" to the Nickel Tank will totally close the loop.

When applying this system to a low temperature process we must take a slightly different approach. The evaporative rate of low temperature processes is not sufficient to sustain an adequate rinse water return directly to the process tank by way of the "Pulse Spray Counterflow Rinse" system. Because of this evaporative deficiency it is necessary to incorporate a heated side tank (Fig.8 Chrome System). This example indicates an average rinse water flow requirement of 39 gal/hr. The evaporative rate of a 115°F Chrome bath is about 10 gal/hour (Fig.5). We must therefore have secondary evaporation from the system if we are to accomplish a closed loop condition. This is achieved by overflowing Rinse #13 into a side tank, and by heating the side tank to 140°F, we can expect an evaporative rate of approximately 28 gal/hr. which will reduce the 39 gal/hr. average rinse flow rate to 11 gal/hr. This can now be returned to the Chrome tank to offset the 1 gal/hr. of natural evaporation and the 10 gal/hr. by the evaporator.



In addition to closing the loop, in this case, we also cool the chrome solution which will reduce mechanical refrigeration requirements. The evaporation of 10 gal/hr. represents over six tons of refrigeration.

AREAS OF CONCERN

There is an old saying amongst platers,"Dragout is a platers best friend". This is because dragout limits the build up of harmful contaminents in the plating bath. As we go from partial to total recovery, contaminents may build to harmful levels that must be dealt with. When recovering bright nickel, for example, it is desirable to use deionized rinse water to prevent the build up of calcium and magnesium. Should this occur, however, it can be removed with a flouride treatment.Sodium, while a potential problem has never proven harmful despite many years of total recovery. Experience has shown sodium leveling off at approximately 20,000 ppm. In some operations, organic contamination could be a problem with total or partial reclaimation. This has been readily controlled with increased carbon filtration and routine additions of hydrogen peroxide to the nickel plating bath. The rinse water system may also on occasion require carbon filtration and/or the addition of small amounts of formaldehyde to prevent white wash in the chrome plate due to organic films or biological growths on the surface of the nickel plate.

In recovering hexavalent chrome, care should be taken to avoid the build up of metallic ions such as nickel, copper, iron, zinc, and trivalent chrome. These may be dealt with by using a cation exchanger on the rinse water prior to returning them to the chrome plating tank.

Recovery of cyanide plating baths may result in the build up of carbonates. The normal methods of removing carbonates are by freezing them out in the winter time or precipitating them out by using barium cyanide or calcium oxide.

In the case of cyanide zinc plating it is customary to preceed the plating operation with a Muriatic acid pickle. This will result in chlorides being dragged into the cyanide zinc process tank which with a closed loop system would build to an intolerable level. The chloride ion is converted at the steel anode basket to chlorine which attacks the steel baskets, cooling coil, brightner system, and sodium cyanide only to return again to the chloride ion and repeat its destructive cycle while never being eliminated from the system. In view of this, we recommend the acid ahead of the cyanide bath be a sulfate based material rather than chloride. This would require the operator to strip his parts and danglers off the plating line. Sulfate being dragged into the cyanide zinc will simply build to a point where it will "freeze out" along with the carbonates as necessary.

APPLICABILITY

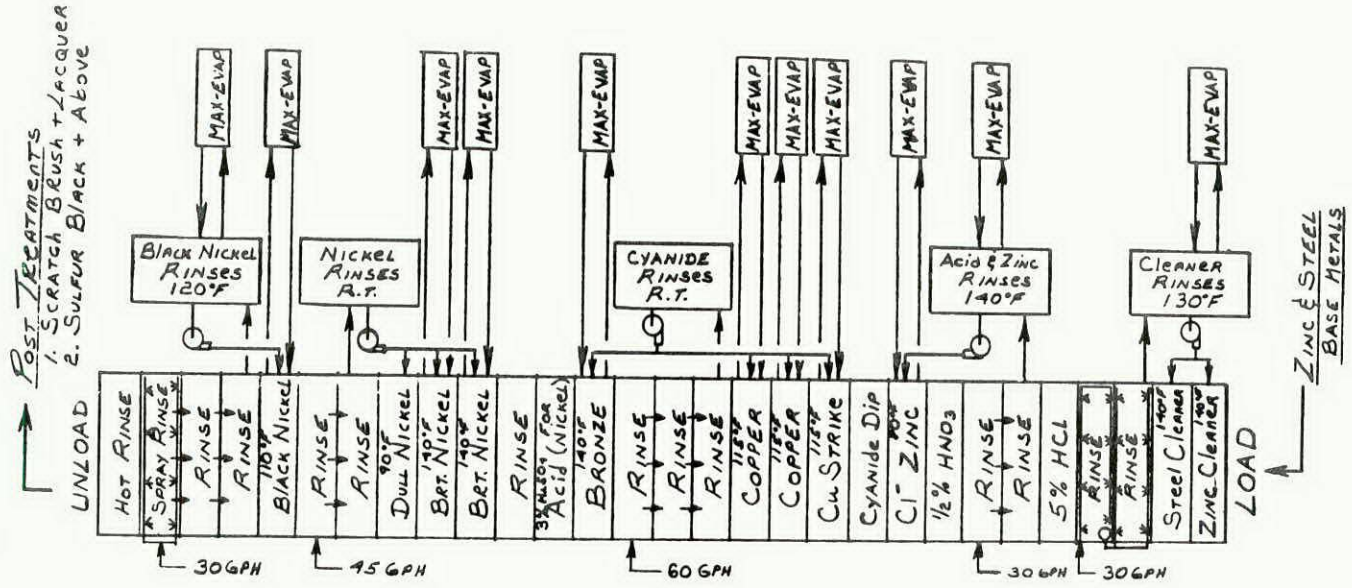
Many laboratory tests have been run on Acid Chloride zinc and Alkaline Non-cyanide zinc processes. The tests involved first running an "AS-IS" hull cell panel on the plating solution. A 300 ml sample of solution was then diluted to 600 ml and heated to 160^{o}F with air agitation for 48 hours while maintaining the solution volume at 600 ml. Thereafter, the volume was allowed to evaporate down to the original 300 mls at which time a second hull cell panel was run. In all cases, this second panel was inferior to the original but was capable of being restored to original appearance with a small addition of brightner.

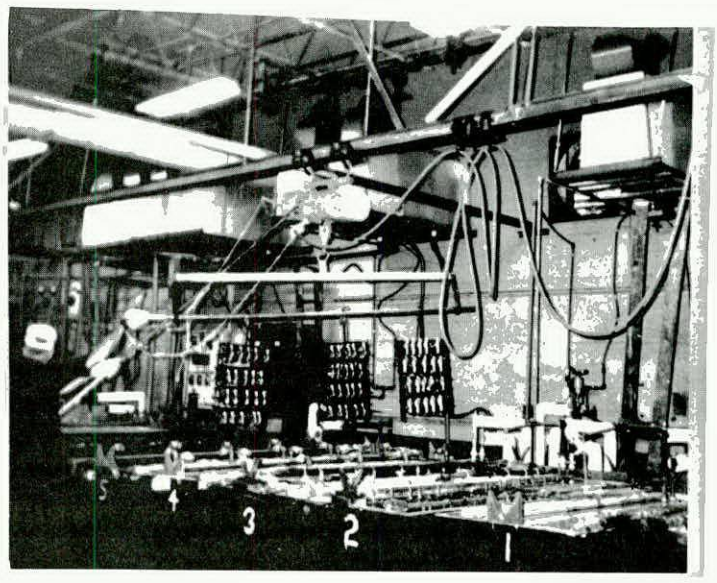
When we close the loop we are treading in unchartered waters and there is a certain risk factor involved. Our industry has been well aware of various treatments involving carbon, hydrogen peroxide, potassium permanganate, and electrolytic dummy plating, which allow us to remove most contaminents should they build to a detrimental level.

There are yet many problems to be experienced and answers to be resolved but, generally speaking, with a little forsight and ingenuity these problems can be avoided or corrected with a minimum amount of expense and effort.

INDUSTRIAL APPLICATIONS

Figure 9 shows the schematic layout of a plant located in Virginia which manufactures casket hardware. This company does not have a sewer line but simply a septic tank for their lavatories. EPA gave them a November, 1985 deadline to stop using an outdoor unlined lagoon for their plating department discharge. They have no waste treatment facilities and the only way they could remain in operation was by using the evaporative reclaim system as shown in the schematic. They have incorporated "Pulse Spray Counterflow Rinsing" and 14 evaporators into their system, (Fig.10 & Fig.11), allowing them to totally close the loop on all rinse waters including the cleaner and acid rinses. The Cleaner and Acid dumps are treated monthly on a batch basis.





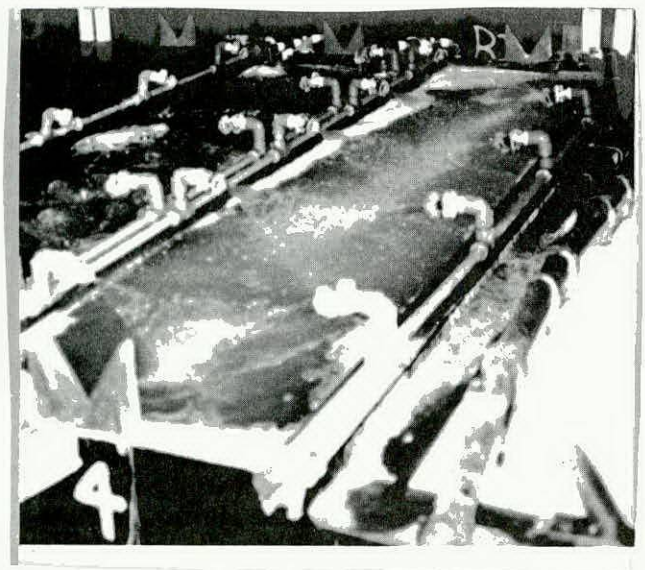
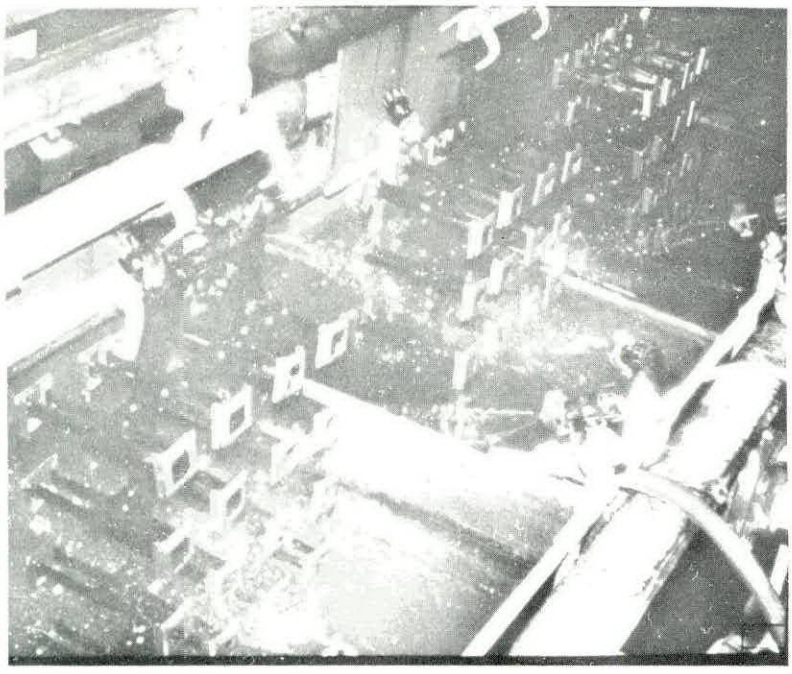


Figure 12 shows a small full automatic nickel chrome plating machine which operates at 106 transfers/hour plating satin nickel and chrome on automotive hardware. There are three nickel rinses and five chrome rinses. By using "Pulse Spray Counterflow Rinsing" and evaporative recovery, their water bill on this machine has fallen from $1,100.00/month to $85.00/month. The final rinse tanks show nickel at 5.6 ppm and chrome at 5.0 ppm. They have no waste treatment system yet the local EPA official recently told the owner they have the cleanest shop he has ever seen.



Clearly "Pulse Spray Counterflow Rinsing" enables the plater to reduce the volume of rinse water required without sacrificing quality of rinsing.

Since 1980 we have located near 200 evaporative units throughout industry on such processes as acid chloride zinc, cyanide copper, hexavalent chrome, trivalent chrome, nickel and acid copper.

CONCLUSION

"Pulse Spray Counterflow Rinsing" and atmospheric evaporators provide a very simple yet effective system for reducing or eliminating waste treatment while saving chemicals. The simplicity of this concept can be easily understood by both plater and maintanence people alike. The owner of a business will experience in most cases, a two to six month payback on investment.

As an industry we have been extremely wasteful of our resources, and if we are to remain viable, healthy, and competative we must become more cost effective to off set the new technology in powder coating, electrophoresis and other organic finishes. We must develop and perfect improved methods of reclaimation bearing in mind that: "A rinse tank is but a diluted plating tank", comprised of perfectly good reusable chemicals.

DON'T WASTE IT -- USE IT !!

E-5

Environmental II
Session E

Groundwater Treatment Aspects Of Remedial Action Plans for Electroplaters/Metals Finishers

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GROUNDWATER TREATMENT ASPECTS OF REMEDIAL ACTION PLANS FOR ELECTROPLATERS/METALS FINISHERS

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Introduction

Groundwater contamination assessment and clean-up has become a high priority on the agenda of environmental protection. The enactment of federal Superfund legislation has been followed by activity on the state and local levels to address contaminated sites not in the scope of federal cleanup efforts. Guidelines for development and implementation of remedial action at hazardous waste sites have been incorporated as part of the National Contingency Plan (NCP) which provides procedures and protocols for all cleanup activities associated with federal Superfund sites. The purpose of the NCP is to establish standardized methods for hazardous waste site activities to ensure that the cleanup activities deal adequately with issues of environmental protection, cost effectiveness and technical feasibility of applied treatment technologies, and protection of the health and safety of site workers and the general public. The NCP concepts have been largely adopted by State Agencies for use in non-Superfund site cleanup activities such as industrial groundwater contamination studies.

The manufacture of printed circuit (wiring) boards and electronic components as well as the surface finishing of various base materials requires the use of chemicals that, when spent, must be properly disposed of. Federal and state hazardous waste agencies currently regulate disposal practices for these chemicals. Unfortunately certain past legal disposal options, such as the pretreatment of industrial wastewater and discharge to waste lagoons may require remedial action to restore the groundwater. In other cases, the corrosive nature of many of the chemicals utilized by the industry caused floor slab and sewer pipe line damage with subsequent contamination of the soil and water under the site.

The potential impact of these contaminants is evaluated by the risk assessment process. The effect of contaminants on the human population and the environment is assessed, with mechanisms of exposure and potential exposure levels investigated relative to the toxicity of individual identified contaminants. Depending on the findings of this risk assessment and the regulatory review process, removal of the contaminants may be required.

In the two case studies presented herein certain groundwater pumping, treatment and disposal alternatives were chosen as the remedial action plan. This paper will update earlier case histories presented by our firm at the 7th Annual AESF/EPA Conference.

CASE STUDY 1

Introduction

Site 1 involves the release of wastewater from a facility engaged in electroplating of electronic components. The facility is located on a six-acre site in an area of light industry bordering on a residential area of condominiums and single family dwellings.

Problems at the facility including wastewater discharge violations and visible signs of wastewater leakage into the soil were the subjects of inspections by the municipal sewer authority and the local Board of Health in 1980 and 1981. In 1983, suspected soil contamination from a leaking wastewater conveyance pipe was verified by soil testing conducted by the owner of the site, which indicated contamination of the soil with metals, cyanides, acids, and volatile organic compounds (VOCs) such as 1,1,1-trichloroethane. The state environmental agency hazardous waste division was notified of the evidence of a release to the environment, and the agency ordered a complete site assessment to be conducted. The site assessment activities were initiated in January, 1984.

Inside the facility, corrosion in the wastewater conveyance trench system was discovered to have allowed leakage of wastewater to the soil below. Contaminated soil beneath the trenches was excavated and disposed as a hazardous waste along with the corroded concrete lining the trenches. This action was taken outside the framework of a Remedial Investigation/Feasibility Study, an action agreed upon by the owner and the regulating agency as a positive and expedient resolution of the problem. The action was taken at the request of the owner to allow an on-going renovation of the building interior to proceed on schedule.

Site History

A site history was compiled to identify past and present chemical usage and waste handling and disposal practices. Existing analytical results on samples of soil and groundwater, wastewater discharge monitoring reports, hazardous waste hauling invoices, and raw materials purchases were incorporated, rumors were heard of drums containing hazardous waste being buried on-site and other information which would be useful in planning a site sampling and analysis plan, as well as providing a preliminary basis for designing a site safety plan.

Field Investigation Activities

Geophysical survey techniques were employed on the site prior to additional sampling efforts in order to provide information about the subsurface geology, the depth to water table, contaminant distribution, and the presence of buried waste drums. Seismic refraction, electrical resistivity, electromagnetic induction, and ground penetrating radar were used to study the site. The data gathered from the geophysical surveys was used to plan the construction and installation of groundwater monitoring wells and to help locate the wells in

areas of probable contaminant occurrence. No evidence of buried waste drums was found and the issue of buried drums was of no further concern.

The field investigation included installation of nine groundwater monitoring wells including one well intended as a background well, located upgradient of the site groundwater flow and at a distance of 170 feet from the facility (Refer to Figure 1). Hydrogeological observations were made to determine soil permeability and other groundwater flow characteristics. Soil and groundwater samples were collected from the well installations and analyzed for a range of test parameters based on the site history. VOCs were the major contaminants of concern, reaching a maximum of 91,000 parts per billion, 1,1,1-trichloroethane, for example, in the groundwater. Other contaminants of significance in the groundwater included cadmium, copper, nickel, sulfate, and fluoride.

Data Interpretation/Risk Assessment

The major contaminant source was found to be leaking underground wastewater collection sumps, with lesser contributions from other sources such as leaking wastewater conveyance pipes and trenches. The wastewater was introduced into a fine sand and silt material that was found to be the predominant soil type above bedrock. The fine grained material limited movement of the contaminants in both the horizontal and vertical directions. It was estimated that very limited off-site migration of contaminants could have taken place, given the calculated rates of travel (approximately four feet per year) and the 20 year period over which the facility had been operating and using chemicals. Movement of contaminants through the underlying aquifer was the only avenue of migration of contaminants away from the site, since the contaminants were not located near the surface and could not be picked up by surface run-off. The nearest receptors in the path of groundwater flow from the site were a group of private water supply wells located approximately 1,700 feet downgradient of the site. The major risk associated with the contamination at Site 1 was degradation of the aquifer water quality that could render the local water supply wells unusable.

Groundwater Recovery and Disposal

Selection of remedial action alternatives began with the decision to recover contaminated groundwater from the aquifer for treatment. The alternatives for groundwater recovery included deep wells with submersible pumps and well point systems for use at shallow depths. While most of us are familiar with deep wells utilizing submersible pumps, a well point system should be explained. This system consists of a group of closely spaced wells connected by a header pipe. A central pump can be used for the entire well point system depending upon the depth, volume pumped and soil permeability. Spacing between well points usually ranges from 2 to 6 feet with flow rates usually less than 5 gpm. In comparison, higher capacity deep wells can be spaced at a greater distance due to their increased drawdown of the aquifer.

Further information for selection of the recovery method was provided in this area by the construction at the site of a groundwater recovery well which was used to perform a pump test to evaluate the response of the aquifer to ex-

tended pumping. The results of this test indicated that deep wells would be more efficient in collecting groundwater on the site than a shallow well point system. A total of four wells would be required to effectively contain the contaminated groundwater and collect it for treatment.

Before considering alternatives for treatment of the recovered groundwater, it was useful to explore the range of possibilities for disposal of the treated groundwater, since the method of disposal would have an effect on the level of treatment required. The three alternatives for disposal of treated groundwater were: use as process water, with final treatment and disposal to the municipal sewerage system; discharge to surface water; and on-site recharge of the aquifer.

Process use and discharge to the sewerage system was attractive from the standpoint of decreased water supply costs and the relatively less rigorous discharge standards imposed by the sewer authority, but was limited by the process water quality requirements and the limited volume that could be recycled versus the amount of groundwater to be recovered for treatment. Discharge to surface water required the most exacting treatment to meet stringent aquatic toxicity standards.

On-site recharge was selected as the most feasible method of disposal. Through proper placement of recovery wells and the recharge system, the treated groundwater could be recycled in a closed loop system, which offered the possibility of soil flushing to extract contaminants which might otherwise be left in the soil. The closed loop concept was also favored by the regulatory agency and would allow initial discharge of treated groundwater at levels exceeding the groundwater quality standards, provided that groundwater quality standards would be met at some point before system shutdown.

Groundwater Treatment

Alternatives for groundwater treatment were considered in three parts; metals, VOCs, and anions such as fluoride and sulfate. Alternatives for metal removal included chemical precipitation followed by conventional sedimentation and granular filtration, and chemical precipitation followed by ultrafiltration. The ultrafiltration alternative was chosen because an existing on-site wastewater pretreatment system utilizing ultrafiltration technology became available for use in groundwater treatment. This approach afforded the advantages of cost effectiveness and ease of implementation while providing acceptable metals removal. A treatability study was performed on a representative sample of contaminated groundwater to assess system performances and effluent quality results. Using lime addition to a pH of 9.5 s.u., the following results were obtained:

Metal	Influent, mg/L	Effluent, mg/L	Groundwater Quality Standard, mg/L
Nickel	20	0.1	0.63
Copper	18	0.1	1.0
Cadmium	0.06	0.003	0.01

Air stripping and granular activated carbon (GAC) were considered as alternative treatment technologies for VOC removal. Both treatment methods were feasible from the standpoint of being able to achieve the desired VOC removals. Operationally, GAC required periodic regeneration of the carbon bed, requiring on-site regeneration equipment or hauling the carbon to an off-site facility. The potential for VOC breakthrough as the carbon approaches its capacity for adsorption requires careful monitoring of the effluent. Air stripping however, provides relatively constant removal performance with minor operation and maintenance requirements, and no associated residual waste disposal costs. Quantities of VOCs that would be discharged into the air from the equipment were not significant and state air regulatory authorities approved of the operation. For these reasons, air stripping was chosen for VOC removal at Site 1.

Removal of the anionic components of the groundwater, sulfate, fluoride, chloride, and nitrate, required the likely use of reverse osmosis or ion-exchange, at significant increases in treatment system equipment costs and operating and maintenance requirements. Estimation of the dilution effects that would be achieved during the groundwater recovery/recharge cycle however, indicated that without treatment, the anions would be reduced to groundwater quality standard levels or below, and that no adverse effects on groundwater quality would occur. Should operating data indicate this is not the case, removal would be required.

Remedial Action Plan Design

The final remedial action plan consisted of four major elements: groundwater recovery wells, chemical precipitation/ultrafiltration, air stripping, and treated groundwater recharge. Following approval of the conceptual design by the regulating agency and public review through the mechanism of the groundwater discharge permit process, implementation of the remedial action plan was initiated.

Final design parameters for the groundwater recovery wells and the recharge system were developed from previously obtained pump test data and permeability testing conducted on-site. Groundwater recovery was achieved with four wells extending into bedrock with a combined design pumping rate of 80 gallons per minute (gpm). Treated groundwater would be recharged to the site through a leaching trench with an area of 3,600 square feet, 420 feet in length.

The air stripper design was completed using data obtained during a pilot test conducted on-site. The final air stripping design specified a 4 foot diameter stripping tower with 11 feet of packed height, with recirculation of the groundwater through the tower for multiple-pass treatment capability. The maximum volume/volume air to water ratio was 150:1 at 80 gpm. The overall design removal efficiency was 99.91%.

Operating Results

This section will be distributed and discussed at the 73rd Annual AESF Technical Conference and will be based on actual operating results from the second quarter of 1986.

CASE STUDY 2

Site Conditions

The site described in Case Study 2 occupies an area of 270 acres, 100 of which are developed with buildings, parking and storage areas, etc. The facility operations include printed wiring board production. A number of VOC spills occurred in the developed area, beginning about 1957. Trichloroethylene was the principal contaminant found at the site. VOC contamination in the groundwater was measured at levels as high as 250,000 parts per billion (ppb) in an area of 3 to 4 acres, with a total area of about 60 acres exhibiting VOC levels of 100 ppb or greater.

The overburden soil is separated from bedrock by a relatively impermeable layer of glacial till, forming two aquifer systems. Leakage of VOCs into the lower bedrock aquifer was influenced by the presence of industrial water supply wells at the site, causing a downward flow component of the groundwater from the overburden to the bedrock.

Remedial Action

Remedial action at the site was concerned with preventing off-site migration of VOCs and removal of VOC from the groundwater. As in Case Study 1, groundwater pumping and treatment was chosen as the preferred remedial action. Disposal alternatives for treated groundwater included process use, direct discharge to the municipal sewerage system, and on-site recharge. The presence of naturally occurring iron concentrations of up to 35 parts per million (ppm) in the groundwater would require iron removal as part of the treatment system if the process reuse alternative was selected. Discharge to the municipal sewer was selected as the most cost-effective alternative.

The groundwater recovery system was designed to withdraw groundwater from the overburden and bedrock aquifers with two separate well systems to prevent further downward migration of VOC contaminated groundwater into the bedrock aquifer. It was determined that such migration would increase the time required to complete groundwater renovation. The overburden recovery system was designed as a shallow well point system composed of 24 well points. An existing deep well was selected for groundwater recovery from the bedrock. The total design withdrawal rate of groundwater from the well systems is 160 gpm.

As in Case Study 1, air stripping was selected as the treatment alternative for VOC removal. Final design of the air stripper was based on a pilot study conducted at the site. The desired VOC effluent concentration for discharge of treated groundwater to the municipal sewer was 50 ppb, total VOCs. The specified system, for a design flow of 160 gpm, was a two tower system in series. Each tower was 3 feet in diameter with a packed height of 24 feet and a removal efficiency for trichloroethylene of 99.5 per cent per tower at a volume/volume air to water ratio of 100:1.

Summary

Two remedial action case studies have been presented that illustrate the remedial action process as conducted by site owners. In both cases, the remedial action process, from site investigation through implementation was conducted over a period of approximately 2-1/2 years. Investigation of the site hydrogeology and contaminant distribution accounts for a large proportion of project duration, but it is time well spent. Complexity is the rule rather than the exception when describing site hydrogeology, and insufficient data will inevitably result in inadequate design and excessive cost impacts. The stepwise approach to remedial action as described herein is intended to ensure that both the technical and economic aspects of a project are properly addressed so that a successful result is achieved.

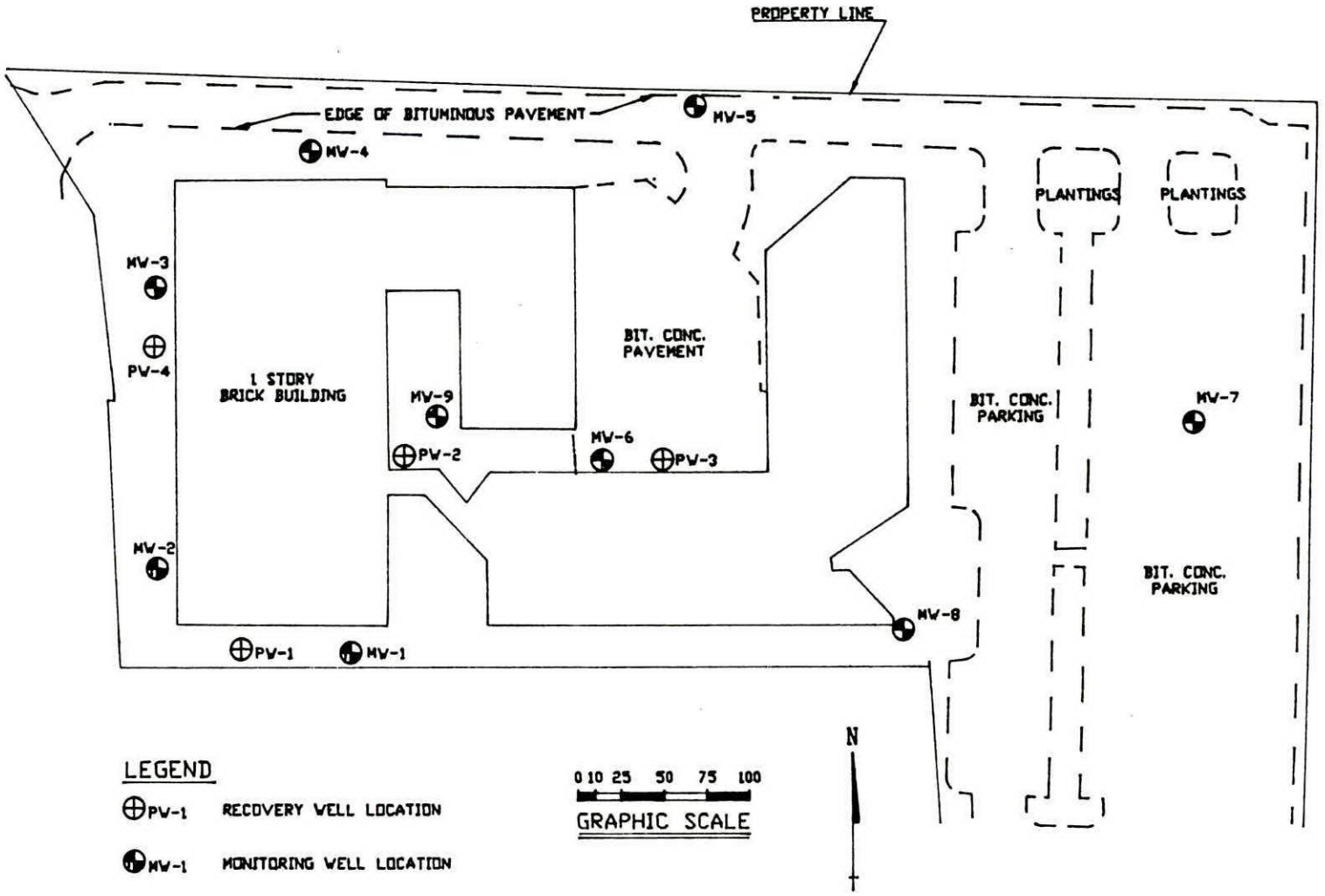

FIGURE 1. SITE PLAN CASE STUDY 1

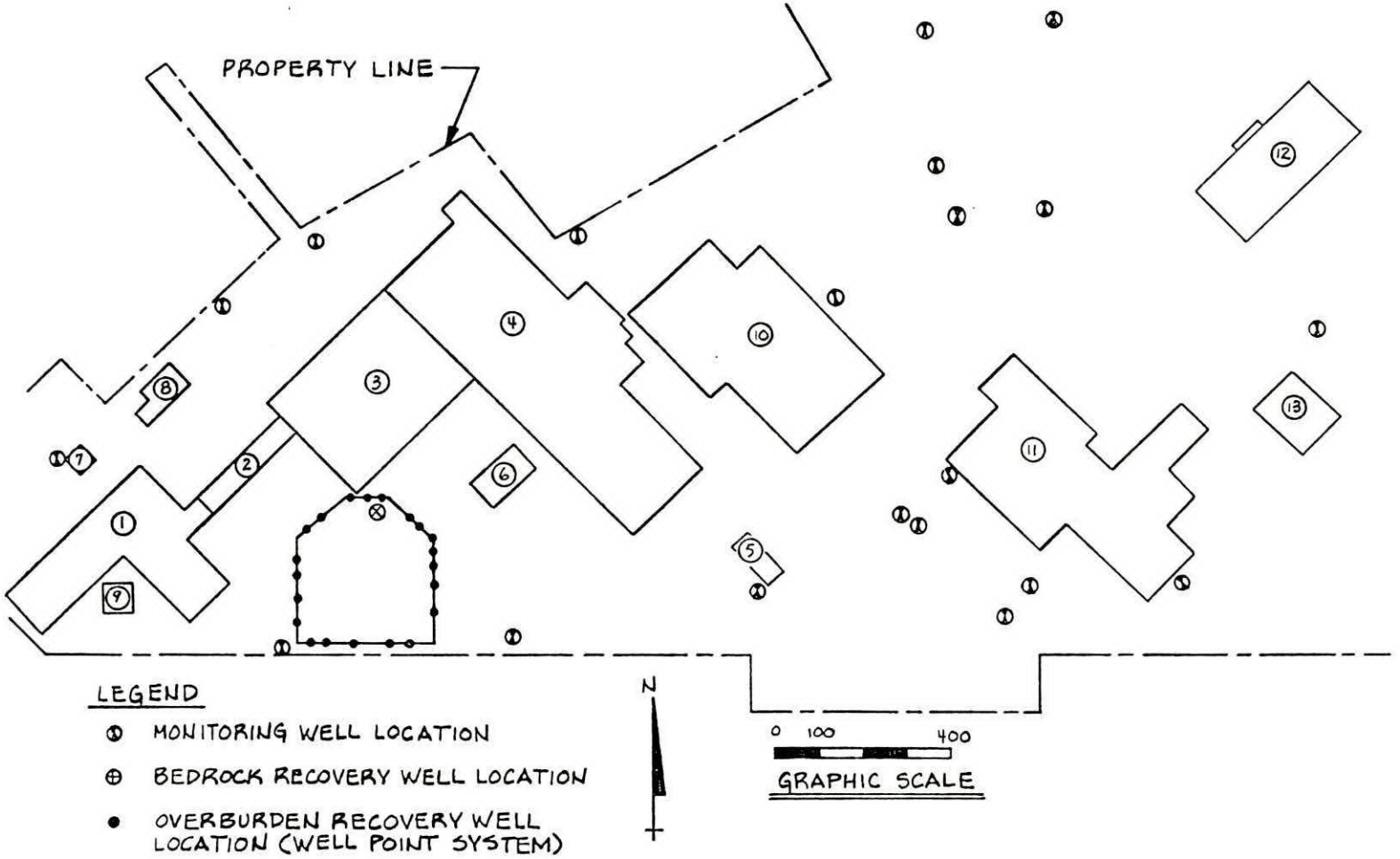

FIGURE 2. SITE PLAN CASE STUDY 2