 disclosed is a process for recovery of cyanide and metals from a liquor containing complexes of cyanide and metal typically generated by a metallurgical or industrial process. The process involves electrochemical dissociation of the metal-cyanide complex and electrowinning of the metal while free cyanide generated in the process is recovered in a membrane treatment step for re-use in a metallurgical process utilising it. An electrochemical apparatus, which may be used in the process, forms a further aspect of the invention. A membrane process alone, for separation of cyanide, from liquors containing cyanide complexes, is a further aspect of the invention.
PROCESS AND APPARATUS FOR RECOVERY OF CYANIDE AND METALS

FIELD OF THE INVENTION

[0001] The invention relates to processes and apparatus for recovery of cyanide and/or metals. The processes and apparatus may involve electrochemical and membrane processes. An electrochemical cell useful in such processes forms a further aspect of the invention.

BACKGROUND TO THE INVENTION

[0002] Cyanide is used extensively in gold processing plants for the leaching of gold from a mill tailing containing it. Certain ores, concentrates and oxidation residues also contain copper and/or other base or precious metals that, like gold and silver, form complexes with cyanide. As a result, mixtures of dissolved complexes, including Cu(CN)₂⁻, Cu(CN)₃⁻ and Cu(CN)₄⁻ may also be formed in a gold cyanide leach solution.

[0003] When this occurs, large excesses of cyanide may be required to ensure that sufficient “free” cyanide is present to leach the gold. This results in high cyanide consumption, which is costly. Moreover, the complexed species are not useful for the further leaching of gold, and cannot be readily recycled to the leach. In certain situations, such complexes cannot be discharged to a tailings dam or alternative disposal system due to prohibitions under environmental regulations.

[0004] As cyanide is a potent contaminant in waste streams, particularly those associated with gold processing operations, technology has been developed for managing cyanide.

[0005] Oxidation may be used to destroy cyanide species known as weak acid dissociable cyanide from waste waters. Such oxidation techniques commonly involve use of an oxidant to destroy cyanide. Hydrogen peroxide has been widely used for this purpose with weak acid dissociable cyanide being oxidised to cyanide. Any metal ions released during the oxidation are precipitated, in an alkaline environment, as hydroxide. However, ferricyanide is not destroyed during oxidation. As well as destruction of cyanide, such a process is not suitable for destruction of the thiocyanate ion (SCN⁻).

[0006] An alternative process involves destruction of weak acid dissociable cyanide by oxidation with a mixture of sulphur dioxide and air. Again, cyanide is oxidised to cyanate and the process is not suitable for removing thiocyanate.

[0007] Further options may involve ion exchange or acidification-volatilisation-re-absorption (AVR) processes. An AVR treatment circuit involves acidification of cyanide liquors or slurries to lower the pH from an alkaline range to pH 3-5 resulting in conversion of free cyanide and weak complexes such as zinc, cadmium and nickel complexes to HCN which is then volatilised by passing air bubbles through the liquor or pulp. An air/HCN stream may then be scrubbed in a lime slurry or NaOH solution to convert HCN back to sodium cyanide for recycling.

[0008] While the AVR process is an option for treating moderate or strong cyanide liquors (over 500 ppm weak acid dissociable cyanide), copper is precipitated as CuCN during the acidification stage. Such product is unsaleable and binds up a third of the available cyanide complexed with the copper, lowering the cyanide recovery.

[0009] The Cyanisorb process is similar to the AVR process above but differs in that clear solutions or slurries are processed at near neutral pH.

[0010] The MNR process was developed by Metalgesellschaft Natural Resources and involves sulphidisation using NaSH and acidification, to pH less than 5, of copper/cyanide rich liquors precipitate synthetic chalcocite (Cu₂S).

[0011] The liquor may then be re-causticised to produce caustic cyanide or acidified further to form HCN gas which may be recovered by absorption. The copper by-product is salable. Nevertheless, material handling of the chalcocite and potential co-precipitation of CuCN and CuSCN may be issues in plant design.

[0012] Solvent extraction and ion exchange techniques are also possible alternatives for treatment of liquors containing free cyanide. However, they do not address recovery of cyanide from cyanide complexes such as copper cyanide complexes.

SUMMARY OF THE INVENTION

[0013] It is the object of the present invention to provide a process for dealing with liquors containing cyanide compounds and complexes, particularly base metal and precious metal cyanide complexes. The process may be applied to recovery of cyanide for use in a metallurgical or industrial process. Advantageously, the process ought not to be chemically intensive in comparison with prior art processes.

[0014] With this object in view, the present invention provides a process for recovery of cyanide and metals from a liquor containing a compound or complex of cyanide and/or thiocyanate and metal generated by a metallurgical process including the steps of:

[0015] (a) electrochemically treating the liquor in an electrochemical cell for electrochemically dissociating the complex present in an electrolyte stream;

[0016] (b) recovering the metal by electrowinning;

[0017] (c) passing electrolyte through a membrane treatment step for separation of cyanide by a membrane process; and, optionally,

[0018] (d) recycling free cyanide to the metallurgical process.

[0019] The process is suitable for recovery of cyanide and/or metal from solutions containing very low concentrations of these components whether in cyanide or thiocyanate form. Thiocyanate compounds or complexes are also considered herein as compounds or complexes of cyanide electrochemically dissociable in accordance with the process of the invention. As to solution concentration, the liquor containing the complexes of cyanide and metal may contain significantly less than 10 g/l metal, a very low concentration.

[0020] An important feature of the process is step (a), the electrochemical treatment step for electrochemical dissociation of the metal-cyanide or metal-thiocyanate complex in an electrochemical cell to form free cyanide which itself forms a further inventive aspect. This step allows higher free
cyanide recovery, notably from thiocyanide present in the liquor. Thiocyanate may also be oxidised to free cyanide in the cell. [0021] The process can be applied to recovery of many different metals and may be particularly suitable for recovery of base metals such as copper, zinc and nickel, particularly from complexes of these with cyanide (base-metal-cyanide complexes). In the case of copper cyanide complexes, often encountered as a by-product from precious metals leaching, the Cu(CN)\textsuperscript{2-}, Cu(CN)\textsuperscript{3-} and Cu(CN)\textsuperscript{4-} complexes are the most significant. All may be present in a liquor from a gold leaching operation for gold ores containing copper or base metals. All the processes may also be used to recover precious metals such as silver, which are complexed with cyanide in precious metal-cyanide complexes.

[0022] Metals may be recovered from the cathode or from the process in a form suitable for recovery by a suitable solid/liquid separation process. For example, copper, silver or other metals may be recovered in a powder or granulated form by conducting solid-liquid separation in a hydrocyclone or similar device.

[0023] The membrane process may be pressure or diffusion driven, being characterised as a process of ultrafiltration, nanofiltration or reverse osmosis, differences between which are described in Lean, L., "Nanofiltration: Trend of the Future!", Water Conditioning and Purification, September 1992, pp 24 to 27 and Cheryan, M et al., "Consider Nanofiltration for Membrane Separations", Chemical Engineering Progress, March 1994, pp 68 to 74, both of which are incorporated herein by reference. These references further describe specific characteristics of membranes for use in these processes though many membranes are proprietary in nature.

[0024] Nanofiltration membranes prevent passage of materials, such as ions, that have size in excess of 10 to 20 angstroms. Ultrafiltration membranes prevent passage of ions having size in excess of 50 to 200 angstroms.

[0025] Reverse osmosis membranes prevent passage of smaller ions and material having size greater than about 2 to 5 angstroms. Membrane processing for recovery of free cyanide may take place in one or more stages involving membrane modules of spiral, fibre, flat plates, tubular or other module design known in the art.

[0026] Such processes, as nanofiltration, ultrafiltration or reverse osmosis, may further be applied to the step of concentrating the recovered cyanide stream to enable re-use if desired. A typical pressure range would be 500 kPa to 8,000 kPa. The recovered cyanide stream or permeate may contain a very low concentration of cyanide in comparison to that required in a metallurgical process, for example a gold cyanide leaching process.

[0027] Therefore, the concentration of free cyanide may be upgraded by further membrane modules in which the cyanide is selectively retained by membranes of decreasing pore size or increasing "tightness". A number of stages may be required to achieve the requisite degree of concentration for recycling of cyanide to the metallurgical process. Such a process may be feasible in two to three stages.

[0028] In the process of the invention, free cyanide, cyanide or thiocyanide complexes and compounds may be present in the liquor. These species may report at the anode of each electrochemical cell in which electrochemical dissociation occurs. Advantageously, the anode should be separated from the cathode at which copper or other metal deposits such that re-complexing with cyanide is limited. Cyanide can be removed from each electrochemical cell by conducting the membrane treatment step within the electrochemical cell to prevent re-complexing with base metal, such as copper. Free cyanide may also be recovered in a membrane treatment step conducted externally of the electrochemical cell. The membrane treatment step may be conducted for spent electrolyte or in a recirculating flow of electrolyte through the electrochemical cell. A number of electrowinning and membrane cells may be employed in a suitable electrochemical apparatus. The cells may be in series or parallel relation.

[0029] In another aspect of the invention, there is provided an electrochemical apparatus for recovering metals by electrowinning from low concentration metal containing solutions, the apparatus including:

[0030] (a) a housing including at least one electrochemical cell and having inlet and outlet means to enable electrolyte to pass through at least one cell;

[0031] (b) an anode for each cell;

[0032] (c) a cathode for each cell at which metal forms and/or deposits and

[0033] (d) flow circulating means for circulating a high velocity turbulent flow of electrolyte through each cell; and

[0034] (e) an electrical connection between the anode and cathode of each cell for completing an electrical circuit between these.

[0035] The flow circulating means may include a baffle means located between the anode and cathode of each cell with the inlet and outlet means located to promote a circulation within the cell. The baffle could alternatively, and advantageousy, serve as anode or cathode with a surrounding or adjacent electrode serving as cathode or anode, respectively. The baffle would preferably be constituted by the anode.

[0036] Alternatively, other means to increase the turbulence, and hence mass transfer in the cell may be employed. These may include, separately or in combination, physical modifications to the anode or cathode to induce turbulence, use of spacers between the anode or cathode, use of gas injection into the cell, use of increased cross flow velocity, pulsatian flow or flow reversal of the electrolyte.

[0037] A number of cells may be located adjacent to each other in series or parallel relation. The cells may be arranged in a number of banks or stages. In one arrangement, an electrowinning unit may comprise a number of anodes and cathodes which may be located in cell units provided with electrolyte inlets and outlets. The anodes and cathodes, which may be in the form of plates, may be retained in supporting frames held in pressure relation by a press. The press may be opened to recover metal deposited on the cathodes. Alternatively, the electrochemical cells may be configured to allow recovery of metal in a suitable solid/liquid separation device such as a hydrocyclone.
The inlet means may include one or more port means such as nozzles, or orifices located, advantageously in spaced relation, to create a flow of electrolyte past the electrodes which is high in velocity in comparison with prior art electrowinning cells. The inlet ports may be arranged in banks or along the length of one side of each cell. Other arrangements are possible. The narrow diameter of ports, nozzles or orifices relative to an inlet manifold supplying electrolyte to the electrochemical apparatus may cause electrolyte velocity to increase. As a result, electrolyte may be injected or jetted into each electrochemical cell. A high degree of turbulence is also induced in the electrolyte flow and this promotes metal ion mass transfer.

Where the electrodes take the form of flat plates, the inlet manifold may be connected to one side of a supporting frame being provided with an inlet gallery through which electrolyte flows, through the nozzles, ports or orifices and ultimately across the electrodes. Another side of the supporting frame may also be provided with outlet port means such as nozzles or orifices respectively connected to an outlet gallery and ultimately an outlet manifold. Again the outlet ports may be arranged in banks or along one side of each cell, typically that side opposed to the inlet ports. Other arrangements, including a staggered arrangement of inlet and outlet port means, are possible. Outlet port means may have larger diameter than the inlet port means.

The diameter of the inlet nozzles, ports or orifices may progressively decrease toward a centre of the one side of the supporting frame such that the velocity profile increases toward the centre of the one side of the electrode supporting frame. This supporting frame may also be electrically connected to a supply of current in a conventional way. It may incorporate a gas vent for venting of anode gas, such as hydrogen, from each cell.

More specifically, the anode and cathode of each cell may be supported by a supporting frame having opposed frame members provided with respective inlet and outlet port means, as described above, communicating each cell with inlet and outlet manifolds, said supporting frame having internal curved walls forming part of each cell. The curved walls further promote the circulating flow of electrolyte within the cell.

A membrane may be incorporated in the electrowinning cell to remove species formed during electrowinning and, particularly when the electrochemical cell is to be employed in the recovery of cyanide. The membrane, of a preferred embodiment of the invention, needs also to be permeable to cyanide with the cyanide permeate side of the cell connected to an outlet or outlet manifold such that cyanide can be removed from the cell without opportunity for re-complexing of cyanide and metal. Retentate is subjected to electrowinning of metal. Retentate may be recycled to the apparatus, treated in further stages or disposed of.

If a reverse osmosis, nanofiltration or ultrafiltration membrane is employed, pressure within the cell can drive the permeate flux.

The outlet or outlet manifold may be connected specifically to receive permeate from the cell and direct it to a cyanide concentration step as above described. The retentate side may be connected, optionally through a separate manifold, to a solid/liquid separation device or hydrocyclone for collection of metal particles recovered by electrowinning. Otherwise retentate may be treated as described above.

The process and apparatus of the present invention may be conveniently and advantageously be used for recovery of free cyanide and metals from solutions containing complexes of these, such as may be derived from precious metal leaching processes.

More broadly, metal recovery is also possible from solutions having much lower metal concentration or tenor than previously known providing the opportunity to operate without expensive concentration upgrading steps such as solvent extraction and ion exchange necessarily employed in prior art processes. For example, solvent extraction is a commonplace step in recovery of copper from a copper leaching process.

In a further aspect of the invention, there is more broadly provided a process for treatment of an aqueous cyanide or thiocyanate bearing stream including a membrane treatment step for separating free cyanide, a cyanide complex or a thiocyanate from a stream containing same. Optionally, free cyanide may be recovered for re-use in a process, particularly a metallurgical process using it.

Such streams may be waste or other streams derived from leach plants, other metallurgical plants or waste water streams from other sources. The membrane processes described above may be directed to this purpose.

BRIEF DESCRIPTION OF THE DRAWINGS

The process and apparatus of the present invention may be more fully understood from the following description of preferred embodiments thereof made with reference to the accompanying drawings in which:

FIG. 1 is a schematic flowsheet for a process for recovering cyanide from a solution or liquor containing metal complexes thereof;

FIG. 2 is a schematic flowsheet for a process for concentrating cyanide in accordance with the concentration step of FIG. 1;

FIG. 3 is a schematic diagram in side section of an electrochemical apparatus for conducting electrolysis of the metal-cyanide complex;

FIG. 4 is a schematic diagram, in end section, of the electrochemical apparatus of FIG. 2;

FIG. 5 is a schematic diagram along section line A-A of FIG. 3;

FIG. 6 is a front view of a cell unit or cell supporting frame for use in an electrochemical apparatus as schematically represented in FIGS. 3 and 4;

FIG. 7 is a first side view of the cell unit or cell supporting frame of FIG. 6;

FIG. 8 is a top view of the cell unit or cell supporting frame of FIGS. 6 and 7;

FIG. 9 is a section view along section line A-A of FIG. 6; and

FIG. 10 is a second side view of the cell unit or cell supporting frame of FIGS. 6 to 9.
DETAILED DESCRIPTION OF THE DRAWINGS

[0060] Referring now to FIG. 1 of the drawings, there is shown a flowsheet for conducting a process in which cyanide and copper metal are recovered from an alkaline aqueous liquor stream 110 containing copper cyanide complexes including Cu(CN)_2^-, Cu(CN)_3^- and Cu(CN)_4^- complexes. Stream 110 may itself be derived from a membrane process for separating gold-cyanide and copper-cyanide complexes as described in U.S. Pat. No. 5,961,833, the contents of which are hereby incorporated herein by reference. Such a liquor stream 110 may be derived from a leach of a copper bearing gold ore. In step 120, the copper cyanide complexes are dissociated in an electrochemical process in which cyanide reports to the anode and copper metal reports to the cathode of electrochemical cell(s) configured to conduct the process. One possible embodiment of electrochemical apparatus for performing this duty is described in further detail below.

[0061] The following electrochemical processes, involving cyanide complexes and thiocyanate, may occur during the process of the invention:

\[
\begin{align*}
\text{Cu(CN)}_2^- & \rightleftharpoons \text{Cu(CN)}_2^2^- + \text{CN}^- \\
\text{Cu(CN)}_3^- & \rightleftharpoons \text{Cu(CN)}_2^2^- + \text{CN}^- \\
\text{Cu(CN)}_4^- & \rightleftharpoons \text{Cu}^+ + 2\text{CN}^- \\
\text{SCN}^+ + 2\text{e}^- & \rightleftharpoons \text{SO}_4^{2-} + \text{CN}^-
\end{align*}
\]

[0062] Therefore, as the process proceeds copper is electrolytically extracted, as a saleable product, perhaps in the form of granules or powder which may be recovered in a suitable solid/liquid separation step 170 including one or more devices such as hydrocyclones.

[0063] In an electrochemical cell operated without a cyanide permeable membrane copper would, subject to kinetics, re-complex with free cyanide to form copper complexes in the reverse process to those reflected by reactions (1) to (3) above.

[0064] However, free cyanide may be recovered from electrolyte in a membrane process. In that way, the re-complexing problem and cyanide wastage may be avoided. There are a number of options for this. Broadly, the process is conducted such that cyanide ions may permeate through the membrane in a process such as reverse osmosis, ultrafiltration or nanofiltration, all of which are pressure or diffusion driven membrane processes and generically described in the literature cited above and incorporated herein by reference.

[0065] In one embodiment, the cyanide permeable membrane may be located in the electrowinning cell. As copper ions migrate to the cathode, cyanide ions pass through a membrane, migrating to a permeate collection manifold. The permeate stream may then be directed to further membrane treatment step, such as for concentration of cyanide for re-use in a metallurgical process for cyanide leaching of copper bearing gold ore.

[0066] In another embodiment, a flow of copper depleted electrolyte may be directed to a membrane treatment step 140 involving reverse osmosis, ultrafiltration or nanofiltration steps in which cyanide is caused to permeate through a suitable membrane under imposition of a pressure gradient across the membrane. Membranes suitable for the membrane treatment step may be sourced under the trade marks DOW NF70 or Desal DK. Other membranes may be suitable noting the importance of pH to membrane selection. The membrane modules for membrane separation of free cyanide may be of spiral, fibre, flat plate, tubular or other known membrane unit type operated at a suitable pressure, for example, in the range 500 kPa to 8,000 kPa (0.5 to 8 MPa).

[0067] A number of membrane modules, which may be arranged in stages may be used for this process.

[0068] FIG. 2 shows a schematic of a cyanide concentration step 160 which itself involves membrane processes which selectively separate cyanide as retentate (concentrate) or otherwise. Stream 150, containing for example 1 g/l cyanide, is directed first to membrane concentration unit 162 with concentrate stream 152, having concentration 5 g/l cyanide, being directed to further membrane concentration unit 164 to generate concentrate stream 154 of concentration sufficient for recycle to a gold leaching process, say 15 g/l concentration free cyanide.

[0069] The lean cyanide stream 153 is directed to membrane concentration unit 166 with concentrate stream 155 being recycled to membrane concentration unit 162. The lean cyanide stream 157 containing a low concentration, say 0.01 g/l cyanide, may be directed to disposal or other treatment steps.

[0070] Cyanide concentration may therefore involve two concentration steps but other concentration process flowsheets could be developed to perform the same duty. More concentration or separation steps could be employed as necessary.

[0071] In the embodiment described above, description was made of free cyanide and copper metal recovery from liquors containing complexes of these. However, the process of the invention is also suitable for recovery of cyanide and other base or precious metals from complexes thereof. The process would also be suitable for recovery of cyanide and silver from complexes thereof. The process is further suitable for recovery of free cyanide from other waste water streams.

[0072] In the broadest aspect of the invention, as described above, the process could be conducted by using a membrane process for recovery of free cyanide in association with a conventional electrochemical cell, in which electrolyte is recycled through the cyanide membrane separation unit.

[0073] However, in a preferred embodiment, the electrochemical process for dissociating copper-cyanide complexes may be conducted in an electrochemical cell or apparatus as described with reference to FIGS. 3 to 10.
Referring now to FIG. 3, there is schematically shown an electrochemical apparatus 10 having a housing 30 incorporating a number of electrochemical cells 21. Housing 30 includes four electrochemical cells 21 each being provided with planar anodes 38 and cathodes 39. Other forms of anode 38 or cathode 39 could be used, for example cylindrical, rod or otherwise.

Between each cathode 39 of cell 21 is a planar anode 38 forming a baffle around which electrolyte circulates in a high velocity turbulent flow across the anode and cathode surfaces. Cathode 39 may completely surround anode 38. Alternatively, an electrochemically inert baffle may be located between anode and cathode plates 38 and 39. In such case, the baffle may be of polymeric material.

It will be understood that anodes and cathodes may be constructed from material known to be suitable for electrowinning application. In this case, stainless steel anodes and cathodes 38 and 39 may be employed. Type 316 stainless steel may be preferred. Electrical connection is made with anodes and cathodes 38 and 39 in conventional manner.

The cells 21 are incorporated in cell units 23 held in a press between end plates 20 which may be of polymeric or other suitable material. In this embodiment the end plates 20 are of polypropylene. The apparatus may be assembled or disassembled by adjustment of pressure screw 18.

Electrolyte enters each cell from an inlet manifold 16 by branch pipes 14 having inlets communicating the inlet manifold 16 with each electrochemical cell 21. Electrolyte leaves each cell 21 through an outlet communicating with outlet manifold 18 through branch pipes 15. Outlet manifold 18 may be connected to membrane treatment step 140 as illustrated in FIGS. 1 and 2. However, electrochemical apparatus 10 may be operated in a recirculating mode with electrolyte being directed through membrane treatment step 140 for recovery of free cyanide, and then back to electrochemical apparatus 10 for further electrochemical treatment. Alternatively, a number of electrochemical stage treatments could be used.

Leaving electrolyte may be depleted in copper which deposits on planar cathodes 39 as a powder or granulated deposit. In a turbulent regime, the metal solid may be transported from cathode 39 surfaces and may be recovered by solid/liquid separation in hydrocyclones for example.

The leaving electrolyte is then passed to membrane treatment step 140 for recovery of free cyanide which may be concentrated for re-use in the metallurgical process as previously described. The membrane treatment step could be conducted within cell 21. For example, anodes 38 could be separated from the remainder of the cell by a cyanide impermeable membrane to achieve this.

The entering electrolyte enters cells 21 through at least one port located where each branch pipe 14 enters each cell 21. As such a port is of lesser diameter than the diameter of the inlet manifold 16, electrolyte velocity is increased and turbulence is likewise increased. Electrolyte is therefore injected or jetted into the cells 21. The walls of the housing 30, the anode 38 (acting as a baffle) and the opposed locations of inlet ports and outlet port(s), the latter being located where each branch pipe 15 exits from each cell 21, act as a flow circulator means which creates a high velocity turbulent circulatory flow of electrolyte that may circulate two or more times about cell 21 before leaving it. In this way, the mass transfer rate of copper from ionic to metallic form is increased with copper recovery being possible even from very low concentration solutions, having copper tenor 1 g/l or even lower. This may also be understood to be the case for other metals.

The circulation effect may be enhanced by orienting the inlet and outlet ports tangential to curved portions 33 of walls 21a of cells 21 as shown in FIG. 4. The curved orientation of the walls 21a enhances the circulation effect.

The supporting frames 210 for each cell unit 23 will now be described in greater detail with reference to FIGS. 6 to 10.

Referring now to FIG. 6, the supporting frame 210 is provided with a number of frame members 211, 212 and 213 which may be made of non-conductive polypropylene or other materials. Supporting frame 210 is supportive of, or connected to, plates 238 and 239 which respectively form the anode and cathode of electrochemical cell 21. Anode and cathode plates 238 and 239 may be of stainless steel or other suitable material. These 238 and 239 may be held in place by a contactor bar (not shown) and a current supply as known in the electrochemical art.

Anode plate 238 may be located approximately centrally of cell 21. Centre line 21a of cell 21 may form the centre line of anode plate 238.

Frame member 211 incorporates a number of inlet ports 240, of narrower diameter than the diameter of inlet manifold 16 or branch pipe 214. Two zones of inlet ports 240 are shown but ports could extend along the entire length of walls of frame member 211 defining cell 21. Electrolyte is pumped to each cell 21 through inlet manifold 16, branch pipe 214 and corner apertures 242 to inlet gallery 241. Inlet gallery 241 communicates with each cell 21 interior through drilled restrictions or apertures, of circular or other geometry, in frame member 211 which form ports 240. In this way, velocity and turbulence of electrolyte are increased. Ports 240 are conveniently located offset from a centre axis 21a of cell 21, and anode 238 to create a turbulent high velocity circulatory flow of electrolyte transversely across the electrodes with the ports 240 acting as jets. Location of anode plate 238 within cell 21, or location therein of an inert baffle, creates a circulatory flow of electrolyte which leaves cell 21 following electrolysis/electrowinning through outlet ports 250. Comer apertures 242 may extend through the entire length of electrochemical apparatus 10. Corresponding apertures may be formed in one or both electrodes, especially cathode plates 239.

The supporting frame 210 opposed frame members 211 and 213 are also provided with internal curved walls 233 which also promote a high velocity turbulent-flow of electrolyte in cell 21.

The leaving flow of electrolyte may be passed through outlet ports 250 to membrane treatment step 140 for recovery of free cyanide while metal can be recovered from the cathode in any convenient manner after the membrane treatment. Ports 250 may also be located offset from a centre axis 21a of each cell 21, advantageously on the opposite side of anode 238 and centre axis 21a to ports 240, which further enhances the circulatory effect. The outlet ports 250, which may have larger diameter than inlet ports 240, are drilled apertures, of circular or other geometry, in frame member 213. In the drawings, outlet ports 250 are centrally located and staggered from the inlet ports 240. The staggering is apparent from FIGS. 6 to 10. FIG. 9, omitting anode 238 for
clarity of illustration, shows the staggered arrangement in which ports 240 and 250 are at different levels within the cell 21. However, the outlet ports 250 could extend along the entire length of walls of frame member 213 defining cell 21. Again, the outlet ports 250 communicate with outlet gallery 251 communicating with an outlet manifold 18 through corner apertures 244, again extending through apparatus 10. In one method, a solid-liquid separator such as a hydrocyclone may be used to recover metal powder from the cells 21 after membrane treatment step 140.

A number of cell units 23 may be mounted together between end plates 20, all being supported by supporting arms 23a of cell unit 23 on a support means (not shown). End plates 20 may be polymeric, say of polypropylene. The cell units 23 may be mounted to be assembled/disassembled by tightening or loosening screw 18 shown in FIG. 3.

The electrochemical apparatus may be operated in recirculating mode to maximise recovery of cyanide and metal. A number of stages may be used, each employing apparatus of the same or similar type to that described above.

The electrochemical apparatus is not restricted in its applicability to metal-cyanide complex electrolysis, as a step in free cyanide recovery, and it may also be applied to recovery of metals, particularly base metals, from low tenor metal ion containing solutions as well as species formed during electrolysic processes for recovery of metals whether in combination, or not, with a membrane separation process for such species.

Modifications and variations to the processes and apparatus of the present invention will be apparent to the skilled reader of this disclosure. Such modifications and variations fall within the scope of the present invention.

The claims defining the invention are as follows:

1. A process for recovery of cyanide and metals from a liquor containing a compound or complex of cyanide and metal generated by a metallurgical process including the steps of:

   (a) electrochemical treatment of said liquor in an electrochemical cell for electrochemically dissociating said compound or complex present in an electrolyte steam;

   (b) recovering the metal by electrowinning;

   (c) passing electrolyte through a membrane treatment step for recovering a free cyanide stream; and, optionally,

   (d) recycling the free cyanide stream for recovery or reuse.

2. The process of claim 1, wherein said complex of cyanide and metal is a base metal-cyanide complex.

3. The process of claim 2, wherein said complex of cyanide and metal is a copper-cyanide complex.

4. The process of claim 1, wherein said complex of cyanide and metal is a precious metal-cyanide complex.

5. The process of claim 1, wherein said membrane treatment step is pressure or diffusion driven for the separation of free cyanide from cyanide complexes and metal ions.

6. The process of any one of the preceding claims wherein thiocyanide is present in said liquor and is oxidised to form free cyanide at an anode during electrochemical treatment of said liquor in said electrochemical cell.

7. The process of any one of the preceding claims in which metal powder formed at the cathode is recovered by solid-liquid separation.

8. The process of claim 6, wherein solid-liquid separation is conducted in a hydrocyclone.

9. The process of any one of the preceding claims further including the step of concentrating cyanide permeate for recycling or re-use.

10. The process of claim 9, including a membrane process for concentrating cyanide.

11. The process of any one of the preceding claims wherein said membrane treatment step for recovering free cyanide is conducted within said electrochemical cell.

12. The process of any one of claims 1 to 10 wherein said membrane treatment step for recovering free cyanide is conducted externally of said electrochemical cell.

13. An electrochemical apparatus for recovering metals by electrowinning from a low concentration metal containing solution, said apparatus including:

   (a) a housing including at least one electrochemical cell and having inlet and outlet means to enable electrolyte to pass through each cell;

   (b) an anode for each cell;

   (c) a cathode for each cell;

   (d) flow circulating means for circulating a high velocity turbulent flow of electrolyte through each cell; and

   (e) an electrical connection between anode and cathode of each cell for completing an electrical circuit between them.

14. The electrochemical apparatus of claim 13, wherein a baffle means is located between the electrodes of each cell.

15. The electrochemical apparatus of claim 13 wherein said baffle means is an electrode, preferably the anode.

16. The electrochemical apparatus of any one of claims 13 to 15, wherein said inlet means includes one or more inlet port means located to create a flow of electrolyte past the electrodes.

17. The electrochemical apparatus of any one of claims 13 to 16, wherein said outlet means includes one or more outlet port means.

18. The electrochemical apparatus of any one of claims 14 to 16, wherein said port means are offset from a centre axis of each cell.

19. The electrochemical apparatus of any one of claims 13 to 17, wherein said anode and cathode of each cell are supported by a supporting frame having opposed frame members provided with respective inlet and outlet port means communicating each cell with inlet and outlet manifolds, said supporting frame members having internal curved walls forming part of each cell.

20. The electrochemical apparatus of any one of claims 13 to 19 wherein each cell includes a membrane for separation of species formed during electrowinning.

21. A process for treatment of an aqueous cyanide or thiocyanide bearing stream including a membrane treatment step for separating free cyanide, a cyanide complex or a thiocyanide from said stream.

22. A process for recovery of cyanide and metals from a liquor containing a compound or complex of cyanide and metal comprising the step of electrochemically treating said liquor in an electrochemical cell for electrochemically dissociating said complex to form free cyanide.

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