Aug. 30, 1949. L. S. RENZONI 2,480,771

PROCESS FOR THE ELECTROLYTIC RECOVERY OF NICKEL

Filed May 18, 1946 4 Sheets-Sheet 1

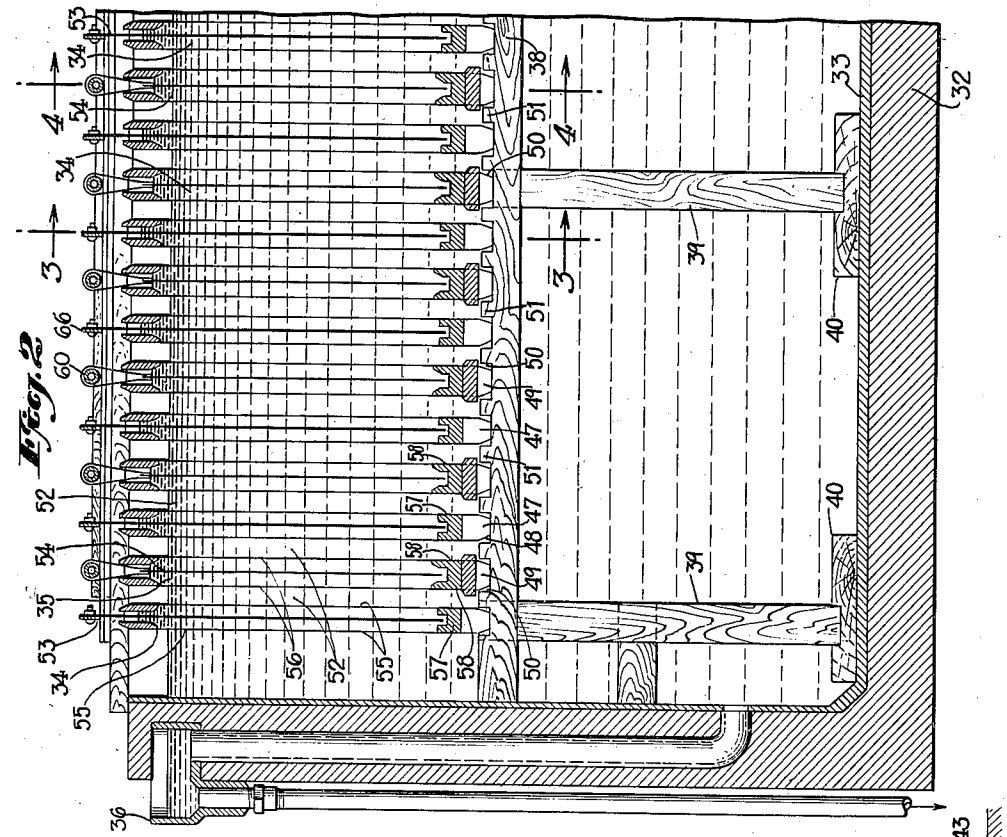


Fig. 2.

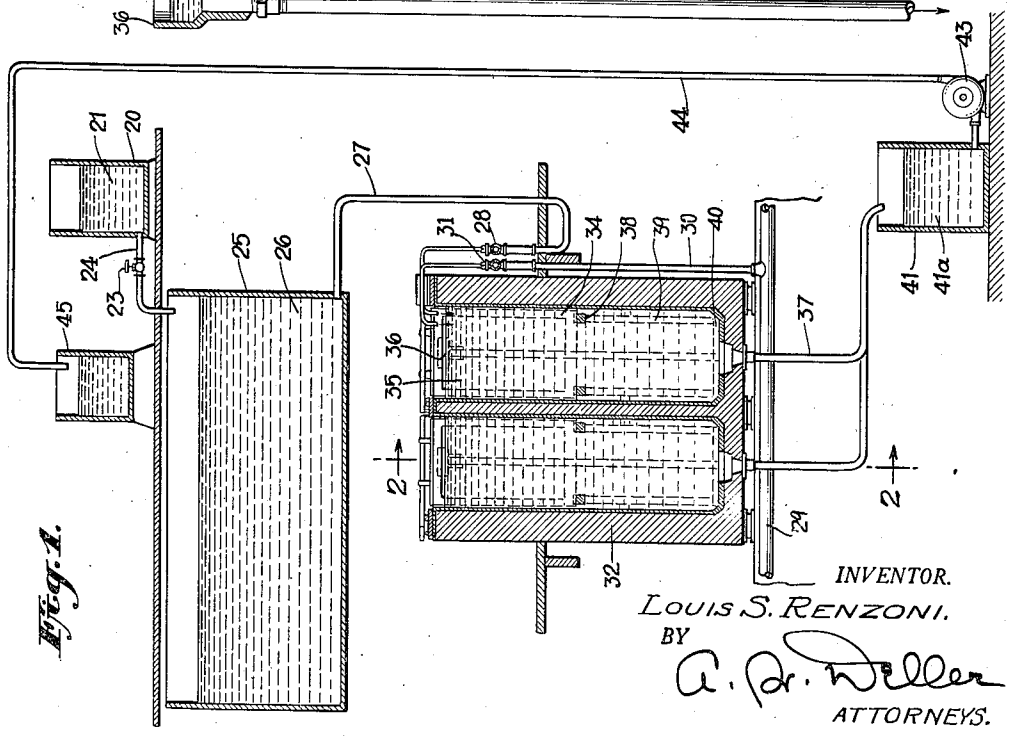


Fig. 1.

INVENTOR.
LOUIS S. RENZONI.
BY
A. Pr. Weller
ATTORNEYS.

Aug. 30, 1949. L. S. RENZONI 2,480,771

PROCESS FOR THE ELECTROLYTIC RECOVERY OF NICKEL

Filed May 18, 1946

4 Sheets-Sheet 2

Fig. 4.

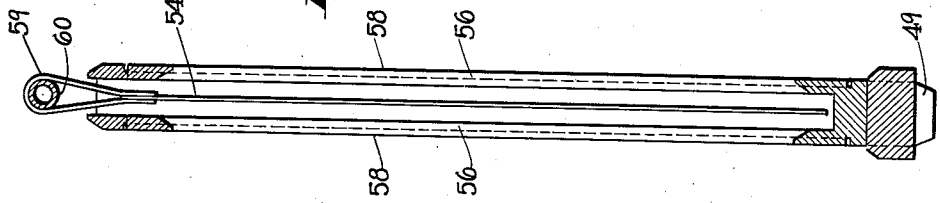
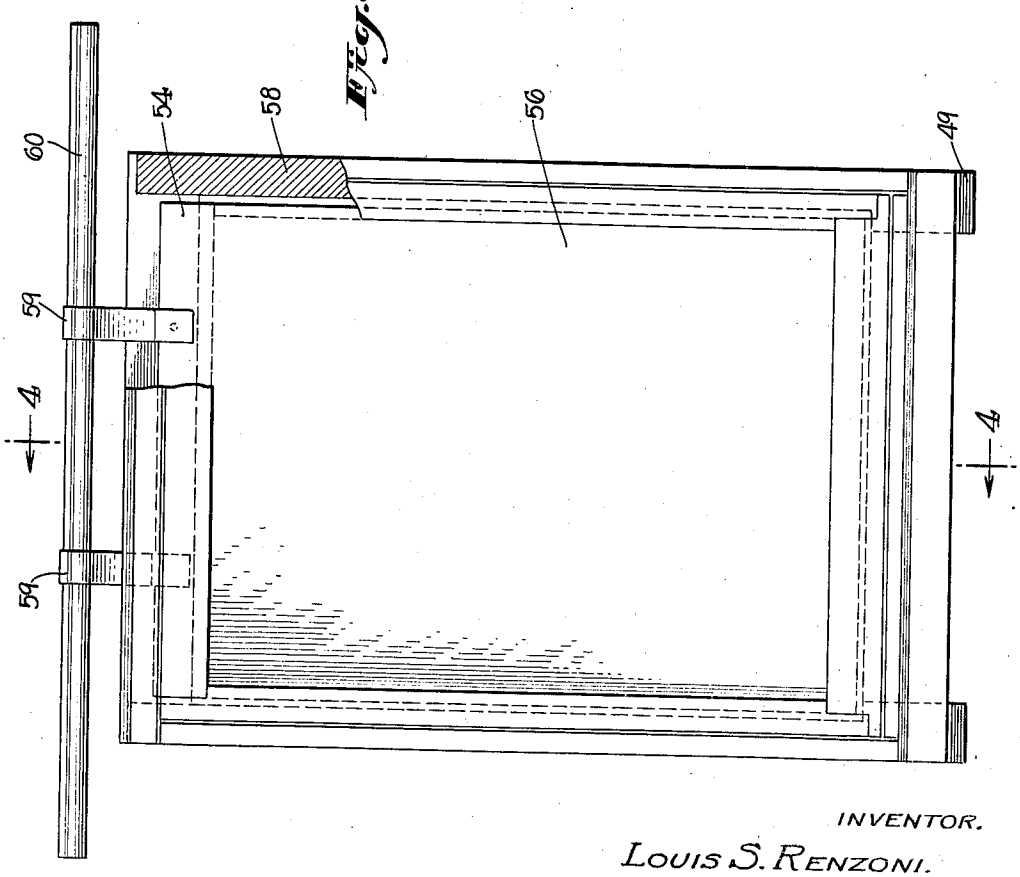


Fig. 3.



INVENTOR.

LOUIS S. RENZONI.

BY

A. Dr. Weller

ATTORNEY.

Aug. 30, 1949. L. S. RENZONI 2,480,771

PROCESS FOR THE ELECTROLYTIC RECOVERY OF NICKEL

Filed May 18, 1946 4 Sheets-Sheet 3

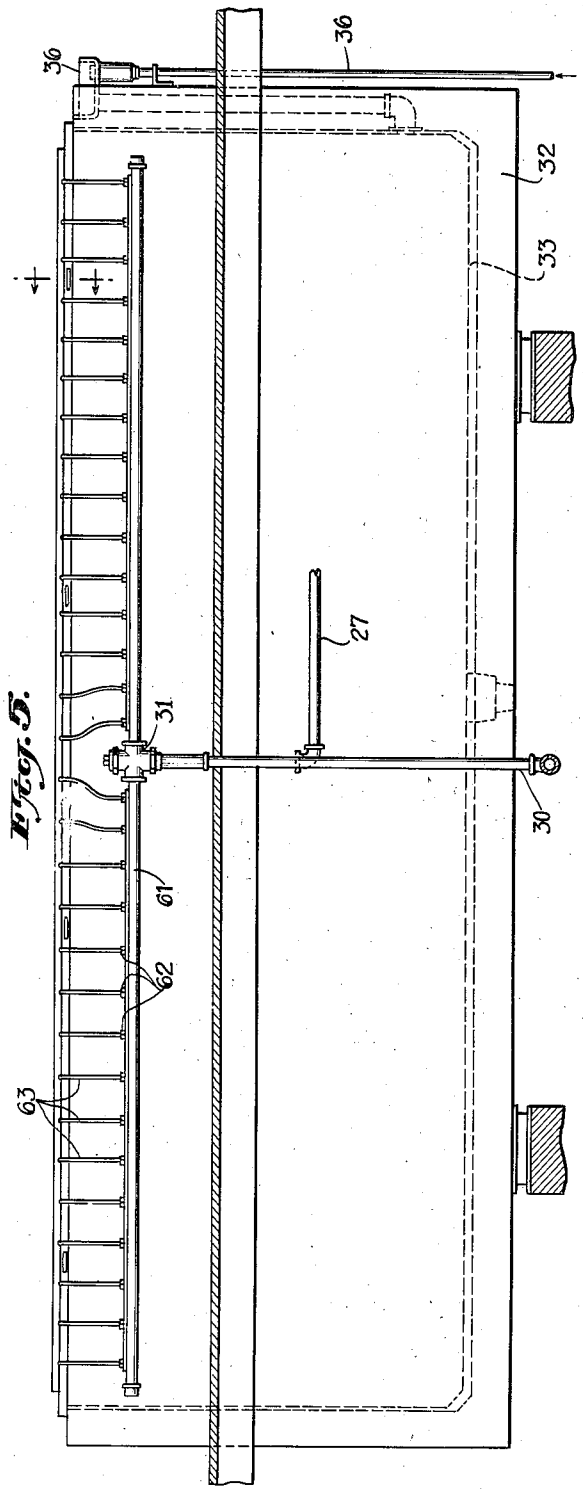


Fig. 5.

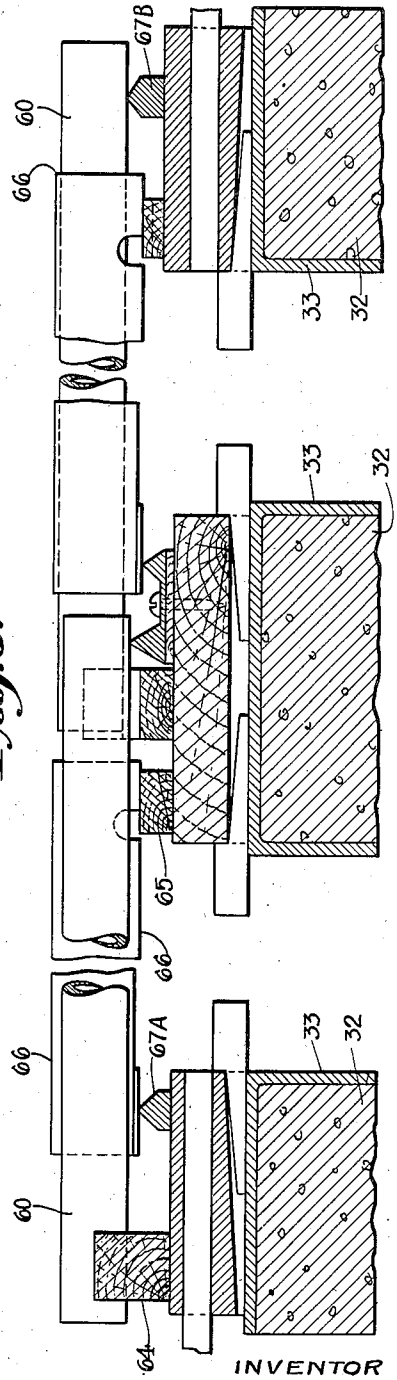


Fig. 6.

INVENTOR
LOUIS S. RENZONI.
BY
ATTORNEY.

Aug. 30, 1949. L. S. RENZONI 2,480,771

PROCESS FOR THE ELECTROLYTIC RECOVERY OF NICKEL

Filed May 18, 1946 4 Sheets-Sheet 4

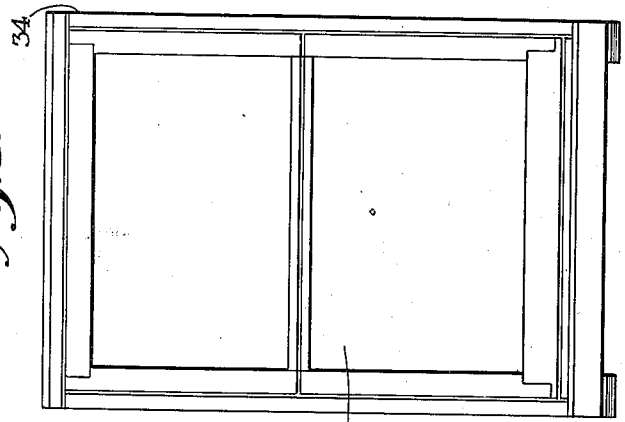


Fig. 8.

Fig. 9.

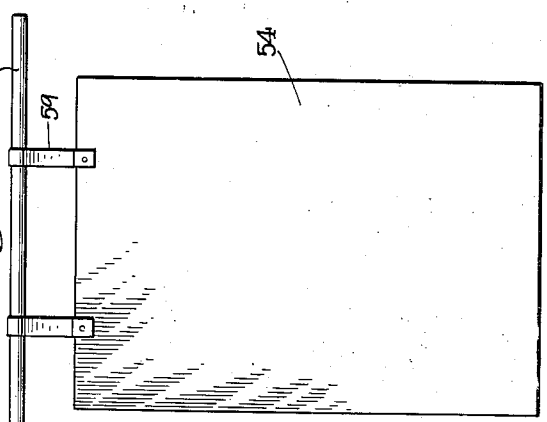


Fig. 10.

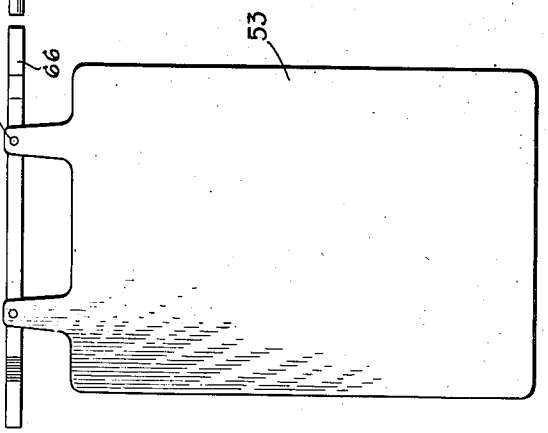


Fig. 11.

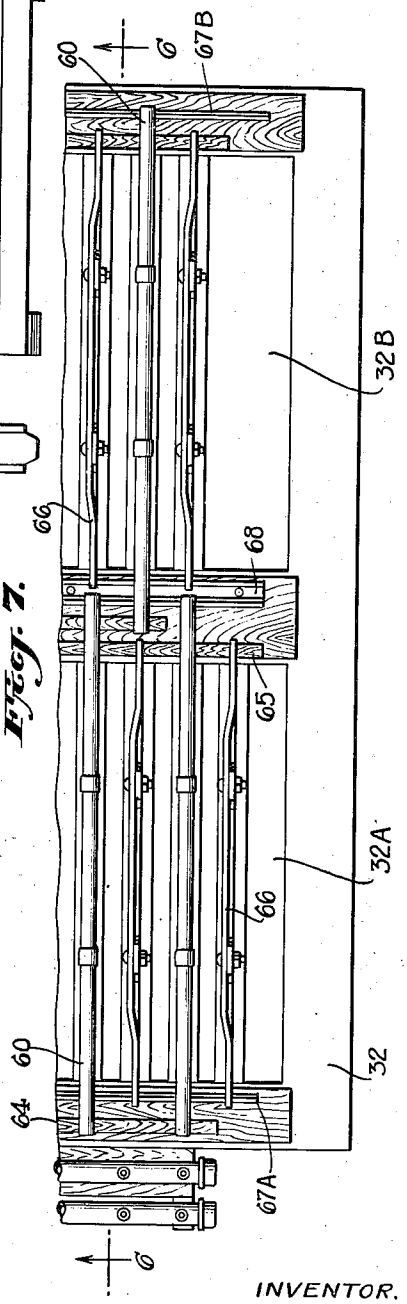


Fig. 7.

INVENTOR.
LOUIS S. RENZONI.
BY
ATTORNEY.

Patented Aug. 30, 1949

2,480,771

UNITED STATES PATENT OFFICE

2,480,771

PROCESS FOR THE ELECTROLYTIC RECOVERY OF NICKEL

Louis Secondo Renzoni, Port Colborne, Ontario, Canada, assignor to The International Nickel Company, Inc., New York, N. Y., a corporation of Delaware

Application May 18, 1946, Serial No. 670,774
In Canada April 12, 1946

9 Claims. (Cl. 204—112)

1

The present invention relates to a nickel liberator cell and a process of electrolysis carried out in that cell.

In the normal course of recovering nickel by electrodeposition from electrolytes containing chloride ions and utilizing soluble anodes, an excess of nickel enters the system over that amount of nickel which is removed at the cathode. In such a system of nickel recovery, it is necessary, in order to maintain a balance between the nickel entering the system and the nickel removed at the cathode, to decrease the amount of nickel entering the electrolyte at the soluble anode without decreasing the amount of nickel removed at the cathode. In systems for recovery of nickel wherein all-sulfate electrolytes are employed, i. e. substantially free of chloride ion, the nickel balance of the system is maintained by replacing some of the soluble anodes with insoluble anodes. However, the practice of replacing soluble anodes with insoluble anodes to maintain a nickel balance, when utilized in a chloride ion-bearing electrolyte system, has proved to be unsatisfactory as, when insoluble anodes are employed in contact with a chloride ion-bearing electrolyte, molecular chlorine is liberated at the anode during electrolysis and leads to numerous operating difficulties. Attempts have been made heretofore to operate cells producing nickel at the cathode and chlorine at the anode, but such attempts have been unsuccessful due to difficulties encountered in handling the chlorine. Furthermore, to provide adequate cathode efficiency for economical operation, it has been found necessary to use either cathode or anode diaphragms to prevent a large percentage of the current from being utilized for hydrogen ion discharge and chlorine reduction. Any such diaphragm arrangements, suitable for nickel electro-refining, have however, been found to deteriorate rapidly due to the action of molecular chlorine, resulting in numerous chlorine leaks, necessitating frequent changes of diaphragms and tank linings. Even more objectionable than the hereinbefore mentioned difficulties has been the resulting addition of chlorinated, water soluble, organic compounds to the nickel electrolyte which resulted in production of strained, warped cathodes throughout the tank house.

It is apparent, therefore, that in order to satisfactorily operate a balanced nickel system, when employing a chloride ion-containing electrolyte, it would be necessary to provide an electrolysis cell and a method for operating the cell in a

2

manner whereby chlorine would not be liberated at an insoluble anode during the electrolysis.

In view of the foregoing remarks, it will be apparent that the art of nickel recovery by electro-deposition, up to the time of the present discovery, was confronted with the problem of obtaining an electrolysis cell that could be operated with insoluble anodes and a chloride-ion containing electrolyte in a manner whereby the system could be operated in balance with respect to nickel, and nickel recovered efficiently at a cathode without liberation of chlorine at an insoluble anode. Furthermore, in providing an electrolysis cell that would operate in a satisfactory manner without liberation of chlorine at an insoluble anode, it was desired that the cell operate satisfactorily without necessity of adding cations or anions to the electrolyte system, which cations or anions would be deleterious to the electrolytic production of high purity nickel at the cathode.

I have discovered a novel liberator cell and a method employing the novel cell with insoluble anodes and a chloride-ion-containing electrolyte whereby the electrolytic system can be operated in balance, with respect to nickel, during electrolysis, and wherein nickel is recovered by electrodeposition at a cathode without liberation of chlorine at an insoluble anode.

It is an object of the present invention to provide a liberator cell capable of maintaining a catholyte substantially free of anolyte and anolyte substantially free of catholyte.

It is still another object of the present invention to provide a liberator cell having an anode compartment and a cathode compartment separated by an intervening compartment, i. e., a middle compartment, whereby during operation of the novel cell, the cathode compartment is maintained substantially free of anolyte and the anode compartment maintained substantially free of catholyte.

The present invention contemplates the provision of a liberator cell having an insoluble anode whereby chlorine is not liberated at the anode during operation of the cell when employing a chlorine-ion-bearing electrolyte.

The present invention further contemplates a method for recovery of nickel by electro-deposition from a chloride-ion-bearing electrolyte by employing the novel liberator cell embodied in the present invention.

It is within the contemplation of the present invention to provide a method for recovery of nickel by electrodeposition from a chloride-ion-

bearing electrolyte by employing a novel liberator cell having insoluble anodes.

The present invention also provides a method for recovering nickel by electrodeposition from a chloride-ion-containing electrolyte by employing a nickel liberator cell having insoluble anodes without liberation of chlorine at the insoluble anodes during operation of the cell.

Other objects and advantages of the present invention will become apparent from the following description taken in conjunction with the drawings in which:

Fig. 1 is a diagrammatic illustration of an installation such as may be employed in carrying out the present invention;

Fig. 2 is a sectional view taken on line 2—2 of Fig. 1;

Fig. 3 is a view partly in section of a cathode compartment;

Fig. 4 is a sectional view taken on line 4—4 of Fig. 3;

Fig. 5 is an elevational view of a manifold feed assembly such as may be employed for feeding electrolyte to the novel liberator cell such as provided by the present invention;

Fig. 6 is a sectional elevational view taken on line 6—6 in Fig. 7 and showing in detail a suitable means of assembly for bus bar connections for anodes and cathodes.

Fig. 7 is a plan view of a suitable means of assembly for bus bar connections for anodes and cathodes;

Fig. 8 is an elevational view of an anode compartment frame;

Fig. 9 is a sectional view of Fig. 8; and

Figs. 10 and 11 are elevational views of a cathode and an anode respectively.

Generally speaking, the novel apparatus of the present invention comprises an electrorefining tank in which are suspended a plurality of alternating anodes and cathodes, each electrode being contained within a compartment therefor, each compartment comprising a diaphragm at each side of the electrode with suitable framework for maintaining the diaphragms in substantially parallel, spaced-apart relationship and each compartment being maintained in spaced-apart relationship with each adjoining compartment by suitable framework thus providing diffusion zones i. e., intervening compartments, between adjacent electrode compartments. Anolyte and catholyte are introduced into the respective anode and cathode compartments at rates sufficient to provide the hydrostatic heads required in each compartment to insure flow of both anolyte and catholyte into the intervening diffusion zones, an overflow being provided in the diffusion zone for the mixture of anolyte and catholyte at a suitable level to assist in maintaining the preferred hydrostatic head. The anolyte employed is an acid solution substantially devoid of chloride ion and is preferably a dilute sulphuric acid solution, while the catholyte is a sulphate-chloride-nickel electrolyte. During operation of the novel cell, nickel is removed from the catholyte at the cathode and the electrolyte, depleted in nickel content, flows through the cathode diaphragm to the middle compartment. At the anode, meanwhile, oxygen is liberated at 100% current efficiency with the simultaneous liberation of hydrogen ions. The liberation of hydrogen ions results in the continuous production of sulfuric acid. Thus, the anolyte passing through the anode diaphragm has an increased acid content. In the middle compartment of the cell, the two solutions, i. e., anolyte and catholyte, are mixed to form acid liquor which is subsequently used for pH correction. The mixing of the two liquors in the middle compartment is not efficient, however, and there is a tendency for the heavy liquor from the cathode compartment to segregate near the tank bottom. For this reason, it is an essential feature of the present invention that the overflow from the electro-refining tank be taken off in the lower regions thereof so that this heavy mixture is withdrawn. The mixture withdrawal outlet will of course be brought to the proper level for overflow in order to maintain the proper relative levels within the anolyte and catholyte compartments and the intervening diffusion zone and this bringing to proper level may be by goose-neck bend or other means well known to those skilled in the art. It is also an essential feature of the present invention that infiltration of the heavy anolyte-catholyte mixture into the anolyte compartment should be avoided and for this reason the suspended anodes and anode compartments should not extend to the bottom of the tank, and in the preferred embodiment, they should not extend more than about two-thirds (⅔) of the depth of the tank. By this arrangement contact between the anodes and the heavy anolyte-catholyte mixture with the undesirable evolution of free chlorine which would result therefrom is avoided. It will thus be apparent from the foregoing that the port of withdrawal of the heavy liquor should be preferably in that portion of the tank beneath the bottom of the anodes.

In reference to respective depths of the anode and cathode compartments, although the preferred embodiment of the present invention is that such compartments should not extend more than about two-thirds (⅔) of the depth of the tank, it is also preferred, but not essential, that the cathode compartments are of the same depth as the anode compartments. The depth of the cathode compartments can be varied, however, particularly made deeper, without materially affecting the operation of the tank. However, I have found that there is no particular advantage in employing a short anode and a long cathode in practicing the present invention, although the use of a cathode longer in length than the anode would be of advantage in a process requiring a high anode current density and a lower cathode current density.

Referring to the drawings, Fig. 1 is a diagrammatic illustration of an installation such as may be employed in carrying out the present invention. In Fig. 1, a multi-compartment electro-refining tank 32, containing a mixed acid electrolyte, is shown having suspended in each of the compartments a plurality of alternating anode compartments 34 and cathode compartments 35 which are more clearly illustrated in Fig. 2. The anode compartments 34 and cathode compartments 35 are supported by compartment-bearing supports 38 in a spaced-apart relationship with each adjoining compartment whereby a diffusion zone is provided between adjacent compartments. Suitable means, such as supports 39 and 40, more clearly shown in Fig. 2, maintain the compartment-bearing supports 38 in desired position. An acid 21, substantially free of chloride ions, and preferably concentrated sulphuric acid, is contained in a suitable acid tank 20. By means of gravity, the acid 21 is allowed to flow through a conduit, such as pipe 24, and control valve 23, into an anolyte supply tank 25 in which the acid 21 flowing therein is diluted to provide an

aqueous anolyte 26, preferably containing about 10 grams per liter of sulfuric acid. By means of gravity, the anolyte 26 is allowed to flow through a conduit, such as pipe 27 and control orifice 28 into the anode compartments 34. Similarly a suitable nickel electrolyte containing chloride ions and sulfate ions is fed through a main feed line, such as pipe 29 and riser 30 into the cathode compartments 35. By means of an orifice, such as shown by reference numeral 31, the rate of flow of catholyte is controlled to a desired rate. In order to maintain a hydrostatic head in the anode compartments 34 and cathode compartments 35, an overflow system, such as overflow system 36, is provided to allow for withdrawal of mixed electrolyte liquor from the tank and diffusion zones in a manner whereby the surface level of the mixed electrolyte solution in the diffusion zones and tank is maintained at a lower surface level than the surface levels of the anolyte in the anode compartments 34 and the catholyte in the cathode compartments 35. The mixed electrolyte solution flowing through overflow system 36 flows by gravity through a conduit such as pipe 37 into an acid liquor tank 41. The acid liquor 41*a* is pumped by a suitable means such as pump 43 through a conduit, such as pipe 44, into a pH correction tank 45. The acid liquor 41*a* may be used for pH correction of purified nickel catholyte or may be employed for other purposes as desired.

Fig. 2 is a sectional view taken on line 2—2 of Fig. 1 and shows the preferred embodiment of a nickel liberator cell such as contemplated by the present invention. In Fig. 2, a refining tank 32 is provided having a suitable lining 33 and an overflow system, such as a goose-neck overflow system 36. A plurality of alternating cathode compartments 35 and anode compartments 34 are suspended in tank 32 in a manner such as shown in Fig. 2 whereby the bottom 47 of each anode compartment 34 rests in a slot 48 of compartment-bearing support 38, and, similarly, the bottom 49 of each cathode compartment 35 rests in a slot 50 of compartment-bearing support 38. The compartment-bearing support 38 is supported in the desired position by means of a suitable support system, such as supports 39 and 40. By means of wood spacers 51 in compartment-bearing support 38, the anode compartments 34 and cathode compartments 35 are spaced apart to provide an intervening compartment 52, i. e., diffusion zone, between adjacent anode and cathode compartments. Each anode compartment 34 has a suitable insoluble anode suspended therein, such as anode 53, and each cathode compartment 35 has a suitable cathode 54, such as a nickel starting sheet, suspended therein. Each anode compartment 34 comprises a diaphragm on each side of the anode, such as anode diaphragms 55, and each cathode compartment 35 comprises a diaphragm on each side of the cathode, such as cathode diaphragms 56. The anode compartments 34 have a suitable framework. such as frame 57, for maintaining the anode diaphragms in substantially parallel, spaced-apart-relationship, and, similarly, the cathode compartments contain a suitable framework, such as frame 58, for maintaining the cathode diaphragms in substantially parallel, spaced-apart relationship. As shown in Fig. 2, the anode compartment 34 and cathode compartments 35 do not extend to the bottom of tank 32, and in the preferred embodiment, the anode compartments 34 and cathode compartments do not extend more than about two-thirds of the depth of the tank. Such an arrangement of the anode compartments and cathode compartments substantially inhibits the infiltration of heavy anolyte-catholyte mixture from the intervening compartments 52 into the anode compartments 34, and thus the heavy anolyte-catholyte mixture does not come in contact with the anodes. The heavy anolyte-catholyte mixture in the intervening compartments 52 is withdrawn from the lower portion of the tank by means of the overflow system 36. As shown in Fig. 2, the surface level of anolyte in the anode compartments 34 and catholyte in the cathode compartments 35 is maintained at a higher surface level than the mixed electrolyte in the intervening compartments 52 and tank 32, thus providing a hydrostatic head in the anode and cathode compartments. In other words, by controlling the rate of flow of anolyte into the anode compartment and catholyte into the cathode compartment, and by proper adjustment of the overflow system 36, the surface level of anolyte in anode compartments 34 and the surface level of catholyte in cathode compartments 35 are maintained at a higher level than that of the mixed acid solution in the intervening compartment 52, thereby providing a hydrostatic head in the anode compartments 34 and cathode compartments 35 with relation to the intervening compartments 52, and providing flow of anolyte and catholyte into the diffusion zones in the intervening compartments.

Fig. 3 is a view partly in section of a cathode compartment, and Fig. 4 is a sectional view taken on line 4—4 of Fig. 3, showing a suitable means of assembly for a cathode compartment such as may be employed in a nickel liberator tank such as shown in Fig. 2. In Figs. 3 and 4, a suitable cathode bus bar 60 supports the cathode 54 in the compartment by means of a cathode connection such as shown by the reference numeral 59. Reference numeral 58 shows a suitable frame construction for the compartment for maintaining cathode diaphragms 56 in substantially parallel, spaced-apart relationship. The bottom 49 of the cathode compartment provides for the resting of the compartment in slots 50 of compartment bearer-support 38, shown in Fig. 2, for maintaining the cathode compartments in spaced-apart relationship with each adjoining compartment, whereby a diffusion zone, i. e., intervening compartment, is provided between adjacent compartments.

Fig. 5 is an elevational view of a manifold feed assembly such as may be employed for feeding anolyte or catholyte to the respective compartments of the novel liberator cell such as shown in Fig. 2. In Fig. 5, a tank 32 having a suitable lining 33 is shown provided with an overflow system 36 hereinbefore described in connection with Figs. 1 and 2. A riser 30 carries catholyte from a main feed line into a header such as pipe 61 which has a series of outlets 62 arranged in a manner such as shown in Fig. 5. Risers 63, preferably soft rubber tubes, are connected to each outlet 62 on pipe 61 and the free end of each riser 63 is curved over the top of tank 32 whereby the catholyte flowing through riser 30, pipe 61, and risers 63 flows into the cathode compartments suspended in tank 32. Orifice 31 connecting riser 30 to pipe 61 maintains the rate of flow of catholyte at the desired rate into the cathode compartments. For feeding anolyte to the anode compartments 34, a manifold system such as

hereinbefore described for the catholyte feed may be employed. Thus, in Fig. 5, a conduit such as conduit 27, is shown which carries anolyte, and which conduit may be connected to a suitable orifice, and assembly of risers, to maintain the desired rate of flow of anolyte to the anode compartments in a manner similar to the assembly of conduit 30, orifice 31, pipe 61 and risers 63 for feeding of catholyte to the cathode compartments.

Fig. 7 is a plan view of the bus bars and electrode suspension means and Fig. 6 is an elevation thereof taken on the line 6—6 of Fig. 7 showing the anode and cathode bus bars and the means for obtaining proper clearances for the anode and cathode compartments suspended in the tank. In Figs. 6 and 7, reference numeral 32 shows a multi-compartment tank, having a suitable lining 33, in which compartments the anode and cathode compartments are suspended as shown in Fig. 2. Cathode bus bar supports, such as wood strips 64, support the cathode bus bars 60. Similarly, anode bus bar supports, such as wood strips 65, support the anode bus bars 66. The anode bus bars 66 and cathode bus bars 60 are assembled in a manner, such as shown in Figs. 6 and 7, whereby a spaced-apart relationship is maintained thereby providing the intervening compartment 52, shown in Fig. 2, between adjacent compartments. Furthermore, Figs. 6 and 7 show a suitable means of assembly for current-carrying members 67A, connecting to anode bus bars 66, which carry current to the anode bus bars. Similarly, current carrying members 67B, connecting to the cathode-bus bars 60, carry current to the cathode bus bars.

In my practice of the present invention, the electro-refining tanks, such as the multi-cell tank of Fig. 7, are connected to each other in series and a plurality of such tanks connected in this manner constitutes an electrical circuit. With reference to Fig. 7, in the tank cell 32A, the anode bus bars 66 are in contact with the anode current carrying members 67A. The cathode bus bars 60, in tank cell 32A, are not in contact with a cathode current carrying member, but only with a conductor, i. e. copper, such as shown by reference numeral 68, having no outside electrical contacts. The conductor 68 serves to distribute the current uniformly and to form an electrical contact between the two tank cells, i. e. 32A and 32B, such as shown in Fig. 7. Conversely, in tank cell 32B, the cathode bus bars 60 make contact with cathode current carrying member 67B, and the anode bus bars 66 contact conductor 68. Thus, in an arrangement such as shown by Fig. 7, considering the flow of current through the solution from anode to cathode, the current entering at the anodes in tank cell 32A flows through the solution to the cathodes in tank cell 32A, and out through the cathode bus bars in tank cell 32A to conductor 68. Thence, the current flows through the anode bus bars 66 and anodes in tank cell 32B, through the solution to the cathode, and through the cathode bus bars 60 to cathode current carrying member 67B.

Fig. 8 is an elevational view, and Fig. 9 is a sectional view of an anode compartment frame such as may be employed in practicing the present invention. In Figs. 8 and 9, reference numeral 34 shows a suitable anode compartment having diaphragms 55 maintained, in the manner shown, in substantially parallel, spaced-apart relationship. Fig. 11 is an elevational view of an anode 53, attached by suitable means, such as lugs 54, to an anode bus bar 66. In my practice of the present invention, an anode assembly such as shown in Fig. 11 is suspended in an anode compartment frame such as shown in Figs. 8 and 9 to comprise an anode compartment for suspension in a tank, such as tank 32 in Fig. 2.

Fig. 10 is an elevational view of a cathode assembly comprising cathode 54 attached by suitable means, such as cathode connection 59, holding the cathode to the bus bar 60. In my practice of the present invention, the cathode assembly shown in Fig. 10 is suspended in the cathode compartment in a manner such as shown in Figs. 3 and 4.

The anode employed in the anode compartments of the novel liberator cell of the present invention is an insoluble anode, satisfactory examples of which are lead anodes or other types of insoluble anodes normally employed with all-sulfate electrolytes in processes for recovery of nickel. In my practice of the present invention, I prefer to employ lead anodes containing about 6% antimony, as I have found that these anodes perform satisfactorily and lead is not added to the electrolyte system as a result of the use of such anodes.

The diaphragms employed for the anode and cathode compartments of the novel liberator cell are generally of the acid-resistant type. In my preferred embodiment of the present invention, a duraklad fabric of vinyl resin is employed for the anode and cathode compartment diaphragms. Still another type of diaphragm that has been found to be satisfactory in practicing my invention is a diaphragm consisting of glass cloth.

In practicing the present invention, when during operation of the cell it is desired to remove the anodes and cathodes from their respective compartments, the anodes and cathodes are removed single from the compartments by suitable means, such as a traveling crane, the hook of which is attached to the anode or cathode bar of the electrode to be removed and the electrode is lifted out of the compartment. Similarly, anodes and cathodes are lowered into place singly into the respective compartments.

The cathodes employed in the cathode compartments of the novel liberator cell may be of suitable types generally used in electro-winning of nickel by electrodeposition. In my preferred embodiment of the present invention, I employ nickel starting sheets, such as are well known to those skilled in the art, for the cathodes in the cathode compartments.

In my novel process for recovery of nickel from a chloride-ion containing catholyte, employing a novel liberator cell, such as provided by the present invention, an aqueous acid solution substantially free of chloride-ion is employed as the anolyte. A suitable anolyte is an aqueous solution containing sulphuric acid. The acid content of the anolyte is determined by the acid requirements of the electrolyte system as a whole but sufficient acid should be present to make the anolyte a good conductor. In my practice of the present invention, the acid requirements of the system are such that the acid concentration of the anolyte is maintained at about 10 to 20 grams per liter of sulphuric acid, and preferably about 10 grams per liter. I employ an aqueous anolyte containing about 10 grams per liter of H_2SO_4 as I have found that at this acid concentration, the conductivity of the anolyte is satisfactory. In other applications, wherein the acid requirements of the system may be greater, the acid concen-

tration of the anolyte may be proportionately increased. The upper limit of acid concentration in the anolyte in any application is determined by the corrosive action of the mixed acid electrolyte formed in the middle compartments, such as middle compartments **52** in Fig. 2. For most practical purposes, an anolyte containing up to about 50 grams per liter of H_2SO_4 has been found to be satisfactory.

The anolyte is preferably maintained at a temperature of about 100° F. to 140° F. as when temperatures exceeding about 140° F. are employed, the diaphragm fabrics and tank linings may be deleteriously affected. Lower temperatures than about 100° F. may be employed, but use of such lower temperatures results in higher power consumption in operation of the novel process described herein for recovery of nickel. A temperature range of about 120° F. to 130° F. has been found to be satisfactory for the anolyte, as use of temperatures within this range provides the desired results and also allows for absorption of heat generated in the event that local short circuits may occur in the system.

In my particular application of the novel process embodied in the present invention, current densities within the range of about 20 to 50 amperes per square foot have been found to be entirely satisfactory, and preferably, are employed in practicing the present invention. Although current densities less than about 20 amperes per square foot may be employed, the use of such lower current densities necessitates employing a large number of tanks to remove the desired quantity of nickel. As for current densities exceeding about 50 amperes per square foot, I have found that use of such high current densities results in production of exceedingly rough cathodes, and therefore, it is preferred that a current density of less than about 50 amperes per square foot may be employed.

In general, the catholytes that may be employed in practicing the present invention are similar to those set forth in my application, Serial No. 472,471, now United States Patent No. 2,394,874, relating to the electro-refining of nickel with sulfate-chloride electrolyte. Thus, an aqueous catholyte that can be satisfactorily employed in the present invention contains about 40 to 60 grams per liter of nickel, about 27 to 30 grams per liter of chloride ion, and about 71 to 120 grams per liter of sulfate ion. The pH of the catholyte is preferably maintained at pH 4.0 to 5.0 at a temperature of 100–120° F. In my preferred embodiment of the present invention, I employ an aqueous catholyte having the following composition:

Constituent	Grams per Liter
Nickel	About 40 to 60.
Sodium	About 20 to 30
Cl	About 27 to 30
SO_4—	About 71 to 120
H_3BO_3	About 15 to 25
Cobalt	About 0.001 to 0.01
Iron	About 0.0001
Copper	About 0.0002 to 0.0005
Arsenic	About 0.0001
Lead	About 0.0001

Although the exact nature of the phenomena explaining the conductance mechanism for the satisfactory performance of the novel liberator cell has not been definitely ascertained, it is believed that the following discussion will be helpful in understanding the principles underlying the conductive mechanism providing for the novel results obtained by employing the present invention. In the cathode compartment of the novel liberator cell, the conditions to be fulfilled to allow the flow of current through the catholyte are that either cations or anions or both anions and cations pass through the cathode diaphragm. In the present application, I impose the condition that all the current must be carried through the cathode diaphragm by the anions. This, I believe takes place in the following manner: at the instant of discharge of a nickel ion, giving up its two positive charges, a sulfate anion or two chloride anions must migrate out of the cathode compartment to maintain ionic equilibrium within the compartment. This flow of free anions through the diaphragm constitutes a flow of electrons or negative electricity towards the anode. Similarly, at the anode compartment, I impose the condition that all the current must be carried through the anode diaphragm by the cations. The mechanism, I believe, is as follows: within the anode compartment, oxygen is liberated at the anode at 100% current efficiency as a result of hydroxyl ion discharge. At the instant of discharge of a hydroxyl ion, giving up its unit of negative charge, a hydrogen ion carrying a unit of positive charge must migrate through the anode diaphragm to maintain ionic equilibrium within the compartment. The continuous flow of these free positive ions towards the cathode constitutes a flow of positive electricity. Combining the two compartments by placing between them a middle compartment containing an electrolyte constitutes an electrolytic cell, the overall operation of which may be described as follows: in the middle compartment, the ions are free to move under the influence of the electric current and the cations will migrate towards the cathode while the anions will move in the opposite direction. The fraction of the total current carried by either the cations or the anions will be determined by their respective mobilities. Thus when current is flowing through the cell, there is a transfer of cations in the direction of the cathode and of anions in the direction of the anode. At any given plane in the middle compartment, the net transfer of cations at the plane is equivalent to the sum of the cations migrating into the plane and of the cations migrating out of the plane. The quantity of matter transferred must be equivalent to one equivalent weight per Faraday. There is, therefore, a boundary of cations moving towards the cathode and a similar boundary of anions advancing towards the anode. In the vicinity of either diaphragm, the advancing boundaries of anions and cations meet a flow of oppositely charged ions which stream through the diaphragm, and a narrow diffusion zone is thus set up in the immediate vicinity of both diaphragms. These diffusion zones form the actual boundaries between the electrode compartments and the middle compartment. At these boundaries, a free exchange of ions can take place and the electrical circuit is completed between the anode and the cathode. Hence it may be considered that the diaphragms act as mechanical barriers preventing the diffusion of ions, while the diffusion zones form the permeable boundaries which allow the free ionic exchange and thus allow for an unhindered flow of current. Although the believed reasons hereinbefore given for the novel results obtained by practicing the present invention are recited above, it is to be understood that the theory for these reasons may change. However, regardless of the reasons un-

derlying the improved results obtained with the present invention, it has been found that by employing the novel cell and process employing that cell, I have provided for efficient recovery of nickel at a cathode from a chloride-ion containing electrolyte without liberation of chlorine at insoluble anodes.

In order that those skilled in the art may have a better understanding of the present invention, the following example is given, employing a novel liberator cell, such as described in Fig. 2, for recovery of nickel from a sulfate-chloride nickel electrolyte without liberation of chlorine at the anode.

Example

In an arrangement, such as shown in Fig. 2, an electro-refining tank having an overflow system is filled with a mixed acid electrolyte in the following manner:

An aqueous solution containing about 10 grams per liter of sulfuric acid is run into the tank until the liquor level reaches the top of the compartment supports **38**. Anolyte, an aqueous solution containing about 10 grams per liter of sulfuric acid, is then introduced into the anode compartments **34** and catholyte, i. e. an aqueous solution containing sulfate, chloride and nickel ions, is introduced into cathode compartments **35**. Both anolyte and catholyte are introduced into the respective compartments at rates of flow sufficiently rapid to maintain an adequate flow through the respective diaphragm to prevent infiltration of foreign ions into the anode and cathode compartments. Sulfuric acid solutions, similar to that introduced into the tank, are introduced into the middle compartmets **52** at the same time as the anolyte is introduced into the anode compartments and catholyte into the cathode compartments, at a reduced rate of flow to maintain the liquor level in the middle compartments below the liquor levels in the cathode and anode compartments, i. e. such as about 2 inches below the liquor levels in the anode and cathode compartments. As soon as the liquor levels in the three compartments, anode compartments **34**, cathode compartments **35** and middle compartments **52**, have reached the desired operating levels, the flow of sulfuric acid solution to the middle compartments is stopped and the flow of anolyte and catholyte is allowed to proceed at the desired rates through the respective orifices. The tank is then ready for operation. The anode compartments, containing 6% antimony-lead anodes, and cathode compartments, containing nickel starting sheets as cathodes are arranged in the tank in the manner shown in Fig. 2. In my practice of the present invention, the novel liberator cell contains 24 cathode and 25 anode compartments. A one inch space separates the anode compartments from the cathode compartments and the intervening spaces constitute the middle compartments.

The purified nickel electrolyte containing about 56–57 grams per liter of nickel, 27–30 grams per liter of chloride ion and 71–120 grams per liter of sulfate ion is fed into the cathode compartments at a rate of 300 milliliters per minute while an aqueous solution containing 10 grams per liter of H_2SO_4 is fed into the anode compartments at a rate of 500 milliliters per minute. During operation of the cell, the mixed acid liquor from the middle compartments and tanks is continuously removed by means of the overflow system. The rate of flow of anolyte at about 500 milliliters per minute into the anode compartments, and catholyte at 300 milliliters per minute into the cathode compartment has been found to be a sufficient rate of flow to provide a hydrostatic head in these compartments with respect to the intervening compartments and to provide a flow of anolyte and catholyte into the intervening compartments. The satisfactory rate of flow of anolyte into the anode compartments and catholyte into the cathode compartments, whereby a hydrostatic head is maintained in these compartments with relation to the electrolyte in the intervening compartments to insure flow of anolyte and catholyte into the intervening compartments is determined by taking into consideration factors influencing maintaining of the hydrostatic head. Such factors include the relative depth of the electrode compartments and the intervening compartments, the specific gravities of the anolyte and catholyte, and the porosity of the diaphragms.

The temperature of the anolyte and catholyte is maintained at about 130° F. The total current flowing through the tank is 6500 amperes and a voltage of 6.5 volts providing an anode and cathode current density of approximately 30 amperes per square foot.

During operation of the cell, the catholyte containing 56–57 grams per liter of nickel, flows to each cathode compartment at 300 milliliters per minute. At each cathode, 4.9 grams of nickel are removed from solution per minute. Thus the depleted nickel electrolyte flowing through the cathode diaphragm has a nickel content of approximately 40 grams per liter. At each anode, oxygen is liberated at 100% current efficiency with a simultaneous liberation of hydrogen ions. This results in the production at each anode of a quantity of acid equivalent to 7.9 grams of H_2SO_4 per minute. Since anolyte containing 10 grams per liter of H_2SO_4 flows to each anode compartment at the rate of 500 milliliters per minute, the anolyte flowing through the anode diaphragm has a total acid content equivalent to 25.8 grams per liter of H_2SO_4.

The anolyte and catholyte flowing through the diaphragm are mixed in the middle compartments to form an acid electrolyte liquor containing approximately 15 grams per liter of nickel and 16 grams per liter of H_2SO_4. The acid liquor flows from the tank by means of the overflow system and is used for pH correction of the purified nickel electrolyte and replaces an equivalent quantity of H_2SO_4 which would otherwise be required for the purpose. In my operation of the present invention, each nickel liberator cell of the type shown in Fig. 2, operating at a total current of 6500 amperes per square foot, removes approximately 375 lbs. of nickel per day from the electrolyte system and produces a quantity of acid approximately equivalent to 625 lbs. of H_2SO_4 per day. During electrolysis, heavy liquor infiltration from the middle compartments into the lower portions of the anode compartments is substantially eliminated, and thus, the anode compartments are substantially free of chloride ions, and as a result, chlorine is not liberated at the anode. Hence, nickel is removed efficiently at the cathodes without liberation of chlorine at the anodes.

The novel electrolytic cell described in the present application is claimed in my co-pending divisional application Serial No. 15,925, filed on March 19, 1948.

Although the present invention has been described in conjunction with certain preferred

embodiments thereof, those skilled in the art will readily recognize that variations and modifications can be made. Such variations and modifications are to be considered to be within the purview of the specification and the scope of the appended claims. Thus, although the present invention has been described in conjunction with a multicell arrangement, as shown in Figs. 1 and 2, it is within the scope of the present invention to include unit nickel liberator cells, as for example a liberator cell comprising a suitable receptacle provided with a suitable overflow and having an anode compartment and cathode compartment suspended therein separated in a manner whereby the space separating the two compartments constitutes a middle compartment, thereby forming a 3-compartment cell. Furthermore, although the present invention has been described in conjunction with an aqueous sulphuric acid anolyte and a chloride-ion-bearing catholyte, it is within the scope of the present invention to include the electrolysis of solutions containing two or more different anions where it is desired to prevent the anodic reaction of one or more of the anions. However, in employing a solution containing one or more anions, the anolyte employed and the product of the anode reaction must be compatible with the electrolyte and process as a whole. Conversely, it is within the scope of the present invention to include electrolysis of a solution where it is desired to prevent cathodic reaction of one of the constituents of the solution.

I claim:

1. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with about 56 to about 57 grams per liter of nickel, about 27 to about 30 grams per liter of chloride ions, about 71 to about 120 grams per liter of sulfate ions, and about 15 to about 25 grams per liter of boric acid, said solution being at a temperature between about 100° F. and about 120° F.; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble lead anode having a content of about 6% antimony and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with about 10 grams per liter of sulfuric acid but substantially devoid of chloride ions, said solution being at a temperature between about 100° F. and about 140° F.; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in said intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the depths of both the anode compartment and the cathode compartment at a rate sufficient to maintain the level of the mixed solutions in said intervening compartment below the respective levels of the solutions in said anode compartment and said cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode at an anode current density between about 20 and about 50 amperes per square foot to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

2. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with about 40 to about 60 grams per liter of nickel, about 20 to about 30 grams per liter of sodium, about 27 to about 30 grams per liter of chloride ions, about 71 to about 120 grams per liter of sulfate ions and about 15 to about 25 grams per liter of boric acid; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble lead anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

3. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with about 40 to about 60 grams per liter of nickel, about 20 to about 30 grams per liter of sodium, about 27 to about 30 grams per liter of chloride ions and about 71 to about 120 grams per liter of sulfate ions; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with about 10 to about 20 grams per liter of sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode

compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

4. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with about 40 to about 60 grams per liter of nickel, about 27 to about 30 grams per liter of chloride ions and about 71 to about 120 grams per liter of sulfate ions; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with about 10 to about 20 grams per liter of sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the depth of the anode compartment at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

5. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with about 40 to about 60 grams per liter of nickel, about 27 to about 30 grams per liter of chloride ions and about 71 to about 120 grams per liter of sulfate ions; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with a small amount up to about 50 grams per liter of sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

6. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with about 40 to about 60 grams per liter of nickel, about 27 to about 30 grams per liter of chloride ions, about 71 to about 120 grams per liter of sulfate ions and about 15 to about 25 grams per liter of boric acid; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

7. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions to provide a pH of about 4 to about 5 and with nickel, sodium, chloride ions, sulfate ions and boric acid; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart

from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

3. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode a solution consisting essentially of water with hydrogen ions, nickel, chloride ions, sulfate ions and boric acid; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with sulfuric acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel

is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

9. A process for the electrolytic recovery of nickel from aqueous nickel-containing solutions which comprises introducing into an acid-resistant, diaphragmous-walled cathode compartment containing a cathode an acid solution consisting of water, hydrogen ions, nickel and chloride ions as essential ingredients; introducing into an adjacent, acid-resistant, diaphragmous-walled anode compartment containing an insoluble anode and spaced apart from said cathode compartment by an intervening compartment having common diaphragmous walls with said anode compartment and said cathode compartment a solution consisting essentially of water with acid but substantially devoid of chloride ions; maintaining the level of each of said solutions in the respective compartments sufficiently high to cause each of said solutions to flow through the respective diaphragmous walls to form mixed solutions in an intervening compartment located between and connecting said anode compartment and said cathode compartment; withdrawing the mixed solutions from said intervening compartment at a level below the anode at a rate sufficient to maintain the level of the mixed solutions in the intervening compartment below the respective levels of the solutions in the anode compartment and the cathode compartment and to maintain the respective flows of said solutions into the intervening compartment; and passing electric current through the solutions between said anode and said cathode to deposit nickel on the cathode whereby nickel is electrolytically recovered from aqueous solutions containing nickel and chloride ions while substantially preventing evolution of chlorine gas at the insoluble anode.

LOUIS SECONDO RENZONI.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
679,985	Palas et al.	Aug. 6, 1901
805,969	Hybinette	Nov. 28, 1905
1,003,092	Dow et al.	Sept. 12, 1911
1,239,012	Hybinette	Sept. 4, 1917
1,375,631	Haglund	Apr. 19, 1921
1,389,829	Heberlein	Sept. 6, 1921
2,394,874	Renzoni	Feb. 12, 1946

FOREIGN PATENTS

Number	Country	Date
9,563	Great Britain	1900