ELECTROWINNING OF ORES

Filed June 3, 1971

2 Sheets—Sheet 2
ABSTRACT OF THE DISCLOSURE

Metalliferous ores are electrowon by grinding them and passing the ground ore in a slurry containing an electrolyte between the electrodes of an electrolytic cell. The electrolyte is so selected that the free surface energy of the ore plus the energy contributed to the ore by the electrical field of the cell exceeds the energy supplied by the ionized components of the electrolyte so that metal plates out on the cathode of the cell.

This application is a continuation-in-part of my prior application Ser. No. 43,403, filed June 4, 1970 and now abandoned.

SUMMARY OF THE INVENTION

This invention relates to a process for the electrowinning of elements from their ores in their elemental states, both metallic and non-metallic, by the proper formulation and manipulation of the components and compositions hereinafter detailed.

It is an object of this invention to recover metals in the combined state or in a free state when placed under the influence of an electrical field and in the presence of a specific electrolyte dissolved in a solvent and by collecting said metals on the cathode or anode of an electric cell.

It is a further object of this invention to recover various metallic or non-metallic components of various ores by an electrolytic processing of ore without separate leaching, extraction, purification, filtration, separation, and concentration procedures.

It is still a further object of this invention to use specific electrolytes for the recovery of specific metallic or non-metallic components.

It is still a further object of this invention to recover anions and cations from solutions in the presence of an electrical field, not only in order to recover the elements, but also for the purpose of purifying the solvent in which the ions are dissolved.

It is still a further object of this invention to recover elements dissolved in waste effluents by processing the flow in an electrolytic cell and to recover the contained elements and also purify the effluent to prevent pollution or permit further use of the solvent.

It is possible by this process to selectively remove individual elements from their ores and also to remove combinations of elements from ores. The unique feature of this process lies in the fact that the elements are removed from the ore in an electrolytic cell without prior chemical treatment and deposited on an electrode of said cell. In short, the only process requirement prior to the removal of the elements is the normal crushing and grinding of the mined ore to a size which permits easy mechanical handling and the formation of a slurry, and access of the electrolyte to the portion of the ore to be ionized.

The treatment of the ore is as follows: (1) The ore from the mine is crushed by standard milling techniques known to workers in the industry. (2) The crushed ore is then milled to a degree of fineness which will permit formation of a slurry of the ground material in the electrolyte chosen for the recovery of the particular element desired. The degree of fineness will vary depending upon such factors as the concentration of the element in the ore, the type of ore, the number of elements to be recovered, the specific gravity of the electrolyte, the cell temperature, the degree of agitation in the cell, and other similar factors.

The inventor feels that the primary cause of action in the electrolyte-ore slurry is based on the free surface energy, and that the element is ionized by the potential established by the electrical field between the electrodes. This belief is based on the fact that in many cases the electrolyte-ore slurry in the absence of an electrical field will not put metallic ions into the liquid phase, but will still act as ideal extractants when the electrical field is in existence such that the ions will not dissolve in slightly acidified thioures, but recovery from barium sulphide ore is 99.88% at a cell efficiency of 85% using this electrolyte.

As previously mentioned it is not a disadvantage for the metallic portion of the ore to be soluble in the electrolyte.

The action could also be explained by another theory of which the inventor is aware in which the formation of active oxidation and reduction cells on the particle surface in the area of the metallic component in the presence of the electrical fluid causes ionization. The requirements of the electrolyte are such that the ionization potentials (see any handbook of chemistry) must be approximately equal to the cell potential set up by the ore-gangue matrix. This potential must, under the influence of the electrical field, permit the ionization potential of the ore to exceed the ionization potential of the electrolyte. In other terminology, the free surface energy of the ore plus the energy contributed to the ore by the electrical field must exceed the energy supplied by the ionized components of the electrolyte. While the inventor has not been able to determine the basic law of nature underlying the relationship involved, he has found that the optimum electrolyte composition and concentration for maximum recovery must be determined experimentally in each case, within the following generalizations: Most sulphide ores are amenable to thiocyanate or thiourea solution which has been acidified with an organic acid of the general type exemplified by citric acid, tartaric acid, or acetic acid. Amphoteric metals are generally amenable to an alkaline hydroxide electrolyte, usually with the addition of some form of chelate such as EDTA. Oxide ores are usually extracted with the highest efficiency from a mildly acidified diethylamine solution.

While the essential novelty of my process resides in the use of an electro-deposition process and the selection of the particular electrolyte best suited to extraction of the metal from the ore, the effectiveness of the process may be maximized by careful attention to the following factors:

1. The particle size, or grind of the ore.—The nature of the process is such that there must be actual physical contact between the electrolyte and the metalliferous component of the ore. The fineness of the grind is that mesh or particle size which will bring about such contact.

For example, zinc in refinery slag is evenly distributed as a component of a glassy slag, and the slag must be crushed to —400 mesh before 90% recovery can be accomplished. Gold veins in quartz can be completely recovered at —100 mesh. Lead can be completely recovered from massive deposits of galena crystals without grinding. In materials of this type such as galena, sandstone copper, limestone zinc, and similar minerals, the grind of the ore is determined by the mechanical material handling requirements of the cell rather than by the electrolyte contact requirements.
2. The rate of deposition, which is determined by the coulombs passed through the cell. The rate of deposition is governed by mechanical and economic considerations rather than by the requirements of the process. One coulomb per day will deposit a proportional amount of metal but would be uneconomical in the extreme. A million coulombs per second would also deposit a proportional amount of metal, but in the process would boil off of the electrolyte and melt the electrodes and would require cooled yard-thick silver busbars. Amperage, therefore, should be at the highest electrode density possible for maximum metal deposition rates, without generating more heat than can be removed readily and economically. In one specific example:

For silver sulphide, in a glassy silicate matrix of the type found in some refinery slags, when ground to minus 325 mesh, in an aqueous electrolyte containing 1% ammonium cyanate, 0.1% citric acid and 0.05% ethyldiethanolcarbamate: 380 amperes per square foot of cathode surface.

3. The voltage should be sufficient to cause site activation, but not high enough to cause excessive non-productive flow. The optimum value for a given ore and electrolyte can be determined by routine experiment. By way of example, for the system described in the preceding paragraph, about 1.2 volts is suitable.

4. The next variable is residence time in the cell. In general the longer the residence time the higher the degree of extraction or the higher percentage of recovery. Also, in general the longer the residence time the higher the cost per unit of recovered metal. These two factors must be balanced for the most economical recovery.

5. Slurry concentration.—It is desirable to run the recovery cell at the maximum thickness of the slurry. Apparently the depleted gaseous medium acts as a semi-insulating medium. The optimum slurry concentration is determined experimentally for a particular ore. Ore is run through the cell at increasing concentration and rate until metallics are found by analysis in the tailings. The throughput rate is then reduced slightly until analysis shows practically no metallics in the tailings.

6. Temperature.—The temperature dependence of some reactions permit higher efficiency at elevated temperatures. For example, the efficiency of recovery of zinc from zinc silicate is greater at 90° C. than at room temperature. However, since the cost of heating the cell must be included in the cost of operating the cell, the electrolyte should, where economically feasible, be compounded for ambient temperatures.

Thus, the particular set of requirements for a given recovery and ore are variable and may be manipulated by the operator to the best economic advantage in a given operation. A given plant may, therefore, be easily modified to utilize varying raw materials and have different product outputs as the exigencies of the economic climate might require. The milled ore is then fed into the electrolyte cell. If wet milling is used, the ore may be milled in the electrolyte and then the slurry pumped directly into the cell. The proper concentration and composition of the electrolyte solution must be maintained for maximum efficiency.

THE DRAWINGS

In the drawings:

FIG. 1 is a graph which shows the relations for some approximations for the first term of the equations hereinafter referred to, with values of $b_4$ from —15 volts to +15 volts plotted along the abscissa, and values of:

$$\log \frac{Qh}{b_4}$$

plotted along the ordinate.

FIG. 2 is a perspective view of a first installation utilizing my invention;

FIG. 3 is a partial sectional view on an enlarged scale, taken along the line II—II of FIG. 1; and

FIG. 4 is an elevational view showing a second installation for utilizing my invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

A first embodiment of the apparatus for carrying out my invention comprises a plurality of frames 11, shaped as shown in FIG. 2. Each frame holds either an anode 12 or a cathode 13, but not both. Successive frames are assembled by means of bolts 10, or the like, with an ion permeable membrane 14 positioned between each two adjacent frames, thus forming a succession of compartments, with alternate compartments containing a cathode and the remainder an anode. The ground ore to be refined is mixed with the electrolyte and introduced through manifold 15 to the anode compartments only, the cathode compartments having already been filled with electrolyte through manifold 16. Electrical current flows from the anodes to the cathodes, carrying with it the metal ions. This metal plates onto the cathode, sloughs off, and falls to the bottom of the cathode compartments, from whence it is removed through the pipe 17. Exhausted slurry falls to the bottom of the anode compartments and may be removed through the pipe 18.

The level of the electrolyte in the cathode compartments is kept slightly higher than that of the slurry in the anode compartments so that there is a slight flow of electrolyte from the cathode to the anode compartments. This prevents a build-up of slurry particles on the membrane.

In the event that the ore particles are to heavy (dense) to keep suspended in the electrolyte, air agitation or hydraulic agitation may be provided by blowing compressed air or fluid through holes drilled in tubes extending through the bottoms of the anode compartments.

A second embodiment of apparatus for carrying out my invention is illustrated in FIG. 4.

This apparatus comprises a cathode 20 upon which the electrowon metal is deposited. This cathode is a vertically supported metal rod or tube having a sufficient surface area for the required current density.

The cathode is encircled by the ion permeable membrane 21, carried by an inert support 22 (i.e. one which is not affected by the electrical current or the ingredients of the electrolyte). The sole purpose of this membrane is to keep the ore slurry from contacting the cathode and thus contaminating the deposited metal with depleted ore particles. Omission of this membrane would not directly affect the deposition of metal on the cathode, but would give rise to the problem of separating the deposited metal from the slurry dirt.

The membrane is in turn encircled by a cylindrical anode 23, sufficiently spaced from the membrane to permit slurry to pass therethrough.

Electrolyte is introduced between the cathode and the membrane and maintained at a slightly higher level than the slurry between the membrane and anode so as to prevent the membrane from becoming plugged with slurry particles.

A spiral guide 24 may be positioned between the membrane and anode to slow the flow of slurry to the rate desired.

In operation, once the space between the membrane and cathode has been filled with electrolyte, the slurry is continuously pumped in at 25 and evacuated at 26, with the pumping rate dependent on the time required to allow maximum economical recovery of the metal. The effluent slurry from several cells may then be passed through a "stripper" cell to remove any remaining values.

The metal is deposited on the cathode in dendritic form, and then breaks off and falls to the bottom of the cathode space, from which it is removed through isolation valve 27.
In the recovery of zinc, nickel, and gold from their ores, we used anodes of antimonial lead in the proportion of eight, equivalent amont to lead and antimo...ode. We have also used other anodes and cathodes for the recovery of these and other metals as later noted.

The electrolyte may be chosen such that it will remove more than one elemental component from the ore. For example, gold, silver, copper, zinc, lead and antimony may be removed from a single complex ore. Metals may be recovered from ore in one of several fashions: In the first the total recoverable elements may be simultaneously deposited on the collecting electrode and separated later by any standard technique; in the second either the cell may be arranged so that the slurry enters areas of varying electromotive force and flux density so that elements will selectively deposit on various areas of the collecting electrode, or the slurry may be pumped through a series of cells each of which has the proper voltage, electrolyte and current density for the deposit of a single element. The procedure used in any given case will be determined by the economics of the process and the purity of the product desired.

This process has been used by the inventor for the successful separation of the following elements from their ores: Magnesium, sulfur, silver, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, germanium, arsenic, selenium, bromine, silicon, yttrium, indium, tin, antimony, molybdenum, tellurium, iodine, palladium, gold, mercury, bariurn, lead, bismuth, tungsten, platinum, thorium, uranium, praseodymium, gadolinium, hafnium, and osmium.

The theory of this invention indicates that the process can also be applied to beryllium, tungsten, titanium, vanadium, rubidium, ruthenium, rhodium, rare earths, and actinide.

Since the choice of an electrolyte is the most difficult and critical feature of my process, a general exposition of the principles utilized in this selection will now be given, followed by several examples of the application of these principles to the selection of a specific electrolyte for use with a specific ore.

A particle suspended in an electrical field in a vacuum becomes a free electrode, and will receive and hold an electrical charge, while in the field, such that the portion of the particle nearest the electron emitting surface of the electrode will become positively charged, and the portion of the particle nearest the electron accepting surface of that electrode will become negatively charged.

If the particle suspended in the field is of uniform composition, the charge will be uniform, and will be a function of the electrical field strength in the area of the particle and the dielectric properties of the particle.

If the suspended particle is of non-uniform composition, and the compositions making up the particle have different dielectric properties, the greater electrical charge will be found in the material having the least dielectric strength, or, in other terminology, the greatest electrical potential will be found associated with the component having the highest conductivity (or least ohmic resistance); or in yet another terminology, the matter most affected by the electrical field is the matter having the greatest electron mobility, that is, the matter most easily ionizable.

In a non-uniform situation, in which the particle is suspended in a non-conducting fluid, the same effects of an electrical field upon a suspended particle will be observed. An analogous situation is observed when the suspending fluid is a conductor, i.e., is an electrolyte.

An electrolyte may be defined as a fluid which conducts an electron flow (current) by means of dissolved materials which, upon being dissolved, dissociate to form ions, which are electrically charged. Helmholtz states that when a metal, or any other substance capable of existing in solution as ions, is placed in water or any other dissociating solvent, a part of the metal or other substances passes into solution in the form of ions, thus leaving the remainder of the metal or substances charged with an equivalent of opposite sign from that carried by the ions. This establishes a difference in potential between the metal and the solvent in which it is immersed. I shall refer to this potential in the following discussion as the "Helmholtz potential."

Electromotive force (EMF) The EMF of a cell is measured by the maximum difference of a potential between its plates. The electromagnetic unit of potential difference is that against which one erg of work is done in the transfer of electromagnetic unit quantity. The volt is that potential difference against which one joule of work is done in the transfer of one coulomb. One volt is equivalent to 10^8 electromagnetic units of potential.

\[ E = \text{Electrochemical equivalent of an ion and is the mass liberated by the passage of unit quantity of electricity. If a current } I \text{ flows for a time } T \text{ and deposits a metal whose electrochemical equivalent is } E\text{, the mass, } M, \text{ deposited is } M = EIT. \]

The value of } E \text{ is usually given in } g, \text{ for mass in grams, } I \text{ in amperes, and } T \text{ in seconds. Basically, free energy is a thermodynamic function of particular interest to a scientist or engineer working with chemical problems. Physically, it is a measure of the energy of a system available (free) to do work at a constant temperature and pressure. In chemical reactions it is a measure of the extent to which substances can react. Free energy is usually denoted by the letter } G \text{ (or sometimes } G\text{, the Gibbs free energy or "thermodynamic potential"), and is usually only considered from the thermodynamic consideration of change, and is expressed as } F \text{ or } G^*.

Mathematically the change in free energy is related to other functions by the following equations:

\[ \Delta G = \Delta H - T \Delta S \]
\[ \Delta G = -nF \]
\[ \Delta G = -RT \ln K \]

where } S \text{ =entropy, } H \text{ =enthalpy, } n \text{ =no. of equivalents, } T \text{ =Faraday's constant, } E \text{ =EMF of cell, } K \text{ =equilibrium constant, } R \text{ =gas constant, } T \text{ =absolute temperature.}

The second equation establishes the relationship between the free energy change and the electrochemical force. This equation is used when the reaction under consideration can take place in a reversible galvanic cell. The EMF may be measured with a potentiometer.

At } \Delta F \text{ values approaching } 0 \text{ or becoming positive, the equilibrium is small, and at } \Delta F \text{ values exceeding } 1 \text{ volt, the process is generally not feasible at the given conditions. Consequently, } \Delta F \text{ indicates the tendency of a reaction to occur. It does not, however, tell how fast it proceeds. This can only be determined experimentally.}

When two or more atoms react to form a compound, they interact in such a fashion that energy is required to alter their relationship. The energy required to separate one of the atoms from a compound is referred to as the "energy of ionization" or the "ionization potential," and is defined as the work (expressed in electron volts) required to remove a given electron from its atomic orbit and place it at rest at an infinite distance. It is customary to list values in electron volts (E.V.) 1 E.V. = 23,053 calories per mole.

Oxidation-reduction energy can conveniently be measured in terms of electrochemical potential. Between a given donor of electrons and a given acceptor there is a certain difference of oxidation-reduction potentials. This difference depends not only on the nature of the two reacting substances but also on the nature of the products of the reaction; it is characteristic of the two oxidation-reduction "couples." For example, when oxygen is reduced to water (\(H_2O\)) its potential is \(-0.81\) volt, but when it is reduced to hydrogen peroxide (\(H_2O_2\)) the potential is \(-2.7\) volt. The more positive the potential, the stronger is the oxidative power of the couple; the stronger is its reducing power.
The foregoing discussion gives definitions of some of the various factors and forces considered when designing on effective electrolyte for use in the recovery of a particular metal or group of metals from their metalliferous state. Other factors which are considered will be discussed below and in the description of methodology.

Ore consists of a mineral formation which contains, either mechanically entrained or diffused, a chemical compound of the economically valuable constituent or constituents. For example, commercial copper may be recovered from the compound copper sulfide, which is distributed through porphyritic rock. For all practical purposes, the value in the ore body, which consists of the mixture of porphyry and copper sulfide, is entirely in the copper metal which is recovered by standard milling, concentrating and smelting processes.

A standard metallurgical procedure is that of leaching, whereby the ore is treated with a chemical which will dissolve the compound containing the metal or metals of value, and not dissolve the non-valuable components of the ore. The dissolved material is then purified and recovery by electrochemical replacement, as in the production of cement copper from a leach solution by the addition of a metallic iron, zinc, aluminum or similar reactive elements. The iron metal gives electrons to the copper ions, which precipitate as metallic copper, as the iron ionizes and goes into solution.

The copper ions may also be removed by electrolysis, ion exchange, pyrolytic reduction and other similar techniques.

In order to directly electrolyze the metallic constituents from the ore, there must be an active part of an electrical circuit, such that the electrical potential will dissociate the compound containing the metal, so that the metallic positively charged ions will travel to the negative electrode (the cathode), and there receive a sufficient number of electrons to become electrically neutral, and thus precipitate on the electrode as metal atoms.

The ideal electrical medium for ionic transport is a fluid one, and from the foregoing discussion we can say several things about the nature of the fluid (electrolyte).

First, it must be capable of carrying ions, that is, ions released from the ore particles must be mobile in the electrolyte so that they can travel to the electrodes.

Secondly, the conductivity of the electrolyte must be high enough to permit rapid transit of large number of ions, so that the deposition rate is commercially sound, yet must not be so conductive that the ore particles are bypassed by the electrical current, that is, that the current passes through the electrolyte without providing ionization energy to the suspended ore particle.

Thirdly, the composition of the electrolyte must be such that the sum total of electrolyte; reaction reactions is zero, that is, that the composition and concentration of the electrolyte after recovery of metals from ore is the same as it was prior to the electrowinning process.

Fourth, the electrolyte must not react with the deposited metal, so that loss of the recovery metal is minimal.

Fifth, the electrolyte must be stable under ordinary conditions, but should be capable of thermal excursions from its design operating temperature without significant loss of efficiency and effectiveness.

Sixth, as in any operating procedure, any given electrolyte, in terms of loss from drop-out, spillage or other loss, must be economically feasible.

**FIRST EXAMPLE**

With the foregoing background information, I shall now set forth the steps required to design an electrolyte for metallic ore containing one metal, in exhaustive detail, to demonstrate the requirements of calculation when only one metal from a mixture of compounds is to be recovered from an ore (an ore which contains only one recoverable metal is called a simple ore; one containing several recoverable metals is called a complex ore).

The first step, upon receipt and recording of the ore, is to make a physical examination. This will, in general, determine the ore body type, that is, whether it is a limestone matrix, a quartz matrix, whether it is an oxidized or sulfide ore, and provide a great deal of information familiar to workers in the field. Since the electrolytic process requires that the electrolyte actually contact the portion of the ore to be ionized, a general idea of the grind requirements of the ore is noted at this examination.

A spectrographic analysis is then made to determine the metallic and non-metallic constituents of the ore (this could be accomplished, with greater difficulty and at a greater expenditure of time by other analytical techniques, such as wet chemical analysis). Any secondary analyses which might be required to determine the composition of the ore are also made.

Assume that we have examined an ore sample and have determined that it is a quartz matrix which contains the valuable (non-diffused) zinc sulfide, and has, by analysis, the following composition:

<table>
<thead>
<tr>
<th>Material</th>
<th>Silicon dioxide (quartz) (SiO₂)</th>
<th>---- percent by wt.</th>
<th>37</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulfide (ZnS)</td>
<td></td>
<td>do</td>
<td>44</td>
</tr>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td></td>
<td>do</td>
<td>7</td>
</tr>
<tr>
<td>Ferric sulfide (Fe₄S)</td>
<td></td>
<td>do</td>
<td>7</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>do</td>
<td>5</td>
</tr>
<tr>
<td>Silver</td>
<td></td>
<td>oz./ton</td>
<td>0.2</td>
</tr>
<tr>
<td>Gold</td>
<td></td>
<td>do</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Physical examination

The ore consists of zinc sulfide laced with quartz crystals. The quartz crystals are fractured and contain ZnS in the fractures. The crystals do not contain zinc sulfide. The grind of this material can be relatively coarse, and need only be fine enough to assure that the quartz is separated at the fracture lines to permit permeation of the electrolyte.

Comments

The material is friable and thus is easily crushed. The 28 percent zinc content, at today's market (14.75¢) is worth $8.23 per ton, thus making the ore of economic value. The additional value would be:

Silver 0.02 oz. x 1.86 = $0.4
Gold 0.01 oz. x 35.00 = $3.5

Recovery of the precious metal content is marginal. If recovered, the costs would be about 15¢ and the equipment for recovery would probably make the payoff period too great for practical recovery. Therefore, let us assume that these values are too low for recovery.

For calculation, the force necessary to dissociate the metal contained is most conveniently expressed as a function of the ratio KT of the free energy of attraction of two ions at their distance of nearest approach,

\[ b_{0} = -e^{2}Z_{1}Z_{2}/DKT_{a} \]

and of the ratio of this distance to the thickness of the ionic atmosphere, \( r_{a} = 6_{a} \), in which \( \epsilon \) is the protonic charge, \( D \) is the dielectric constant, \( k \) Boltzmann's constant, \( T \) the absolute temperature, and \( k \) the Debye function, which is defined as \( k = (4\pi\epsilon^{2}N/1000DKT)Z_{1}Z_{2}Z_{3}^{2} \), in which \( N \) is Avogadro's number, \( C \) the concentration of species \( i \), in moles per volume (in liquids, liter, in solids, 1000 cc.), \( Z_{1}, Z_{2}, Z_{3} \) are the valences of the \( t, s, \) and \( i \) ions, respectively, \( r_{a} \) the closest distance of approach of a \( t \) ion to an \( s \) ion.
The expression for the activity coefficient of a species \( t \) is:
\[
\ln y_t = Z_t \sum_{t=1}^{\infty} \left( \frac{C_t Z_t}{Z_t} \sum_{t=1}^{\infty} b_{t}\gamma_{t}^{-1} \ln \left( \frac{x_{t}}{Z_t} \right) \right)
\]

The first sum gives the effect of pair interactions of a molecule of species \( t \) with every other ion in solution. The second sum gives the effect of change of ionic strength when a \( t \) ion is added upon the interaction of all possible ion pairs in the solution. Note that the explicit expressions of the concentration occur as ratios of the equivalent concentrations of ions \( t \) or \( r \) to the ionic concentration, so that the only functions of concentration are \( f(x) \) and \( g(x) \). It is convenient to list each of the lower members of the series and to give a general expression for the higher ones:

- \( f_{1} = -x^{-3/2} \)
- \( f_{2} = e^{-x^{1/2}}/\sqrt{x} \)
- \( g_{1} = x^{1/2} \)
- \( g_{2} = e^{-x} \)

The limiting value of \( f_{r} \) for \( r = 4 \) is proportional to \( X_{t}^{3} \), and the limiting value of \( g_{r} \) is proportional to \( X_{t}^{r+1} \) for \( r = 4 \) and to \( X_{t}^{2} \) when \( r > 4 \) so that the limiting value of the contribution of terms in \( r = 4 \) is proportional to \( X_{t}^{3} \). The zeroth term reduces to Van Der Waals' \( f \) times the total concentration. It is compensated in part by a similar term in which molar volume replaces \( b \) when \( ln y \) is reduced to constant pressure.

The first term vanishes if all the ions are of the same size.

The second term corresponds to the Debye-Hückel expression. If all values of \( a_{t} \) are the same, it agrees with the D-H expression to all terms in \( X_{t}^{2} \) but continues to increase for large values of \( X_{t} \) instead of approaching an asymptote. Debye follows the V.D. Waals method of giving the central molecule a radius equal to its diameter and treating the other molecules as points.

The third term vanishes for symmetrical solutions \( (z_{t} = z_{r}) \) and need not concern \( u \).

The great difficulty of a power series in \( b_{t} \) is that, although the series is always convergent, it converges very slowly for large values of \( b_{t} \). The maximum initial slope

\[
b_{t}^{-1/3}(1-3)\]

occurs for \( r \) approximately equal to \( |b_{t}| \). In water at room temperature \( b_{t} \) is approximately \( -72Z_{t}^{2}/2525.06 \). So, for two trivalent ions with a radius of 5A., the maximum is not reached by the tenth term. This, of course, explains the great difficulty of recovering such trivalent ions as \( C_{2}^{3+}, A_{2}^{+} \) from aqueous solutions.

The function

\[
B_{t} = \int_{0}^{b_{t}} X_{t}^{3}(e^{-x} - 1 - x + x^{2}/2 - x^{3}/6) \, dx
\]

which is always positive and, for finite values of \( B_{t} \), is less than \( b_{t} \). When \( B_{t} \) is small, or when the difference between the two curves is small, the true values is much nearer the full than the broken line. The full lines seem to give excellent approximation for \( b_{t} < 10 \), but the uncertainty increases for larger values. \( B_{t} \) passes through O at \( b_{t} = 0 \). For negative \( b_{t} \), \( B_{t} \) increases rapidly enough to compensate for any decrease shown in FIG. 1, so that \( B_{t} \) increases at least as rapidly as

\[
b_{t}^{-2}.
\]

For small positive \( b_{t} \), \( B_{t} \) increases a little more rapidly than for equivalent negative values, and for large positive \( b_{t} \) there is an exponential increase, so that \( B_{t} \) increases much more rapidly than

\[
b_{t}^{-2/3}.
\]

Because of the asymmetry of \( B_{t} \) as a function of \( b_{t} \), \( b_{t} \) is smaller when \( Z_{t} \) has the same sign as \( Z_{r} \) than when the signs are opposite, but because of the factor

\[
b_{t}^{-3/2},
\]

it is larger for divalent ions of the same sign than for two univalent ions of opposite sign, and larger for a trivalent ion of the same sign than for three univalent ions of opposite sign. The interaction of polyvalent ions is associated to lower valence ions of the opposite sign, and leads to association constants which depend greatly on the other ions present.

Referring to FIG. 1, optimum dissociation electrostatic field strength for the various ions pairs as calculated lies between the two slanted broken lines.
Referring to the zinc ore used as an example, we may now calculate ionic dissociation energies for pairs and triplets as follows:

<table>
<thead>
<tr>
<th>Pair</th>
<th>( \Delta G^\circ )</th>
<th>( \Delta G^\circ /\text{ mole} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{2+}, \text{O}^{2-} )</td>
<td>-0.02</td>
<td>-0.02</td>
</tr>
<tr>
<td>( \text{Fe}^{3+}, \text{O}^{2-} )</td>
<td>-0.11</td>
<td>-0.03</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}, \text{O}^{2-} )</td>
<td>-1.77</td>
<td>-0.02</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}, \text{O}^{2-} )</td>
<td>-0.63</td>
<td>-0.03</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}, \text{O}^{2-} )</td>
<td>-0.88</td>
<td>-0.03</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}, \text{O}^{2-} )</td>
<td>-0.68</td>
<td>-0.03</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}, \text{O}^{2-} )</td>
<td>-0.72</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

Average \(-1.74\)

From the foregoing, we see that we have available in the mineral, calculated as voltage, \(-1.74\) volts of free energy. Since the potential required to dissociate the zinc sulfide in this case is \(-6.63\) volts, the electrolyte must supply \(-2.89\) volts of free energy.

Further, the electrolyte must be capable of carrying large current loads, since the minimum electrode current density, for economic reasons, should be 100 ASF (amps per square foot; obtained by dividing the total amps passing through the cell by the total submerged electrode area). It must also be either inert, i.e., not reactive with ore components, or must be regenerated by the electrode reactions, i.e., if \( \text{Zn}^{2+} \) is reacted with \( \text{H}_2\text{SO}_4 \) by the reaction \( \text{Zn}^{2+} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2 \), the reaction is actually (in water) \( \text{Zn}^{2+} + 2\text{H}_2\text{O}^{-} \rightarrow \text{ZnO}^{2-} + 2\text{H}_2 \). If the solution is electrolyzed, the cathode reaction is \( \text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn} \), and the anode reaction is \( 2\text{H}_2\text{O}^{-} \rightarrow \text{H}_2 + \text{O}^{2-} \), thus the active ions \( \text{H}_2\text{O}^{-} \), are regenerated in the recovery (electrolytic) process.

The preferable situation is one in which no reaction occurs and thus there is no leaching of the ore, which results in change in the electrolyte balance. Calculation is much easier, for one thing, if complex factors due to electrolyte change are not introduced.

From the tables, the system citric acid: thiourea has a calculated \(-2.76\) V of free energy available when the concentration is four percent thiourea and the thiourea: citric acid ratio is 4:1. Experimentally, the dissociation constant of zinc sulfide in the system is approximately \(6 \times 10^{-7}\), which is reasonably insoluble. The \( k_d \) of \( \text{FeO} \cdot \text{Fe}_2\text{O}_3 \) in the system is \(8 \times 10^{-21}\) and \( k_d \) of \( \text{SO}_2 \) is \(4 \times 10^{-22}\). No reaction, therefore, may be expected between the magnetite and the silica and the electrolyte.

Thus we may establish, for this ore, thiourea: citric acid as the electrolyte.

We must now examine the electrolyte for other requirements.

First: Current carrying capacity. The resistance per cm.\(^2\) of the solution is 6.3 ohms. Since minimum electrode spacing is 1", electrodes at 1" spacing have a cell resistance of 6.3 x 2.54 = 16 ohms. By Ohm's law \( E = IR \), therefore, \( E = 100 \times 16 = 1600 \) volts. Obviously, this is an absurdity, particularly since the dissociation voltage for the reaction \( 2\text{H}_2\text{O}^- \rightarrow 2\text{H}_2 + \text{O}^{2-} \) is \(2.419\) volts. (Actually, in this electrolyte, the dissociation voltage for \( 2\text{H}_2\text{O}^- \rightarrow 2\text{H}_2 + \text{O}^{2-} \) is \(4.87\) volts.) We can then by substituting in Ohm's law, determine the maximum allowable cell resistance:

\[
R = \frac{E}{I} = \frac{4.87}{100} = 0.0487 \Omega.
\]

The easiest way to reduce the electrolyte resistance is to add conductive ions, however, we must be sure that we adding close to zero free energy value in so doing. Several salts are listed which meet this requirement, such as \( \text{KCl} \), \( \text{NaCl} \), \( \text{Na}_2\text{SO}_4 \), \( \text{K}_2\text{SO}_4 \), etc. Care must be taken that the additive selected will not react with either ore or electrolyte components. It is also desirable that the ionic radii of the added ions be the same as those of the element being recovered (see foregoing discussion in which it is shown that when the ions are the same, the first term of the evaluation equation vanishes).

Thus far, for 100 gallons of electrolyte, we have:

<table>
<thead>
<tr>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
</tr>
<tr>
<td>Citric acid</td>
</tr>
<tr>
<td>Sodium chloride</td>
</tr>
</tbody>
</table>

If the recovery of silver were of significance, either sodium sulfate or potassium sulfite would be used, since the presence of the chloride would form insoluble silver chloride with the silver ions migrating through the electrolyte.

Characteristically, sulfide ores are poorly wet by water, so that the interface between the electrolyte and the zinc sulfide is an area of high resistance. This is eliminated by adding a surfactant to the electrolyte:

<table>
<thead>
<tr>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
</tr>
<tr>
<td>Citric acid</td>
</tr>
<tr>
<td>Sodium chloride</td>
</tr>
<tr>
<td>Surfactant</td>
</tr>
<tr>
<td>Antifoam</td>
</tr>
</tbody>
</table>

The surfactant may be of the alkyl benzyl sulfonate type, and the antifoaming agent of the silicone type, available from Dow-Corning, but any of the surfactants or antifoaming agents now conventionally used in the electrolytic treatment of metals will do.

Experimentally, a small amount of the iron does, in fact, plate from the ore to the electrode. Common practice is to use a tartrate to suppress this; therefore, we add 6 ounces sodium tartrate.

Balancing the electrolyte, we find that we now have -2.79 v. of free energy. To bring this to the optimum of -2.89, we add one of the cyclohexylamines, which have very high free energies. Selecting, because of the citric acid, methyl isopropylcyclohexylamine, and have, as a final formulation for the ore specified:

<table>
<thead>
<tr>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
</tr>
<tr>
<td>Citric acid</td>
</tr>
<tr>
<td>Sodium chloride</td>
</tr>
<tr>
<td>Surfactant</td>
</tr>
<tr>
<td>Antifoam</td>
</tr>
<tr>
<td>Sodium tartrate</td>
</tr>
<tr>
<td>Methyl isopropylcyclohexylamine</td>
</tr>
<tr>
<td>Water, q.</td>
</tr>
</tbody>
</table>

Since the electrolyte is calculated to the ore, there are certain effects which are too complex to admit of calculation, such as crystal strain energy, matrix effects, and others not known to the author, which will have some effect on the optimum ionic concentrations of the electrolyte components, therefore, some pragmatic adjustment of the actual concentrations is required by experimentation to effect maximum recovery and cell efficiency of the electrolyte.

This is done by electrolyzing the ore in a series of electrolytes in which the components are individually varied by a few percent, and noting the effect of the change on the recovery rate (grams per ampere hour) of the metal. These adjustments, although relatively time consuming, are minor in technique and degree.

Utilizing fundamentally the same mathematical procedure, I have calculated electrolytes for several ores. The following examples have been experimentally verified, as will be shown following the calculated values.
We see that we have no free energy available, and that our electrolyte is not only going to have to supply −4.00 volts necessary to overcome the negative free energy of 4.00 volts, but it also must supply 2×−2.57=5.14 volts to dissociate the NiFe from the S, and the Ni from the Fe, for a total energy requirement of −9.14 volts. Needless to say, such electrolyte systems are rare, and systems which are also stable or regenerative are extremely rare. This obviously explains the trade statement that nickel ores cannot be electrolyzed. However, while rare, such systems do exist. Among them are K₃Cr₂O₇·9H₂O and Fe₂O₃ (−10.23 v.) and KMnO₄·H₂SO₄·KB₄F (−11.1 v.) and K₂CO₃·Fe₂O₃·MnO₂ (−9.63 v.). The first requires a pH of 3.17, the second 1.15 and the last a pH of 11.8 for maximum free energy. The use of alkalis is forbidden by the high Al₂O₃ content of the ores; Aluminum is amphoteric and would readily form aluminates, either destroying the electrolyte balance or requiring economically impossible quantities of caustic to maintain the electrolyte composition. The second requires greater amounts of acid than the first to obtain the low pH, and would probably require acids with high dissociation constants, such as the mineral acids which would readily react with the Fe compounds. Also, the potassium permanganate is unstable, and would require an inert atmosphere at the cell, and would react with any organic matter included in the material flow through the cell. The first is easily prepared, economical, and the pH may be readily attained with an inexpensive organic acid, such as acetic, which has a low dissociation constant, and which will not react with any of the analyzed components of the ore. Agricultural grades of these chemicals are readily available throughout the world and are inexpensive.

Thus, we may use a basic formulation:

\[
\begin{align*}
K_2Cr_2O_7 & \quad \text{pound} \quad 11.3 \\
MnSO_4 & \quad \text{do} \quad 17.6 \\
FeCl_3 & \quad \text{do} \quad 5.8 \\
Acetic Acid & \quad \text{do} \quad 3.9 \\
Surfactant & \quad \text{ounce} \quad 8 \\
Antifoam & \quad \text{do} \quad 4
\end{align*}
\]

Looking at the free energy of the electrolyte, we find −11.07 v., which has to be reduced to minimize the iron content of the plated metal. Iron cannot be avoided in the deposited metal due to the formation of Fe ions when the FeNi dissociates, and will deposit equimolar with the Ni, however, conventional electrolytic purification or smelting procedures will refine the nickel. For example, melting the deposited cathode metal and blowing it with oxygen prior to casting will drastically reduce the iron content.

\[
\begin{align*}
\text{NiS}_2O_3 & \quad \text{pound} \quad 11.3 \\
\text{FeO} & \quad \text{do} \quad 17.6 \\
\text{FeCl}_3 & \quad \text{do} \quad 5.8 \\
\text{Acetic Acid} & \quad \text{do} \quad 3.9 \\
\text{Surfactant} & \quad \text{ounce} \quad 8 \\
\text{Antifoam} & \quad \text{do} \quad 4
\end{align*}
\]
The electrolyte may comprise:

- Ammonium carbonate, grams: 13.7
- Ammonium hydroxide 29%, ml: 47
- Ammonium chloride, grams: 1.1
- Ammonium cyanide, do: 1.0
- Detergent, as in Example III, do: 0.4
- N-propylcyclohexylamine, grams: 0.4
- Antifoam, as in Example III, do: 0.4
- Sugar, lb: 8.75
- Water q.s., gal: 30

When dissolved, add:

- Ammonium tartrate, grams: 0.3

1. Sodium or potassium cyanide may be substituted in proper molecular ratio.

V.—For use on an ore containing copper oxide and copper sulfide in a ratio of 60% oxide to 40% sulfide:

- Pyridine, mol: 0.1
- Pyridine chloride, mol: 45.0
- Sodium hydroxide, percent: 5.0
- Gelatin, do: 0.01
- Ammonium hydroxide, do: 4.0
- Water q.s., do: 100.0

VI.—For use on a 99% pyrolose ore containing 62.93% manganese, balance substantially all oxygen:

- Sulfuric acid, lb: 8.3
- Ammonium sulfate, lb: 35.1
- Cellulose, oz: 6
- Acetic acid, oz: 3
- Isobutyl-n-propylcyclohexylamine, oz: 8
- Sugar, oz: 8
- Detergent, as in Example III, oz: 3
- Antifoam, as in Example III, oz: 2
- Water q.s., gal: 30

VII.—For use on an ore consisting essentially of calcium carbonate and calcium silicate in a ratio of 3 parts of carbonate to 5 parts of silicate and containing 6 oz. of gold per ton:

- Sodium cyanide, lb: 8.3
- Sodium sulfide, lb: 15.8
- Detergent, as in Example III, oz: 4
- Triethanolamine, oz: 6
- Isopropylcyclohexylamine, oz: 3
- Sodium carbonate, lb: 4
- Water q.s., gal: 10
- Antifoam, as in Example III, as required.

This may be diluted approximately 10:1 for use, and the dilution adjusted to best recovery.

VIII.—For use on copper sulfide ore:

- Sodium dichromate, lb: 1.64
- Sulfuric acid, gal: 5.5
- Copperas, lb: 31
- Cellulose, lb: 13
- Hydrochloric acid, long do: 8
- Methyisopropylcyclohexylamine, oz: 9
- Detergent, as in Example III, oz: 4
- Antifoam, as in Example III, oz: 6
- Sodium tartrate (add last), lb: 2.3
- Water q.s., gal: 30

IX.—The following electrolyte has been successfully used to extract traces of gold and silver from mine tailings:

- Sodium carbonate, lb: 15
- Ammonium acetate, lb: 13
- Sodium cyanide, lb: 25
- N-propylcyclohexylamine, oz: 8
- Detergent, as in Example III, oz: 8
- Antifoam, as in Example III, oz: 6
- Sodium hydroxide, lb: 75

Sugar, oz: 4
Ammonium hydroxide 29%, lb: 30
Water q.s., gal: 30

The foregoing examples are given as actual electrolyte compositions and voltages based upon the analysis of the ionization potential of the particular ores for which the electrolytes were compounded. It should be remembered that the same mineral in a different base rock or matrix may require a different electrolyte. Since each element and compound in the ore contributes a value to the calculation of the electrolyte ionization potential, changes in composition require corresponding calculations to formulate the appropriate electrolyte.

The foregoing electrolytes set forth as examples pertaining to specific ores may be introduced into an installation of the type illustrated in FIG. 2 or any cell capable of passing the ore electrolyte slurry between the anode and the cathode. The cathode may be made of an electrically conductive material which may be the same element being recovered from the ore or may be of a dissimilar type of material from which the recovered metal can be chemically, electrically, or mechanically removed, as in the case of the zinc electrode used in the recovery of zinc, whereby the cathode is melted at the time the recovered zinc is melted; or similarly, as in the case of the stainless steel electrodes used for the electrical recovery of zinc whereby the built-up zinc sheet is mechanically stripped from the stainless steel electrode. The anode may be made of a non-consumable electrically conductive material such as platinum, iron, lead, gold, carbon, or similar materials. The anode and cathode are spaced from each other and from the membrane, if such membrane is used, for optimum recovery, which spacing and method of determining the spacing is well known to workers in the art. For example, an inter-electrode spacing ranging from 1/4 to 3 inches has proven to be an optimum range for most electrolytes, with the membrane, where used, suspended between the electrodes in such a fashion to allow a commercially adequate thickness of metallic deposit upon the cathode. The filter membrane is an indissoluble material which has openings of a proper size to prevent the passage of ore particles. Such materials are typified by woven polypropylene, woven nylon, cotton, plastic or woolen cloth; porous membranes made of flexible or non-flexible materials, such as porous Teflon, left or porous ceramic materials, or by membranes of the types used in osmosis and dialysis, which may be used if the ore slurry and method of ore suspension should require a membrane to prevent entrapment of ore particles in the deposited metal. The properties of various materials for the construction of the anode and cathode are described in any handbook of chemistry and physics, such as that published by the Chemical Rubber Company; and the desired materials are readily available from manufacturers of the materials used for such purposes.

In laboratory tests of the electrolytes used in the foregoing examples an electrolyzer of standard design was used. This laboratory electrolyzer is commonly known to all those skilled in the art. Platinum electrodes and a polyethylene cloth membrane were employed with a spacing of ½ inch between the anode and cathode area of 6.28 in.2 and an anode area of 6 inches in 2 immersed 2 inches in the slurry. Other conductors may be used as electrodes, providing that they are non-consumable in the process, and based on their electrical characteristics which may be found in a table listing the properties of metals as conductors which may be found on page 80 of the 1968-69 edition of the Handbook of Chemistry and Physics, a standard reference work, published by Chemical Rubber Company, as well as in other standard texts.

Using the specific ores for which the electrolytes were developed in the examples set forth herein and as referred to in the following paragraph, column 1 shows the re-
spective mesh; column 2 shows the respective cathode voltage used; and column 3 represents the current density used; however, considerable variation is allowable. It will be appreciated that the values given in the foregoing examples were selected to produce optimum results for the specific apparatus, ores, and electrolytes disclosed. In terms of voltage, the plate voltage is determined by the equation appearing on page 19 in the paragraph beginning with line 8 of this specification. The amperage loading must be determined experimentally for each cell designed since it is a function of the cell design and is affected by such things as electrode space, electrolyte temperature, and electrode conductivity. Efficient plating of most metals on the cathode occurs at a load of approximately 10 amperes per square foot and below. Dendritic deposition occurs in the range from 25–50 amperes per square foot loading. These cathode loadings can be affected by additives. For example, the addition of a commercial brightener will frequently allow higher amperage loadings—such as the addition of 0.5% of Udeleye No. 34 nickel brightener to the electroless nickel electrolyte permits solid plate-out at 75 amperes per square foot. The techniques for obtaining maximum deposition in any given case are well known to workers in the art. Udeleye 34 is an addition agent which is a proprietary compound. Other similar compounds are manufactured by other companies such as Dow Chemical Company; but all are proprietary, and the formulations are neither published nor known to the public. Sugar, glycerein, and gelatin are addition agents which frequently will permit higher amperage loadings but do not have the scope, range, and capacity of the proprietary compounds.

Either dendritic or solid plate may be achieved by proper manipulation of plating rate, solution temperature, additives, and current density. Generally, higher the current density the greater the possibility of dendritic deposition. Either type of plate may be advantageous. Dendritic deposition allows continuous cell operation since the deposited metal may be easily removed from the cell. Solid deposition is readily used in many industrial processes. It is cleaner (less entrapped electrolyte) and melts with less oxidation. Solid plate could allow finish plate from the ore; i.e., bumpers, circuit boards, and other objects could be plated in a slurry cell. **ADVANTAGES**

The following advantages are found in this process for the recovery of metals from their ores:

1. Recovery can be made in excess of 99%.
2. Cell efficiencies in excess of 85% can readily be achieved.
3. Since the electrolyte may be recovered from the depleted ganse removed from the cell, the only chemical costs involved are the replacements of water and chemicals lost through evaporation and irrecoverable dragout.
4. Use of this process permits recovery of metals at the mine site, eliminating many transportation and process costs.

5. Electrolytes can be formulated so that all of the metals in a complex ore can be simultaneously extracted or in such a manner that they are selectively extracted.
6. This electrolytic system may be compounded for the purification of some industrial plant wastes thus preventing contamination of water systems.
7. In many, but not all, ores this system will eliminate the need for concentration systems.
8. Some non-metallic elements may be recovered by this process.

What is claimed is:

1. The method of refining metallic ores which comprises the steps of intimately contacting the metallic components of said ore with an electrolyte within an electric field of an electrolytic cell, adjusting and maintaining the surface energy or ionization potential supplied by the ionized components of said electrolyte at a level that is less than the sum surface energy or ionization potential of the ore plus the energy contributed to the cell.
2. The method claimed in Claim 1 in which the ionization potential of said electrolyte is substantially equal to that of said ore.
3. The method claimed in Claim 2 in which said ore contains a plurality of different metals which are ionized on an electrode of said cell.
4. The method claimed in Claim 1 in which said cell is heated.
5. The method claimed in Claim 1 in which said electrolyte and a ground ore are formed into a slurry which is passed through said cell as a moving bed having the maximum thickness at which loss of metal to the tailings is avoided.
6. The method claimed in Claim 1 in which said electrolyte is inert with respect to the components of said ore.
7. The method claimed in Claim 1 in which said electrolyte is regenerated by the reactions which ionize the metal in said ore.
8. The method claimed in Claim 1 in which said electrolyte has a low electrical resistance.
9. The method claimed in Claim 1 in which the radii of the ions in the electrolyte are substantially equal to those of the metallic ions to be separated from said ore.
10. The method of Claim 1, including the steps of calculating the ionization potential of the ore and preparing an electrolyte having a substantially equal ionization potential.
11. The method claimed in Claim 1 in which said metal is zinc and said electrolyte consists principally of thiourea, an organic acid, and sodium chloride.
12. The method claimed in Claim 1 in which said metal is nickel and said electrolyte consists principally of K2Cr2O7, MnSO4, FeCl3 and an organic acid.
13. The method claimed in Claim 1 in which said metal is gold and said electrolyte consists principally of KCN, NaOH, and an organic acid.
14. The method of Claim 1, in which said ore is sulfide ore and said electrolyte is a thiocyanate or thiourea solution which has been acidified with an organic acid.
15. The method of Claim 1, in which said ore is an ammoniacal metal ore and said electrolyte solution contains an alkali hydroxide.
16. The method of Claim 1, in which said ore is an oxide ore and said electrolyte is a mildly acidified dichromate solution.
17. The method of Claim 1, in which said ore is a zinc sulfide ore and said electrolyte comprises thiourea, citric acid, one or more salts selected from the group consisting of KCl, NaCl, Na2SO4 and K2SO4, a surfactant which reduces the resistance between the interface
of the zinc sulfide and the electrolyte, and an antifoaming agent.

18. The method of Claim 1, in which said ore is a (NiFe)₉S₈ ore and said electrolyte comprises K₂Cr₂O₇, MnSO₄, FeCl₃, acetic acid, a surfactant, an antifoaming agent and triethanolamine.

19. The method of Claim 1, in which said ore is a gold-quartz ore and said electrolyte comprises KCN, NaOH, a surfactant and an antifoaming agent.

20. The method of Claim 1, in which said ore is a copper carbonate ore and said electrolyte comprises Na₂CO₃, NaOH, NaCN, CH₃COONa, a detergent, and an antifoaming agent.

21. The method of Claim 1, in which said ore is a nickel laterite ore and said electrolyte comprises (NH₄)₂CO₃, NH₄OH, NH₄Cl, a detergent, and antifoaming agent and water.

22. The method of Claim 1, in which said ore is a copper oxide and copper sulfide ore and said electrolyte comprises pyridine, pyridinium chloride, NaOH, gelatin, and water.

23. The method of Claim 1, in which said ore is a pyrolusite-manganese ore and said electrolyte comprises sulfuric acid, ammonium sulfate, acetic acid, sugar, a detergent, an antifoaming agent and water.

24. The method of Claim 1, in which said ore is a calcium carbonate-calcium silicate ore and said electrolyte comprises NaCN, Na₂S, a detergent, an antifoaming agent and water.

25. The method of Claim 1, in which said ore is a copper sulfide ore and said electrolyte comprises sodium dichromate, sulfuric acid, HCl, a detergent, an antifoaming agent and water.

26. The method of Claim 1, in which said ore is extracted gold and silver from mine tailings and said electrolyte comprises Na₂CO₃, ammonium acetate, NaCN, N-propylocyclohexylamine, a detergent, an antifoaming agent, NaOH, sugar, NH₄OH, and water.

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R. L. ANDREWS, Assistant Examiner

US. Cl. X.R.