United States Patent [19]

Williams

[11] **3,859,195**

[45] **Jan. 7, 1975**

[54] **APPARATUS FOR ELECTROCHEMICAL PROCESSING**

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[73] Assignee: **E. I. du Pont de Nemours and Company,** Wilmington, Del.

[22] Filed: **Oct. 17, 1973**

[21] Appl. No.: **407,248**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 290,642, Sept. 20, 1972, abandoned.

[52] **U.S. Cl.**.................. **204/272,** 204/130, 204/151
[51] **Int. Cl.**........................... **B01k 3/00,** B01k 1/00
[58] **Field of Search**........... 204/130, 140, 153, 151, 204/272

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Primary Examiner—T. M. Tufariello

[57] ABSTRACT

An apparatus for electrochemical processing characterized by extended surface electrodes maintained at a substantially uniform electrical potential while presenting a relatively low pressure drop to liquids in treatment passed through the apparatus.

9 Claims, 16 Drawing Figures

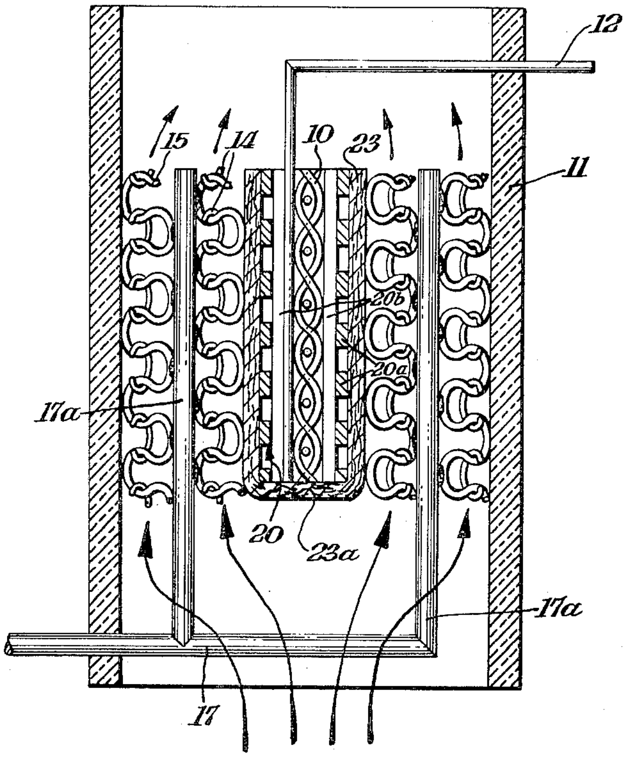


Fig. 1.

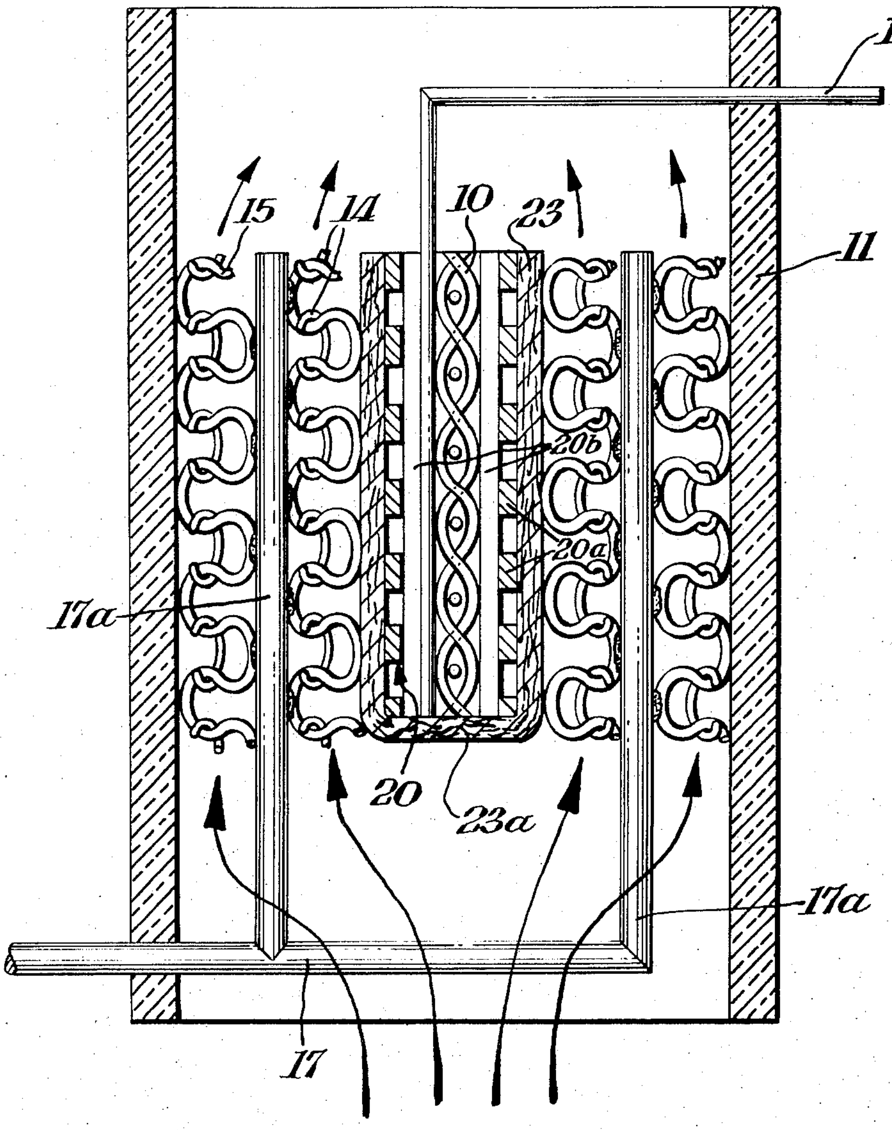


Fig. 3.

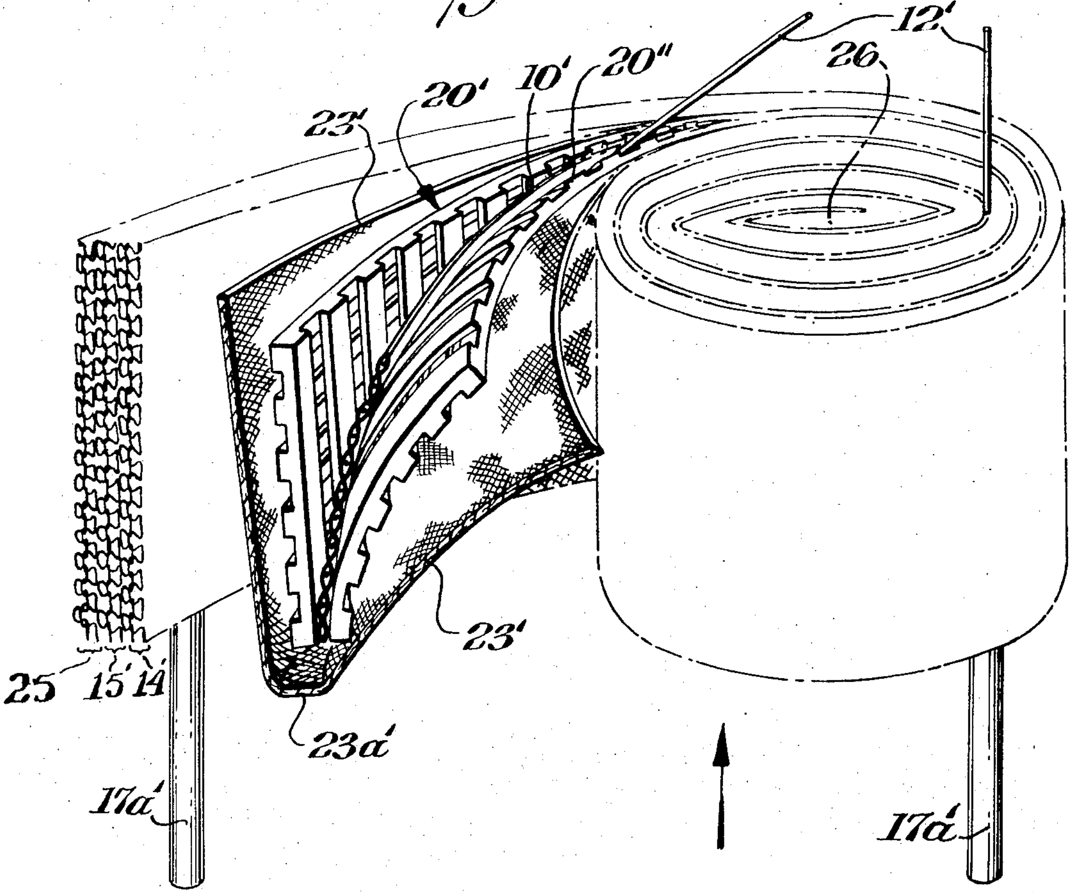

12'
26
20''
10'
20'
23'
25
15'
14'
23a'
23'
17a'
17a'

Fig. 2.

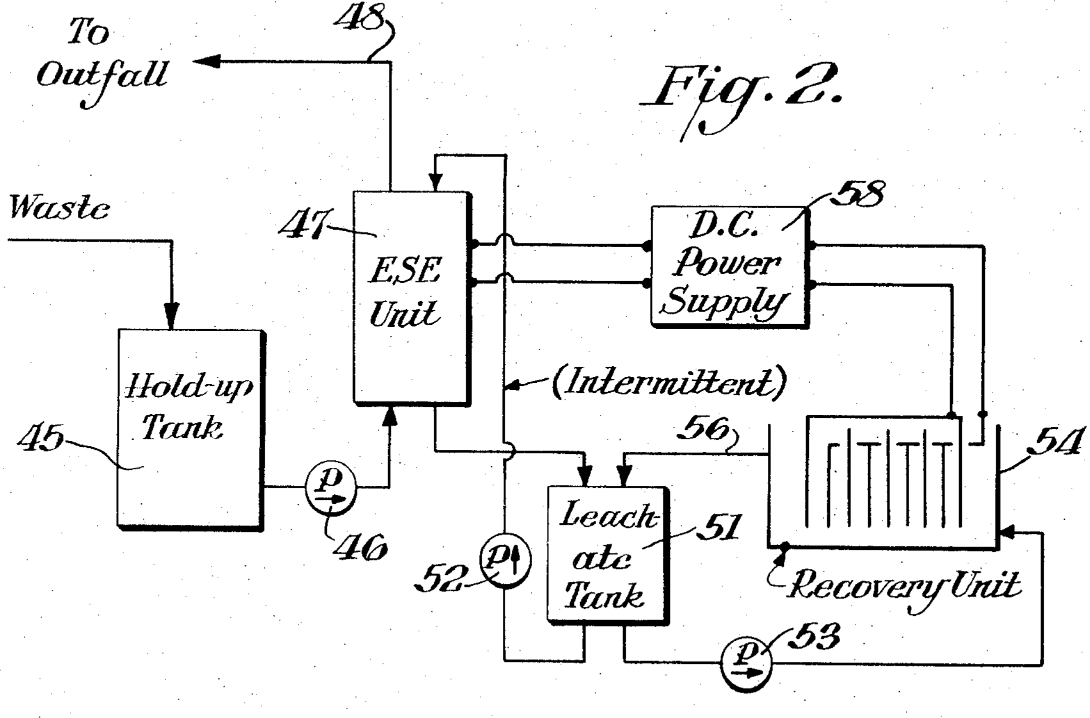

To Outfall
48
Waste
47
ESE Unit
D.C. Power Supply
58
Hold-up Tank
45
(Intermittent)
56
54
P
46
P
52
Leachate Tank
51
Recovery Unit
P
53

Fig. 4A.

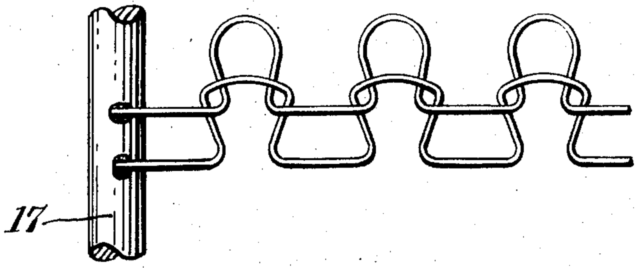


Fig. 4B.

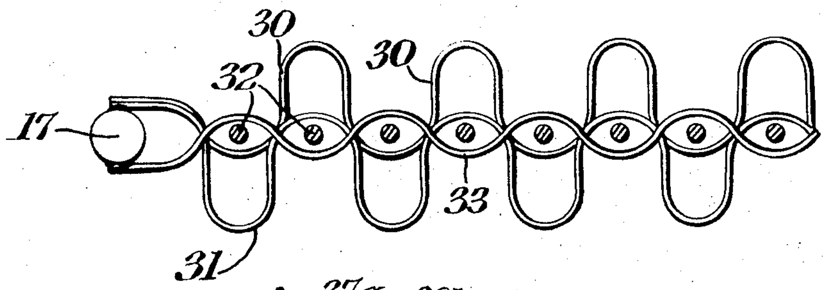


Fig. 4C.

Fig. 4D.

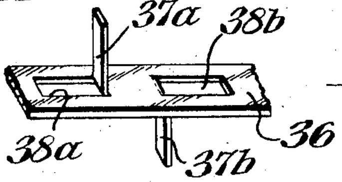


Fig. 4E.

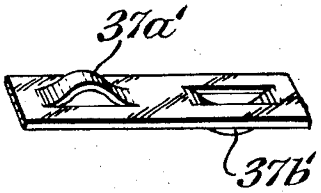


Fig. 5A.

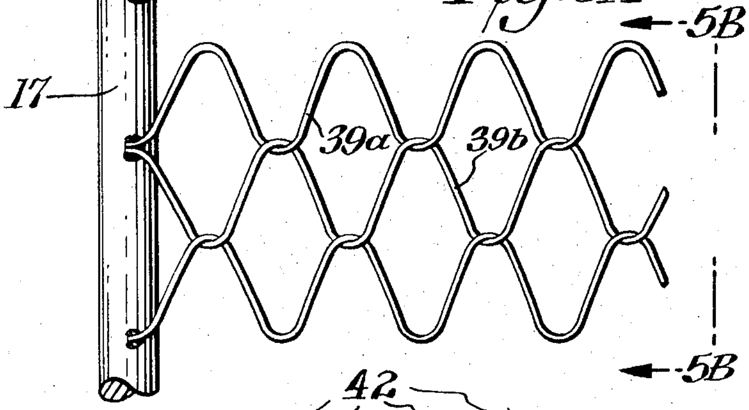
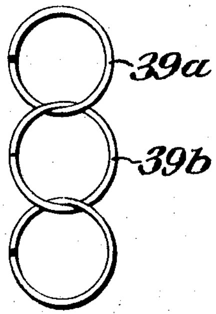


Fig. 5B.



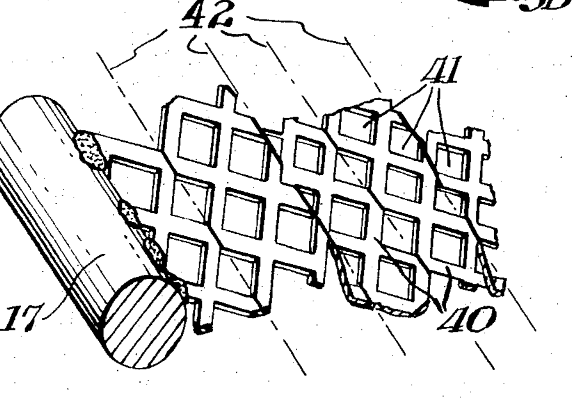


Fig. 5C.

Fig. 6A.

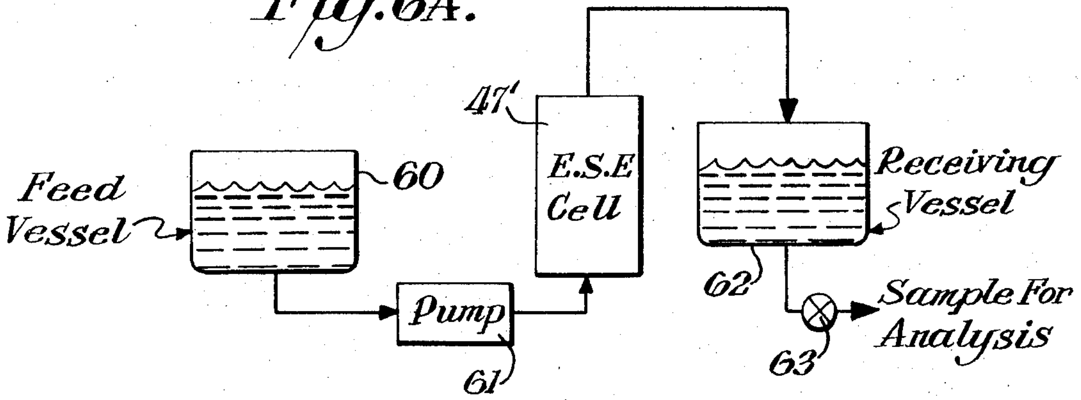


Fig. 6B.

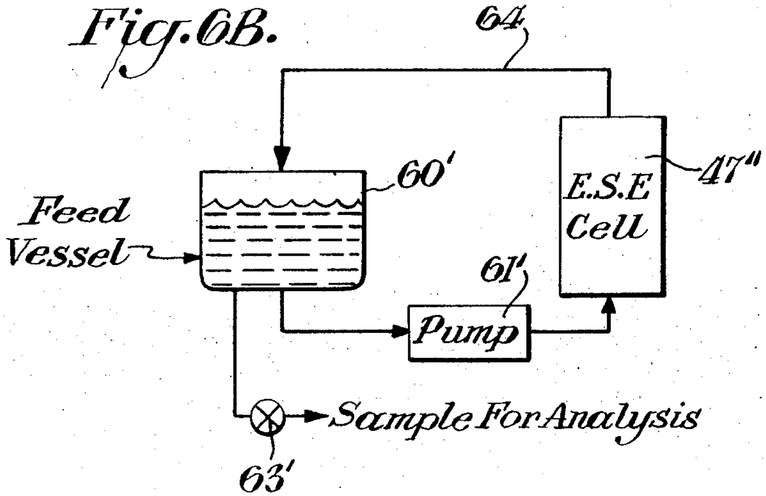


Fig. 7.

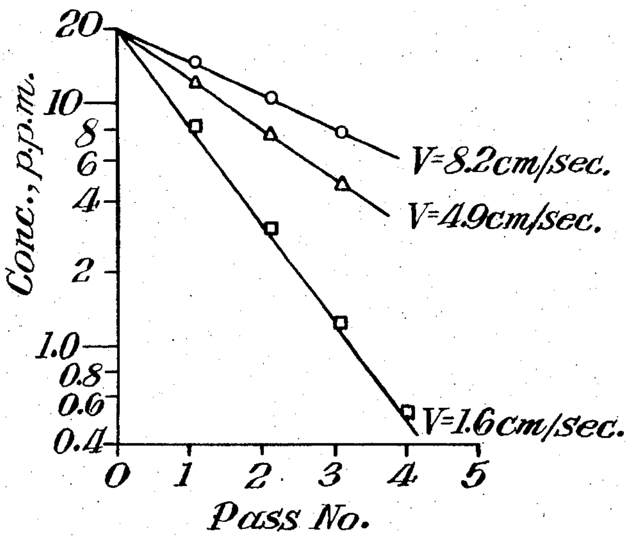


Fig. 8.

Electrolysis of Industrial Effluent "C"

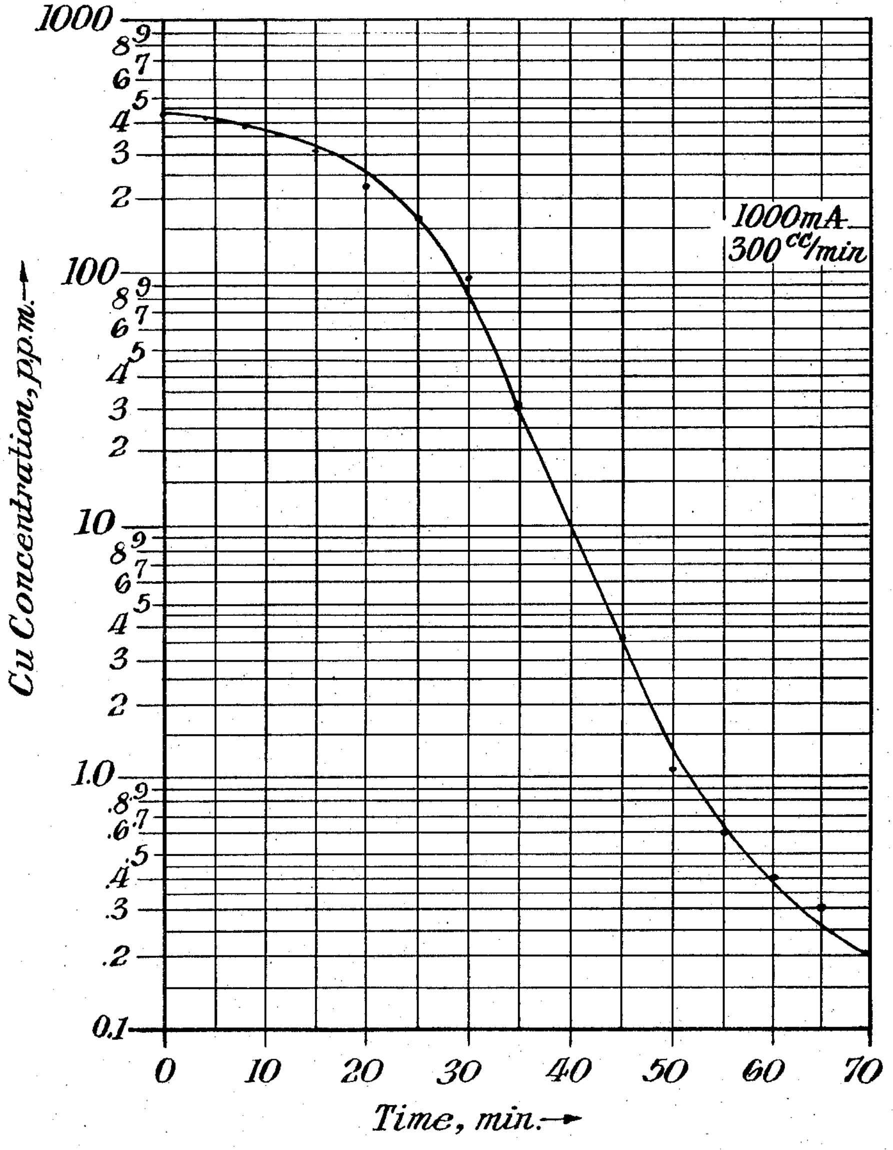
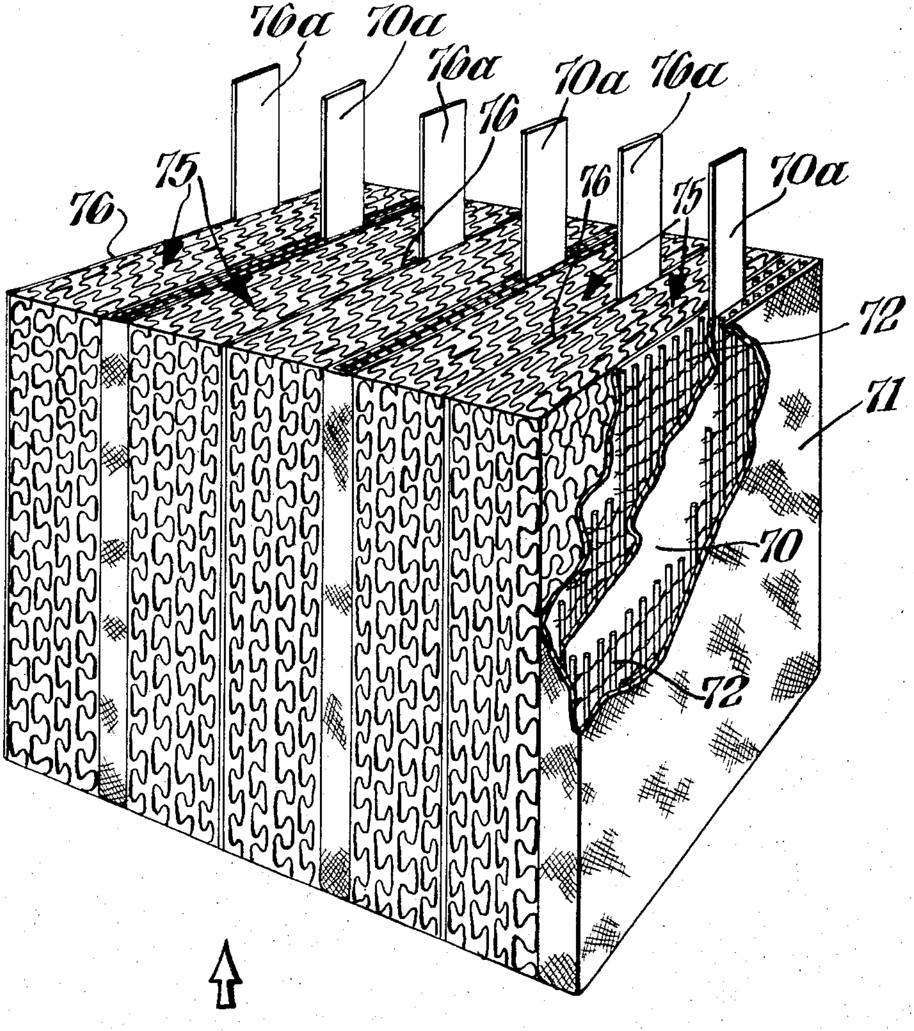


Fig. 9.



APPARATUS FOR ELECTROCHEMICAL PROCESSING

CROSS REFERENCE TO RELATED APPLICATIONS

This Application is a continuation-in-part of U.S. application Ser. No. 290,642 filed on Sept. 20, 1972 now abandoned.

BRIEF SUMMARY OF THE INVENTION

Generally, this invention comprises an apparatus for the electrochemical treatment of an electrically conductive solution by effecting separation, reaction or other processing of a given ingredient of the solution. The apparatus is an electrolytic cell comprising at least two inter-functioning electrodes disposed within a vertically oriented leak-tight housing, at least one of which electrodes has an extended surface area over which a substantially uniform reaction-producing electrical potential is maintained throughout that portion of the area of the electrode in confrontation with the electrolyzing area of the remaining electrode, the separatory (or reactive) one of the electrode pair being relatively openn to access of electrically conductive solutions passed through the cell, whereas the remaining electrode is isolated from the solution by enclosure within an electrically insulative envelope permitting ionic conduction while barring ready passage of the soluution therethrough.

DRAWINGS

The invention is described with reference to the following drawings, in which:

FIG. **1** is a partially schematic side elevation sectional view through a first (cylindrical) embodiment of cell constructed according to this invention,

FIG. **2** is a block diagram of an arrangement of apparatus effecting separation of heavy metal from a dilute electrically conductive solution as process liquid,

FIG. **3** is a somewhat schematic partially opened view of a preferred embodiment of spiral wrap electrode structure for use with this invention,

FIGS. **4**A–**4**C are partially schematic representations of two different knitted and woven electrode element designs of uniformly reticulated open construction which can be utilized with this invention,

FIG. **5**A is a partially schematic side elevation view of a third electrode structure of "cyclone fence" design,

FIG. **5**B is an end view of the structure of FIG. **5**A taken on lines **5**B—**5**B thereof,

FIG. **5**C is a partially schematic fragmentary perspective view of a fourth electrode structure fabricated from expanded metal,

FIGS. **6**A and **6**B are, respectively, diagrammatic flow sheets of continuous mode operation and of batch mode operation with solution recycle according to this invention,

FIG. **7** is a plot of copper removal according to this invention wherein Cu content in ppm is plotted as ordinate versus pass number through the apparatus as abscissa,

FIG. **8** is a plot of copper removal according to this invention from a typical industrial effluent containing Cu as adulterant wherein Cu concentration is plotted in ppm as ordinate versus time in minutes as abscissa,

FIG. **9** is a partially schematic perspective view of a rectangular electrode embodiment of this invention.

DETAILED DESCRIPTION

This invention will be described primarily as applied to pollution abatement in the cathodic removal of heavy metals at low concentrations from dilute electrically conductive solutions, or waste effluents; however the invention is equally applicable to high concentration uses, anodic processing and also the effectuation of electrochemical reactions, such as oxidation and the like, all as hereinafter detailed.

In ordinary electrochemical processing of aqueous solutions, e.g., in electroplating, the ionic components are present in relatively high concentrations and thus migrate to the electrodes at rates consistent with practical current densities and at relatively high coulombic efficiencies for the desired reactions. However, in many situations, such as most aqueous wastes from industrial plant operations, the ionic components are present at levels two or three orders of magnitude lower than those encountered in plating practice. If electrochemical treatments are to be applied to the low concentrations of contaminants in such aqueous wastes, it is found that conventional apparatus known to the art possesses very low electrical efficiency, coupled with excessive cell residence time, which renders it impractical to reduce the concentration of the contaminants to the safe levels prescribed by law, e.g., one part per million.

Research on conventional electrochemical cell operation reveals that, when the concentrations of species involved in electrochemical reactions are very low, other competing electrochemical reactions can concomitantly ensue, proportionately reducing the efficiency of the desired reactions. Thus, in aqueous metal solutions, incidental production of hydrogen at the cathode instead of plateout of the desired metal component, such as copper, constitutes electrical current waste. In some instances objectionable mixed metal deposits are also produced, instead of the desired pure metal, whereas, in other instances, the deposits are of inferior physical character, such as loose powders rather than adherent films.

Attempts have been made to solve the problems described by utilizing porous carbon electrode equivalents, including fixed and fluidized beds of carbon particles surrounding the metallic bus supplying current, thereby relying only on point-to-point contact of the carbon particles to maintain conduction. Electrodes fabricated from porous carbon have also been used, through the pores of which the liquid electrolyte is forced to flow; however, these suffer from high pressure drop as well as rapid blinding resulting from accumulation of the plated-out component within the fine pores.

Blocks of carbon can be arranged to provide a high area electrode surface per unit volume of the bed; however, there are disadvantages, such as: (1) carbon has a higher specific resistivity than most metals, so that an electron current flowing within a solid carbon matrix displays a substantial voltage drop between the supply bus and the remote regions of electrode surface. Nonuniformity of electrode surface potential permits concomitant multiple electrochemical processes at different electrode regions, instead of restricting operation to a desired single process. (2) Conventional porous carbon has a very fine pore size of, typically, 0.001 inch–0.006 inch (25 to 150 μ) and is, therefore, quickly clogged with an electrochemical deposit. (3) Fluid flow resistance is very high as a result of both fine pore size and low porosity (e.g., typically, the void fraction is 0.5 or less), requiring either high pressure operation or a very low flow rate.

Packed beds of carbon particles can, by careful selection of particle size and shape, afford a more open deposit area for the deposition of electrochemical product, which has a longer servce life, before blinding, together with a lower pressure drop. However, a new difficulty is encountered, namely, reliance on point-to-point particles contact for the electrode circuit path, which evinces a higher electrical resistance between the supply bus and the bed extremities, so that current efficiency is reduced even below that of a block carbon electrode structure. Moreover, the void fraction of packed beds is usually only about 0.50, making only half of the bed section available for passage of the solution in treatment.

Fluidized beds of carbon particles display even more severe disadvantages, in that: (1) there is a substantially higher particle-to-particle electrical resistance, because the area of particle contact are smaller and there exist only low interparticle pressure, since the bed is at least partially floated by the process stream throughput, (2) part of the time some particles are completely out of contact with any others, contributing zero electrode activity and, where corrosive solutions are being treated, actually reducing overall efficiency by loss of previously deposited material through corrosive attack, and (3) deposits built up on individual fluidized particles change the fluidization properties of the particles, making for objectionable inconstancy and nonuniformity of electrode behavior.

Use of metallic extended surface electrode structures is disclosed in U.S. Pat. No. 2,588,450 in the form of a loose stainless steel wool pad as cathode disposed within a cylindrical basket fabricated from an insulative material which is perforated on the periphery to divert the electrolyte flow to an anode disposed coaxially with respect to the cathode. The cell is utilized for the electrodeposition recovery of gold from caustic solution, and the electrolyte is introduced first into the center of the cathode, after which it flows generally laterally through the basket side wall and thence to the encircling anode, so that contact of electrolyte with the electrodes is sequential from cathode to anode.

U.S. Pat. No. 3,244,604 shows electrolyte flow-through woven mesh cathodes ¼ to 4 inches thick, used for removing metal ion impurities which are present at concentrations below about 500 ppm in aqueous caustic solutions. The cathodes are pads of woven nickel wire stiffened by a nickel screen to which electrical connection is made. Anodes and cathodes alternate in vertical array in the direction of electrolyte flow and there is, of course, no separator inhibiting electrolyte flow-through with respect to the anodes, since the electrolyte has to flow with equal facility through all of the electrodes in the vertically disposed stack.

Neither of the disclosed constructions employ simultaneous subjection of electrolyte to both anode and cathode operation at common transverse levels, and this is an important feature of this invention.

THIS INVENTION

For the conduct of electrochemical reactions, the essential electrical potential of a point in an electrolyte, hereinafter referred to as the "reactionproducing potential," is equal to the sum of the following:

1. The equilibrium reversible half-cell potential at the conditions of the electrolysis (i.e., temperature, pressure, concentrations of species at the electrode-electrolyte interface, etc.),

2. The activation overpotential, this being the extra electrical potential over and above the equilibrium reversible half-cell potential required to drive the desired reaction at a given rate. This overpotential is a function of the real current density at the electrode-electrolyte interface, and

3. Ohmic voltage drop in the electrode material. This voltage drop is the integral sum of the ohmic voltage drops along each of the paths of current flow leading from the electrode-electrolyte interfaces to the said point in the electrode.

This invention advantageously influences all three of the factors determinative of electrode point potential in the following respects:

a. The electrodes, constructed of extremely fine filaments which provide large surface area and enhance the mass transfer coefficient, minimize the concentration difference between the bulk of the electrolyte and the electrode-electrolyte interface at any given level of operation. Correspondingly, the departure from the equilibrium reversible half-cell potential predicted from the bulk concentrations is minimized.

Accordingly, in a situation where competing reactions can occur, the potential region corresponding to this undesirable condition is less closely approached, so that the specificity, or coulombic efficiency, for the desired reaction is enhanced.

b. The activation overpotential, which is a function of the current density, is minimized at any given level of operation by the high real surface area of the extended surface electrode. This contributes even morre importantly than (a) supra to selectivity and enhanced coulombic efficiency for the desired reaction.

c. The high conductivity of the preferred electrode materials, together with the use of welded or other low resistance connections to buses, minimizes ohmic voltage drop for any given level of operation.

By reduction of each of the enumerated voltage contributions, the power required for a given level of cell operation is substantially reduced. A further contribution to higher power efficiency is the close juxtaposition of anode to cathode in cells of this invention. This is achieved by enclosing one of the interfunctioning electrodes of the pair within a separator presenting both sides of this isolated electrode in electrolyzing disposition with respect to a co-functioning electrode.

Referring to FIG. **1**, a cylindrical embodiment of electrochemical cell according to my invention comprises the high surface cathodic design shown, which is here utilized to remove heavy metals (e.g., Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Co, Hg and Pb) from dilute aqueous solution. In this service, only a relatively small anode is required and this can, accordingly, constitute a compact rolled-up metal screen **10** which is centrally located along the longitudinal axis of the cell enclosure which, in this instance, can typically be a tube **11** fabricated from glass, polymeric resin or the like. If desired, a metallic enclosure **11** can be employed, provided that the anode supply bus **12** is electrically insulated therefrom, in which case the inside wall surface of the enclosure constitutes additional cathodic area.

The anode supply bus **12** of FIG. **1** is introduced in fluid-tight relationship through a passage drilled radially in the wall of enclosure **11** and is bent downwardly into firm contact with adjacent plies of the screen over the full length thereof, preferably being weld-attached thereto.

The cell of FIG. **1** is provided with two concentric cathode element sleeves **14** and **15** coaxially disposed with respect to the common axis of enclosure **11** and anode **10**, although a greater or lesser number can be utilized if desired. An essential feature of this invention is the utilization of cathode elements which have a very large extended surface, while at the same time insuring substantially equipotential maintenance over the electrochemically effective surface as well as presenting an open structure permitting low pressure drop passage of electrolyte therethrough. Bulky open mesh designs of the structures shown in FIGS. **4A** and **4B** have proved highly effective because of their uniformity in construction and because of their physical flexibility in assembling apparatus such as those shown in FIGS. **1** and **3.** However, uniformly reticulated structures generally, such as the species shown in FIGS. **4C** and **5A–5C**, can also be used.

Extended surface electrodes employed in my cells can be made from evenly distributed highly conductive continuous run corrosion-resistant metal filaments 2 to 4.5 mil dia., fabricated into knitted form having a void volume in excess of about 85 percent and a surface area in excess of about 5 cm^2/cm^3 of electrode volume. While FIG. **1** details extended surface cathodes, it will be understood that, where anodic electrodes are to be utilized in electrochemical processing, the same electrode structures are ideal for anodic service and, in fact, the electrical supply leads can be simply reversed in polarity to convert cathodic operation into anodic operation. Cathode bus connections are effected through branched upright bus connectors **17***a*, weld attached to radially opposed pairs of cathodic elements **14, 15** and attached at the bottom ends to a cathodic bus **17** extending radically out through the wall of enclosure **11** to a suitable conventional d-c source, not detailed.

As shown in FIG. **1**, anode **10** is mounted within a spacer cage **20**, which can be of generally open cylindrical form constituting circular strips **20***a* joined on the inside surfaces to upright strips **20***b*, pairs of which latter elements define vertical passages between them for escape of gas released at anode **10.** A porous construction is preferred for spacer cage **20**, a preferred material of construction for an electrically insulating cage being a unitary bulky polymeric product (e.g., polyethylene) produced by extrusion through a rotating grooved annular extrusion die. The producct is an open net-like structure made up of coarse filaments laid over one another at right angles and bonded at crossing points.

Optionally, an electrically conductive (metal) spacer cage of generally similar construction as that hereinabove described can be employed, in which case cage **20** constitutes a radial extension of anode **10** since it is in conductive contact therewith.

Enclosing the anode-spacer cage subassembly is a porous cup-like nonconducting electrode separator **23** having its base end **23***a* disposed in the direction of process liquid input which, in FIG. **1**, is shown as from the bottom as denoted by the directional arrows. Separator **23** can be typically fabricated from spunbonded polyethylene.

The purpose of separator **23** is to forestall electronic conduction between anode **10** and cathode **14, 15** by isolating against metal-to-metal electrode contact, while still furnishing an ionic passage through the solution spanning the electrodes. The permeability of separator **23** should be moderately high for good ionic conductivity while still being low enough to prevent gross mixing between the anolyte and catholyte solutions.

It is also permissible to fabricate separator **23** from electrically insulative ion-exchange membrane materials, such that ions of at least one component in the solution can pass through the separator, thereby completing the ionic current path, while forestalling direct metal-to-metal electronic conduction between the electrodes within the cell as well as direct solution flow between electrolyte chambers.

In summary, the cell structure described supra utilizes very large extended surface electrodes arranged so as to (1) accommodate liquid electrolyte flow therepast with only moderate pressure drop, (2) provide short path distance from any point in the electrolyte in process to the effective extended surface electrode in order to facilitate rapid ionic discharge and (3) insure exceedingly uniform potential maintenance between bus connectors **17***a* and cathodes **14, 15** by keeping the electrical resistivity to a minimum not only within the electrode structure per se but also from point-to-point throughout the electrode structure en route to buses **17.**

The absolute magnitudes and relative quantitative importance of the physical parameters of the extended surface electrodes described depend, importantly, upon the particular electrochemial process to be effected. For example:

1. In the cathodic deposition of heavy metals such as Cu existing in low concentrations in dilute H_2S0_4 solutions, the current densities required for stoichiometric equivalence to the metal content removed, with conventional liquid flow velocities through the cathode, will be relatively low. The voltage drop across the conductive path between supply bus **17**, bus connectors **17***a* and the extremity of any filamentary path in the cathode mesh is the product of current (I) and path resistance (R). If fine filaments are used in the cathode structure in order to secure large surface per unit volume of the mesh, the increase in R resulting from the small diameter filaments is largely offset by the high conductivity. Thus, the existing IR drop is relatively minimal, so that the voltages at all points on the cathode surface are approximately the same as the supply voltage of bus **17** and bus connectors **17***a*.

2. In the cathode removal of one metal while preserving an accompanying metal of nearly equal deposition voltage in solution, it becomes far more important that in (1) supra to assure a close approach to equipotential cathode surfaces, and filaments of heavier gage are preferred in this regard.

3. When the concentrations of materials being treated are higher than in the usual wastes, e.g., in electrowinning, the operation is less affected by rate of

mass transfer of ions to an electrode because more ions are available and the current densities are higher in meeting the stoichiometric requirements, so that it becomes even more important that in (1) and (2) supra to assure equipotential electrode surfaces. Here it is often feasible to sacrifice some electrode open fluid space, concomitantly increasing the conductive filament cross-sections.

4. As an extension of case (3) supra, in situations where no deposit forms on the electrodes, e.g., anodic oxidation or cathodic reduction forming soluble products, likelihood of plugging porous electrodes is greatly reduced, therefore it is practicable to substitute lower porosities in favor of heavier electrode cross-sections.

Referring now to **FIG. 3,** there is shown a preferred design of cell according to this invention employing one-piece spirally wrapped cathode, anode electrode structures which are particularly advantageous in providing a large electrode surface in form adapted to insertion into a tubular, leak-tight housing, such as a conduit. Elements in **FIG. 3** corresponding to the same elements in **FIG. 1** are denoted by the same reference numerals, except that these are primed. The external housing **11** is omitted in the showing of **FIG. 3** and, to more clearly expose the anode-spacer structure, the outer terminal portions of the interwrapped elements are pulled apart radially to bring sizable surface portion into better view.

The cathode, or outer member shown in **FIG. 3** is portrayed as having three schematically represented cathode elements, i.e., **14'**,**15'**, and **25**, each consisting of a flattened stainless steel wire tubular knit structure pressed into tight electrically conductive contact with its neighbor. Also, since anode **10'**, which can be a screen or foil of electrochemically inert material (e.g., platinum), is effective on both of its side surfaces, individual spacers **20'** and **20''** are employed on opposite sides of the anode, the pair constituting the equivalent of spacer cage **20, FIG. 1.** The equivalent of cup-like separator **23** is the sharply folded double ply element **23'**bottom, which encases the subassembly **20'**, **10'**, **20''** on the bottom edge and both sides, it being understood that the process liquid again is supplied from the botton, as denoted by the directional arrow, whereas exit of treated liquid and any gaseous products is via the top.

Positive supply bus branches **12'**, **12'** are advantageously spaced along the length of anode **10'**, to better distribute the supply of electrolyzing current and voltage in accordance with the demand imposed by equal incremental lengths of anode surfaces. The same principle is applied with respect to negative supply bus connectors **17*a*'**, **17*a*'**. The structure of **FIG. 3** is shown in somewhat loosely rolled condition, so that there exists a longitudinal passage **26** at the inner extremity of the spiral. With tighter roll wrapping, this bore virtually disappears, or can be plugged by a non-conducting rod, so that no bypass through the cell is presented to process solution flowing axially thereof.

The structure of **FIG. 3** can be neatly fitted into a circular tube enclosure and, even though it is tightly wrapped into very compact space, only moderate resistance is interposed to solution flow.

Referring now to **FIGS. 4** and **5,** there are shown details of extended surface electrode formation. Thus, FIG. 4A (and end view 4B) show a knitted bulky wire structure, such as used in the apparatus of **FIG. 1,** made by interlooping adjacent courses of long length wire denoted **27,** which are weld-joined to bus connectors **17*a*.**

Very satisfactory operation has been obtained using cathode mesh structures of the configuration shown in FIGS. 4A and 4B employing from about twenty to about one hundred and twenty individual wire layers. It is a convenience to utilize flattened tubular knit sleeves fabricated from Type **316** stainless steel wire having two filaments in each loop, the filament diameters being any of 2 mil, 3 mil or 4.5 mil (corresponding, respectively, to 0.051 mm, 0.076 mm and 0.115 mm diameters), as marketed commercially by Metex Corporation, Edison, N.J. Referring to **FIG. 3,** and utilizing a single spacer made up of Du Pont Vexar polymeric netting measuring about **15** mils (0.38 mm) thick and a separator **23'** measuring about 6 mils (0.152 mm) thick, it was practicable to obtain a four-wrap cathode structure, each wrap of which constituted twenty-five overlaid double layer flattened knit sleeves, or a total of two hundred radially disposed individual mesh layers, which assembly fit snugly into a Pyrex pipe enclosure having an inside diameter of 51 mm.

A great variety of materials having a wide range of dimensions can be utilized in extended surface electrodes as taught in this invention, however, the following general combination has given exceptionally good results: (1) spiral arrangement of electrodes as shown in **FIG. 3,** (2) use of a pair of spacers **20'** (one on each side of the anode) insuring unhindered egress of any gases generated, especially at the anode **10'**, (3) a separator constituting an envelope open only along the cell electrolyte outlet side made up of a strong web material such as ion exchange membranes, textile fabrics, paper and spunbonded products having a permeability to ionic passage equivalent to a pore size of about 0.2 mil, (4) knitted mesh of continuous metallic filaments as basis for the extended surface electrode such as shown in FIGS. 4A and 4B, (5) electrode mesh size **6-20** courses/inch (**2.4-8** courses/cm), (6) extended surface electrode area 30–50 cm^2/cm^3, (7) ratio of electrode area cathode/anode 5–50 in service of removing trace heavy metals from waste solutions, (8) void volume in extended surface electrode, 90–95 percent, (9) extended surface electrode filament size, 2–5 mils (50 μ), (10) treated solution flow velocity, 1–10 cm/sec, and (11) anode current density, 5–200 ma/cm^2, based on the anode' s simple projected area (i.e., the product of width *x* height).

Cells constructed and operated as described supra have the following characteristics: (1) average distance from any point in liquid in process flowing through extended surface electrode to a filament surface is 0.7 mm., (2) when operated at a high anode current level (e.g., 60 ma/cm^2) the maximum voltage drop from the bus bar to the most remote location in the extended surface electrode structure is less than about 0.160 volt and (3) the pressure drop through a typical 51 mm. dia. "jellyroll" spiral electrode assembly for a 75 mm. active length of the roll of extended surface electrode (cathode) is as follows for two sizes of filament in knitted mesh (**FIG. 4A** design):

TABLE I

PRESSURE DROP VS. FLOW RATE

Flow Rate		Filament Size	
gpm	cm³/min.	2 mils(0.051 mm)	4.5 mils(0.115 mm)
1.0	3,785	9.8 cm H_2O	3.3 cm H_2O
2.0	7,570	20.7	7.6
3.0	11,355	38.5	13.4
4.0	15,140	60.5	20.4
4.5	17,032	70.8	24.0

In FIG. **4C** there is shown a "Turkish towel-like" wire cloth mesh structure having continuous conductive filaments **30** and **31** forming a looped pile extending outwardly from both sides of the woven structure. The ends of filaments **30** and **31** are securely bonded to the bus connector **17***a* by welding, brazing or the like for low electrical resistance.

In this structure the loops are woven in as part of the warp and constitute the wire structure of the electrode. Filler fibers **32** run at right angles to the loops and can, or need not, be electrically conductive. The purpose of the filler fibers is primarily to complete the weave and hold the entire structure together for mechanical integrity. If filler fibers **32** are conductive, it is preferred that their ends be joined to an additional bus structure in a manner as hereinbefore described for filaments **30** and **31** in order to insure lowest possible electrical resistance within the cathode structure materials. Warp filament **33**, and others not shown but reversed in orientation with respect to opposite individual loops, are companionate threads binding the filler fibers **32** in place. If the warp filament **33** is conductive, it is preferably welded at the end to bus connector **17***a*. However, it need not be conductive and, in this case, circuit contact with the bus is dispensed with.

If a cut pile is employed instead of a loop pile, the entire structure is preferably electrically bonded together by a dip soldering or brazing.

FIG. **5A**, a plan fragmentary view, and FIG. **5B**, an end view, together show a "cyclone-fence" type electrode structure made up of helically interwound adjacent metal filaments, such as **39***a*, **39***b*, weld-joined at their ends to cathode bus connector **17***a*. The relatively large diameters of the helices (refer FIG. **5B**) constitute, in multi-layer assemblages, an exceptionally open electrode structure not readily plugged by suspended solids in the electrolyte in process.

Finally, FIG. **5C** shows, in perspective, a conventional expanded metal electrode structure in which the sheet **40** is first provided with a line of slits and thereafter pulled longitudinally to open the slits into diamond apertures **41**. The outwardly projecting ends are weld-joined to cathode **17***a* and successive sheets **40** are creased or corrugated transversely along lines **42** to furnish the desired separatory offset between adjacent sheet members.

The foregoing description is particularly directed to the preferred embodiment "jelly-roll", or spiral assembly, cell construction; however, extended surface flow-through electrodes having high conductivity and porosity can equally well be assembled in flat stack form, resembling a "club sandwich" arrangement. Thus, this invention is readily applicable to commercial plate-and-frame electrolysis cell designs and the like.

Referring to FIG. **9**, there is shown a cell embodiment according to this invention utilizing planar electrodes which, in this instance, are disposed in vertical coparallel rectangular array with the solution to be subjected to electrochemical processing introduced from the bottom, as indicated by the flow directional arrow. The containment housing is omitted in this FIG. for simplicity in the showing as is also the right-hand cathode sub-assembly, it being preferred to associate each anode with a pair of cathode assemblies, one on each side.

The anode **70** is, in this instance, a solid metal plate, typically fabricated from platinum about **25** mils thick. Anode **70** is disposed within a separator envelope **71** of good ionic permeability, as hereinbefore described, which nevertheless effectively isolates the anode from ready circulation of electrolyte liquid through the anode region. Spacers **72**, also constructed as hereinbefore described, are interposed between each face of anode **70** and the inside faces of separator envelope **71**.

Electrical conductor tabs **70***a*, welded, brazed or otherwise secured in good electrical conductive joinder with anodes **70**, afford circuit connection points with an anode current supply bus, not detailed.

The cathode sub-assemblies denoted generally at **75** are here shown, for simplicity, as each made up of only four contiguous layers of wire mesh construction as hereinbefore described (e.g., two superposed pieces of knitted stainless steel sleeve construction each providing a double layer cathode element, electrical conduction being maintained throughout by tight physical contact between adjacent layers). Stainless steel plates **76**, typically, 40–60 mils thick, each having an upstanding tab **76***a* for electrical connection with a negative polarity current supply bus **17**, not shown, are provided on the sides of the cathode sub-assemblies remote from the associated anodes, thereby completing the overall cell assembly.

Referring to FIG. **2** there is shown a schematic flow diagram for treatment of a typical industrial waste stream such as, for example, a dilute aqueous sulfuric acid solution containing small quantities of copper sulfate, which, in this case, is advantageously initially accumulated in hold-up tank **45**. A pump **46** propels the waste stream through an extended surface electrolysis unit of this invention, denoted generally at **47**, from whence treated product is exhausted to outfall, or other desired destination, via discharge line **48**.

For purposes of simplification of the following description, it is assumed that unit **47** is a single cell. Then, after a given period of operation, depending on the size of the cell of unit **47** and the quantity of metal which is removed from the waste solution, the cathode space of the cell becomes partially filled with the deposit of the metal which plates out upon the elements of the cathode structure. This increases the pressure differential across the cell to a point where it is economical to remove the cell from service briefly for regeneration. This is conveniently effected by the balance of apparatus shown in FIG. **2**.

Thus, a moderately concentrated acid solution, such as nitric acid, is stored in leachate tank **51** so that, when electrolysis is halted in unit **47**, the acid is forced, by pump **52**, through the electrolytic cell of unit **47** with return back to tank **51**. The leaching solution speedily dissolves plated-out metal from the cathode structure to produce a highly concentrated acid leachate solution thereof. The leachate solution can be accumulated in tank **51** until a convenient time arrives to subject it to electrolytic recovery in a conventional electrolytic recovery unit, denoted generally at **54,** to which the solution is supplied via pump **53.** The acid, stripped of its metal content, is recycled back to tank **51** via line **56** for repeated regeneration service. The conventional direct current power supply, denoted generally at **58,** is shown as furnishing electrolyzing current independently to both units **47** and **54.**

Others methods exist for removing accumulated metal from the extended surface electrode of unit **47.** Thus, a plugged cell can be taken out of service and a fresh cathode substituted for the filled cathode structure, after which operation is restored. Then, in a separate system, the clogged electrode is made anodic with respect to another electrode immersed in a small volume of concentrated electrolyte, and metal is anodically dissolved away to produce a highly concentrated metal solution resembling the leachate solution.

It should be mentioned that the electrolytic cells of this invention are well-suited to multiple use and, in this connection, can be readily employed in either series, parallel or combination series-parallel liquid flow convention as dictated by the circumstances. Thus, in one instance where the waste stream involved has a very large volumetric flow rate, a multiplicity of small-sized cells were employed in parallel connection in preference to designing a single large cell to carry the entire load. similarly, in cases where a considerable quantity of metal is to be removed from a waste solution, it can be convenient to treat the waste stream by series flow through a succession of extended surface electrode cells, the first of which, in order, remove the large quantities of the metal whereas later ones in the series clean up the traces.

The series arrangement described has the advantage that the first cells gradually become loaded with metal, and can then be removed for regeneration, while later cells in the series chain take over the burden. Fresh cells progressively added at the end of the chain constantly maintain the metal removal capability; however, the particular point of maximum metal removal shifts progressively along the cell chain during prolonged operation.

The electrical supply for the hereinabove described cell arrangements is completely independent of the liquid flow conventions. Thus, if multiple cells are operated in liquid flow parallel, all of the potentials required for equal cell plateout would be the same, so that electrical parallel power supply is advantageous. Conversely, if the cells are arranged in liquid flow series, each separate stage usually has a particular optimal operating voltage, in which case separate power supplies of preselected voltage output are usually preferred.

In the following examples, two general modes of operation were utilized: (1) single pass and (2) recirculation.

Referring to FIG. **6A**, the single pass mode utilized a solution supply vessel **60** from which solution to be treated was withdrawn via pump **61** and routed to the extended surface (ESE) electrolysis cell denoted generally at **47′**, with discharge therefrom into a receiving vessel **62** from which solution samples for analysis could be withdrawn at will via stopcock **63.**

Referring to FIG. **6B**, the recirculation mode utilized a solution supply vessel **60′** from which solution to be treated was withdrawn via pump **61′** and routed to the extended surface electrolysis cell denoted generally at **47″**, with recirculation therefrom, via line **64**, back to supply vessel **60′**. Stopcock **63′**, connected with vessel **60′**, permitted drawoff of solution samples for analysis as desired.

EXAMPLE I

A cell was assembled as detailed in FIG. **3** incorporating an extended surface cathode, a polymeric separator, two polymeric spacers and a screen anode layered together as a sandwich-like stack which was then rolled into a spiral for insertion in tubular methyl methacrylate polymer tube.

For this test the cathode (**14′**,**15′** and **25**) was knitted sleeve material 0.002 inches (50.8 microns), 2-filament, S.A.E. 316 stainless steel mesh having ten courses/in (3.9/cm). The separator **23′** was Du Pont Tyvek 1058, a spun-bonded high-density polyethylene of 1.6 oz/yd^2 (0.0054 gm/cm^2), about 6 mils (152 μ) thick, with individual fibers in the range of 0.2 mil (5 μ) dia. The spacers **20′** and **20″** were Du Pont Vexar 30 CDS **89**, an extruded netting of high density polyethylene, having a thickness of 30 mils (0.76 mm) with eight strands/in. crossing each other at a 90° angle, giving a diamond pattern. The anode **10′** was 80 mesh (31.5 mesh/cm) woven platinum screen having individual filaments 0.0042 inch (107 μ) dia.

The cathode was made up of sixty folds of sleeve 2.5 inches (6.35 cm) wide (i.e., four pieces, each folded **15** times constituting 120 individual layers), weighing a total of 60 gms.

The anode dimensions were 2.5 (6.35 cm) wide × 6 inches (15.2 cm) long. The two Vexar spacers were the same length as the anode, but 2.75 inches (7.0 cm) wide. A piece of Tyvek 7 (17.8 cm) long × 6.0 inches (15.2 cm) wide constituted the separator. It was folded around the spacers and the anodes and then placed on the layered cathode. The electrodes and interleaved components were then rolled into a tight spiral and inserted into the 2.0 inches (5.08 cm) inside diameter methyl methacrylate polymer tube.

The solution treated was a synthetic aqueous "waste" having a starting concentration of 20 ppm by weight of copper (added as copper sulfate) and sufficient sulfuric acid to give a pH of 1.0. The effluent concentration of copper was determined by atomic absorption spectroscopy after each pass, with the copper concentration decreasing as tabulated infra.

Operation was conducted pursuant to mode **1** (FIG. **6**A) except that, after each analysis, the treated solution was returned to vessel **60** for another pass through the cell **47′**. This cycle was repeated four times.

Operating conditions for this Example were as follows:

The solution was at room temperature and required no temperature adjustment as a result of the electrolytic treatment.

The solution velocity (superficial) was 100 cm/min, giving a residence time of 4.2 secs/pass.

Electrical current was supplied at a rate stoichiometrically sufficient on the first pass to remove all copper from the solution, and this current was maintained at the same lever (2000 ma) throughout all subsequent passes.

Table 2

Effluent Concentrations

Pass No.	Copper Concentration (ppm)
0	20
1	8.2
2	3.4
3	1.3
4	0.6

EXAMPLE II

The same cell and synthetic waste employed in Example I was treated here with operation in the same mode but at progressively higher flow rates and using proportionately higher electrical currents. Thus

Run	Feed Rate, liters/min.	Velocity, cm/sec.	Current ma
A (Example I)	2.0	1.63	2,000
B	6.0	4.9	6,000
C	10.0	8.2	10,000

The corresponding effluent concentrations are plotted in FIG. **7** as a function of the number of passes through the cell at the different solution velocities reported.

EXAMPLE III

A cell was constructed as described for Example I, except that the cathode consisted of twenty layers (18.1 gms total) of 316 stainless steel knitted mesh made from 0.002 inch dia. filaments with two strands/loop and ten courses/inch.

The separator was Tyvek 1058 and the spacer was Vexar PDS **89**, a polypropylene netting 15 mils (380μ) thick. Due to space limitations, only one layer of Vexar spacer was used with the anode in the Tyvek separator envelope. As in EXample I the anode was a 2.5 × 6.0 inch piece of 80 mesh woven platinum screen. The components were layered into a sandwich, rolled into a tight spiral and inserted into a glass tube 1.0 inch in dia.

The solution treated was a synthetic waste composed of copper sulfate, sulfuric acid and water (copper content = 103 ppm and pH = 1.0). The cell was operated in mode **1** (FIG. **6**A) by passing the fresh copper-containing solution in approximately one liter quantities at a flow rate of 500 cc/min, corresponding to a superficial velocity of 1.67 cm/sec, while maintaining the current supply at the listed levels with the results tabulated as follows:

Table 3

Effect of Current on Copper Removal
(starting with an initial Cu conc'n. = 103 ppm.)

Current (ma)	Voltage (volts)	Copper Conc'n. (ppm)
100	2.1	98
200	2.4	93
500	3.4	83
1,000	4.5	67
2,000	6.6	61

EXAMPLE IV

A cell was assembled exactly as described in Example III, and operated as in Example I. Two different alkaline solutions, each containing approximately 20 ppm of dissolved copper, were individually treated. Their compositions were as follows:

A. 17.0 ppm of copper from copper sulfate, 2.75 gms/liter of $(NH_4)_2\ SO_4$, pH adjusted to 8.0 with NaOH; and

B. 17.9 ppm of copper from copper sulfate, 3.0 gms/liter of $(NH_4)_2\ SO_4$, and 1.0 gm/liter of NaCl, pH adjusted to 8.9 with NaOH.

The solution to be treated was pumped from vessel **60** through cell **47'** (mode **1**) at a flow of 300 cc/min. (1.0 cm/sec superficial velocity) in repetitive passes and current was supplied at 300 ma. The effluent copper concentration was determined by atomic absorption spectroscopy after each pass through the cell and is tabulated as follows for the two synthetic waste solutions:

Table 4

Effluent Concentrations from Alkaline Electrolysis

Pass No.	Solution A (Cu in ppm)	Solution B (Cu in ppm)
0	17.0	17.9
1	8.8	12.2
2	4.2	6.8
3	1.8	2.7
4	1.0	1.4
5	0.4	0.9

EXAMPLE V

A cell was constructed as described for Example III, except for the following: SAE 304 stainless steel was used as cathode, no spacers were included in the separator envelope and the anode was 80 mesh platinum screen measuring 2 (5.1 cm) × 4 inches (10.2 cm).

The solution treated was a sample of an actual industrial effluent "A". It had previously been determined that the composition of this waste stream fluctuated over a wide range, depending upon the particular plant operations in progress at any given time. However, the sample tested here had an initial soluble copper content of 15.5 ppm, a pH = 2.8 and a chloride content of approximately 900 ppm. There were traces of other heavy metals, e.g., Fe, Ni and Cr, and a heterogeneity of dissolved organics, each in low concentrations. Sulfate was the principal anion present.

After filtering to remove suspended solids the solution was fed at 500 cc/min (1.67 cm/sec superficial velocity) in repetitive passes to the cell supplied with applied current as listed:

TABLE 5

Treatment of Industrial Effluent "A"

Pass No.	Current (ma)	Copper Conc'n. (ppm)
0	—	15.5
1	500	5.6
2	250	2.8
3	150	1.8
4	100	0.7
5	100	0.6

EXAMPLE VI

The cell of Example V was operated in the same manner as described for Example V but used to treat a sample of a different actual industrial plant effluent "B". This aqueous effluent was variable and heterogeneous in composition, but, as received for test, contained 48.5 ppm of copper, an approximately equal content of iron and had a pH = 1.5 due largely to the presence of sulfuric acid.

After a period of aeration to remove dissolved sulfur dioxide, the solution was pumped to the cell in repetitive passes at a rate of 500 cc/min (i.e., 1.67 cm/sec superficial velocity). The current fed during each pass, the effluent copper concentrations and the attendant coulombic efficiencies are tabulated as follows:

Table 6

Treatment of Industrial Effluent "B"

Pass No.	Current (ma)	Voltage (volts)	Cu Conc'n. (ppm)	Efficiency (%)
0	—	—	48.5	—
1	1,000	3.0	15.5	82
2	500	2.5	5.4	51
3	300	2.3	2.1	55
4	200	2.2	0.9	30

In order to determine what disposition was made of the iron, Example VII was conducted.

EXAMPLE VII

The cell of Examples V and VI was used to treat industrial effluent "B" in the manner of mode **1** (FIG. 6A). Here the object was to remove the toxic copper ions from the solution selectively, leaving the iron in solution for either subsequent treatment or discharge. The results of two tests, each consisting of one pass through the extended surface cathode cell, are as follows:

Table 7

Treatment of Industrial Effluent "B"

Test No.	B-1	B-2
Flow Rate, cc/min	500	300
Current, ma	1500	750
Voltage, volts	4.0	3.4
Initial iron content, ppm	48.5	48.5
Effluent iron content, ppm	49.5	49.3
Initial copper content, ppm	44.0	44.0
Effluent copper content, ppm	18.2	12.5

This Example shows that the extended surface cathode was effective over a current range of at least **2**:**1** as regards selective removal of copper without accompanying iron removal. No significance is attached to the fact that effluent iron content is slightly higher than influent iron content, as this could be due to analytical difficulties.

Hydrogen gassing at the cathode is, however, a natural consequence of the relatively current supply rate of Test B–**1**, and it is possible that the generation of hydrogen bubbles screened the cathode, making it somewhat less effective than in Test B-**2** as regards copper removal. In any case, considering both Tests together, it is clear that there exists an optimal current for a particular solution processed in a particular cell. In this Example, it is believed that this optimal current lies below the Test B–2 level rather than above it, because the coulombic value for the copper content of the as-received effluent "B" is 660 ma.

EXAMPLE VIII

The cell of Example III was operated in mode **2** (FIG. 6B), that is, the solution treated was circulated from solution accumulation vessel **60'** through cell **47''**, and thence back to vessel **60'**, which latter was well-stirred during the test. Samples of solution were withdrawn via stopcock **63'** for analysis at preselected time intervals denoted.

The solution employed here was 2400 cc of a synthetic lead-containing waste prepared by dissolving sufficient $Pb(NO_3)_2$ in water to bring the lead concentration to 23 ppm. The pH of the solution was adjusted to 1.33 with nitric acid. The solution flow rate through the cell during the test was maintained at 300 cc/min, while the applied current was maintained at 500 ma. The progressive lowering of lead content is shown by the following.

Table 8

Electrolysis of Synthetic Lead Wastes

Elapsed Time (min)	Lead Concentration (ppm)
0	23
4	13.8
8	10.3
12	9.5

EXAMPLE IX

The cell of Example III was operated as in Example VIII. The initial aqueous feed solution in this case was 2,400 cc of acidic mercuric chloride solution containing 30 ppm of mercury at a pH of 1.3 as adjusted with hydrochloric acid. The solution circulation rate through the cell was 300 cc/min and the applied current was 500 ma. The reduction of mercury content achieved was as follows:

Table 9

Electrolysis of Synthetic Mercury Waste

Elapsed Time (min)	Mercury Concentration (ppm)
0	30
4	15
8	10
12	5
16	2.5
20	2.0
24	1.5
28	0.7
32	0.5
36	0.4
40	0.3

EXAMPLE X

The cell of Example III was operated as in Example VIII. The initial aqueous feed solution consisted of 2,400 cc of acidic silver nitrate solution containing **20** ppm of silver at a pH of 1.35 as adjusted with sulfuric acid. The solution was circulated at a rate of 300 cc/min and the applied current was 500 ma. The reduction of silver content achieved was as follows:

Table 10

Electrolysis of Synthetic Silver Waste

Elapsed Time (min)	Silver Concentration (ppm)
0	20
4	9.8
8	4.2
12	2.6
16	1.7
20	1.0
24	0.8
28	0.7
32	0.6
36	0.5

EXAMPLE IX

A cell was constructed identical to that described in Example III, except that 22 gms of knitted mesh were used as the cathode instead of 18.1 gms. Operation was as in Example VIII, with the initial feed solution being 1,200 cc of wash water from a Kodak M-6 X-ray film processing machine. This solution contained 234 ppm of silver and was at a pH of 4.7. The solution was circulated through the cell at a rate of 300 cc/min. with an applied current of 1,000 ma. The silver content of the solution was reduced as follows:

Table II

Electrolysis of Film Wash Water

Elapsed Time (min)	Silver Concentration (ppm)
0	234
5	95
10	50
15	36
20	30
25	23
30	20
35	13
40	10

EXAMPLE XII

The cell of Example III was operated as in Example VIII. The initial feed solution was a sample of an actual aqueous industrial effluent "C". Experience showed that the effluent composition could be expected to fluctuate, as do most industrial wastes, but this sample contained 425 PPM of copper at a pH of 0.3. There were negligible suspended solids present, while the dissolved solids were in the range of 10 to 15 percent. The low pH resulted from a mixture of hydrochloric and sulfuric acids. This solution was circulated through the cell at 300 cc/min with an applied current of 1,000 ma.

The reduction in copper content is shown in the plot of FIG. **8.**

EXAMPLE XIII

A cell was constructed without an extended surface cathode to demonstrate the comparative advantages of such electrodes.

Thus, two platinum foil electrodes, each 5 mils (127 microns) thick with dimensions of 2 cm × 5 cm, were positioned longitudinally 1.2 cm apart and facing each other in a 1 inch dia. glass tube. The liquid to be treated was circulated through the tube and past both electrodes.

The cell was operated in the manner of Example VIII (FIG. **6,** mode **2**) with a recirculation rate of 300 cc/min and an applied current of 200 ma. The aqueous solution under test was 200 cc of pH = 1.7 containing initially 105 ppm of copper from copper sulfate and 10 cc/liter of phosphoric acid. Copper was removed from solution, but at low efficiency, as shown in the following Table:

Table 12

Electrolysis with Foil Electrodes

Elapsed Time (min)	Copper Concentration (ppm)	Current Efficiency (%)
0	105	—
60	67	3.2
120	42	2.1
180	25	1.4

EXAMPLE XIV

To demonstrate a process application of extended surface electrodes, the system shown in FIG. **2** was assembled.

Five cells constructed as described in Example I were assembled in vertical stack or column formation, one on top of the other, to make up the ESE unit. The liquid in treatment was pumped into the bottom of the column and exited out the top. A line from the top of the ESE unit carried the effluent back to the feed (hold up) tank **45** where the copper concentration was adjusted to maintain a constant feed composition in the cell stack. Each of the five cells was powered by a separate D-C power supply, and provision was made for sampling the liquid stream between adjacent cells in the stack.

The aqueous solution treated was an acidified dilute solution of copper sulfate containing 20 ppm of copper at a pH = 2.5. Sulfuric acid was used for pH adjustment. The solution resistivity was adjusted to 40 ohm-centimeters by the addition of sodium sulfate. This solution was pumped through the ESE unit at a rate of 3 gpm (11.7 liters/min), giving a superficial fluid velocity of 9.7 cm/sec. Thus, for the five cells in series, each cell having a working length in the flow direction of about 7 cm, the contact time for the solution treated was approximately 3.6 seconds.

Each cell was operated at constant current by its individual power supply. The applied voltages were low; for example, throughout the 14 hours of the run, the voltage to the first cell never exceeded 5.25 volts, even though the current 17 amps. Because lower currents were applied to the other cells, their voltages were correspondingly lower.

The effluent copper concentration was measured at intervals for both the feed solution and for the solution exiting from each of the five cells. The results are set out in appended Table **13,** along with the pressure drop (ΔP) across the cells. Thus, the column headed "Cell I" reports the copper concentration, in ppm, of the solution exiting the first cell, the column under "II" gives the same information for fluid exiting the second cell, etc. The pressure drop across the first cell is ΔP_1, whereas the total pressure drop across all five cells is ΔP_5. Of course, the pressure drops increase with passage of time due to the gradual accumulation of copper in the cathode structures.

Table 13

MULTI-CELL ELECTROLYSIS

Flow Rate: 3.0 gpm

	Feed	Cell I	Cell II	Cell III	Cell IV	Cell V	Pressure Drop, psi * ΔP_1	Pressure Drop, psi ** ΔP_5
Current Amp.	—	17	11	8	5	3.5		
		Copper Concentrations						
Elapsed Time, hrs.								
2	20.9ppm	15.5ppm	11.5ppm	7.7ppm	5.9ppm	4.1ppm	1.25	5.75
4	20.2	16.0	9.1	7.5	4.3	3.0	1.5	6.25
6	19.5	14.2	8.4	6.3	4.0	2.4	2.0	7.0
8	20.6	15.8	11.4	9.3	5.8	4.1	2.5	8.2
10	19.7	14.5	10.3	7.9	5.0	4.0	2.8	8.8
12	20.0	16.5	10.3	8.3	4.1	3.1	3.2	9.4
14	20.4	16.4	11.5	8.2	4.5	3.1	3.5	10.0

*Pressure drop across first cell.
**Pressure drop across all five cells.

At this point in the operation of the system, the input of fresh solution (20 ppm of Cu content) was halted and the power supplied switched off. The column of cells was drained, flushed with water for 30 seconds, drained again, then contacted with an acidic leaching solution to remove the accumulated copper from the stainless steel cathodes.

For the leach operation, a volume of 9.0 liters of approximately 20 percent nitric acid was used. It had been used once previously for a similar leaching operation, so that its copper content was 22,800 ppm (2.28 percent) as initially fed to the cell column. The leachant was circulated through the cell group assembly at a rate of approximately 6 liters/min for a period of 24 minutes. At that point, no further traces of copper were seen to remain in the cell column and leaching was discontinued, the column was drained, then flushed with water for 30 seconds and drained again.

Flow of the synthetic aqueous waste solution was resumed through the cell column and electrical power again supplied to the individual cells. The copper content of the leachate was determined to be 40,700 ppm. Nitrate analysis of the solution showed the leaching operation to be essentially stoichiometric.

The cycle hereinabove described was thus 14 hours of extended surface electrode operation; drain, leach, etc., approximately 30 minutes.

The leachate was then circulated at the relatively low flow rate of about 1 liter/min from leachate tank **51**, FIG. **2**, to recovery unit **54** and thence back to the leachate tank, which latter was a 5 gallon (19 liter) polyethylene jug.

Recovery unit **54** was a conventional electrolytic copper recovery cell housed in a methyl methacrylate polymer tank 15.2 cm wide × 15.2 cm deep × 36.8 cm long. The leachate was pumped into the tank at one end near the bottom and flowed over a weir 12.7 cm above the tank bottom before exiting at the opposite end of the tank. A multiplicity of alternated flat anode and cathode plates constituted the electrodes of the recovery cell, these being hung transverse the tank from polymeric holders, so that the plates were at 90° to the general direction of solution flow. Two cathode plates were interposed between three anode plates, all electrode plates measuring 10.2 cm wide × 12.7 cm high, separated one from another a distance of 1.9 cm and immersed to a depth of 10.2 cm. The anodes were 80 mesh (31.5 mesh/cm) platinum screens made up from filaments 107 um dia. The cathodes were 16 gauge type 316 stainless steel plates.

The three anode screens were connected in parallel electrically, as were also the two cathode plates.

Power was supplied to the electrode of recovery unit **54** from a separate d-c supply at a rate of **22** amperes. This corresponds to a cathodic current density of 50 ma/cm^2. After **5** hours of operation, a total of 99 gms of copper had been deposited on the two cathodes. The copper concentration of the leachate had been reduced to 29,800 ppm. Overall, the electrical efficiency for recovery of copper from the leachate was 76 percent.

In similar test conducted in the same general manner, but with mechanical agitation of the solution, electrical efficiencies as high as 98 percent were obtained. Such solutions, after copper depletion, are ready, after appropriate NHO_3 make-up addition, for reuse in the next leaching operation.

Example XV

Industrial effluent "G", an aqueous solution of a cationic type red dye, containing approximately 300 ppm of that dye in addition to 0.1 percent by weight of glycolic acid, 2 percent dimethyl formamide and 150 ppm of chloride ion, was circulated through an energized extended surface area cell for the purpose of decolorizing the solution.

For this test an extended surface cathode cell was assembled as follows: the anode was 80 mesh (31.5 mesh/cm) woven platinum screen made up from individual filaments 0.0042 inch (107 μm) dia. The anode was a single sheet measuring 2.5 (6.4 cm) × 5.0 inch (12.7 cm). The cathode was **15** layers of knitted 0.002 inch (50.8 μm) 2-filament, type 316 stainless steel mesh 2.5 (6.35 cm) × 5.0 inch (12.7 cm), weighing 14.3 gms. A single piece of Vexar screen, of the type described for Example III, was placed beside the described anode into a Tyvek envelope, of the type described in Example III, the whole subassembly being placed in a 60 mm dia. whatman extraction thimble cut off at the closed end to form an open cylinder. The

Whatman extraction filter is marketed by W. & R. Balston, Ltd., Maidstone, Kent, England, and has the shape of a hollow cylinder closed at one extremity by a hemispherical end. It is made from heavy paper pulp, having a thickness of about one mm, and is used in standard laboratory extractions by the Soxhlet technique. The cell separator layer was cut to fit smoothly once around the cylindrical cathode with no overlap at the ends. The Whatman filter served as a peripheral seal against electrolyte bypassing around the electrolyzing apparatus. The entire assembly was placed inside a 1.0 inch (2.54 cm) inside diameter glass tube so as to give the configuation shown in FIG. **3.**

To start this run, 400 cc of effluent "G" solution was placed in a reservoir vessel **60'**, FIG. **6B**, and recirculated (mode **2**) through the cell hereinabove described at a rate of 300 cc/min (correspoding to a superficial linear velocity of 1.0 cm/sec). Current to the cell was then supplied at 500 ma, which required approximately 10 volts across the cell. Every hour, 5–10 cc samples of the solution in the reservoir **60'** were taken for spectrophotometric analysis by measuring the absorption peak at 525 mμ. During the course of this experiment, the destruction of the red-colored dye was seen to occur visually. The data taken were as follows:

Table 14

Decolorization of Industrial Effluent "G"

Elapsed Time from Start of Current Application (hrs.)	Relative Dye Conc'n. of Solution in Reservoir 60'	Real Dye Conc'n. (approximate) ppm
0	1	300
1	0.684	205
2	—	—
3	—	—
4	0.113	34.2
5	0.051	15.1
6	0.025	7.5
7	0.025	7.5

An independent experiment confirmed that destruction of the dye probably occurred at the cathode; however, because of lack of knowledge of the precise mechanism of decolorization current efficiencies were not calculated.

EXAMPLE XVI

A synthetic aqueous cyanide waste was circulated through an energized extended surface anode cell to demonstrate the oxidative destruction of cyanide ion through the following probable mechanism:

$2\,CN^- + 4\,OH^- = 2\,CNO^- + 2\,H_2O + 4\,e^-$, which reaction has a potential of 30 0.970 v. vs. the standard hydrogen electrode (refer "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C." by A. J. de Bethune and N.A.S. Loud).

The synthetic waste was made by dissolving sodium hydroxide to a concentration of 0.01 N NaOH solution (pH = 12) hydroxide to a concentration of **0.01** N NaOH solution (pH = 12). To this solution was added NaCN to a concentration of 274 ppm, which corresponds to 145 ppm cyanide ion content.

The extended surface area was fabricated as follows: The extended surface area anode was 80 mesh (31.5 mesh/cm) woven platinum screen fabricated from filaments 0.0042 inch (107 μm) dia. Five layers of this screen, each formed by folding a 12 inch long piece back on itself to form a 6 inch length, were used for the anode, forming an assembly 2.5 (6.35 cm) × 6 inch (15.2 cm) and weighing 59.5 gms. The cathode was made from a single piece of the same platinum screen measuring 2.5 (6.35 cm) × 6 inch (15.2 cm). A single piece of Vexar screen of the type described in Exampale III was placed, as a spacer, along with the described cathode, into a Tyvek envelope separator of the type described in Example III. The whole subassembly was placed in a Whatman extraction thimble of the type described in Example XV and cut to the dimensions of the subassembly in the manner hereinbefore described in Example XV. The entire assembly was placed inside a 1.0 inch (2.54 cm) inside diameter glass tube to give a configuration such as shown in FIG. **3.**

At the start of this experiment, 1 liter of solution was placed in feed vessel **60'** and recirculated through the cell **47''** in mode **2** (FIG. **6B**) at a rate of 100 ml/min. (corresponding to a linear velocity of 0.33 cm/sec.). Current to the cell was then supplied at 500 ma. Samples of 10–15 ml were taken via stopcock **63'** at specific intervals for cyanide ion concentration analysis by titration with $AgNO_3$ solution in the presence of paradimethylaminobenzalrhodamine as indicator.

Table 15

Destruction of Cyanide in Synthetic Cyanide Waste
Experiment No. 1

Elapsed Time from Start of Current Appl'n. mins.	CN^- Concentration of Solution in Feed Vessel 60' (ppm)
0	145
10	125
20	129
40	117
50	115
60	116.5
80	115
100	112

A second experiment was made under the same conditions on a solution prepared exactly as described for Experiment No. 1 supra, but containing only 103 ppm CN^- ion.

The data obtained was as follows:

Table 16

Destruction of Cyanide in Synthetic Cyanide Waste
Experiment No. 2

Elapsed Time from Start of Current Appl'n. mins.	CN^-Concentration of Solution in Feed Vessel 60' (ppm)
—	103
10	101
20	102
30	103
40	94.6
50	95.7
70	92.5
90	95.6
110	85
130	88.0
150	86.2

EXAMPLE XVII

The cell of Example III was operated as in mode **2,** FIG. **6B.** The solution treated was non-aqueous, composed of dimethylformamide in which 53.4 gms/liter of tetraethyl ammonium perchlorate were dissolved. The solution had a resistivity of 98 ohm-centimeters. Copper sulfate was added to produce a copper concentration of approximately 20 ppm. The pH of this solution was measured initially, and readings of 8.5 and 8.8 obtained; however, it is doubtful that these values are true pH levels, for the reason that only a relatively small number of hydrogen ions probably existed in the solution.

A total of 300 cc of the solution was circulated through the cell at a flow rate of 300 cc/min (superficial velocity 1.0 cm/sec). The applied current was 300 ma. Copper concentrations as determined by atomic absorption were as follows:

Table 17

Electrolysis of Non-Aqueous (Dimethylformamide) Solution

Elapsed Time mins.	Copper Concentration ppm
0	20
2	1.4
4	0.9
6	0.6
8	0.3
10	0.2

EXAMPLE XVIII

The cell of Example XVI, with the extraction thimble wrapping replaced by a single wrap of Teflon fluorocarbon sheet measuring 0.031 inch (795 μm) thick and 2.5 inch (6.4 cm) wide, was used to reduce an aqueous quinone solution of approximately 100 ppm concentration to hydroquinone by making the extended surface electrode the cathode.

The solution was prepared by dissolving 400 mgs. of quinone (first dissolved in methanol) in four liters of distilled water, so that the final methanol content was 0.30 percent and the pH = 5.5.

At the start of the experiment, one liter of the solution hereinabove described was placed in feed vessel **60'** (FIG. 6B, mode **2**) and recirculated through ESE cell **47''** at a rate of 100 ml/min (corresponding to a linear velocity of 0.33 cm/sec). Current was supplied to the cell as 125 ma. Samples of 10–15 ml volume were withdrawn via stopcock **63'** at preselected intervals for spectrophotometric analysis. The gradual formation of hydroquinone was traced by measuring its characteristic absorption peak at 2930 A.

The results obtained were as follows:

Table 18

(Experiment No. 1)

Elapsed Time, mins.	Quinone Conc'n., ppm	Hydroquinone Conc'n., ppm
0	97.5	15.0
20	68.3	36.0
40	47.5	56.0
60	34.0	67.7
80	18.5	80.7
100 11.0	108.0	

The overall coulombic efficiency was 36 percent.

Another experiment was carried out under the same conditions as hereinabove described, except that the current supplied to the cell was 250 ma.

Table 19

(Experiment No. 2)

Elapsed Time, mins.	Quinone Conc'n., ppm	Hydroquinone Conc'n., ppm
0	113.0	4.5
20	68.8	47.0
40	39.0	80.0
60	19.0	94.0
80	9.8	101.0
100	4.4	106.0
120	2.5	108.0

The overall efficiency was 26.5 percent.

EXAMPLE XIX

This Example demonstrates the necessity for spacers **20, 20'** and **20''**, as shown in FIGS. **1** and **3**, respectively.

Seven cells of the design of Example I (FIG. 3) were inserted in vertical stack formation within a tubular glass conduit with electrical connections made to each as detailed in Example XIV supra. Through this extended surface electrolysis unit, the solution treated was pumped from the bottom inlet with exit out of the top at a rate of approximately 3 gallons/min.

The aqueous solution treated was an actual industrial plant waste containing a varying amount of copper ions in the range of 1 to 10 ppm. The solution was filtered and adjusted to a pH of usually about 3 before it was passed to the cells. Each cell was operated at a current density appropriate to the copper level in the solution at the point of cell entrance, and the current supply ranged from about 2 to about 8 amperes/cell, giving current densities from about 10–40 ma/cm^2.

The cell stack reduced the copper concentration of the solution treated by at least 90 percent. The stack was operated continuously for 600 hours without loss of performance, except for one cell in which a Vexar spacer slipped, apparently during assembly of the cell, which permitted the Tyvek separator **23** (FIG. **1**) to contact the platinum screen anode. It was found that the Tyvek separator degraded seriously at those points where it contacted the anode, allowing the cell to short out before the **600** hours operation was achieved.

The cause of the degradation is not known for certain; however, it could have been oxidation occurring at the anode surface.

Another problem to be safeguarded against is that of electrical shorting due to metallic dendrite growth occurring on the cathode and extending toward the anode. Dendrite formation is somewhat unpredictable, depending as it does on the metal ion concentration of the treated solution, the existence of localized high current density paths between the electrodes and, probably, other variables.

In any case, dendrite penetration through the separator elements **23, 23'**, FIGS. **1** and **3** respectively, must be prevented, as it has been found that electrical shortout dendrites can form in as brief a period as 45 minutes when electrolyzing copper solutions containing from 500 to 1,000 ppm Cu.

As hereinbefore described, Tyvek 1058 has worked well as a separator material, this being a spunbonded sheet formed by the random distribution of very fine translucent continuous fibers (about 0.0002 inch dia.) which are self-bonded by heat and pressure. The composite Tyvek 1058 is about 0.006 inch thick and constitutes approximately 30 fiber layers. Under visual examination, each of these layers presents average triangular openings defined by any three randomly oriented fibers presenting maximum openings measuring 0.0008 to 0.0016 inch. However, since there is a multiplicity of superposed layers, the effective openings for ionic transport are equivalent to devious pores of approximately 0.00016 inch size. Separator structures, as described, have the appearance of translucent sized book paper and are strong enough to prevent dendrite penetration therethrough while still permitting good electrode-to-electrode ionic transport.

In comparison, a Tyvek 1621 sheet, which has been treated to possess openings of about 0.012 inch maximum dimension visible to the unaided eye, i.e., about **100** times larger than the effective size of Tyvek 1058 sheet, did permit dendrite penetration and consequent electrical cell short out.

What is claimed is:

1. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing provided, at the lower end, with an inlet port for electrolyte introduction, and at the upper end with an outlet port for discharge of said electrolyte, at least one of said electrodes being of uniformly reticulated open construction so as to oppose low resistance to electrolyte flow therethrough and having an extended surface area over which a substantially uniform reaction-producing electrical potential is maintained with respect to surrounding electrolyte throughout the portion of said area in confrontation with the electrolyzing area of the remaining electrode, and said remaining electrode being disposed within an electrically insulator separator envelope closed on all sides except at the edge adjacent to said outlet port fabricated from an electrolyte-inert material which is relatively liquid-tight in construction so as to bar the ready passage of said electrolyte therethrough but which is permeable enough to permit ionic passage between said electrodes.

2. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing according to claim **1** wherein said separator envelope is fabricated from an electrically insulative web consisting of one of the group made up of ion exchange membranes, textile fabrics, paper and spunbonded products having a pore size barring penetration of dendrites built up by metal depositing on the cathode electrode of said interfunctioning electrodes.

3. An electrolytic cell according to claim **2** wherein the permeability to said ionic passage is equivalent to a pore size of about 0.2 mil.

4. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing according to claim **2** wherein said separator envelope is a spunbonded high-density polyethylene having a density of substantially 1.6 oz./yd.^{2} (corresponding to 0.0054 gm/cm^2), and **6** mils (corresponding to 152μm) thick, made up of individual fibers in the range of 0.2 mil (corresponding to 5μm) diameter.

5. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing according to claim **1** wherein said uniformly reticulated electrode having an extended surface area over which substantially uniform reaction-producing electrical potential is maintained with respect to said surrounding electrolyte throughout the portion of said area in confrontation with the electrolyzing area of said remaining electrode is a composite made of a plurality of double layers of electrically conductive metal having good corrosion resistance to said electrolyte, each of said double layers being opposite sides of a flattened tubular knit formation fabricated from wire measuring in the range of about 2–4.5 mils (corresponding to a range of about 0.51–0.115 mm) diameter.

6. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing provided with a separator envelope according to claim **1** wherein said electrodes and said separator envelope are sufficiently flexible to be wound into a layered spiral composite fitting tightly within said leak-tight housing and being closed off centrally and peripherally to bar electrolyte bypass flow around said electrodes and said separator.

7. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing according to claim **1** wherein there is interposed between said separator envelope and said remaining electrode a relatively thin spacer fabricated from material substantially inert with respect to said electrolyte having a ribbed structure defining full-length open vertical passages confronting said remaining electrode and isolating said separator envelope from contact with said remaining electrode.

8. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing according to claim **7** wherein said spacer constitutes an extruded netting of high density polyethylene having a thickness of between about 15–30 mils (0.76 mm) made up of about eight strands/iunch with said strands intersecting each other in a 90° diamond pattern.

9. An electrolytic cell comprising at least two interfunctioning electrodes disposed at a common transverse level within a vertically oriented leak-tight housing according to claim **1** wherein said electrodes are generally planar in form.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,859,195 Dated January 7, 1975

Inventor(s) John M.Williams Page 1

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 2, "μ" should be --μm--; line 26, "area" should be --areas--; line 27, "pressure" should be --pressures--.
Col. 5, line 46, "radically" should be --radially--.
Col. 6, line 41, "electrochemial" should be --electrochemical--; line 62, "that" should be --than--.
Col. 7, line 4, "that" should be --than--; line 34, "neighbor" should be --neighbors--; line 41, delete "bottom"; line 44, "botton" should be --bottom--.
Col. 8, line 45, "area" second occurrence should be -- areas --. **line 49, "μ" should be --μm--.**
Col. 9, line 56, after "cathode" insert --connector--.
Col. 11, line 26, "has" should be --had--; line 30, "similarly" should be --Similarly--.
Col. 12, line 13, after "in" insert --a--; line 21, "μ" should be --μm--; line 23, "μ" should be --μm--; line 29, "μ" should be --μm--; line 34, after "2.5" insert --inches--.
Col. 13, line 41, after "2.5" insert --inch--.
Col. 14, line 15, after "flow" insert --rate--.
Col. 15, line 62, after "relatively" insert --high--.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,859,195 Dated January 7, 1975

Inventor(s) John M. Williams Page 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 18, line 54, after "current" insert --was--.

Col. 20, line 32, "electrode" should be --electrodes--; line 58, after "2.5" insert --inches--.

Col. 21, line 54, after "of" delete "30" and insert -- + -- line 64, after "area" insert -- cell --

Col. 22, line 3, after "2.5" insert --inches--; line 3, "inch" should be --inches--; line 6, after "2.5" insert --inches--; line 6, "inch" should be --inches--.

Col. 23, line 33, "inch" should be --inches--; line 62, move "100" over to be under "80" on the line above; line 62, move "11.0" over to be under "18.5" on the line above; line 62, move "108.0" over to be under "80.7" on the line above.

Col. 25, line 35, "insulator" should be --insulative--.

Col. 26, line 4, "and" should be --about--; line 50, "iunch" should be --inch--.

Signed and sealed this 6th day of May 1975.

(SEAL)
Attest:

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