ELECTROLYTIC RECOVERY OF METAL FINISHING WASTE WATER

by

Roy Druce, B.Sc.

INTRODUCTION

The presence of dissolved metals in metal finishing waste waters has become the subject of strict governmental regulation in recent years. Maximum permissible concentrations, in most cases, are now on the order of just a few parts per million.

These effluent limitations have had particular impact on the electroplating segment of the industry which has large quantities of metal-bearing waste rinse waters for disposal.

Plating rinse waters are, in essence, highly diluted electrolytes. Since electrolysis is the only technique which offers the possibility of direct, single-stage, reusable metal recovery from such solutions, it would appear to be a practical and economic means for bringing rinse water metal content down to current standards.

Conventional plating technology, however, is not easily extended to such reduced concentrations. As a consequence, a number of non-electrolytic alternatives have been offered the metal plater.

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1 Presented at HAZTECH Canada Conference and Exhibition, May 12-14, 1987, Mississauga, Ontario, Canada.

2 General Manager, BEWT Recovery Technologies Inc., Whitby, Ontario, Canada.
This paper will examine the most frequently encountered of these alternatives. It will review the principles of electrolysis as they relate to dilute solutions and discuss some practical electrolytic systems currently available.

Finally, the paper will describe in some detail the emergence of a greatly improved, highly efficient, cost-effective electrolytic metal recovery cell that appears to be the closest approach yet to a solution of the electroplater's waste water problems. This cell technology was developed in England some ten years ago and has had its field-testing in hundreds of installations abroad, yet, it has only recently been introduced to Canada and the United States. For that reason, its description may be of some interest to this Conference.

**BACKGROUND**

When plated items are lifted from the plating bath, they carry with them a certain amount of the metal-rich plating solution. This is referred to as the "drag-out" and it is normally washed off in one or more rinse tanks. Usually the first rinse (or drag-out) tank contains a static water bath. Additional washing may be done in spray rinse or running water tanks which overflow directly into the sewer discharge line.

With repeated washings, the static bath becomes enriched in metal ions until, ultimately, it no longer performs its washing function satisfactorily and must be replaced with clean water. As the concentration of plating solution in this bath increases, carryover of metal ion to succeeding rinses increases proportionately.
The static baths and running rinse waters contain the metal plating salts in dilute solution, but, to obtain the low levels of effluent concentration now permitted, they usually require further dilution, or treatment to remove the metal ions before discharge.

Chemical precipitation has been the traditional method for treating electroplating waste waters to remove metal content when required. Metals are precipitated out of the effluent in the form of hydroxide sludge. Since costs favor a large precipitation plant situated at pipe-end, the sludge often contains mixed precipitants of no value.

Expenses for disposal of metal-bearing sludge have risen dramatically in recent years. This has been caused primarily by a decrease in landfills accepting such waste and much tighter control over their operations. These higher disposal costs added to the required expenditures for chemical reagents (without any offsetting savings from metal recovery) have given electroplaters considerable incentive to explore other methods of waste water treatment.

**NON-ELECTROLYTIC RECOVERY SYSTEMS**

**Reverse Osmosis**

Reverse osmosis is a separation method utilizing a semipermeable membrane which permits some constituents of a solution to pass through while retaining other components. In processing electroplating effluent, water permeates the membrane while the metal salts are rejected and concentrated. The recovered water is of good enough quality to be reused as rinse water. The RO membrane, however, shows poor rejection of cyanides and borates associated with copper. This could be a problem when copper solutions are
handled.

Reuse of the metal concentrate does not seem to have been widely accepted. The reason is that economics of the process force installation of a plant at the pipe-end after all solutions have been mixed instead of at the source of a particular metal solution. As a result, concentrates of mixed metals are formed which have little value or are difficult to separate and reuse.

**Ion Exchange**

This is a liquid/solid extraction in which metal ions in the solution are replaced by hydrogen or sodium ions present in the ion exchange resin.

Ion exchange can recover metal ions down to concentrations acceptable for direct discharge and, by using a cation exchange resin followed by an anion exchange resin, complete cleaning of the rinse water can be achieved, making it suitable for reuse. Pretreatment may be needed, however, because of the strong dependence of the resin absorption capacity on the pH of the solution. This is particularly unfortunate as the pH of the effluent stream naturally lowers as metal is removed, thereby requiring further pH adjustment.

Some compounds, such as cyanides, may interfere with the process in a way that leads to recovery of the metal in a highly acidic solution. Often this is treated by precipitation of the hydroxide.

The high cost of ion exchange results from its complexity, the great deal of automation required for efficient running, and high reagent cost. The process is frequently linked to an electrolytic system for metal recovery, placing additional costs on top of an already expensive process.
Solvent Extraction

Solvent extraction is the liquid/liquid analog of ion exchange. The exchanging chemical is dissolved in an immiscible solvent (generally organic) which is mixed with the rinse waters. On settling, the two liquid phases separate and the metal ions are now present in the organic phase. Stripping with the concentrated acid results in concentrated acid/metal and regenerated organic streams.

Although it is a simpler operation than ion exchange, solvent extraction has certain disadvantages. Some solvents are particularly poisonous. Since some entrainment of the solvent in the aqueous phase always occurs, it could add to the problem of pollution rather than solve it. In some cases, dissolved solvent in the rinse water could stain the work. As with all concentration methods, a further stage (electrolysis) is required to obtain metal in usable form.

PRINCIPLES OF ELECTROLYTIC RECOVERY

In principle, the electrolytic process is quite simple. The reaction that takes place when a potential is applied to an electrolytic cell with a copper sulphate electrolyte, for example, is as follows:

Cathode Cu^{++} + 2e^{-} \rightarrow Cu

Anode H_{2}O + SO_{4}^{2-} \rightarrow H_{2}SO_{4} + \frac{1}{2}O_{2} + 2e^{-}

The products, as can be seen, are copper metal, sulphuric acid, and oxygen gas.

Any metal which can be electroplated in this way can, in theory, be removed or at least reduced in concentration from a dilute effluent stream by the same electrolytic process. The simplest way of doing this is to
insert two sheet metal electrodes into the effluent and apply a potential of a few volts DC. Direct current flowing through this simple electro-chemical cell will result in metal being deposited at the cathode (as shown above) and a complementary reaction at the anode (oxygen evolution, oxidation, or dissolution, depending on conditions).

The elementary arrangement suffers from several drawbacks. The rate at which metal is removed from the solution by plating onto the cathode is very low. This is because, in a dilute solution, the metal ions become depleted near the cathode and are replaced only slowly by diffusion from the bulk of the solution. The result is in a poor quality deposit (often a powder) and requires a relatively large piece of equipment to deal with the flow.

In addition, current efficiency (the proportion of cell current usefully employed in depositing metal) is very low, often under 20% for a metal concentration of 100 ppm. The remaining current is wasted in side reactions, such as hydrogen evolution.

In order to increase the rate at which metal ions diffuse to the cathode, it is necessary to introduce some form of turbulence or agitation into the cell. Many attempts have been made to design cells of this type and a few that have at least some practical value may be worth mentioning.

**PRACTICAL ELECTROLYTIC RECOVERY SYSTEMS**

**Plate Electrodes in Flow Cells**

This configuration is very similar to that employed in the electrowinning and electorefining of copper. The main feature is its simplicity: a tank containing the electrolyte has plate anodes and cathodes
suspended into it, the mass transfer of metal ions being enhanced by recirculation of the electrolyte. The metal deposit, however, is in the form of a powder which has less value than plated deposits.

**Fluidized Bed Electrodes (F.B.E.)**

In the context of effluent treatment, this technique has been proposed in the form of a cathode of copper particles fluidized by the electrolyte. Such a system has relatively high mass transfer and the ratio of electrode area to volume is higher than in other types of cell. Problems arise from the electrically conducting nature of the fluidized particles. Potential distribution across the electrode tends to be uneven, limiting the effective thickness of the fluidized bed to very low values. Redissolution of the deposit and agglomeration of particles also occur in metal deposition reactions.

**OTHER ELECTROLYTIC OPTIONS**

Extremely fast flow systems in parallel plate geometry can theoretically give sufficiently high mass transfer, but the power requirement is very high.

Rotating cathode cells lead to very complex and expensive systems. They are not particularly suited for metal recovery, since metal powders of low value are produced.

Packed beds of conducting materials have been studied and, although their performance seems promising, they are very difficult to scale up. Furthermore, they behave like a concentrator, similar to solvent extraction or ion exchange, and require a further stage to produce metal.
DEVELOPMENT OF THE HIGH EFFICIENCY ELECTROLYTIC METAL RECOVERY CELL

In 1976 the Electricity Council Research Centre at Capenhurst, Chester, England, embarked on a program aimed at improving the electrolytic recovery of metals from dilute solutions.

Existing systems were studied. Attention focused on the fluidized bed electrode concept (described in the preceding section) because of its high mass transfer characteristics. Experiments were conducted to overcome problems associated with the conducting nature of the fluidized bed. It was shown that a non-conducting fluidized bed of glass beads about 500 microns in diameter, in conjunction with plate electrodes, improved performance. The smooth plates, however, offered little resistance to fluid flow and also promoted undesirable channeling. Expanded metal mesh electrodes solved these problems. A romboid patterned mesh, rather than flat or wire mesh, proved most effective. It was determined also that the anodes should be 3-4 cm smaller than the cathodes in both dimensions to avoid excessive growth on edges, contact areas, etc.

An operating cell incorporating the above features was designed. This cell consists of a rectangular chamber with a flow distributor at the bottom (Figure 1). The electrolyte is pumped through the distributor and fluidizes the glass beads contained within the cell. The glass beads are expanded to a predetermined height providing a high turbulence zone into which the mesh electrodes are placed.
METAL FINISHING WASTE WATER APPLICATION

The high efficiency cell described above has been incorporated in a unit specifically designed to recover metal from electroplating rinse waters. This unit is used in a closed-loop configuration to process the contents of the first rinse tank (Figure 2). Rinse water, bearing drag-out from the plating bath, is pumped to a reservoir adjacent to the electrolytic cell chamber. It then goes through the chamber where the metal is removed. The rinse water leaves the chamber through an overflow weir, returns by gravity to the reservoir, and from there is recirculated back to the rinse tank.

By continuous cycling, the metal concentration in the rinse tank is maintained at a low level and dragout losses into following rinses are negligible. The system generates no waste streams requiring subsequent treatment. Metal concentrations in the final rinse can be as low as 1 ppm.

Metal Recovery

This unit is suitable for use wherever a dilute solution containing one of the following metals is present: copper, nickel, nickel-iron, zinc, cadmium, brass, tin, cobalt, silver, or gold. It is designed to recover metals from solutions down to 50 ppm. Depending on the system, current efficiencies of up to 95% can be achieved.

Metal is deposited as a high purity, hard plate on the cathode. When sufficient deposit has formed, the cathode can be removed manually and reused immediately as an anode in the plating bath. For this purpose, the substrate mesh is manufactured of an inert metal, such as titanium. Alternatively, the complete electrode may be sold for its scrap value. In
this case, the mesh may be manufactured in the same metal as the deposit.

**Site Location**

For best results with the high efficiency electrolytic cell unit, the solution to be treated should contain only one metal. In practical terms, this means locating the cell close to the source of contaminated water, before it becomes mixed with other wastes. Normally this does not present a problem, since the system requires relatively little floor space and units can be provided economically for each metal being plated.

**Water Savings**

In addition to the economic benefit of reusable, recovered metal, this system can reduce water costs substantially. Since the metal concentration in the first rinse tank remains approximately constant, the rinse water needs to be changed much less frequently. For the same reason, more accurate adjustment of subsequent rinse flows is also possible, further reducing water requirements.

**Other Cost Savings**

Compared to other metal recovery systems, capital costs are quite low and the value of recovered metal can well exceed the cost of operation. This assures an early payback on investment. See Table 1 for comparative cost figures.
SUMMARY AND CONCLUSIONS

Strict governmental regulations on metal-bearing waste water discharges have given electroplaters greater concern over waste water treatment.

Conventional precipitation treatment has become largely uneconomic because of the rising cost of sludge disposal. More desirable methods would help pay their way through reusable metal recovery.

Electrolysis, while offering direct, single-stage metal recovery from electrolytes, is not easily extended to dilute solutions such as rinse waters. Some fairly practical systems are available, however, and these usually avoid the complexity and expense of nonelectrolytic alternatives.

A highly efficient electrolytic metal recovery cell, developed and in widespread use abroad, has recently been introduced to Canada and the U.S. Its cost-effectiveness suggests investigation by electroplaters.