

[54] PROCESS FOR THE ELECTROLYTIC REFINING OF HEAVY METALS

3,707,448 12/1972 Veloso ..... 204/105 M

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[57] ABSTRACT

[21] Appl. No.: 309,899

This invention provides an improved electrolytic process for obtaining the elemental metal by electrodepositing from an aqueous solution of a halide of the metal. The improvement comprises the presence of an alkali metal halide or an alkaline earth metal halide dissolved in the electrolyte solution. This process is preferably applicable to obtaining the respective metal from the halides of nickel, cobalt, tin, iron and manganese.

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[51] Int. Cl. .... C22d 1/24, C22d 1/14, C22d 1/18

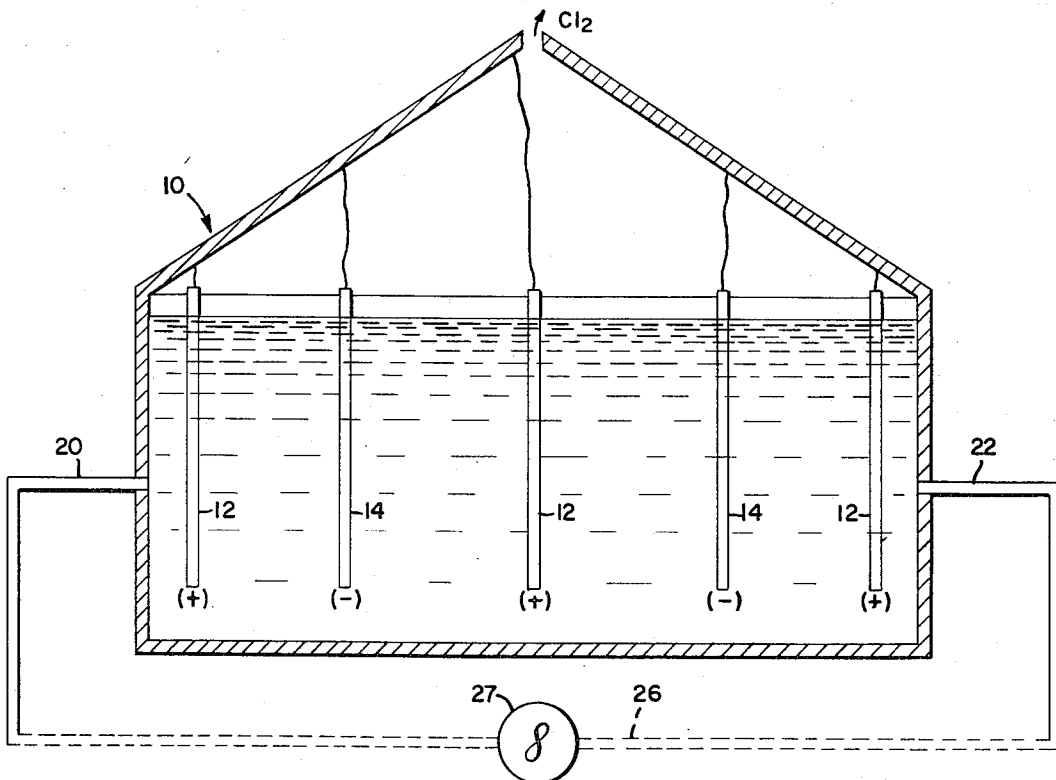
[58] Field of Search..... 204/113, 105 M, 118, 122, 204/128, 98

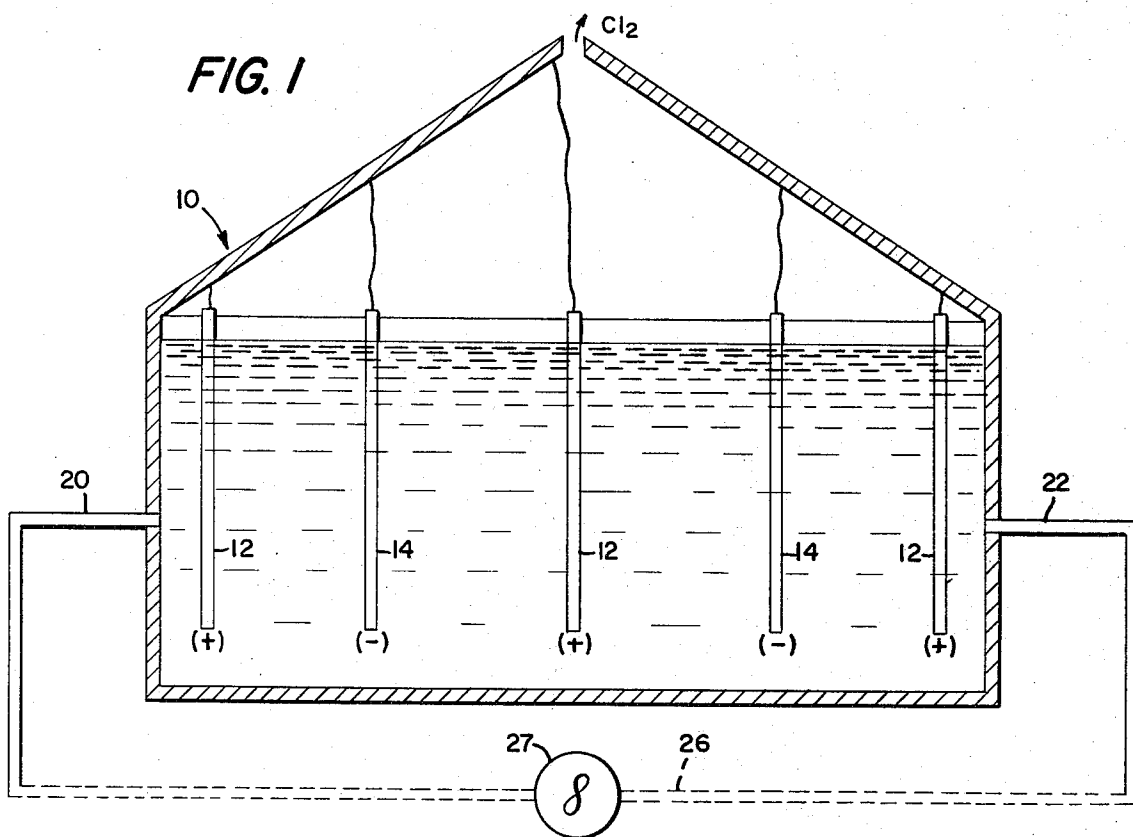
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28 Claims, 5 Drawing Figures





SHEET 2 OF 5

80gpl NICKEL ELECTROLYTE  
ANODE-CATHODE SPACING - 2-INCHES

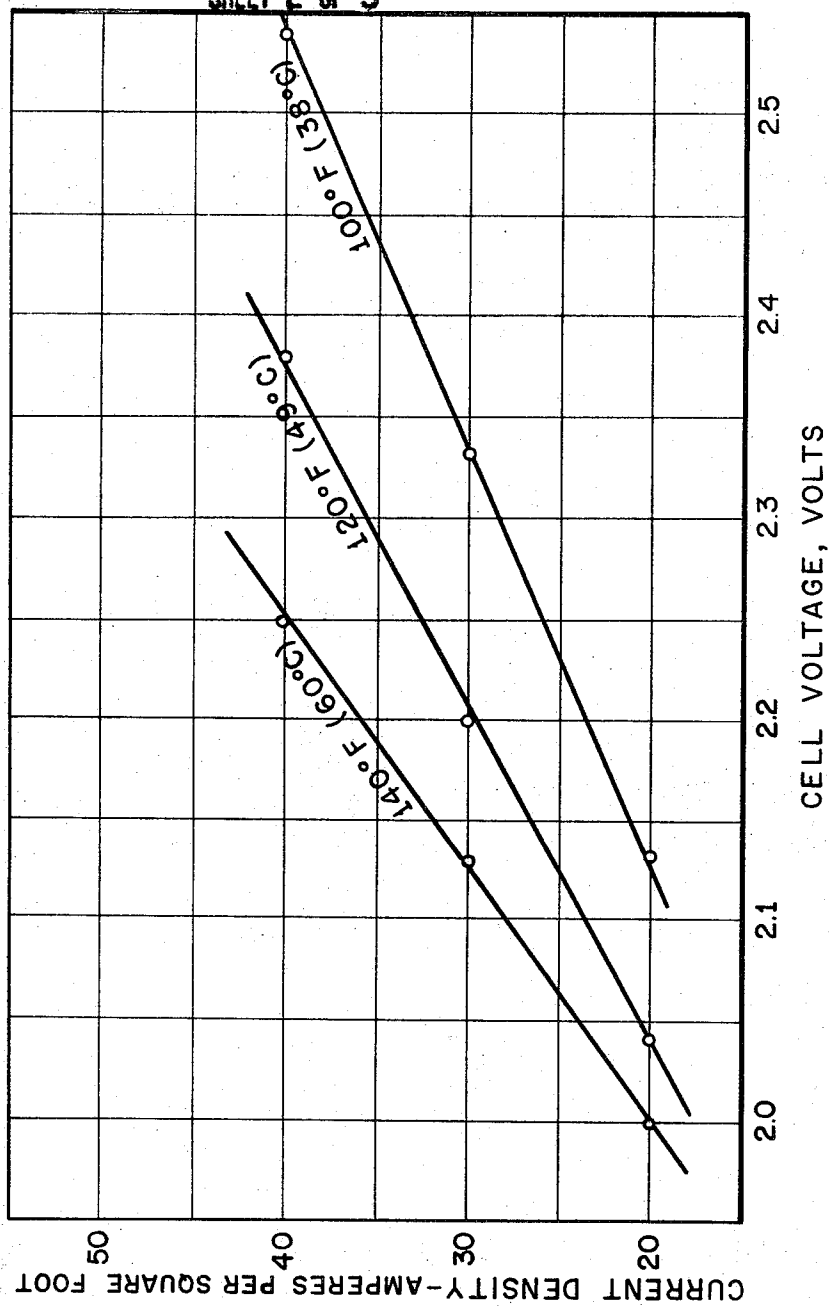


FIG. 2

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80 gpi COBALT ELECTROLYTE  
ANODE-CATHODE SPACING - 2-INCHES

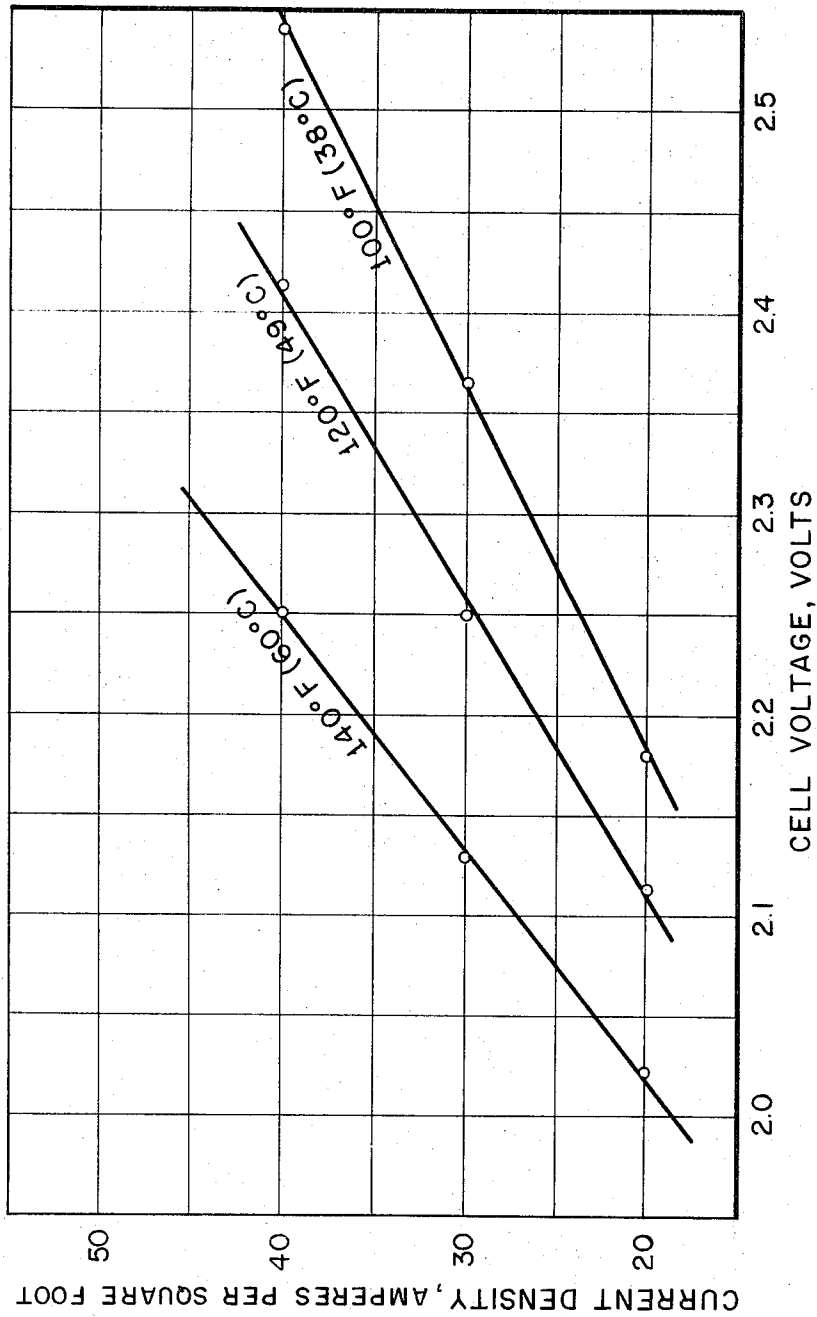


FIG. 3

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NICKEL ELECTROLYTE

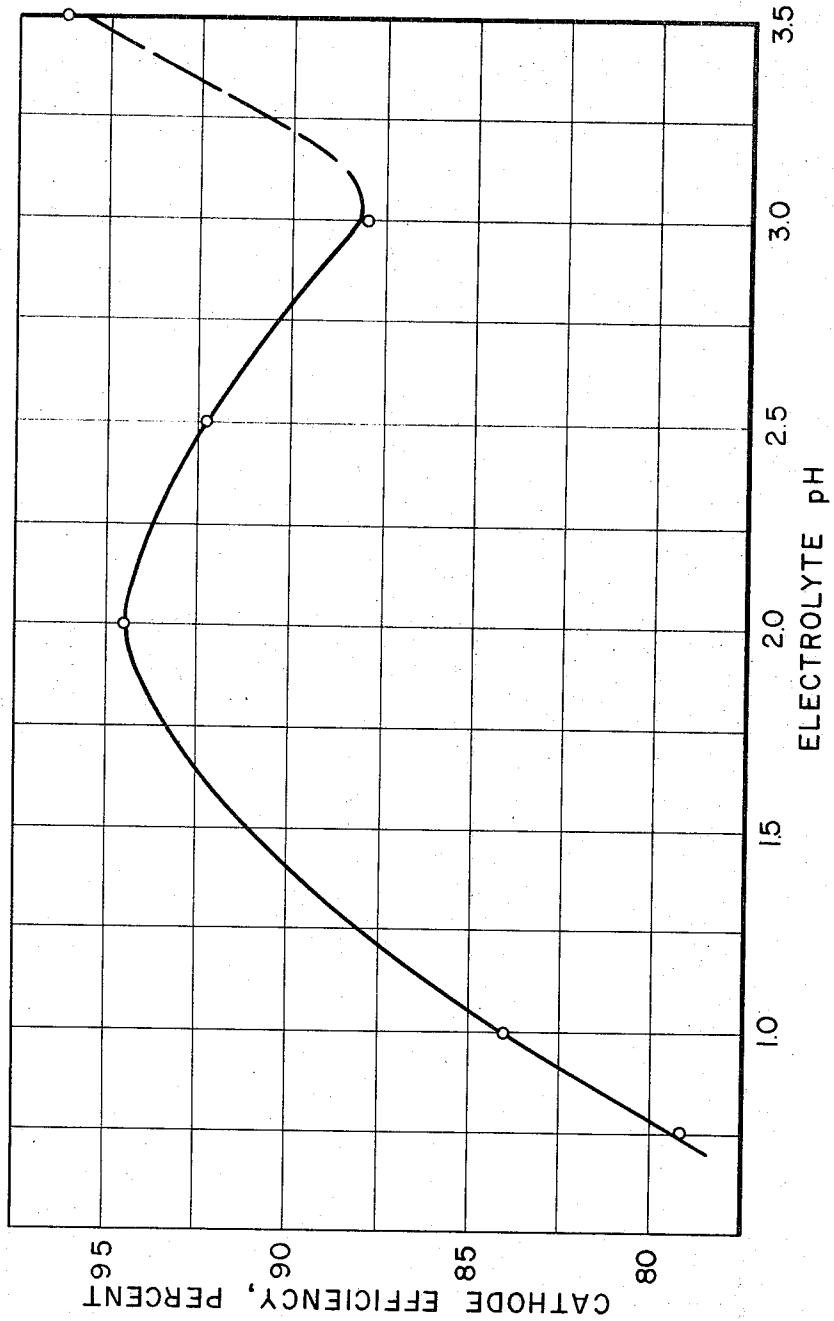


FIG. 4

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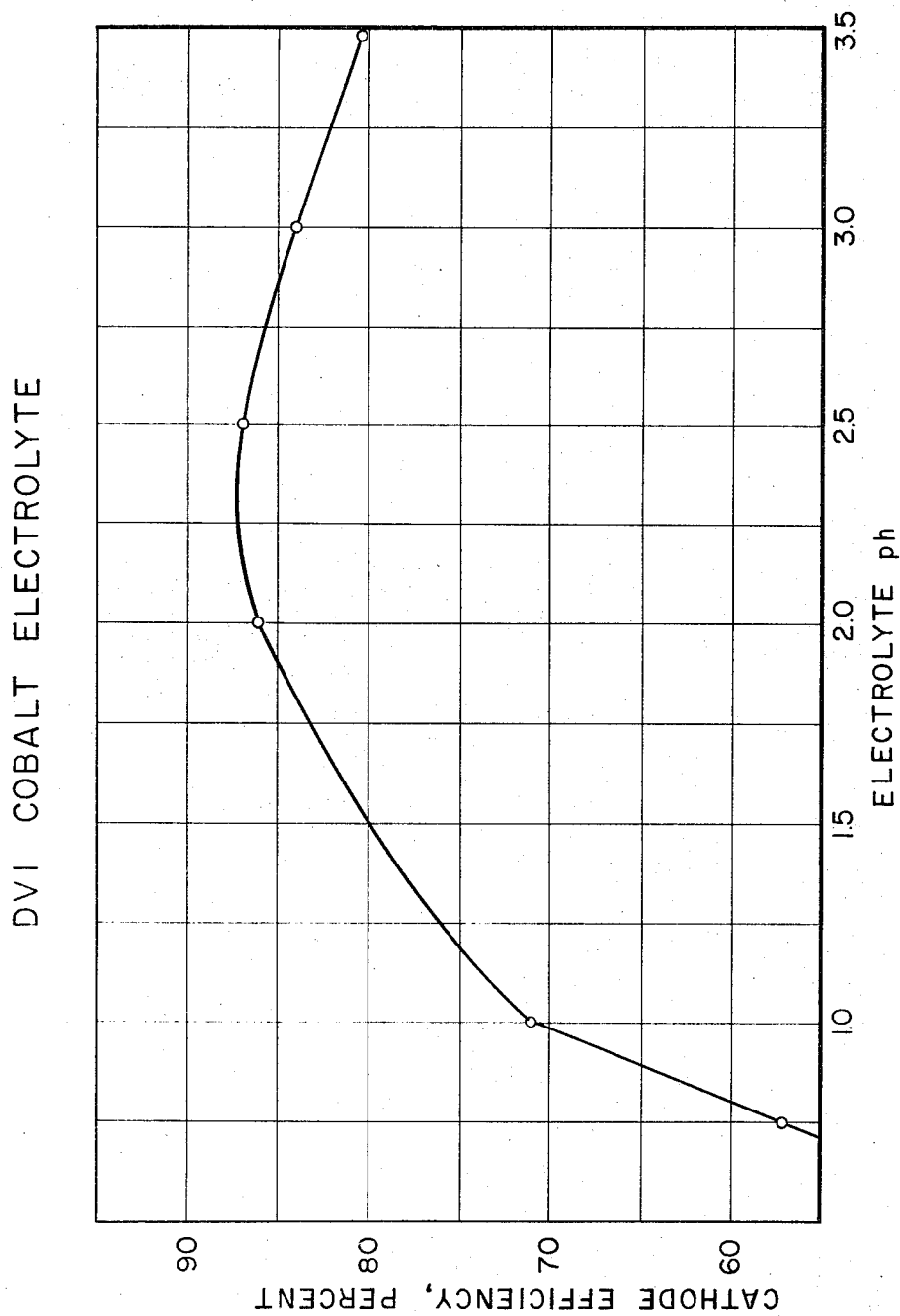


FIG. 5

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## PROCESS FOR THE ELECTROLYTIC REFINING OF HEAVY METALS

A process sometimes used commercially for the electroplating of nickel utilizes an aqueous electrolyte solution of nickel halide. Similar cobalt electroplating processes have been carried out utilizing aqueous solutions of cobalt halide. Generally, among the halides, the chlorides are preferred as they are the most economically attractive.

Further, the chloride ion is the most mobile of the halide ions and, therefore, most efficient in any electrolysis operation. The electroplating operation not only results in the plating out of the pure metal at the cathode but also, under certain circumstances, results in the evolution of the elemental halogen, e.g., chlorine gas, at the anode.

One example of a nickel chloride electrolysis cell is described in *Chlorine, Its Manufacture, Properties and Uses, ACS Monograph Series No. 154*, J. S. Sconce, Editor (Reinhold, 1962), see page 230. Nickel metal is electroplated as an intermediate step in the production of  $\text{Cl}_2$  from  $\text{HCl}$ . Two cells are used at a given time; one cell acts as a nickel plating electrolysis cell and the second acts as a nickel dissolving cell. The roles of the two cells are periodically reversed. For example, nickel deposits on the cathode and chlorine is released at the anode of one of the cells, which contains an aqueous solution of  $\text{NiCl}_2$  as the electrolyte, while nickel chloride is being formed in the second cell to feed the first cell. When the nickel has been deposited to the desired extent on the cathode of the first cell, the operations of the cells are reversed: the electrolysis is halted in the first cell and the nickel deposit is dissolved by feeding hydrochloric acid to the first cell to form nickel chloride and hydrogen. The nickel chloride solution produced in the first cell is fed to the second cell in which the nickel chloride is electrolyzed to plate out nickel and to form chlorine. When there is a heavy deposit of nickel on the cathode of the second cell, the operations of the cells are again reversed.

Any excess hydrochloric acid in the nickel chloride solution fed to the electrolysis cell is neutralized by a base, e.g., sodium hydroxide, resulting in the formation of, e.g., sodium chloride, salt, which remains in solution, building up to a level at which it precipitates out in the nickel-dissolving cell. The effluent from the nickel dissolving cell is filtered to remove any precipitated sodium chloride prior to its being recycled as a feed stream back to the chlorine-forming electrolysis cell.

Sconce describes a procedure for using nickel as an intermediate in the production of chlorine and requires the plated nickel to be as readily soluble in hydrochloric acid as possible. Thus, the process described by Sconce is directed towards forming as reactive a nickel plate as possible, i.e., having a high surface area, and being highly porous, spongy and "treed."

Such a nickel plate is obtained by utilizing a very high concentration of nickel in the solution in the cell. This results in a nickel plating which has the high surface area desirable for the chlorine-producing process, but not a plating suitable for the production of the metal, per se. Similarly, in the process described by Sconce, it is not necessary to maintain a constant pH because the presence of hydrochloric acid or of hypochlorous

acid is not undesirable when the quality of the nickel plated out is not relevant.

In earlier nickel chloride electrolysis operations, for the preparation of a nickel plate, the nickel chloride is generally admixed with a buffering agent, e.g., boric acid, to prevent the decrease in pH generally associated with such chloride electrolysis operations. The decrease in the pH is generally caused by the reaction of the chlorine gas with water to form hypochlorous and hydrochloric acids.

The problem of controlling pH and preventing the formation of hydrochloric and hypochlorous acid (HCLD) (both of which readily degrade plated metal) is difficult and is perhaps the major reason why, in most commercial operations throughout the world, the sulfate salt is utilized as the electrolyte in a cell in which the anode and cathode are separated by a semi-permeable diaphragm. Otherwise, halide electrolysis is preferable. The deposits of pure nickel metal from the chloride solution, compared to deposits obtained utilizing a sulfate electrolysis solution, are finer grained, harder, smoother, stronger and less brittle. Furthermore, compared to the sulfate ions, the halide ions are more efficient carriers of electricity and can thus operate at lower voltages and at higher current efficiencies. There is further less tendency to pit and form module growths and "trees" on the deposits.

It has been suggested to use all-chloride baths, buffered with boric acid, for cathodic electroplating of nickel in a cell which does not require a diaphragm. The buffering agent must be very carefully monitored and maintained during the course of the electrolysis, or cathodic electroplating. This requires relatively expensive and complicated controls and lessens the commercial value of the nondiaphragm process.

It had further been suggested, at a time when wood was a relatively cheap and desirable material of construction, that the addition of sodium chloride to a nickel chloride plating bath, buffered in the usual manner, would allow the use of wooden cell tanks for the electrolysis process.

The use of nondiaphragm cell, as opposed to a cell wherein the anode and cathode compartments are separated by a semi-permeable diaphragm, is desirable as simplifying the construction and the operation of the cell with a concomitant decrease in cost. The required use of a buffering agent, however, tends to outweigh these advantages, at least in part.

It must be pointed out that there is a significant difference between the problems found in electroplating of a metal to form a relatively thin skin of the plated metal and in electro-refining, where larger bulk quantities of the metal are formed and for which the use of buffers becomes substantially impractical.

For a discussion of the electroplating of nickel from chloride electrolyte, see an article by Wesley et al. in *Transactions of the Electrochemical Society*, Volume 75, page 209 (1939) and an article by Blum, et al. *Transactions of the Faraday Society*, Volume 31, page 1203 (1935) and for subsequent improvements thereon, see the article by Pinner et al., *Monthly Review of the American Electroplaters Society*, Volume 32, page 237 (1945).

Suprisingly, it has now been found to be possible to carry out the electroplating and electrorefining of nickel and other heavy metals from their halides, in a single compartment cell, without a diaphragm, and

without the use of a buffering agent, by the addition of an inert source of halide ion to the electrolyte solution. The presence of the additional halide tends to maintain the pH of the electrolyte solution substantially constant during the electroplating of the heavy metal onto the cathode and the evolution of halogen at the anode and to yield a high quality metal deposit. In a most preferred embodiment, the feed solution to the electrolysis cell is substantially saturated in the neutral source of halide.

This invention, therefore, provides an improved process for refining electrolytically a heavy metal to form a fine-grained, hard, smooth, strong, dense and not brittle deposit of the metal, and to evolve a halogen, from an aqueous electrolyte solution containing dissolved therein a halide of the desired heavy metal, the electrolysis being carried out utilizing an insoluble anode, the improvement comprising the presence in the electrolyte solution of an inert halide (which can be an alkali metal halide or an alkaline earth metal halide) which is inert under the conditions of the electrolysis of the heavy metal. The inert halide is preferably present in an amount of at least about 60 percent of its saturation concentration in the electrolyte solution. The maximum concentration of the inert halide in the electrolyte solution is limited only by solubility and is optimally the saturation concentration of the neutral halide in the electrolyte solution.

The electrodepositing of metal from an aqueous solution of the metal halide is generally applicable to some of the so called "heavy metals" or "transition" elements of Groups VIIA, VIII, IV B and II B of the Periodic Chart of the Elements. Generally, this process can be used to deposit a metal which is itself not reactive with halide ion in solution at the concentration present in the electrolyte of the present invention. The halide salts of the deposited metal must be soluble in all of the metal's lower valence states, if the metal is a multi-valent element and is fed in a compound at one of the higher valence states. The process is most effectively used for the electrowinning of nickel, cobalt, manganese, tin, iron and zinc from aqueous solutions of the respective halide salts. The halide used is usually the chloride, although iodides and especially bromides are also commercially useful. If desired, a mixture of halides of two different platable metals can be utilized. For example, a mixture of nickel halide and cobalt halide can be electrolyzed to obtain alloys of nickel and cobalt at the cathode.

The alkali metal halide or alkaline earth metal halide present in the electrolyte in accordance with the present invention must be strongly conductive and should not introduce a cation which itself is electrolyzable under the conditions of the cell or which in other ways effect the plating of the desired heavy metal. The alkali metal halides and alkaline earth metal halides are useful in all cases. Useful halides of an alkali metal or an alkaline earth metal include, for example, the chlorides, iodides and bromides of sodium, potassium, cesium, lithium, magnesium, barium, calcium, strontium and rubidium.

Mixtures of two different metal cations and different halide anions can be present, e.g., two different alkali metal halides or one alkali metal halide and one alkaline earth metal halide, can be used, as long as, e.g., the concentration of the salts is at least about 60% of their combined saturation. That is, if a certain amount of a

mixture of alkali metal halides and/or alkaline earth metal halides can be added to an electrolyte solution before forming a precipitate of at least one of the alkali metal halides or alkaline earth metal halides, 60% of that amount is an operable minimum amount of the mixed halide.

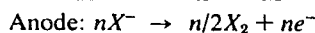
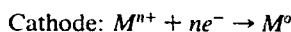
Although it is generally desirable to utilize the same halide ion for both the compound of the metal to be plated and for the alkali metal or alkaline earth metal halide, different halide ions can be utilized. This may create a problem in that the halogen which is generated at the anode may not be pure. However, it has been noted that the use of different halides can aid in maintenance of the desired high quality metal cathodic deposit, which is the primary consideration.

The pH of the electrolyte solution in the cathodic deposition operation affects the cathode current efficiency, and the quality and the internal stress properties of the metal electrodeposited on the cathode. Accordingly, it is highly desirable to maintain the pH of the electrolyte within the cell constant within certain optimum limits. This can be accomplished by the presence of the alkali metal halide or alkaline earth metal halide in the electrolyte solution in accordance with this invention.

The improvement of the present invention for example, is generally applicable to the so called "all-Chloride" nickel electroplating or electrorefining process, wherein all of the metal to be electrowon, e.g., nickel, is present as the halide. The parameters and the compositions for such procedures are generally set forth, for example, in *Graham Electroplating and Engineering Handbook*, (1971), page 247.

The so called "all-chloride" electroplating procedure was originally conceived for nickel and is readily extended to other heavy metals, especially cobalt. Early work on these processes is described, for example, in an article by Wesley et al. in *Transactions of the Electrochemical Society*, Volume 75, page 209 (1939) and in an article by Blum, et al., *Transactions of the Faraday Society*, Volume 31, page 1203 (1935) and for subsequent improvements thereon, see the article by Pinner et al., *Monthly Review of the American Electroplaters Society*, Volume 32, page 237 (1945).

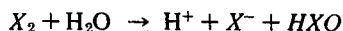
Generally, the improvement of the present invention is applicable to an electrowinning or an electroplating process carried out in electrolytic cells containing an aqueous solution of the metal halide, the cell having at least one each anode and cathode. The reactions taking place in the cell are as follows:



where  $M$  is the heavy metal,  $X$  is the halide and  $n$  is the valence of the metal.

Optimally, the solvent, water, should not enter into any reaction. However, a side reaction that can occur is between the elemental halogen and water which results in the formation of a hydrohalic acid and a hypohalous acid, as follows:





Thus, as a result of this undesirable side reaction, the pH of the electrolyte solution is sharply lowered. This side reaction, of course, also decreases the yield of halogen. The side reaction is especially troublesome when electrolyzing chlorides.

This procedure can be carried out within the parameters for operating "all chloride" or the related types of electrodeposition processes. Generally, the electrolyte solution fed to the cell can contain from about 0.3 up to about 2 gm-atoms per liter of the heavy metal, present as the halide, and preferably up to about 1.5 gm-atoms per liter of heavy metal. The maximum desirable concentration in the solution of the heavy metal to be electrodeposited onto the cathode is limited by the quality of the metal deposit required. Concentrations of the heavy metal in the electrolyte solution fed to the cell higher than the above tend to result in less desirable physical forms of heavy metal deposits.

The desirable pH for the electrolysis of most of the heavy metals, such as nickel and cobalt, is optimally in the range of from about 2 to about 2.5 but can be as low as about 1 and as high as about 3.5 without decreasing efficiency or quality of the product to below a commercially acceptable level. The pH, in accordance with this process, can be maintained substantially constant, or at least the change in pH can be limited, at the value initially set by the presence of the inert halide, without a buffering agent.

Cathode current density for these electrolysis processes is not critical and can vary depending upon the rate at which it is desired to deposit the metal. It is often necessary to balance the desired rate against the desired cathode efficiency. Generally, at a cathode current density of from about 10 to about 50 amperes per square foot, and preferably from about 30 to about 40 amperes per square foot, a useful commercial process can be effected: the cathode efficiency is at a sufficiently high level to render the process economically feasible.

The operation of this process is preferably carried out by feeding in rich electrolyte solution and withdrawing spent electrolyte solution continuously, thus maintaining an electrolyte concentration within the desired range in the cell. If desired, a recirculating or batch cell, can be utilized, i.e., the same solution is recirculated several times through a cell past the electrodes.

The efficiency is measured as the cathode efficiency. Preferably, an efficiency of at least about 75 percent and optimally at least about 85 percent should be obtained. However, efficiency is a function of economics and is not crucial to the operation of the process of the present invention.

The cathodes which are preferably used in the process of the present invention are "starter sheets," formed of the same metal as is to be deposited. This permits the formation of a discrete cathode product which can be removed and utilized as solid metal. The use of an insoluble, inert, cathode, nonreactive in the electrolyte solution, such as stainless steel, results in a deposited metal which must be chipped off or marketed as a sandwich product, or which is deposited as thin pliable sheets which can be peeled off from the cathode.

The so called starter sheet can be readily prepared from a conventional soluble anode-type, electrolyte cell. For example, in the starter sheet formation process, an aqueous electrolyte comprising 300 grams per liter  $NiSO_4 \cdot 6H_2O$ , 20 grams per liter sodium chloride and 30 grams per liter boric acid, is prepared having a pH of 4.0. The electrolyte is maintained at a temperature of 125° F. The electrolysis cell utilizes a soluble metal anode e.g. nickel of the metal desired to be electroplated e.g. nickel. The cathode has a surface from which a thin sheet of the metal can be readily removed or peeled. Suitable cathodes for making starter sheets include specially treated stainless steel cathodes, which permit ready removal of thin ductile sheets of the electroplated metal.

Alternatively, the preparation of the starter sheet can be carried out in an all chloride bath.

Preferably, the anode for use in the process of the present invention is of the type insoluble, or substantially inert, or nonreactive in the electrolysis system.

Suitable materials for forming insoluble electrodes, for use as the anode, include materials such as graphite, insoluble lead anodes, especially antimonial lead, platinum, platinum-coated materials, such as platinum-coated titanium and ruthenium-coated materials, such as ruthenium-coated titanium.

Each cell can include a single cathode and a single anode or can include a battery of positive and negative electrodes. For example, a series of plates, either all insoluble electrodes, such as platinum, but preferably alternating insoluble anode and metal starter sheet cathodes, can be utilized wherein the electrodes are separated by from about 2 to about 6 inches and preferably from about 2 to about 3 inches.

In conventional operation, the two end electrodes are anodes, so that the intermediate cathodes are plated on two sides.

It is pointed out that the total halide ion concentration in the cell electrolyte comes from the alkali metal halide and/or alkaline earth metal halide and from the heavy metal halide. As the heavy metal is electroplated at the cathode, halogen is being generated at the anode. This serves to remove halide ion from the solution. Thus, after a period of operation of a batch cell, or at the effluent end of a multi-electrode cell, the halide ion concentration is decreased.

When using an alkali metal halide or alkaline earth metal halide, the feed to the cell is optimally saturated in the salt. For salts which have a relatively flat saturation-concentration temperature curve, the electrolysis feed solution can be mixed at room temperature. If there is a substantial change in saturation concentration with temperature, the electrolyte should be mixed at substantially the temperature of operation.

The electrolysis cell is generally operated at an elevated temperature sufficient to insure satisfactory cathode quality and a sufficiently high cathode efficiency. It is generally understood that the higher the temperature the lower the voltage required to maintain a given current density.

Although generally it is found that too low a temperature tends to decrease electrode efficiency, the maximum temperature is generally determined purely by nonelectrical considerations. Above a certain temperature, the problems of handling the feed and product materials become difficult. However, if desired, any

temperature up to the boiling point of the electrolyte solution can be utilized.

Generally, an electrolyte temperature of at least about 35° C. is desirable in order to obtain at least a fair cathode quality and a sufficiently high cathode efficiency. However, under certain special conditions a lower temperature could be used if necessary. It has generally been found that temperatures greater than about 70° C. are unnecessary. Preferably, the electrolysis cell is operated at an electrolyte temperature of from about 45° to about 60° C.

The process of the present invention accordingly results in an improved electrolysis procedure whereby heavy metals can be electro-refined at a high efficiency to obtain the desired heavy metals and also a most useful by-product, the pure halogen. The all chloride process is believed to be superior to the use of other salts, e.g., nickel sulfate, in electrowinning procedures. It has been shown to result in a higher efficiency, generally up to a 50 percent savings in power consumption, a wide plating range, and a lower tendency to pit and form nodule growths, and trees on the cathode deposit. The procedure can operate at higher cathode and anode current efficiencies and is generally easier to control because of the simple composition of the solution. The tendency towards decreasing pH, i.e., increasing acidity, is limited by the present improvement which permits this superior process to be operated without a buffer and without a diaphragm between anode and cathode compartments. This results in a further improvement in the procedure, giving a higher quality cathode deposit having low internal stress, high current efficiency and cathode quality and substantially eliminating edge growths or treeing. The addition of a buffer, such as boric acid, is avoided and the requirement of maintaining a constant or nearly constant composition of such buffer as well as of the metal halide to be plated is therefore eliminated.

Referring to the drawings:

FIG. 1 is a schematic cut-away elevation view of an electrolysis cell useful in accordance with the present invention.

FIGS. 2 through 5 are graphs representing correlations between various parameters for operating nickel and cobalt electrolysis cells in accordance with this invention.

Referring to FIG. 1, a rectangular covered electrolysis cell indicated generally by 10 containing an anode 12 at each end and intermediate cathodes 14 and anode 12 is useful for operating the present invention. Each anode 12 and cathode 14 is connected to an electric source, not shown. The cathodes 14 are the preferred starter sheets of the desired plating metal.

Inlet 20 and outlet 22 are located behind the anodes at each end of the cell. The cell can be operated batchwise with recirculated electrolyte when recirculation line 26, indicated by dashed lines, and pump 27 are connected to the inlet 20 and outlet 22, respectively.

The following examples represent the preferred embodiments of the present invention and are not intended to be exclusive of the scope of the invention.

#### EXAMPLE I

A nickel electrolyte was prepared at room temperature as an aqueous solution comprising 80 grams per liter of nickel as  $\text{NiCl}_2$  and substantially saturated in sodium chloride (200 g/l.), to provide a total of 4.6 gm-

atoms of chloride ion/liter of solution. A sample of approximately three liters of the above electrolyte solution was fed to a glass-lined rectangular cell 4 inches long containing a graphitic anode at two opposite ends and a cathode formed of a thin nickel starting sheet, approximately 0.010 inches thick, midway between the anodes.

The cell was provided with means to recirculate the electrolyte so that it flowed past the first anode, the cathode and then past the second anode and then was recirculated to the first anode.

The electrolyte was heated to a temperature of 60° C., the pH measured and found to be approximately 2.0. The surface area of the anode was approximately 4 by 6 inches by 1 inch and of the cathode initially 3 by 4 inches by 0.01 inch thick. The cell was operated with the electrolyte recirculating until the nickel content of the electrolyte dropped to approximately 11 grams per liter and the chloride ion concentration to about 3.6 gm-atoms/liter. When the concentration of nickel was reduced to below approximately 20 grams per liter and the chloride ion reduced by an equivalent amount, to about 4.1 gm atoms/liter,  $\text{Cl}^-$ , the quality of the nickel plating out at the cathode was substantially reduced.

The pH of the solution was found to remain substantially constant during the electrolysis until the nickel concentration was decreased to about 20 grams/liter. Chlorine was generated at the anode and was removed overhead. Nickel of a high quality and even surface was deposited onto the cathode starter sheet. The nickel deposits were light colored and unusually smooth.

The electrodes were electrically activated initially to a voltage of about 2.13 volts. At a cathode current density of approximately 30 amperes/ft<sup>2</sup> the cathode efficiency was 91 percent.

#### EXAMPLES 2 THROUGH 6

The process of Example 1 was repeated but the pH of the electrolyte was varied as shown in Table I by the addition of HCl or NaOH. The voltage and cathode current density were varied concomitantly with the changes in pH.

Table I

EFFECT OF NICKEL ELECTROLYTE pH			
Example	pH	Cathod Efficiency percent	Deposit Quality
2	3.5	96.3	fair — poor
3	3.0	88.1	fair — good
4	2.5	92.3	very good
1	2.0	90.5	very good
5	1.0	84.2	good
6	0.75	79.1	fair — highly stressed

As shown the cell operates with reasonable efficiency and at least a fair quality deposit can be obtained over a wide range of pH. Thus, feed solutions of varying pH's, e.g., as obtained from various ore refining operations, can be utilized. In each case the pH remains substantially constant at the initial value throughout the electrolysis procedure.

#### EXAMPLES 7 and 8

The process of Example 1 was repeated except varying the voltage to obtain the cathode current density

during electrolysis as shown in Table II, and the cathode efficiencies determined; the data are set forth in Table II.

TABLE II

Example	Current Density (amps/ft <sup>2</sup> )	Cathode Efficiency %
7	20	92.2
1	30	90.5
8	40	88.0

In all examples cathode plating of high quality was obtained.

## EXAMPLES 9 through 11

The process of Example 1 was repeated except that the voltage was changed so that a current density of 20 amperes per square foot was obtained and operating temperatures for the electrolyte were varied. The results are set forth in Table III.

TABLE III

Example	Temperature, 20°C	Cathode Efficiency percent	Cathode Quality
9	27°C	—	poor
10	38°C	89.4	fair
11	49°C	92.1	good
7	60°C	92.2	very good

As shown a broad range of temperatures can be utilized, if desired, for the electrolysis process of the present invention. In all cases, the pH of the electrolyte remained constant during the entire course of the electrolysis.

## EXAMPLE 12

The procedure of Example 1 was repeated but substituting potassium chloride for sodium chloride; the solution was saturated with KCl at room temperature prior to addition to the electrolysis cell, and contained 200 g/l KCl. A cathode plate of very good quality was obtained utilizing the potassium. The pH of the solution remained constant at 2.0 throughout the electrolysis.

## EXAMPLE 13

The procedure of Example 1 was repeated but utilizing calcium chloride (300 g/l) as the halide source in place of NaCl. The quality of the cathode deposit was found to be very good and the cell operated at a satisfactory cathode efficiency.

## EXAMPLE 14

An electrolyte solution was prepared comprising 80 g/l of cobalt, as (CoCl<sub>2</sub>), 200 g/l of NaCl, (substantially saturated at room temperature). A sample of this electrolyte solution (3 liters) was added to the cell described in Example 1 but containing a cathode comprising a cobalt starting sheet 3 inches × 4 inches × 0.01 inch thick. The electrolyte was heated to a temperature of 60°C. and a charge of 2.13 volts was applied between the electrodes at a cathode current density of 30 amperes per square foot. The procedure was operated batch-wise (recirculation) until the cobalt concentration was decreased to approximately 15 g/l cobalt and 4 gram-atom/liter chloride ion. A satisfactory cathode efficiency of 86 percent was maintained

during the entire process; however, at the lower concentration of cobalt the quality of the cathode deposit began to deteriorate. The cobalt deposits were light colored and extremely smooth. The pH of the electrolyte remained constant at 2.0 throughout the entire electrolysis until the lower concentration was reached.

## EXAMPLES 15 through 18

The procedure of Example 14 was repeated, except that the initial pH of the electrolyte solution was varied as shown in Table IV below, utilizing HCl to decrease pH to below 2.0 and NaOH to increase pH. The voltage and cathode current density were varied concomitantly with changes in pH.

TABLE IV

Example	pH	Cathode Efficiency percent	Deposit Quality
15	3.0	84	fair
16	2.5	87	very good
14	2.0	86	very good
17	1.0	71	good
18	0.75	57	good

As shown from the above table the electrolysis cell can be operated at a wide range of pH s so that a variety of feed streams, such as from various hydrometallurgical procedures, can be utilized without requiring initial neutralization or pH adjustment.

## EXAMPLES 19 through 21

The procedure of Example 14 was repeated, except that the voltage was changed so that a current density of 30 amperes per square foot was obtained and the temperature of the electrolyte solution was varied as shown in Table V below.

TABLE V

Example	Temperature °C.	Cathode Efficiency percent	Cathode Quality
19	27°C	84.6	fair
20	38°C	87.0	good
21	49°C	86.3	very good
14	60°C	86.1	very good

As shown from the above data, a range of temperatures can be utilized but an increase in temperature does result in an improvement in cathode quality.

## EXAMPLES 22 and 23

The procedure of Example 14 was repeated except for varying the voltage to obtain the cathode current density during electrolysis as shown in Table VI, and the cathode efficiencies were determined: the data are set forth in Table VI.

TABLE VI

Example	Current Density (Amps/ft <sup>2</sup> )	Cathode Efficiency %
22	20	87.5
14	30	86
23	40	86

The attached drawings show the correlation between cell voltage and current densities for nickel solution (FIG. 2) and cobalt solutions (FIG. 3) 80 g/l heavy

metal, at various temperatures, and the effect of pH of the electrolyte on cathode efficiency for nickel (FIG. 4) and cobalt (FIG. 5).

The patentable embodiment of this invention which are claimed are as follows:

1. In a process for refining by cathodically electrodepositing a heavy metal at the cathode while simultaneously evolving an elemental halogen at the insoluble anode from an aqueous electrolyte solution containing dissolved therein a halide of the heavy metal, the heavy metal being selected from the group consisting of cobalt, nickel, zinc, iron, tin and manganese, the improvement which comprises the presence in the electrolyte solution of a halide of a second metal selected from the group consisting of alkali metal and alkaline earth metal, the concentration of the halide of the second metal being at least about 60% of its saturation concentration in the electrolyte solution, whereby a hard, dense and smooth deposit of the heavy metal can be deposited at the cathode, in the absence of a buffering agent.

2. The process of claim 1, wherein the heavy metal is nickel.

3. The process of claim 2, wherein the halide of a second metal is an alkaline earth metal chloride.

4. The process of claim 3, wherein the halide of a second metal is magnesium chloride.

5. The process of claim 3, wherein the halide of a second metal is calcium chloride.

6. The process of claim 2, wherein the halide of a second metal comprises sodium chloride.

7. The process of claim 2, wherein the halide of a second metal comprises potassium chloride.

8. A process in accordance with claim 1, wherein the elemental halogen is chlorine.

9. A process in accordance with claim 8, wherein the halide of the second metal is sodium chloride.

10. A process in accordance with claim 9, wherein the halide of the heavy metal is nickel chloride.

11. A process in accordance with claim 9, wherein the halide of the heavy metal is cobalt chloride.

12. The process of claim 1, wherein the heavy metal is cobalt.

13. The process of claim 12, wherein the halide of a second metal is an alkali metal chloride.

14. The process of claim 12, wherein the halide of a second metal is an alkaline earth metal halide.

15. The process of claim 12, wherein the halide of a second metal is selected from the group consisting of sodium chloride, magnesium chloride, calcium chloride and potassium chloride.

16. The process of claim 1, wherein the anode and the cathode are in a single chamber such that there is uninterrupted fluid flow between the anode and the cathode, in the absence of a buffer material in the elec-

trolyte solution.

17. The process of claim 1, wherein the concentration of the heavy metal in the electrolyte solution is not greater than about 2 gram-atoms/liter of the metal.

18. The process of claim 1, wherein the pH of the electrolyte solution is maintained substantially constant during electrolysis without the addition of a buffer material.

19. The process of claim 1, wherein the halide of a second metal is a chloride.

20. The process of claim 1, wherein the electrolysis is carried out utilizing as the cathode a "starter sheet" formed of the heavy metal to be plated.

21. The process of claim 1, wherein the electrolysis is carried out at a temperature of at least about 35°C.

22. The process of claim 1, wherein the concentration of the heavy metal in the electrolyte solution is in the range of from about 0.3 gm-atoms per liter to about 1.5 gm-atoms/liter.

23. The process of claim 1, wherein the pH of the electrolyte is in the range of from about 1 to about 3.5.

24. The process of claim 1, comprising feeding the aqueous electrolyte solution to an electrolyte cell wherein the feed solution is substantially saturated in the neutral source of halide ion.

25. A process for obtaining an elemental heavy metal from a halide of the heavy metal by cathodically electrodepositing the heavy metal while obtaining an elemental halogen, the process comprising subjecting to electrolysis, between an insoluble anode and a cathode, an aqueous solution comprising dissolved therein a halide of a heavy metal selected from the group consisting of cobalt, nickel, tin, zinc, iron and manganese, to be electrodeposited, and a halide of a second metal selected from the group consisting of alkali metals and alkaline earth metals, the total concentration of halide ion in the aqueous solution being sufficient to eliminate any substantial change in the pH of the aqueous solution during electrolysis without the addition of a buffer solution and being such as to provide a concentration of the halide of the second metal of at least 60% of its saturation concentration in the electrolyte solution, so as to evolve an elemental halogen at the insoluble anode and to deposit elemental heavy metal at the cathode as a dense, smooth and hard deposit.

26. The process of claim 25, wherein the total concentration of halide ion in the electrolyte solution is at least about 3.6 gram-atom/liter of halide ion.

27. A process in accordance with claim 25, wherein the elemental halogen is chlorine.

28. A process in accordance with claim 1, wherein the elemental halogen is selected from the group consisting of chlorine, bromine and iodine.

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