PROCESS OPTIONS FOR WASTE MINIMIZATION AND METAL RECOVERY FOR THE METAL FINISHING INDUSTRIES

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ABSTRACT

There is growing environmental concern with the methods of waste disposal used for handling hazardous materials in the metal finishing industry. A resulting need exists to develop and implement the best existing and potential technologies for waste minimization and resource recovery. The objectives of this study were to identify and briefly describe both existing and potential future methods for minimizing and recovering metallic wastes in the metal finishing industries. Included in the evaluation are the advantages and disadvantages of the various methods available and under development. Existing minimization techniques include countercurrent rinsing, drag-out reduction, and waste segregation. Recovery methods investigated include evaporation, ion exchange, reverse osmosis, electrodialysis, and re-smelting of metallic wastes. Discussions on future methods also cover combination technologies with the trend toward development of closed-loop processes. Investigation has shown that additional research must be done to make the developing technologies economically feasible. These challenges are being met by increasing contributions from the technical community, particularly chemical engineers. Finally, the metal finishing industries must be willing to join in the development and implementation of these new technologies if we are to successfully answer environmental concerns.

BACKGROUND

Electroplating of metals became feasible in 1840 and has grown until it now ranks as an important specialty industry, with nickel, copper, and chromium as examples of the most important plating metals (1). Electrodeposited metals serve either a decorative or structural purpose, or sometimes both, by providing a pleasing appearance and/or various desirable engineering properties. Electroplating finds application in many areas, including electronic, automotive, aerospace, and household products.

An example of this dual purpose application is chromium plating, which has both decorative and "hard" or industrial-use. These hard chromium coatings possess such desirable engineering properties as heat, wear, corrosion and erosion resistance, and a low coefficient of friction (1). Chromium is deposited primarily from a chromic acid (CrO_3 as H_2CrO_4) solution, which is highly toxic.

A major concern in metal electroplating is the high toxicity of plating chemicals and, therefore, the process requires extensive measures to prevent release of hazardous material to the environment. Releases come primarily from discharge of improperly treated rinsewater, though spray from the plating bath surface (particularly while using aeration for mixing), spills, and occasional plating bath disposal (because of uncorrectable composition) can also be of concern. In addition, since chemical precipitation of heavy metals is the primary method of treatment of these waste materials, disposal of hydroxide sludge is a significant problem. When confronting these problems, concern must include the short and long-term effects on the health of the plating shop workers and the public in general.

Concern for public safety has lead to growing environmental regulations on the federal, state, and municipal levels. Regulations include the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments of 1984 (2,3). As with all manufactures, the plating industry must deal with unfounded fears of the public about anything involving chemicals, especially when the chemicals are deemed "toxic" by public institutions, such as the government or the press. To command public confidence, not only must we continue to responsibly handle these hazardous materials, but we must make our successes known to the public, which, at a technical level, will involve developing improved means for disposal and ultimately recovery of valuable resources through process improvements and new technologies.

The minimization, recovery, and treatment methods employed for wastes produced by any electroplating process, however, can be very complicated. The subject is an area of chemical engineering, involving chemical reactions (both chemical and electrochemical) and unit operations (such as mixing and filtration) (1), typically referred to as electrochemical engineering. Developing feasible solutions must involve full consideration of all technical, legal, and economic implications.

STEPS IN WASTE MANAGEMENT

A successful waste management program requires using a systematic approach. One possible approach has four major steps (4). Step I involves planning and organization. The program goals must be determined and a task force organized. Step II is the assessment stage where the specific process is evaluated and is the most important step. The assessment stage can be summarized with five basic operations:

1. collecting and compiling process and waste stream information,
2. prioritizing waste streams,
3. site inspection,
4. generating options, and
5. screening options.

Once the various options have been evaluated, Step III in the waste management program is a feasibility analysis of both the technical and economic factors. Step IV is implementation of the chosen waste management program.

A successful waste management program involves a number of general techniques, the first being inventory management, which includes both inventory and materials control. Possible controls consist of hazardous chemical inventory size reduction, as well as material loss and damage reduction during handling and production. A second useful technique involves production process modifications in the form of maintenance programs, material changes, and process equipment modifications (4). The final technique of a sound waste management program is that of waste minimization and recovery. A successful management program will implement all three techniques simultaneously.

Generally, those methods involving waste minimization and recovery demonstrate some form of integrated waste treatment system (5), which tends to treat wastes at the source. A typical block diagram of an integrated waste system is illustrated in Figure 1 (5). The advantages of such a system include simplified supervision and control, reduction of waste treatment costs, simplified sludge handling, and improved rinsing. The major drawbacks include a necessity for additional process equipment and operation expense, as well as possible degradation of plating if not operated properly.

OBJECTIVES

The objectives of this study were to identify and briefly describe both existing and potential future methods of waste management for minimizing and recovering metallic wastes in the metal finishing industries, including evaluation of the advantages and disadvantages of the various methods available and being developed.

EXISTING/CONVENTIONAL METHODS

CURRENT DISPOSAL TECHNOLOGY

Chemical precipitation is currently the primary method used in the treatment of electroplating waste streams (1,5,6). The most common precipitation technique is hydroxide treatment, which involves altering the pH of a solution with sodium or calcium hydroxide to precipitate the heavy metal hydroxides. The drawbacks to hydroxide precipitation, however, include the dependence of precipitate solubility on pH and the difficult dewatering characteristics of the resulting sludge. Another chemical technique uses soluble and insoluble sulfides, with the advantages of wider acceptable pH range and much better thickening and dewatering characteristics of the metal sulfides produced. However, the major drawbacks include the presence of toxic sulfides and possible evolution of hydrogen sulfide gas in the process. The metal hydroxide sludge produced after dewatering must be fixed to prevent leaching, typically with portland cement, and then disposed of in a landfill. Future constraints on land disposal will increase the pressure to eliminate precipitation as a method of waste treatment.

MINIMIZATION TECHNIQUES

The first option one should consider to reduce wastes is minimization because it is the least expensive reduction technique and is often quite easily implemented. The cost of waste treatment depends largely upon the volumetric flow rates of waste and the concentration of pollutants in the waste water (7) areas where minimization efforts should be focused.

To reduce volumetric flow rates, modified rinsing methods should be analyzed. Since the rinse process is the primary contributor to waste streams, a countercurrent application (such as in Figure 1) may be more appropriate. For example, simply using a two-tank counter current rinse system, water usage (and subsequent waste water production) can be reduced by 99% over a single tank system (7).

The primary contributor to the quantity of waste material produced by plating operations is drag-out, which is the liquid material that adheres to the plated parts and rack when removed from the plating tank. Drag-out may be controlled and hopefully minimized by adjusting such factors as bath density and viscosity, geometry of pieces, drainage time (the most readily controlled factor), positioning of pieces, and velocity of withdrawal (5). Other options that may reduce chemical drag-out include using spray rinses or air knifes above the plating bath and reducing the bath concentration itself (7).

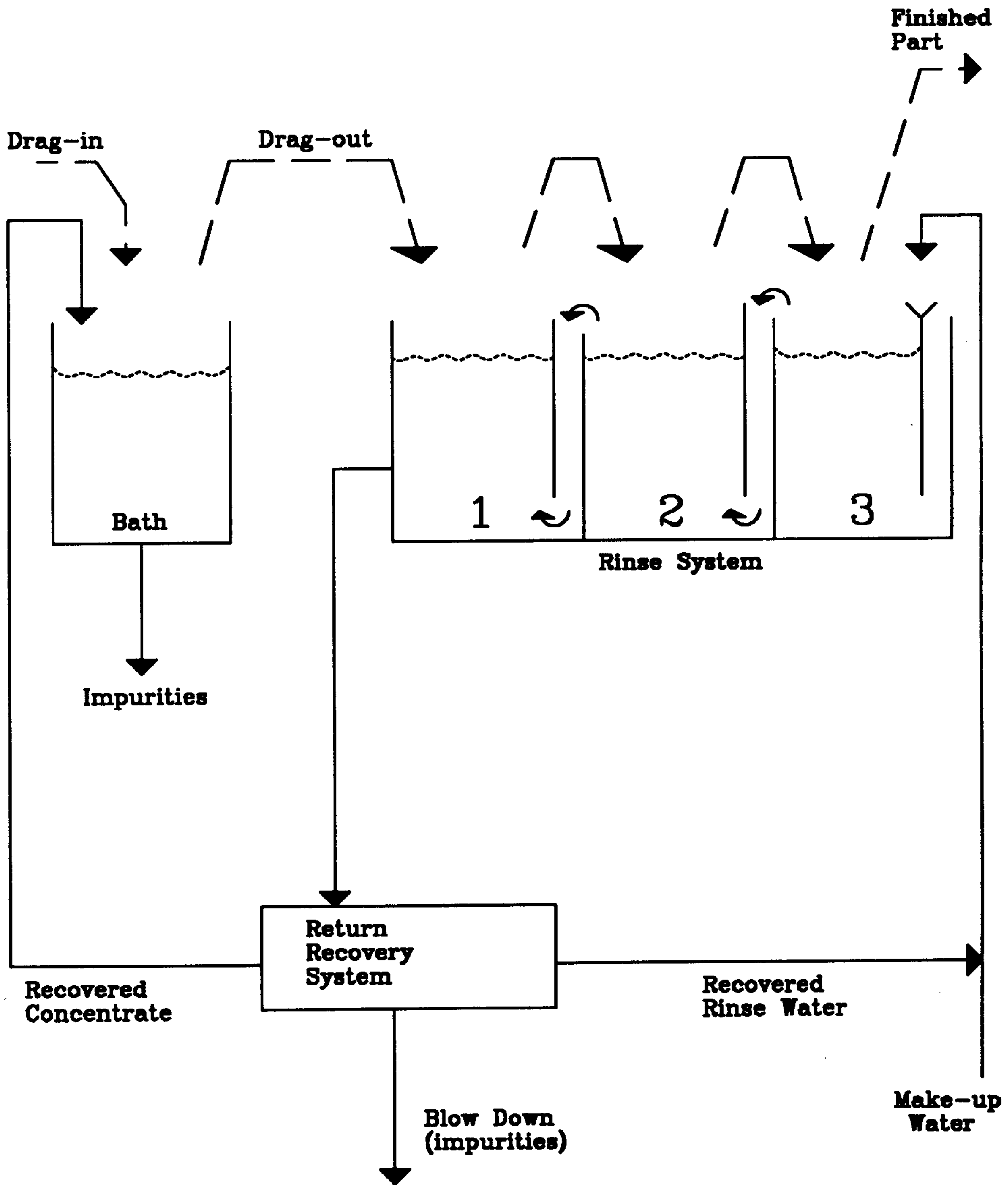

Figure 1: General integrated waste treatment system.

Other minimization options are also available. Segregation of wastes is an important technique for reducing treatment loads. When wastes are mixed, they become diluted and require larger treatment facilities for cleaning and re-separation. Also a mixture of wastes is given the hazard classification corresponding to the most dangerous material present, leading to higher disposal and liability costs. Reducing the frequency of tank dumps is another option that will lower treatment costs (5). Using less hazardous materials in the actual plating processes may also be beneficial. Other cheap and effective tools for waste minimization include using flow regulators, conductivity probes, reuse of contaminated rinses, and good housekeeping (cleaning) practices (7).

RECOVERY TECHNIQUES

When low cost plating line modifications or rinse-and-recycle modifications are not available, chemical recovery may be an option. A number of useful techniques exist for plating material recovery and range from simple evaporation to electrodialysis. With all of these methods, waste chemicals are recovered, as the name implies, and are sold or reused in some part of the process.

Evaporation is the oldest, simplest, and most durable of the recovery methods. Three evaporation techniques find common use (6). The first is atmospheric evaporation, which can use waste process heat as an energy source. The second is vacuum evaporation, which allows liquids to boil at lower temperatures, thereby preventing thermal degradation of bath additives, such as organic brighteners (7). The major problem with vacuum evaporation is the need for more sophisticated equipment and expense. The third option is a simple film evaporator.

The advantages to evaporation techniques include versatility, reliability, and recovery of nearly 100% of dissolved solids. Nevertheless, the disadvantages include a large initial investment, large energy requirements, possible need for stream pretreatment, and return of the entire stream to the plating bath (i.e., impurities are not removed, but concentrated) (5,8,9).

Ion exchange is another recovery option. Of any method, it is the best in flow rate per dollar invested, but the worst in water conservation (6). Ion exchange removes metals and impurities by using polymeric resins that replace the harmful, or valuable, ions in solution with safe, inexpensive ones. The great advantage of ion exchange is its ability to reduce the concentration of dissolved metals to very low levels; the fluid discharged from the column typically contains less than 0.5 ppm of the toxic material (10). Ion exchange works best for dilute solutions and is effective for a large number of metals (9). The major drawback is that the exchange resins, usually in the form of beads, must be regenerated by flushing with a suitable acid, caustic or brine solution, leading to added expense and downtime, as well as another stream that must be treated and/or recovered. A useful configuration of ion exchange columns involve having at least two connected in parallel to allow for continuous operation while regeneration occurs.

Reverse osmosis (RO) is a more complicated recovery method. It requires applying pressure to a concentrated solution to overcome the natural osmotic pressure and force permeation of water through a membrane (5). The concentrate may then be treated or reused and the pure permeate (water) recycled. Reverse osmosis units come in three basic configurations: spiral, tubular, and hollow fiber (5). A few drawbacks of RO include an inability to produce a sufficiently concentrated return stream and no removal of impurities (9). There may also be degradation of the membrane caused by plugging with salts or permeate compression.

Electrodialysis is a recovery method that lends itself to closed systems and is often used to reclaim metals (6). As the name implies, electrodialysis is electrolytically assisted dialysis, where an applied potential forces ions to migrate through an ion selective semi-permeable membrane. Electrodialysis is good for high drag-out rates and is also effective for concentrating rinse waters to high strength (6). The efficiency, unlike reverse osmosis, improves with increasing metal salt concentration and the only major drawback is a need for careful maintenance and operation (9).

A final recovery method that finds application is electrolytic recovery and is usually applied for drag-out tanks or spent strong solutions. It involves an electrochemical reduction of ions to elemental form onto a cathode for subsequent removal. The process requires a drag-out recovery tank, an electrolytic recovery tank (usually with stainless steel cathodes), and a recirculation pump (5). High flow rates or good agitation are also needed to circulate the bath. The major advantage is that it tends to minimize the load on the waste treatment system and pollution discharge rates while also avoiding the conversion of metal ions to sludge.

Once the metals ions have been reduced, three options for handling the metal/cathode combination exist. The metals may simply be disposed of when plated onto a cheap, plastic substrate. A high surface area cathode may also be employed where a fibrous or filamentous substrate collects the metals, which are then chemically stripped for resale. The final removal option is employed when a high purity metal extract is desired. A solid slab of high purity metal may be reduced onto a flat cathode for mechanical stripping and resale on secondary metal markets (9). The disadvantages of electrolytic recovery include problems operating with dilute solutions (low conductivity), a large electrical energy requirement, and the diffusion controlling factors (8).

FUTURE/POTENTIAL METHODS OF WASTE TREATMENT

By far, chemical precipitation has been the most popular waste treatment method, but due to the increasing costs of landfilling, new methods of hazardous waste treatment have been focusing on waste minimization. The ultimate goal is to achieve "closed-loop" operation where all raw materials entering the process line exit as part of the finished product. In this regard, conventional processes have been improved, more effective combinations of existing technologies have been developed, and new, creative technologies continue to be researched.

A problem with conventional electrodialysis processes has been fouling of the membranes. Nearly all new electrodialysis installations utilize a reversible process in which the cell polarity is periodically reversed, thereby reversing the flow to and from the concentrate and depleting chambers (11). Flow reversal tends to redissolve or physically purge precipitates and surface films, but requires membranes that can function in either the anion- or cation-selective modes, and platinum-coated titanium electrodes that can function either as cathodes or anodes.

Conventional electrolytic recovery techniques have recently evolved into fluidized bed electrochemical reactors, which has improved the economics of removal and recovery of metals from dilute solutions. (12). The typical cell consists of a set of apertured, expanded-metal-mesh electrodes immersed in a bed of small glass beads. The bed is fluidized to about twice its packed depth by pumping rinsewater upward through a distributor particle bed. The glass beads continuously scrub the surface of the electrode and promote mixing, which brings fresh solution to the electrode surface. This type of electrochemical reactor has been successfully used to recover gold, silver, cadmium, nickel, nickel-iron alloy, copper, and zinc (12).

A new variation of an older concept involves application of ultrafiltration (UF) and hyperfiltration (HF) to electroplating waste minimization and has been particularly effective for the removal of suspended solids, oil and grease, large organic molecules, and complexed heavy metals from wastewater streams (11). In UF and HF, a membrane retains materials based entirely on size, shape, and molecule flexibility. Feed solution is pumped through a membrane module and the membrane acts as a sieve to retain materials that are too large to pass through its pores. The retained materials (concentrate) then exit the module separately from the purified solvent (the permeate). The difference between UF and HF is only in its selectivity. Hyperfiltration typically removes species with a molecular weight between 100 and 500 g/mol; ultrafiltration removes species with a molecular weight greater than 500 g/mol (11).

Since individual waste minimization processes cannot always achieve the desired degree of recovery, combinations of individual processes have been developed which utilize the major advantages of the separate processes. Several examples of a combination of ion exchange and electrolytic recovery exist. Typically, the solution produced from regeneration of an ion exchange column is much more concentrated than the influent waste stream and may be ideal for further treatment by electrowinning. Electrolytic recovery converts the toxic metals in solution to their elemental form, often as metal sheets that can be reused, sold for scrap, or otherwise safely disposed. However, electrowinning is not as effective as ion exchange for reducing dissolved metals to low concentrations and, therefore, the residual solution is directed back to ion exchange for further treatment, thus creating a "closed loop" (10).

Another alternative is the re-smelting of traditional electroplating waste sludge to recover the metals, which has been implemented for reprocessing of iron, nickel and chromium-mixed sludge (13). The resulting ingots are sold to stainless steel manufacturers. The major advantage of this process is the elimination of the long-term liability associated with landfilling. However, the process is highly energy intensive and not easily applied to small scale operations with the current technology. Presently, only a few reprocessing facilities exist in the mid-Atlantic region of the U.S., leading to potentially prohibitive shipping costs.

New, creative technologies are constantly being researched. Among these is the electrodialytic ion exchange (EDIX) cell, which consists of alternate bipolar and cation permeable membranes between an anode and cathode, as shown in Figure 2 (14). The wastewater stream enters the regenerate chamber where metal and hydrogen ions migrate across the cation permeable membrane into the concentrate chamber. To balance the negative ions remaining in the regenerate chamber, water is separated into hydrogen ions and hydroxide ions by electromotive force within the bipolar membranes. The hydrogen ions replace the migrating positive ions while the hydroxide ions migrate to the anode and react to form oxygen gas and water. In the concentrate chamber the formation of hydroxide ions balance the positive ions that have migrated from the regenerate chamber through the cation permeable membrane, while the hydrogen ions formed migrate to the cathode and are reduced to form hydrogen gas. Initial process analysis of the EDIX system indicates that a single pass process is not capable of providing a water stream suitable for disposal, but does greatly reduce the metal ion concentration and could possibly be used in series and/or in conjunction with other processes to create a closed-loop process (14).

Other creative research has focused on using vermiculite and partially converted shellfish waste (15) as a medium to adsorb metal ions from solution. The ions are then recovered by eluting the medium and directing the resulting concentrated stream back to the plating bath.

New technologies are becoming more economically feasible due to the increasing costs and restrictions of current disposal methods (i.e., disposal of precipitate sludge in landfills). The trend is definitely toward closed-loop configurations, although never fully obtainable due to unavoidable contaminant build-up that can result in reduced product quality. Nevertheless, the closed-loop efforts greatly reduce the amount of sludge produced and can still pay for themselves through reduced sludge-removal costs.

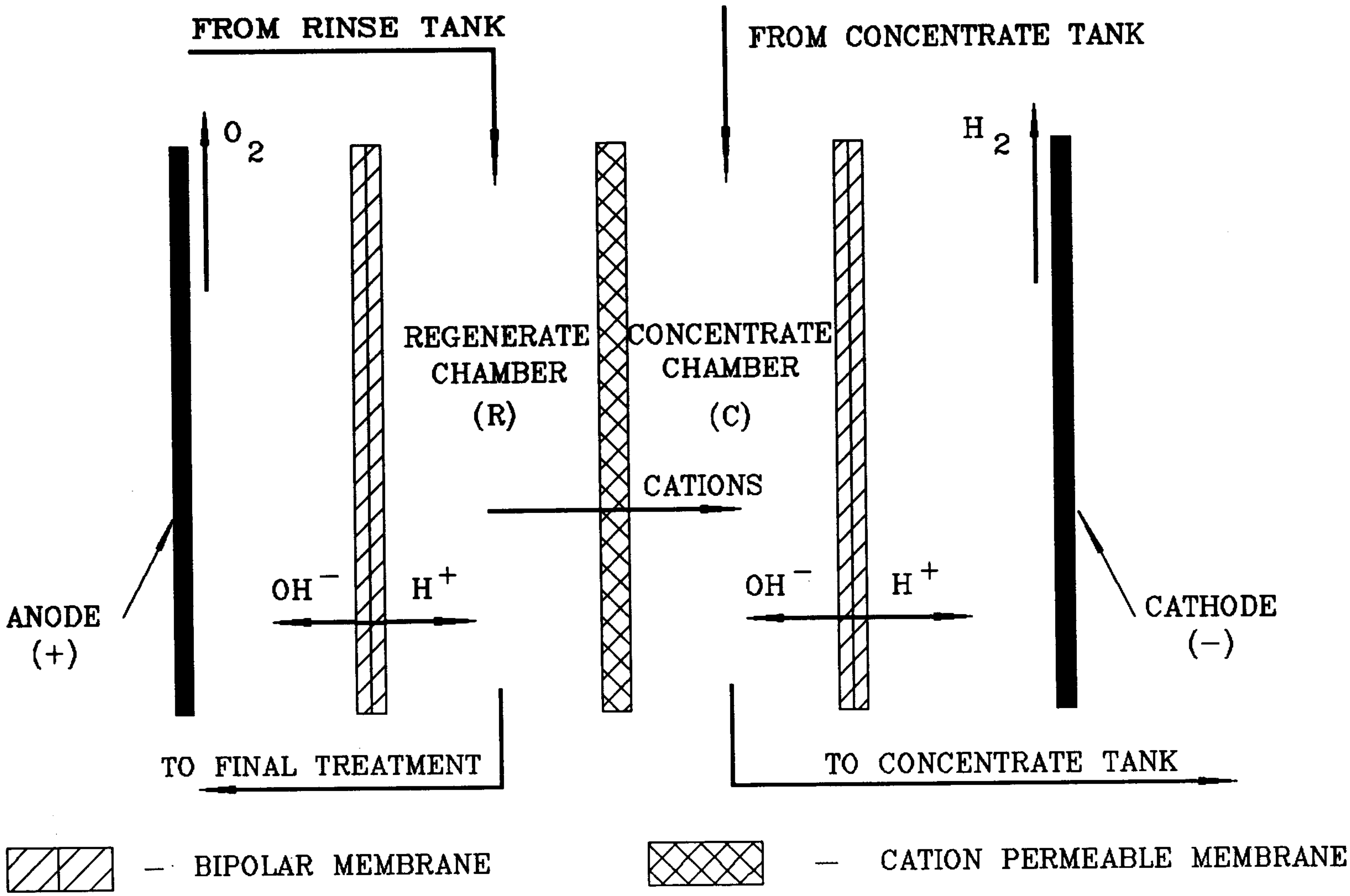

Figure 2: Schematic diagram of the electrodialytic ion exchange (EDIX) cell.

Finally, microcomputers can be utilized as a powerful tool to evaluate the performance of new and existing treatment systems (16). Programing languages, such as FORTRAN and BASIC, and spreadsheets can be used to develop mathematical models of systems to evaluate their operating feasibility without physically building prototype models and conducting laboratory experiments, thereby saving time and expense. Also, these models are convenient for evaluating existing systems, as well as developing an economic evaluation of alternatives (16). To fully utilize these tools, the electroplating industry will require increased technical expertise in the fields of chemical, electrochemical and environmental engineering.

CONCLUSIONS

1. There is a need to continue developing near closed loop processes for reuse of raw materials before they become treatable wastes, which involves emphasizing waste minimization, stream segregation, and contaminant minimization.
2. New technologies, such as in the area of electrodialysis, are being developed. They will need to be tested under actual operating conditions.
3. Computers in general, and microcomputers in particular, are a valuable, but under utilized, tool in the surface finishing industry for evaluating existing and future technologies. Training and exposure to example applications will be necessary to change this situation.

RECOMMENDATIONS

Continued development of new technologies, and combinations of them, are needed in order to approach the closed loop operation goal. To accomplish this, the surface finishing industry must be willing to support research efforts and to try new technologies as they develop. Improving waste minimization and recovery methods will also require a higher level of technical expertise in the industry to allow for proper evaluation of technical and economic options, as well as operation of these new processes. Hiring chemical engineers with environmental and electrochemical backgrounds is essential for technical/economic analysis and additional specialized training of operators.

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