ELECTROCHEMICAL REACTOR SYSTEMS FOR POLLUTION CONTROL AND THE REMOVAL OF TOXIC METALS FROM INDUSTRIAL WASTEWATERS*

Bernard FLEET

SCADA Systems Inc., Rexdale, Ontario, Canada M9W 5M8 and
The Department of Chemistry,
University of Toronto, Toronto, Ontario, Canada M5S 1A1

A review of electrochemical reactor systems for the recovery of metals and for pollution control applications is presented. The major engineering factors which influence the design of reactors are evaluated and the key features of two-dimensional and three-dimensional reactor designs are discussed. Some examples of the application of electrochemical reactors to the recovery of metals from dilute solutions are given in the form of case studies, covering both pollution control and resource recovery processes. Finally a comparison is made of the relative technical and economic merits of electrochemical recovery pollution control systems and conventional chemical waste treatment routes.

1. INTRODUCTION

1.1 *Chemical Waste Management*

In reviewing developments and prospects for the use of electrochemical reactors in recovering metals from industrial wastewaters and for pollution control in general, it is useful first to define the problem and the types of application for which these systems are to be targetted.

Pollution by toxic metals including cadmium, copper, chromium, lead, mercury, nickel, and zinc is generated by a wide range of manufacturing industries such as mining, metal finishing/plating, electronics, semiconductor and printed circuit board manufacturing as well as several other industries that use metal treatment as a part of their overall manufacturing processes. Waste management practices in these industries vary widely. In some cases effluent streams are simply diluted to meet regulatory limits but more commonly a chemical treatment process is used where caustic soda, lime or sulphide is added to the waste stream to convert the dissolved metals into a semi-solid "sludge". After partial dewatering this toxic metal sludge is either packed into steel drums or occasionally "fixed" with calcium sulphate or cement waste before being dumped into a land disposal site. These sites range from municipal waste dumps to "secure" chemical landfills to abandoned mineshafts or deep wells.

There is now indisputable evidence[1] that land disposal of toxic wastes is only a temporary solution to the problem. All of these storage or disposal sites leak to varying degrees with the result that many of the toxic species find their way into natural watercourses and subsequently into the biological food chain. Increasing awareness of the risks associated with hazardous chemical waste disposal is causing governments to initiate stricter environmental legislation, which in turn is causing many industries to re-evaluate their waste management options. There are strong trends towards seeking on-site, zero discharge, resource recovery technologies[2,3].

Clearly, there are many environmental waste management problems where electrochemistry is able to offer an effective solution[2-5]. However, before these new electrochemical processes can be implemented two important questions need to be answered.

First, are the economics and environmental climate suitable to encourage industries to make the investment in new waste management strategies. Second, are there alternative resource recovery technologies available and if so how do they compare in performance and costs with the electrochemical route.

The purpose of this review is to attempt to answer these questions by surveying the status of the various commercial and research prototype electrochemical reactor systems for pollution control and metal recovery. It also attempts to define the role of electrochemical reactor systems in solving some major problems of environmental waste management.

2. BACKGROUND TO ELECTROCHEMICAL ENGINEERING

2.1 *Electrometallurgy*

Electrometallurgy, broadly defined as the electrolytic plating or recovery of metals from solution, is among the earliest examples of applied science. Examples of crude electroplating date from early Egyptian and Assyrian times[6], while the first literary reference to electrochemistry is recorded in Pliny's Histories[7] and describes the silver plating of tin. By the 1850's, just 50 years after the introduction of Volta's electrochemical pile, electroplating was already an established practice. Electrolytic recovery of metals as an industrial process also followed closely on Faraday's and Davy's pioneering works with the first electrowinning cells being reported in the late 1860's following the introduction of the dynamo.

The earliest recorded example of the application of electrochemical principles to the recovery of metals occurred on the present territory of Czechoslovakia, in Banská Bystrica at the mine of Herrungrund, early in the sixteenth century[8]. This involved the recovery of copper from cupriferrous mine waters by electrochemical replacement with iron. A variety of decorative copper plated ironware was produced by this process.

2.2 *Electrochemical Engineering Aspects of Metal Recovery*

Electrochemical engineering as a science dates from the mid-1960's coinciding with several advances in electrochemistry, particularly in the fields of mass transport theory, materials science and instrumentation. The impetus given to electrochemical technology by Heyrovský's work should also not be overlooked. The development of polarography as a technique for the study of electrode processes also provided a stimulant for many workers to expand these ideas to other fields of electrotechnology. The influence of other scientific disciplines on the development of electrochemical engineering has been summarised by Selman[9].

In conventional electrochemistry the mechanism of the electrode process and its

kinetics are often the factors of major concern. In electrochemical engineering, on the other hand, the actual mechanistic details of the process are not so important as its specificity or process efficiency. More importantly we are concerned with the rate of the process, the current efficiency and a measure of reactor efficiency, the space-time yield. This latter factor determines whether a process is economically or commercially viable since it can be used to compare performance of different electrode designs as well as comparing an electrochemical process with the space-time yields for alternate non-electrochemical technologies.

The design of electrochemical reactors offers an entirely different set of challenges than those found in classical electrochemistry. In a conventional electrochemical system one is often dealing with a microelectrode of usually uniform surface area and activity under conditions of very well defined current control either diffusion limited or kinetically controlled or in cases of convective control with very well defined mass-transport conditions. In electrochemical engineering on the other hand one is dealing with a bulk electrode, of constantly varying surface area and activity as metal is deposited. In addition, there are often difficulties in maintaining uniform potential control and current distribution over the electrode surface. It is also necessary to consider the reverse stripping process of recovering the metal after collection. Problems of scaleup, materials corrosivity and other engineering design problems must also be addressed.

The theoretical background to electrochemical engineering is now well established[10-18]. The principles controlling the major parameters in reactor design and operation, potential/current control, potential/current distribution, mass transport characteristics, role of electrocatalysis and the role of electrode material, etc., are fairly well understood. The keystone undoubtedly has been the development of convective diffusion theory by Levich[10] which has led to the proper evaluation of concentration profiles in a wide range of electrolytic systems. The concept of the boundary layer defines the concentration profiles of electroactive species in the bulk solution, in the boundary diffusion layer and at the electrode surface. The role of convective diffusion in both laminar and turbulent forced convection modes has also been defined and has led to the development of mass-transport relationships for a wide range of electrode/cell geometries.

2.3 Reactor and Process Design

The design or selection of an electrochemical reactor for a specific application or metal recovery process depends on a variety of factors. The first consideration is the process itself, the type of metal or other chemical species to be recovered, the con-concentration level and chemical composition of the process stream and finally the desired removal rate or treatment efficiency. Unless the application is well established, it is first of all necessary to investigate the electrode process. For most

metal deposition processes, basic data on the electrode process may be obtained from the literature including source references such as Pourbaix diagrams[18] which define pH–potential equilibria. In the absence of this data, laboratory bench scale experiments may be required to define process conditions and provide data for scaleup.

In the design of electrochemical reactors, there are four major areas for consideration. First is the overall cell design, including electrode materials of both cathode and anode and the requirement, if any, for a diaphragm or separator. The second is the problem of potential control of the working electrode. Next is the control of current distribution over the working electrode surface area and finally there is the definition and control of the mass-transport characteristics of the system.

The electrode potential of the working electrode is a complex parameter involving current distributions within the working electrode and the solution, conductivities of the bulk electrode and the process solution and the concentrations of all reactants and products for all of the possible electrode processes. In classical electrochemical experiments, potentiostatic control is achieved by electronically comparing the voltage difference between the working and reference electrodes, and the required operating potential (set point) and feeding the difference back to a rectifier such that the rectifier provides an output through the counter electrode to maintain the desired condition. In electrochemical engineering applications, however, potentiostatic control suffers from a number of practical problems. The first is the problem of ground loops from cell currents which can drive destructive currents through the reference electrode, effectively destroying its performance. More significantly, the reference electrode suffers from location problems as it is normally linked to the cell via a Luggin type capillary probe. It can therefore, only monitor the potential at one small site in the working electrode which may have very little relevance to the overall electrode potential. This approach may be useful in initial design studies for electrode potential mapping but its real application as a control technology is minimal.

The current distribution within the electrode which in turn controls the current efficiency of the electrode, is dependent on the mass transport characteristics of the system and on the control of potential over the working electrode surface. Mass-transport is the parameter which controls most situations. The known Nernst diffusion model describes the situation at the electrode/solution interface. Three distinct regions can be identified; the stationary diffusion layer of solution adjacent to the electrode surface, the boundary diffusion layer where, under electrolytic operating conditions, a concentration gradient and a solution flow velocity profile may be observed, and finally the bulk layer.

2.4 Reactor Control

Since potentiostatic control of most electrochemical reactor systems is impractical, the next option is voltage control. This route, however, is also often of limited

value[19]. The voltage-current relationships of most cells are dominated by inter--electrode conditions, electrolyte resistance, diaphragm resistance, and mode of operation, monopolar or bipolar, etc. Typically, cell voltages are of the order of 4 to 10 volts for monopolar operation, while most working electrode potentials are in the range 0 to 1·0 volts. Clearly, cell voltage has some limitations for controlling working electrode potential, especially when the influence of concentration and temperature changes are considered.

In most cases, especially in the case of metal recovery from dilute solution, constant current control is the most useful operating approach from both a practical and theoretical standpoint. Since the electrode potential cannot be controlled in a "potentiostatic" sense it can be controlled by a combination of controlled current and controlled mass-transport. For a typical current voltage curve for a mass-transport controlled process operating under constant current conditions then the electrode potential will be given by the point at which the imposed current value inersects the i–E curve. Mass-transport characteristics are, therefore, critically important in controlling electrode potential. For a given electrode-cell geometry, there is a well defined range of mass-transport and imposed current conditions that will achieve the desired electrode process efficiency. At the same time there are often significant problems in controlling mass-transport conditions within a reactor. This is especially the case with three-dimensional electrodes where mass-transport conditions in the reactor can change dramatically during the course of a process. For example, in a metal deposition process, electrode surface and effective area of electrode will change continuously and in many cases significantly influence hydrodynamic performance.

The other major critical area of advancement in electrochemical engineering has been in materials science. The materials requirements for electrochemical reactors are often very critical due to the corrosivity of the process media and extreme reactivity of some electrogenerated species. The development of novel electrocatalysts, especially the introduction of the dimensionally stable ruthenium/iridium oxide based DSA anodes has played a vital role in the development of commercially viable reactor systems. The development of membrane/separator materials with much improved mechanical stability, ion-permeability and conductivity has also been played a key role.

2.5 Engineering Parameters

In electrochemical engineering, three parameters are often used to define the performance of an electrode or electrochemical reactor, current efficiency, process efficiency and electrode/cell space-time yield. In some cases, particularly with high surface electrode cells, an additional parameter, the percentage conversion or removal per pass may also be specified.

The process efficiency, Φ, is defined as moles of metal removed as a function of initial metal concentration in the process stream

$$\Phi = \frac{\text{moles of metal removed}}{\text{moles of metal in process stream}} \cdot 100 \ . \tag{1}$$

The current efficiency, β, is defined as the ratio of cell current used to deposit metal on the working electrode as a fraction of the total current passed through the cell,

$$\beta = \frac{\text{theoretical current for metal deposited}}{\text{total charge consumed}} \cdot 100 \ . \tag{2}$$

The space-time yield parameter provides a measure of electrode/cell performance, allowing comparison, for a given electrolytic process between different electrode configurations and also between electrochemical systems and competitive, non--electrochemical technologies. The space-time yield term Y_{ST} is defined for an electrode as;

$$Y_{ST,E} = \frac{A_s i}{czF} \tag{3}$$

and for a cell,

$$Y_{ST,C} = Y_{ST,E} \frac{1}{1 + V_A/V_B} \ , \tag{4}$$

where A_s is the specific electrode area, i the current efficiency, c the concentration change during one solution pass through the reactor and V_A and V_B the volumes of anode and cathode compartments. The importance of the foregoing discussion is that in the design of electrochemical reactors for metal removal, the major objective is to maximise the space time yield and thus minimise the size and capital cost of the system for a given process or level of metal recovery.

3. ELECTROCHEMICAL REACTOR SYSTEMS FOR METAL RECOVERY

3.1 *Application Area*

Three major application areas of electrochemical reactors in metal recovery can be defined:

Electrowinning of metals from ores and primary sources,

Electrorefining of metals from aqueous solutions or molten salts

Electrolytic recovery of metals from waste sources and industrial effluents (electro-chemical detoxification).

Whilst the cell design requirements for electrorefining are usually quite specific, many cell designs used for both electrowinning and electrochemical effluent treatment are often very similar and in many cases the applications overlap. With the exception of the electrolytic processes for aluminium, magnesium and sodium, applications of electrochemical applications of electrowinning have mainly been directed to the recovery of copper, nickel and the precious metals. However, electrolytic processes have been developed for a wide range of metals[20] but due to the world depression in metal values only a small fraction of these processes are presently either being developed or operated on a commercial scale.

3.2 *Classification of Reactor Designs*

The plethora of electrochemical reactor designs are, in many cases, difficult to classify. Various approaches have been attempted[21,22]; one approach is based on defining the motion of process solution in relation to the direction of current flow through the working electrode (Fig. 1). This definition describes three main modes of process flow; a "flow-by" mode where solution flows past the surface of the electrode and two flow-through modes, "flow-through parallel to current" and "flow-through perpendicular to current". A simpler classification (Scheme 1) is based on working electrode geometry, i.e. whether the cell/reactor employs a planar (Two-Dimensional) or bulk electrode (Three-Dimensional). Two-dimensional reactor systems are typically planar electrode, low surface area designs, whereas three-dimensional designs mostly comprise high surface area systems with extended electrode surfaces typically based around porous electrode materials, packed particles or fibres. While most
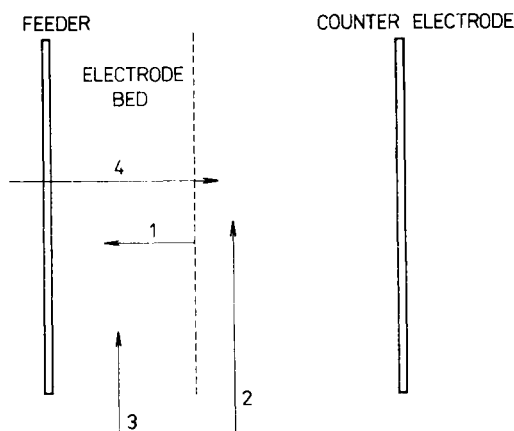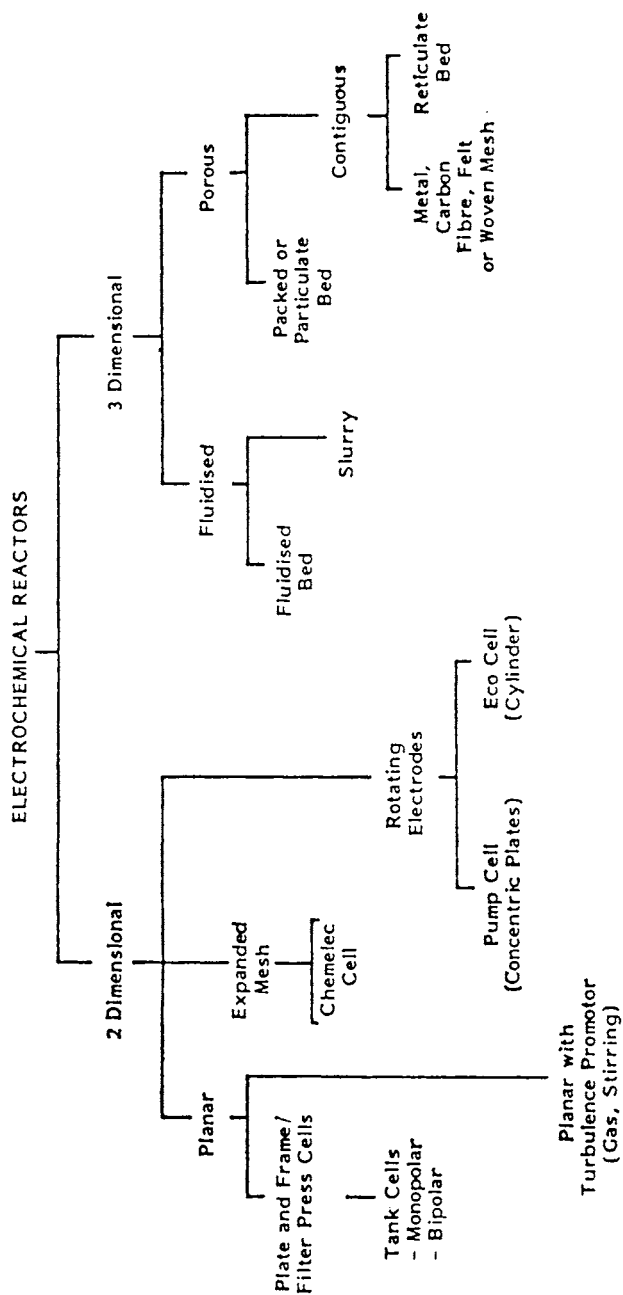

FIG. 1

Mass transport modes in electrochemical reactors. 1 Current flow; 2 flow-by; 3 flow through perpendicular to current flow; 4 flow through parallel to current flow

current research and development effort in electrolytic metal recovery seems to be directed towards high surface area reactors, it should be also noted that the two

ELECTROCHEMICAL REACTORS

- 2 Dimensional
  - Planar
    - Plate and Frame / Filter Press Cells
      - Tank Cells
        - Monopolar
        - Bipolar
      - Planar with Turbulence Promotor (Gas, Stirring)
  - Expanded Mesh
    - Chemelec Cell
  - Rotating Electrodes
    - Pump Cell (Concentric Plates)
    - Eco Cell (Cylinder)
- 3 Dimensional
  - Fluidised
    - Fluidised Bed
    - Slurry
  - Porous
    - Packed or Particulate Bed
    - Contiguous
      - Metal, Carbon Fibre, Felt or Woven Mesh
      - Reticulate Bed

SCHEME 1

classifications of reactor system referred to above should not be viewed as competitive. Rather, they should be viewed as a spectrum of available reactor and working electrode designs, from which the optimum reactor and process design can be selected for a given application. A review of the major designs of rector system, most of which have found application in metal removal from industrial wastewaters is presented below.

4. TWO-DIMENSIONAL REACTOR SYSTEMS

Classical electrochemical reactor designs invariably evolved from direct scale-up of simple laboratory electrolysis experiments. The most common example of this concept is the tank cell where an array of electrodes are immersed in a plastic or metal tank. More sophisticated versions involve forced convection, rotating or moving electrodes and a wide range of plate and frame or filter-press-type cells.

In the two-dimensional class of reactors three main types will be considered, tank cells, plate and frame cells and rotating electrode systems.

4.1 *Tank Cells*

Tank cells are one of the simplest and most popular designs of cell for both electro-organic and inorganic processes. Commercial designs which are available in a wide range of sizes and electrode areas can operate both in the monopolar or bipolar mode. They usually function as an undivided cell with a single electrolyte/process stream; the incorporation of membrane/separators is inconvenient and in cases where cathode and anode chambers need to be separated a plate and frame construction is usually preferred.

Although the widest commercial use of tank cells has been in electroorganic synthesis[23,24], they have also found application in pollution control and metal recovery, mostly for electrowinning applications. The Lancy Cell[25] is a typical example; it comprises a planar electrode cell of modular construction offering a range of cathode areas from $0.5 - 5.0$ m^2. A similar type of modular tank cell design with a membrane isolated anode compartment and planar stainless steel cathodes has been developed by SCADA Systems[26]. The main applications for this type of reactor system is in the electrowinning of high concentration process streams such as spent plating baths, etchants, and ion-exchange eluates. Typically these cells can economically treat process streams to provide effluents in the $100 - 300$ ppm range after which they may require further processing by a high surface area reactor. Another example of a tank cell used as a resource recovery system is the Capenhurst Cell[27], which has been designed for regeneration of etchants in the printed circuit board industry. These spent etchants usually contain the dissolved Cu(II) as well as the reduced form of the oxidant etchant, typically Fe(II) from $FeCl_3$ or Cu(I) from $CuCl_2$. In the

Capenhurst process the cell recovers copper at the cathode while in the anode compartment the active etching species is regenerated.

A bipolar version of the tank design, the Bipolar Stack cell, consists of an assembly of parallel, planar electrodes separated by insulating spacers. Flow of electrolyte between electrodes may be either by natural or forced circulation. This design of cell is easy to construct since it simply comprises a stack of alternating electrodes and spacers with electrical connections being made to the two end electrodes. The number of electrodes in a stack typically ranges from 10 to 100. Process flow is usually by gravity feed so that the cell has none of the complex hydraulics and plumbing features of plate and frame cell designs. One example of this design, the bipolar trickle tower reactor consists of a regular array of bipolar perforated carbon discs separated by an insulating mesh. The original work[28] on this design described the removal of metals and simultaneous cyanide destruction from cyanide containing rinse streams.

4.2 *Plate and Frame Cells*

One of the most popular cell designs, primarily for large-scale electroorganic synthesis and to a lesser extent for metal recovery is the plate and frame design also known as the filter press. The basic design incorporates parallel plate electrodes, separated by insulators, gaskets or diaphragms and mounted on tie rods or a filter press (Fig. 2). Process flow is usually achieved by either series or parallel flow through internal gasketing. This arrangement, which also minimises solution bypass, has some distinct advantages over the simpler tank cells, most notably the far better defined hydrodynamic characteristics. The plate and frame concept has proved very popular for electroorganic synthesis due to its flexibility of design with the wide range
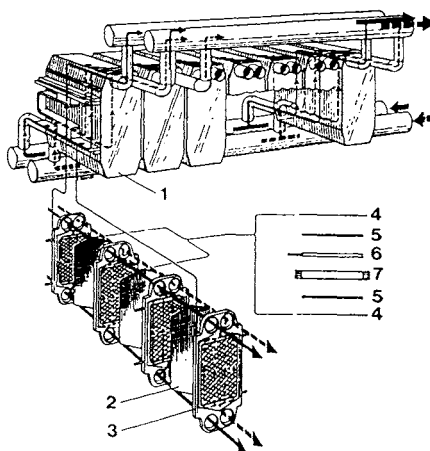

FIG. 2

Plate and frame design (courtesy of Electrocell AB). 1 Module; 2 membrane; 3 electrode element; 4 membrane; 5 frame, inner; 6 electrode; 7 frame, outer

of working electrode materials, anodes and membrane/separators, variable hydro-dynamics and operating conditions including monopolar or bipolar and divided or undivided cell operation.

One of the most versatile plate and frame cells is the SU cell developed by Electro-cell AB in Sweden[29]. Based mainly on the work of the Lund group, Electrocell has developed a range of reactor designs from the laboratory-scale microcell up to a several m^2 pilot-scale version. The range of interchangeable electrodes, membranes and frame materials allows for versatility in applications which range from electro-organic synthesis through metal recovery to chloralkali processes.

4.3 *Mass Transport in Planar Electrode Cells*

The limited metal removal rates for planar electrodes has led to a variety of ap-proaches for enhancing mass-transport in this type of cell. These have included mechanical stirring, solution forced flow, and gas sparging. Rotating the working electrode has also proved to be one of the most practical routes for enhancing mass transfer. Other methods have tried to increase electrode surface area by roughening or even the use of wire mesh electrodes; these routes approach the domain of three--dimensional electrodes.

Although not strictly a two-dimensional cell design, the Chemelec Cell[30] developed by Bewt Engineering (U.K.) uses an array of expanded mesh cathodes with alternate noble metal coated, DSA type planar anodes in an undivided cell arrangement (Fig. 3). Based on the original concept[31] developed at the Electricity Research Council (U.K.), the unique feature of this design is that it uses a fluidized bed of inert glass ballotini to promote mass-trasnport. This cell has been successfully applied to a range of metal recovery and pollution control applications in the metal finishing, printed circuit board and photographic industries.

4.4 *Rotating Cells*

Rotating the working electrode has been one of the most obvious ways of increasing mass transfer rates, particularly in metal recovery applications. One attractive feature of this approach is the ability to adjust the cathode rotation speed to the shear stress of the electrode to dislodge the deposited metal in powder form. Mecha-nical scraping has also been used in addition to direct shearing of dendritic deposits. By analogy to the analytical rotating disc and ring-disc electrodes, this configuration of cell should also have application where short-lived intermediate species are involved in the process for example in the electrolytic generation of oxidants or reductants for effluent treatment. Although the ability to produce high purity metal powders is an attractive feature of this design, in routine industrial practice rotating electrodes do have some mechanical limitations.

A rotating cylinder cathode has featured in several commercially developed systems for metal recovery. The Eco Cell[32] was one of the earliest designs based on this concept, where the rotating drum cathode was scraped by a wiper to dislodge deposited metal which is then passed through a hydrocyclone to produce a metal powder. A cascade version of this cell with six chambers separated by baffles was also demonstrated and was claimed to reduce a 50 ppm copper input stream to 1·6 ppm in the output[33]. Commercial development of this design is now being carried out by Steetley Engineering (U.K.).

A laboratory prototype of an ingenious design of rotating disc electrode cell has been described by Tenygl[34] for the production of hydrogen peroxide for potable or industrial wastewater sterilization. By using a partly submerged rotating disc array, a thin film of electrolyte is maintained in contact with air, thus enabling a much higher concentration of hydrogen peroxide to be formed than in the alternative homogeneous solution route. The peroxide in the thin solution film is continuously fed into the bulk solution by the rotation process.

The pump cell concept[35], devised by Jansson and coworkers in Southampton (U.K.) is another variant of the rotating cell. In the simplest version (Fig. 4) the process stream enters the thin layer between the rotating disc cathode and the stationary cell body. The electrolyte is accelerated to high mass transfer rates and the cell becomes self priming. In metal recovery applications the deposited metal film is discharged from the cell in the form of fine powder. It is also relatively straight-
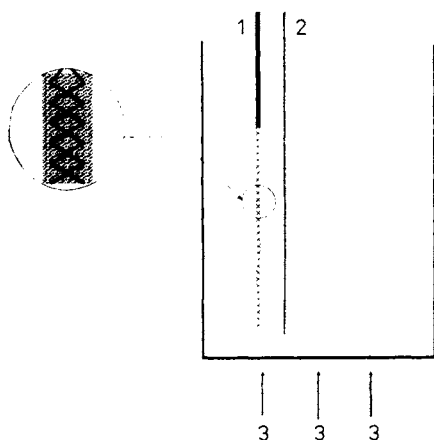

Fig. 3

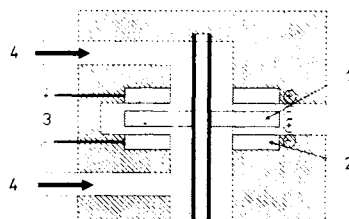Chemelec cell. 1 Expanded mesh steel or Ti cathode; 2 Ti/RuO$_2$ coated anode; 3 process inlet

Fig. 4

Bipolar pump cell; magnetically driven rotor on ceramic shaft. 1 Rotor; 2 stator; 3 current connections; 4 flow direction

forward to scale-up this cell design to produce a multiplate bipolar stack; a 500-amp version of this cell has been tested.

Another version of the rotating electrode concept has been developed by Gotzell-man KG (Stuttgart, F.R.G.). In this design known as the SE Reactor Geocomet Cell[36], a concentric arrangement of rod-shaped cathodes rotates inside inner and outer anodes. The deposited metal is dislodged by the rotating rods and falls to the bottom of the cell. The anodic destruction of cyanides in metal plating process rinses is also claimed to be possible with this arrangement.

5. THREE-DIMENSIONAL REACTOR SYSTEMS

The development of high performance, high surface area electrode reactor systems has undoubtedly been one of the most active research and development areas in electrochemical engineering. The demand for systems with high space-time yields has been driven by the need for economic metal recovery systems for both pollution control and resource recovery applications.

It should be noted at the outset that the distinction between two-dimensional and three-dimensional reactor systems is often far from rigid, with many designs such as wire mesh and expanded metal electrodes falling in between the two types.

The unifying feature in all of these designs is that the cell chamber is filled or partly filled with the working electrode material. The enhancement in mass-transport characteristics obtained with these designs in comparison to conventional two-di-mensional planar reactors has had dramatic consequences for the commercial de-velopment of electrochemical engineering. First, the orders of magnitude increase in space-time yields obtained with many of these designs has resulted in substantial decreases in capital and operating equipment costs for a given process. This in turn has made the electrochemical processes more competitive with alternative, non--electrochemical technical routes. Second, they opened up important new application areas, such as low level metal recovery, which were either technically or economically impractical with the far less efficient two-dimensional cells. Some trade-offs were involved, particularly in the area of potential control and uniformity of current distribution. Despite early difficulties in maintaining the desired potential and current distribution in three-dimensional electrodes, the leverage in improved space-time yields more than compensates for this limitation. With further research in the areas of better computer modelling techniques and advanced process control systems even this limitation may eventually be overcome.

5.1 *The Fluidised-Bed Electrode*

The invention of the fluidized bed cell by the University of Newcastle group[37] both marked an important landmark and created a major stimulus to the field of electro-

chemical engineering. Despite the elegance of this cell design, it was the inherent limitations of the fluidised-bed concept that provided a focus for the development of alternative high surface area reactors.

The principle of the fluidised-bed cell is shown in Fig. 5; the conductive electrode particles are contacted by a porous feeder electrode, while the process stream causes fluidisation of the electrode bed. The main limitation to the design is that fluidisation of the bed causes loss of electrical contact between the particles, resulting in an extensive ohmic drop occurring within the cell so that uniform potential and current distribution is virtually impossible to maintain. The original design by Goodridge et al.[37], however, illustrates why the cell was initially so attractive. The electrode had a specific area of $200 \ m^2/m^3$ and was thus able to support large currents at an effective current density of around $0.01 \ A/cm^2$. Despite these advantages, it was more than 15 years from the initial concept before any significant commercial demonstration of the concept was achieved.

Most of the commercial development of the fluidised-bed cell has been carried out by Akzo Zout Chemie in the Netherlands[38]. The Akzo cell design overcame
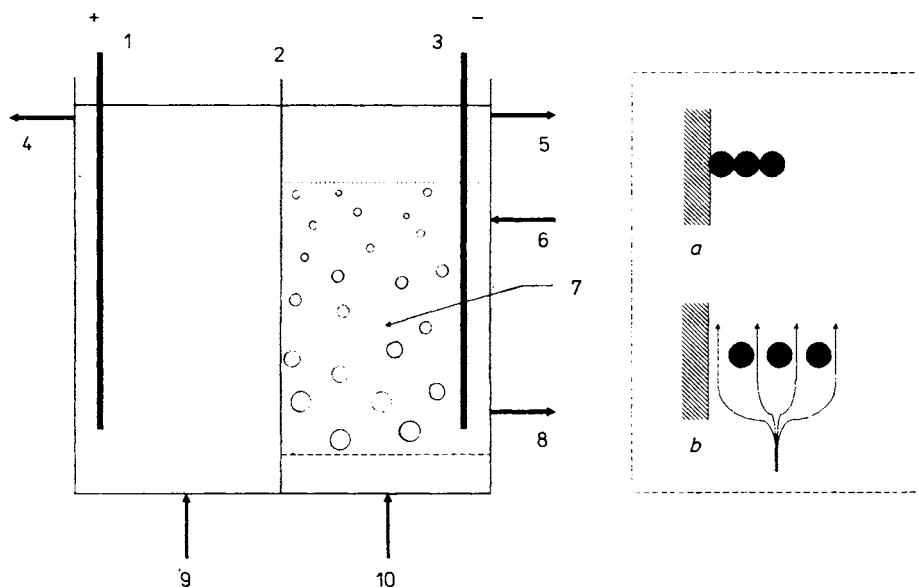
FIG. 5

Fluidised-bed cell. 1 Anode; 2 cathode (current feeder); 3 diaphragm; 4 anolyte; 5 catholyte (process steam); 6 supply of small metal particles; 7 fluidised-bed; 8 discharge of grown metal particles. a Solution at rest, particles in contact, particle potential $E_p =$ feeder potential E_f; b particles fluidised, potential $E_p = E_f + iR$

some of the scale-up limitations of the original design by the use of a large number of rod feeders to the cylindrical, 0·35 m diameter, cathode bed. The cell also contained six symmetrical rod anodes encased in cylindrical diaphragms. Applications to copper removal from chlorinated hydrocarbon waste and mercury from brine have been demonstrated by Akzo. The technology is currently licensed and is being developed by the Billiton Group of Shell Research, also in the Netherlands[39].

The Chemelec Cell described earlier[29] is also an example of the use of the fluidised--bed concept to promote mass-transport. In this case, however, the working electrode is an expanded metal mesh and the inert fluidised bed simply acts to enhance mass-transport.

5.2 *Contiguous Bed Electrode Designs*

Many of the problems of fluidised-bed cells appear to have been overcome by the development of three-dimensional contiguous bed reactors[40,41]. Evolving in many cases from porous electrode designs used in battery or fuel cell applications, these electrode designs are characterised by very high specific surface areas and space time yields. At the same time the ability to control potential and current distribution through the electrode bed is far better than in the earlier fluidised bed designs.

The first demonstration of the use of this electrode principle to metal recovery and pollution control applications was the use of carbon fibres as a high performance cathode[41]. Subsequently this electrode concept was developed commercially by HSA Reactors in Canada[42] and is currently being produced under licence by Baker Brothers (Stoughton, Mass), Hitachi (Japan) and Sorensen (Kassel, F.R.G.). The initial plate and frame cathode designs of the HSA Reactor, although very efficient, proved difficult to strip of deposited metal and were replaced by a tank cell design which used demountable cathode elements consisting of woven carbon fibre supported on a metal screen feeder (Fig. 6). This design was tested by the U.S. Environmental Protection Agency for appliation to metal recovery and cyanide destruction
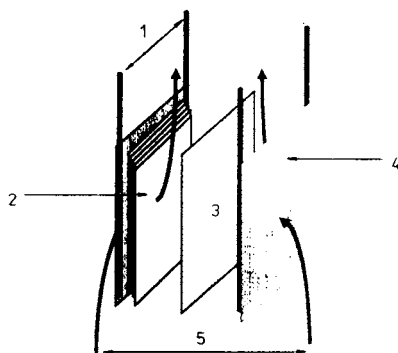

FIG. 6

High surface area reactor. 1 Cathode current feeders; 2 layered carbon fibre cloth; 3 anode, DSA type or steel; 4 stainless steel or Ti mesh cathode support; 5 process solution flow

in the metal finishing industry[43]. A pilot reactor was also demonstrated for the treatment of Gold Mill effluent to remove zinc and other trace impurity metals from the effluent after gold recovery (Barren Bleed stream) simultaneously liberating sodium cyanide for recycling to the pregnant stream extraction process[44]. Some preliminary experiments to demonstrate the prospects for treatment of organic effluents, particularly the treatment of Kraft Mill effluent from the Pulp and Paper industry were also carried out with limited success.

An alternative electrode material for contiguous bed electrode design is reticulated vitreous carbon. This material, which is prepared by pyrolysing polyurethane foams to give a vitreous carbon surface has shown great promise as an electrode material for electrochemical engineering since it is possible to fabricate electrode material with a wide range of pore size and void proportion. The Retec Cell[45] uses a tank configuration with reticulated vitreous carbon cathodes for treatment of metal bearing rinse streams. After metal collection, the cathodes are then removed for stripping in a separate cell.

5.3 Packed-Bed Cell Designs

An alternative design to the contiguous electrode is the use of a packed particulate bed of electrode material. Kreysa and Reynvaan[46,47] have studied the design of packed bed cells for optimal recovery of trace metals. The Enviro Cell[48], based on their work, consists of a packed bed of carbon granules and has been mainly applied to metal removal from industrial process streams. These authors also point out the desirability of altering the cathode bed geometry to compensate for depletion effects.

A different design of packed bed reactor has been developed by the Nanao Kogyo Company[49]. The major features of their cell are the packed particulate bed cathode with central cathode feeder and symmetrical anodes separated by a diaphragm. The cell also uses the bipolar mode of operation.

An interesting design of static three-dimensional electrode is the Swiss-Roll cell[50,51]. As the name implies, this design uses thin flexible sheets of cathode, separator, and anode rolled up around a common axis and inserted into a cylindrical cell. Flow is axial to the bed and the small interelectrode gap provides for a low cell voltage. A similar version of this concept was developed by DuPont[51] and was known as the extended surface electrode or ESE Cell. This system was demonstrated at the pilot scale for metal removal from wastewaters.

The complexities of any attempt to rigidly classify reactor designs is well illustrated by the plate and frame system developed by the Swedish National Development Company and described earlier under the two-dimensional cell category[28]. A different version of this cell[52] uses a packed-bed electrode for wastewater metal removal but unlike most other packed bed designs, the SNDC reactor uses the flow-by mode as in conventional plate and frame type operation.

This review by no means exhausts the range of electrochemical reactor and electrode/cell designs that have been used for metal recovery. It does attempt, however, to survey the major electrode design concepts which have either demonstrated performance or show promise of future development for application to metal recovery.

6. APPLICATIONS OF ELECTROCHEMICAL REACTOR SYSTEMS IN METAL RECOVERY

A comprehensive review of the wide range of applications of electrochemical reactor systems in metal recovery and pollution control is beyond the scope of this review and will not be attempted here. Rather, it is proposed to briefly review the various waste management strategies in which electrochemical systems can be employed and to examine the economic factors that control the implementation of these electrochemical technologies in waste management. Finally, some specific case studies will be presented, illustrating specific examples of the application of electrochemical reactor systems to facilitate metal recovery, resource recycling and zero-discharge strategies for industrial waste management.

6.1 *Waste Management Strategies*

The approach to any chemical waste management problem can vary widely depending upon the type of industry, the size and nature of the particular plant and the local environmental regulations. The two extremes of waste management strategy are first on-site treatment and recovery and second, offsite transport and disposal. Within these two extreme strategies there are clearly a number of compromise situations. These might include, for example a plant where the more easily treated wastes are handled on site while the more difficultly treated wastes are sent offsite for treatment or land disposal.

For on-site treatment there is a choice between custom designed continuous treatment systems and transportable treatment systems. The latter are mobile treatment systems which can be brought into a plant to treat certain type of wastes which can be stored ready for batch treatment.

As an alternative to on-site treatment or land disposal, many European countries have now set up centralised waste treatment facilities. These systems are more useful for organic chemical wastes since they rely very strongly on incineration technologies. Clearly the selection of an optimum waste management strategy for any given industry and geographic location is an enormous task. For any company or plant the choice depends on two main factors. First is the environmental regulations and their level of enforcement; the second is the economics and performance of the various treatment technologies and waste management strategies.

6.2 *The Economics of Waste Management*

The economics of waste management is a complex issue since there is no direct cost benefit or economic payback associated with the installation of a waste management system. While the major driving force is undoubtedly government regulations, the key incentives for waste management can be summarised as follows:

a) Increasingly stringent environmental regulations leading to greater surveillance of industry's operating practices, decreasing permissible discharge limits and limited availability of sites for land disposal of solid and liquid hazardous chemical wastes.

b) The increasing value of many metals and process chemicals providing justification for implementation of resource recovery and recycling systems.

c) The rising costs of process water and higher sewer discharge costs providing justification for use of wastewater treatment allowing recycling of most of the plant of process water, often with the added advantage of generating a high purity, deionised water streem.

d) An increasing awareness by many industries of the direct economic benefits of waste management in terms of improved product quality and reliability as well as improved worker safety and operating conditions.

Assuming that for metal pollution generating industries some type of waste management system is mandatory, then the waste management strategy to be adopted should be based solely on an evaluation of the technical performance and economics of the various competing waste management technologies and strategies. As an example, for a metal finishing or metal plating plant two alternate waste management strategies could be considered. The first route is the standard chemical treatment approach, involving reduction of chromium, oxidation of cyanides, pH adjustment and precipitation of heavy metal sludges, sludge filtration, followed by offsite transport and land disposal of the sludges. The second approach is a zero-sludge, resource recycling approach using a series of integrated electrochemical recovery and ion-exchange systems to treat the various metal pollutants at their point of generation (point-source treatment).

Defining the former conventional chemical treatment system as "treatment and disposal" and the latter electrolytic system as "resource recovery", the following economic comparisons can be made.

Capital cost: Resource recovery systems are three to five times more costly than comparable treatment/disposal systems for the same capacity since a separate treatment process is required for each type of waste stream. Treatment/disposal systems, on the other hand, combine and treat collectively all of the waste streams.

Operating Costs: Both routes require some treatment chemicals with the treatment/ /disposal route being the more costly. Labour costs are generally similar for both approaches although with the resource recovery approach labour costs can generally be decreased by around 30–40% by addition of automatic controls.

Cost Benefits: While the resource recovery approach allows recovery of some metals and other process chemicals, their value is usually quite low in comparison to overall operating costs. Resource recovery systems do however, have a significant cost benefit in that they enable a large proportion, up to 90% or more, of plant process water to be recycled as high purity water.

Waste disposal costs: The major difference between the two approaches is in the costs of offsite waste transport and disposal. With public pressure and environmental regulations moving rapidly towards restricting land disposal of toxic wastes, the costs of dumping at available landfill sites is increasing exponentially. The resource recovery approach on the other hand allows the plant to treat the bulk of its toxic wastes on site and in many cases can reach a "zero-discharge" status.

Future intangible costs: Many companies now perceive that there are significant legal risks associated with dumping toxic wastes in land disposal sites since any future leakage from a landfill can be enormously costly. In the United States, for example, the costs of remediation of some abandoned chemical dump sites have been estimated to be as high as $ 3 000 (U.S.) per ton (including the costs of site surveys, pollutant analysis and treatment methodology development) when the original cost of dumping the waste was probably less than $ 100 per ton.

Recent studies[2,3] have concluded that given effective environmental legislation, the overall costs of resource recovery waste management technologies, of which electrolytic recovery is one of the more important, are very competitive with conventional treatment routes. While the exact comparison will vary according to the size and nature of the plant, all conclusions favour the use of some from of resource recovery, such as electrolytic treatment, in order to effect significant waste reduction.

6.3 *Metal Finishing*

Electrochemical reactors have shown great promise for treating waste streams from metal finishing operations. This industry generates a highly toxic and complex waste
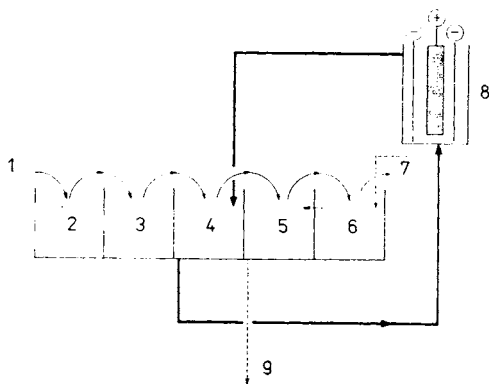

FIG. 7

Point-source treatment of electroplating rinses. 1 Direction of plating work flow; 2 pre-plating; 3 plating bath; 4 static or drag-out rinse tank; 5 first running rinse; 6 second running rinse; 7 process water input; 8 electrolytic recovery cell; 9 discharge to sewer or waste treatment

stream containing a range of metals including copper, cadmium, lead and chromium, cyanides and some organics. Because of the lack of uniformity of most metal finishing operations it is difficult to define an optimum treatment strategy. One of the most generally useful treatment approaches for this industry is based on the use of electrochemical reactors used as point source treatment units. In this process they are linked in a "closed-loop" configuration on the rinse tank immediately following plating operations (Fig. 7). In this situation, the rinse tank R_1 is a drag-out or non-flowing rinse so that the metal plating solution adhering to the plated parts is captured. The electrochemical reactor continuously removes accumulated metals from this drag-out rinse and thus maintains the metal concentration at a suitably low level, typically in the range $10-100$ ppm. Thus, the carry over of this metal containing solution to the next running rinse tank is minimised as is the discharge from this tank to the sewer. In most cases this approach can ensure that the effluent from this particular source is well below the discharge limit. In most cases, however, electrochemical reactors are not able to provide a complete solution to metal finishing waste management problems, since they are unable to treat all of the metals used in this industry. Also, it is not usually technically or economically feasible to install a recovery system on the final effluent from a plating plant to remove the last residues of toxic metals since at this stage process flows are usually quite large and large capacity and thus expensive systems would be required for their treatment. Applications of electrochemical reactors in metal finishing waste management have included the treatment of acid copper, cyanide copper, cadmium, nickel, tin, lead, gold, silver and platinum rinses, cyanide destruction and some few applications of process bath control.

The electrolytic recovery of metals from metal finishing effluents usually involves two steps; collection or plating of the heavy metals followed by some form of stripping from the working electrode. The stripping process can be carried out in several ways; by chemical dissolution either in situ or in a separate stripping tank, by electro-chemical stripping via reversal of electrode polarity or by galvanic stripping. In the case where the metals are plated out as a solid metallic sheet they may in some cases be reused as anode material or alternatively sold as scrap. Chemical or electrochemical stripping can also be used to produce a metal salt solution for reuse in the manu-facturing processes.

6.4 *Printed Circuit Board Manufacturing*

Chemical waste management in the Printed Circuit Board industry is generally less complex than in the Metal Finishing industry since the manufacturing processes are more systematic and better defined. This industry generates toxic wastes comprising acid and chelated copper from circuit board plating/etching, tin/lead from solder coating and masking and nickel and gold from edge connection preparation.

Although a number of waste management strategies have been described[2,3], one of the most promising would seem to be based on a combination of ion-exchange and electrolytic recovery (Fig. 8). In this approach the dilute metal-bearing process rinse streams are first segregated and treated by an ion-exchange process. The higher concentration waste sources (spent process baths, circuit board etchants, etc.) are treated directly with an electrowinning cell using planar stainless steel cathodes in a tank cell with a membrane isolated anode and turbulence promotion. This electrowinning process can reduce metal concentrations from initial values in the $5-20$ g/l range down to $100-200$ ppm. Residual solution after treatment is then recycled through the ion-exchange process to remove remaining metals. This closed-loop combination of ion-exchange and electrolytic recovery is applicable to all of the metal bearing waste streams generated by this industry and also can be applied with some process modifications to waste streams generated by other electronic products industries such as semiconductor and intergrated circuit manufacturing.

Furthermore, by incorporating a demineralisation step into this process, a complete resource recovery, zero-discharge waste management system can be achieved, with recovery of all of the toxic metals and recycling of over 90% of process water as high purity, deionized water. The economics of this approach are particularly suited to medium to large size plants with total daily process water usage over 200 000 litres per day. For smaller plants some alternate strategies may be more appropriate.
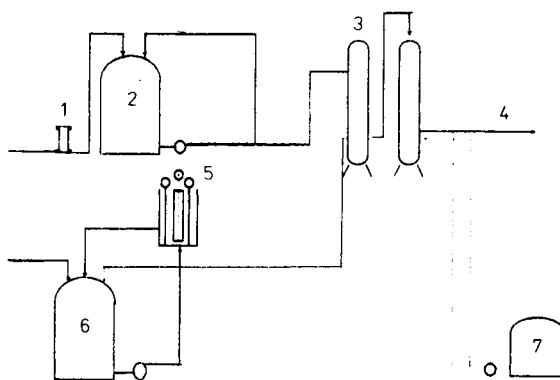

FIG. 8

Integration of ion-exchange and electrolytic recovery. 1 Filter; 2 collection tank for segregated dilute metal stream; 3 ion-exchange columns, collector and guard; 4 discharge to sewer or demineralization for recycling to process; 5 electrowinning cell for treating high concentration metal sources and ion-exchange eluate; 6 high concentration metal sources storage; 7 eluent reservoir

6.5 *Mining*

While electrolytic processes have been described for a range of mining and primary metal recovery processes, in most cases, the currently depressed economics of the metals industry has prevented their commercial exploitation. One area where electro-chemical processes still offer considreable promise is in gold mining. At the present time this industry relies very heavily on the Merrill–Crowe process which consists of adding powdered metallic zinc to a cyanide extract of the gold ore. This causes precipitation of the gold while at the same time generating a highly toxic waste stream containing cyanides and zinc and other metal cyanide complexes. An alternative process for lower grade gold ores is the Heap–Leach process (Fig. 9) in which a cya-nide process stream is percolated through a mound of ore to extract the gold which is then collected in a plastic lined tank. In most cases a carbon adsorption process is used to recover the gold by adsorbing the gold cyanide complex on carbon particles or an activated carbon column.

Electrolytic cells have long been used for final electrorecovery of gold after con-ventional processing and cyanide extraction using either the Merrill–Crowe or carbon--in-pulp processes. The cell designs used to date have not generally adopted recent advances in electrochemical engineering and it seems clear that the full potential of electrochemical techniques has yet to be realized in this industry.
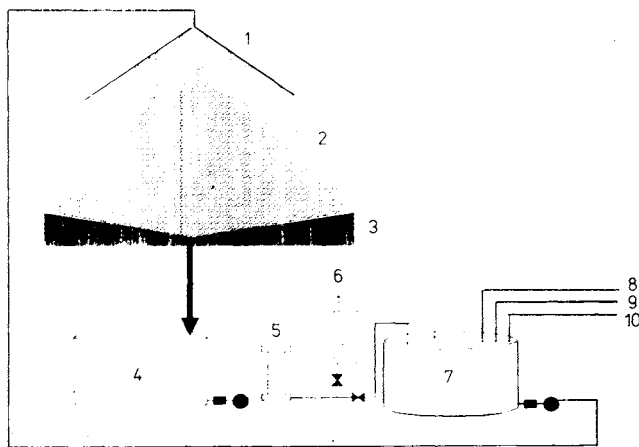

Fig. 9

Heap leach gold recovery. 1 Sprays; 2 crushed ore; 3 asphalt or plastic lined pad; 4 collection tank; 5 carbon filter collector for gold and metal cyanides; 6 electrolytic cell; 7 process return tank; 8 process water; 9 caustic soda; 10 cyanide solution

There are several possible conceptual process schemes incorporating electrolytic recovery which could both improve the economics of conventional gold processing which in most cases would simultaneously eliminate many of the hazardous waste problems faced by this industry.

These include:

a) Direct electrowinning of gold from gold cyanide process streams: This electrolytic treatment of the pregnant leach stream, by recovering gold and other impurity metals, also liberates free cyanide, a valuable process chemical. By recycling the cyanide back to the extraction process, the generation of a toxic waste stream is eliminated. Due to the volume of water used to make up process solutions, etc., a small fraction of the treated process stream cannot be recycled and requires discharge. In this case the cyanide in this stream can be destroyed by treatment with chlorine generated in the anode compartment of the reactor.

b) Electrowinning of Heap–Leach extracts: The Heap–Leach process is commonly used to treat low grade ores (< 10 − 12 ppm), the electrochemical reactor could be used to treat the cyanide extract after carbon in pulp extraction (Fig. 9). There is also the possibility of using high performance cathode cells to treat the heap leach extract directly without the need for an intermediate carbon adsorption pre-concentration step.

c) Difficultly treatable gold ores: Conventional gold recovery processes are not suitable for treating certain types of ores, particularly ore bodies containing large amounts of clays, slimy ores or carbonaceous ores. In these cases, cyanide leaching followed by either carbon adsorption/elution and electrowinning or direct electrowinning from cyanide extract are viable treatment options.

6.6 *Other Applications*

Several other electrolytic metal recovery processes have been demonstrated including silver from photographic film and film processing wastes, palladium from spent catalysts, mercury from chlorine cell effluents, lead from battery manufacturing and a variety of metals from extractive metal processes.

7. CONCLUSIONS

Electrochemical reactors are now well established as a major technology for recovery of metals in a wide range of waste management and pollution control applications. The systems developed to date have demonstrated the ability to treat most toxic heavy metals over a broad concentration range (parts per million up to several grams/litre) and recover the metal in a useful form, either as solid sheet metal, metal powder or a concentrated metal salt solution.

These systems are generally comparable in terms of economics and performance with most competitive technologies and being modular in construction are fairly simple to scale-up. While in many cases electrochemistry is unable to provide the total solution to a given waste management problem, it often can play a major role. For many waste management problems, there are no viable alternatives to electrochemical systems.

Three-dimensional, high surface area electrode systems are the most effective for pollution control, particularly for low-level metal recovery applications, although in many cases they still face some problems in terms of effecting uniform control of potential and current distribution. Nevertheless, the economic leverage provided by the higher space-time yields of these designs is so great that they are finding widespread use. The design and development of this type of system, particularly its application to a broad range of toxic waste management problems continues to be one of the most active research areas in electrochemical engineering.

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