

Sept. 18, 1945.

A. R. GLOBUS

2,385,269

PROCESS OF ELECTROLYTICALLY EXTRACTING METAL

Filed May 10, 1941

4 Sheets-Sheet 1

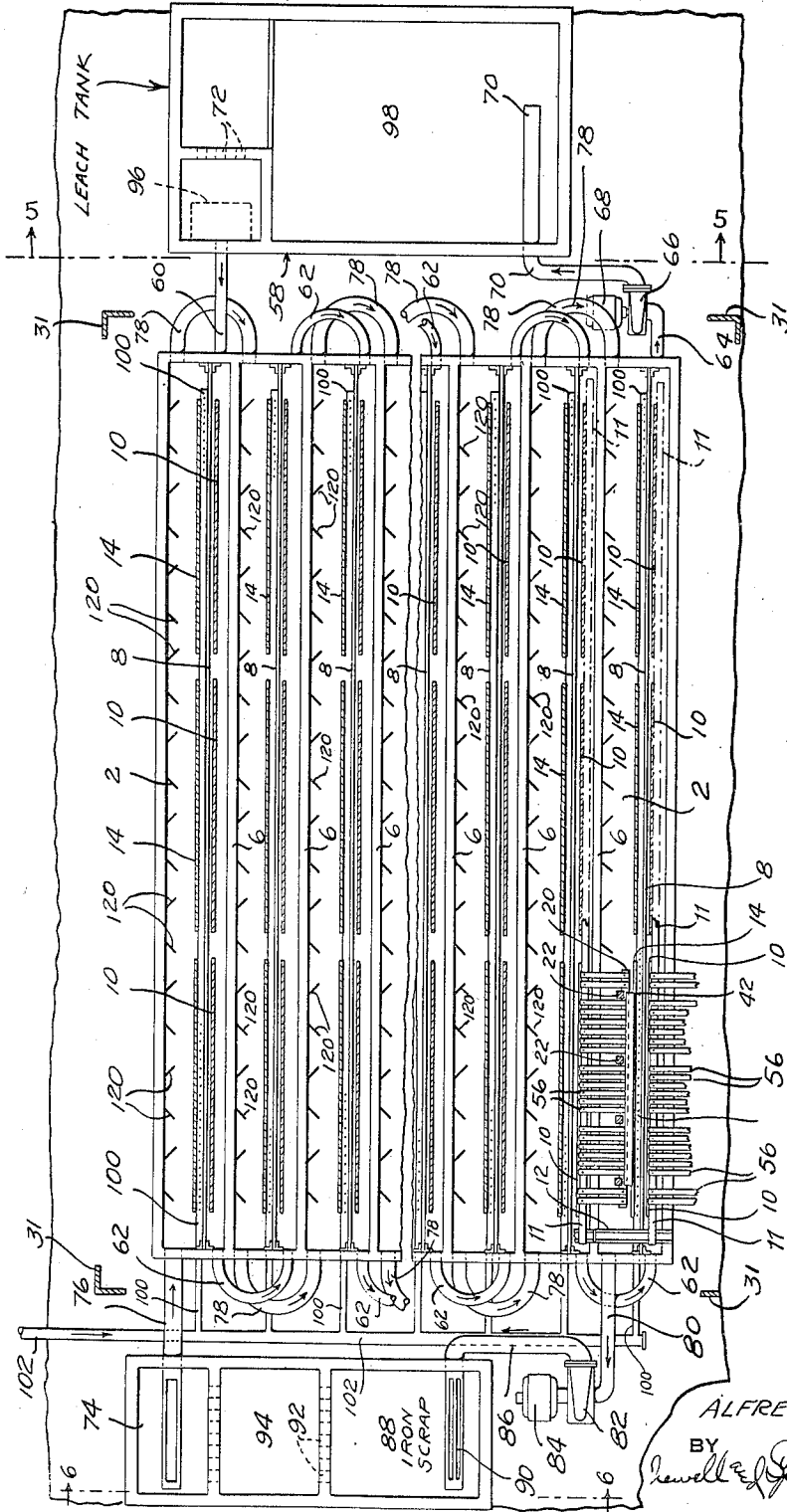


Fig. 1.

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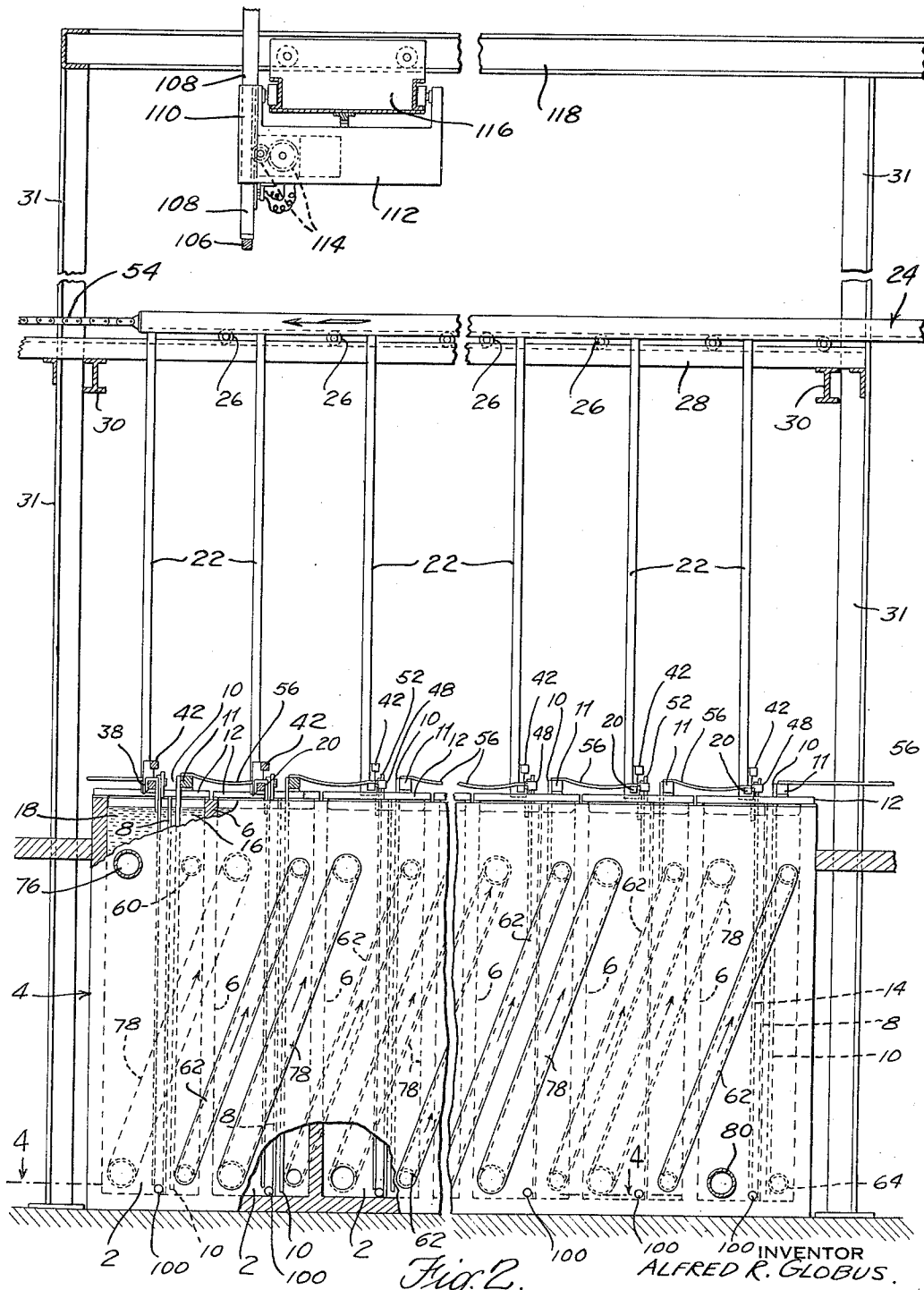


Fig. 2.

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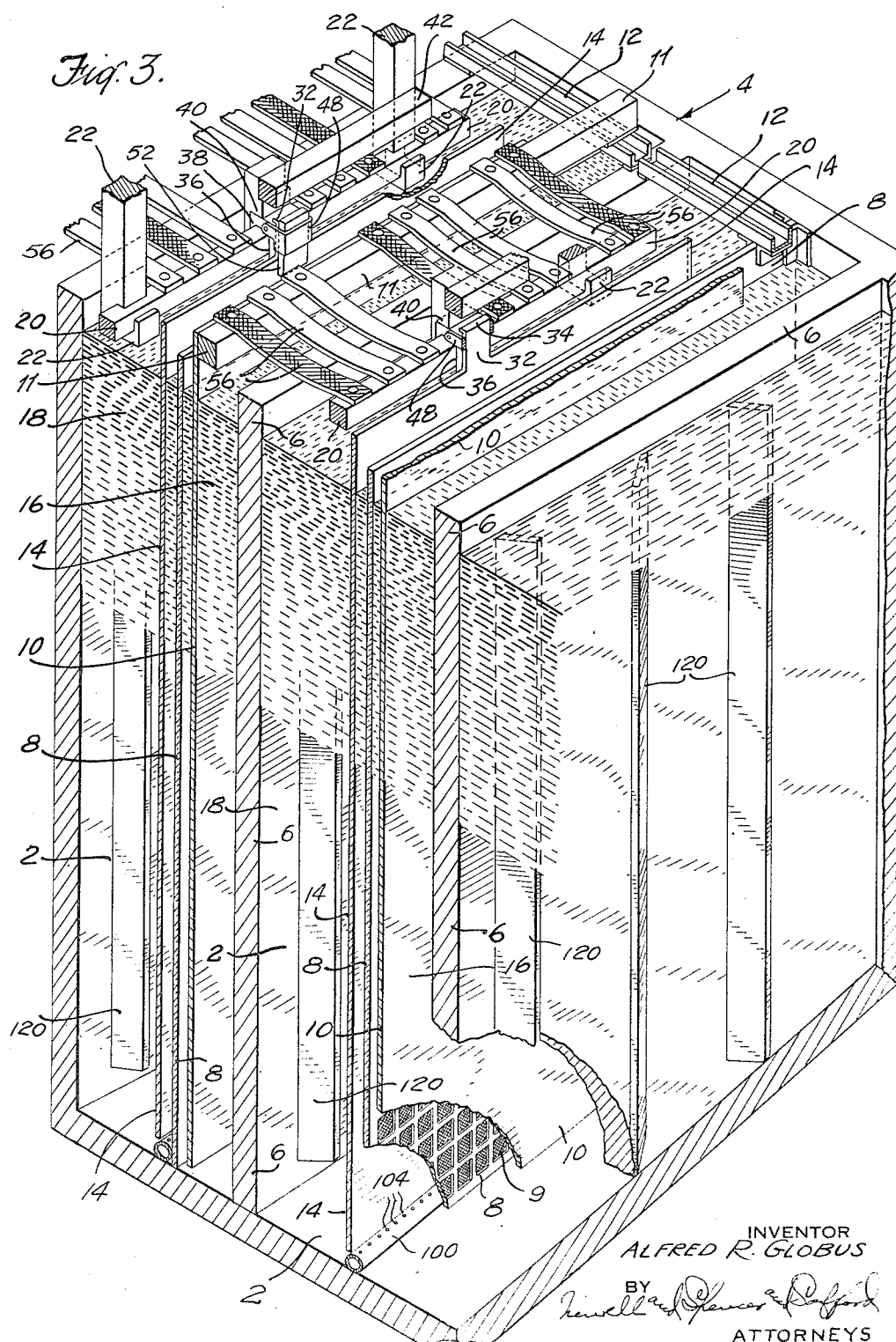
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PROCESS OF ELECTROLYTICALLY EXTRACTING METAL

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4 Sheets-Sheet 3



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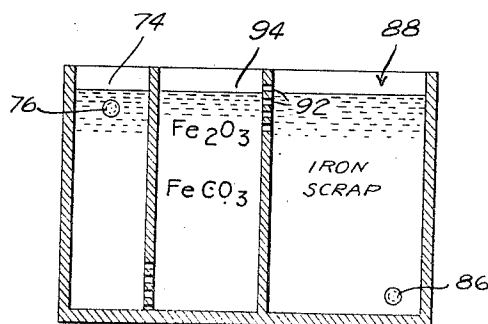
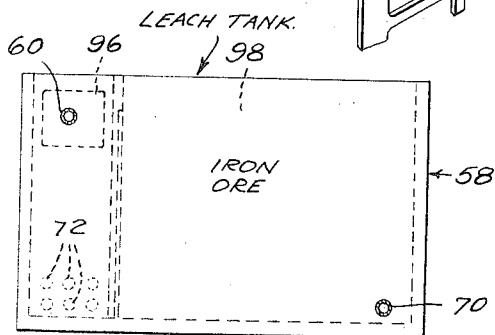
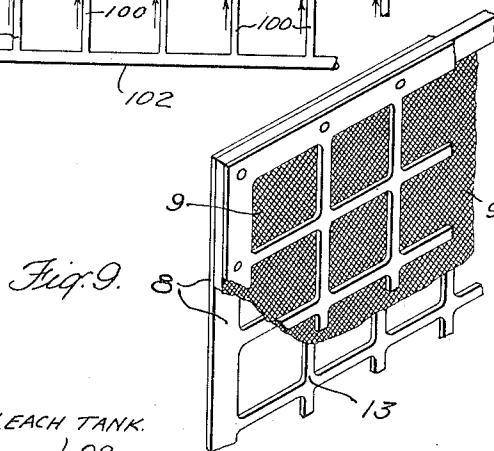
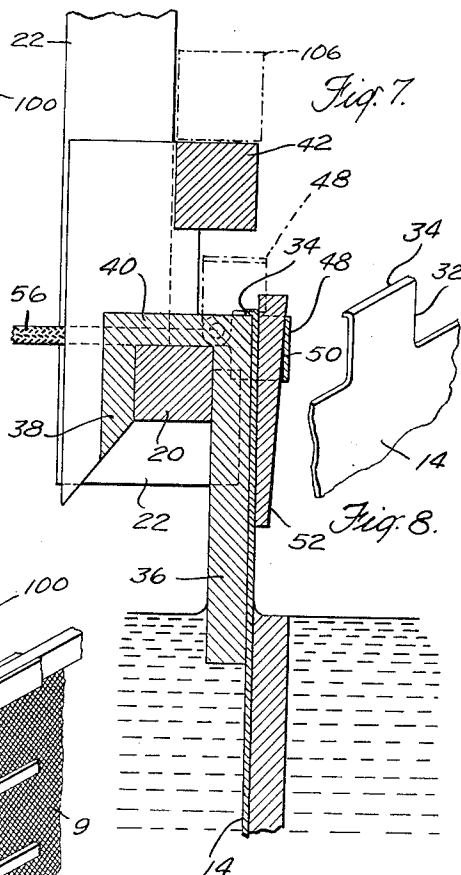
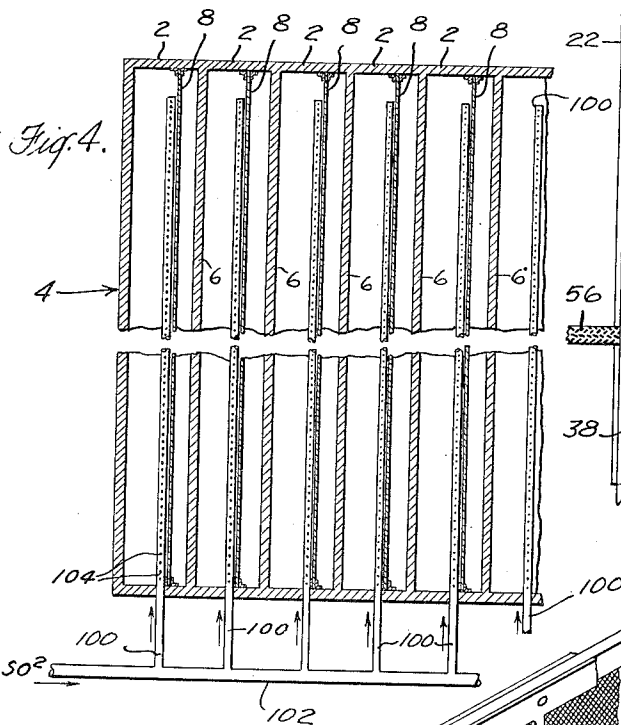
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PROCESS OF ELECTROLYTICALLY EXTRACTING METAL

Filed May 10, 1941

4 Sheets-Sheet 4



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UNITED STATES PATENT OFFICE

2,385,269

PROCESS OF ELECTROLYTICALLY
EXTRACTING METAL

Alfred R. Globus, Brooklyn, N. Y., assignor of eleven and one-ninth per cent to Otto H. Henry, Caldwell, N. J., eleven and one-ninth per cent to James C. Hartley, Silver Mine, Norwalk, Conn., and eleven and one-ninth per cent to H. Dorsey Spencer, New York, N. Y.

Application May 10, 1941, Serial No. 392,871

10 Claims. (Cl. 204—112)

This invention relates generally to electrolytic processes. More particularly the invention relates to improved processes for effecting the electrolytic refining of metals or the electrowinning or electrolytic extraction or separation of metals from their ores, compounds, mixtures, alloys, scrap and waste.

Although the electrolytic refining of metals and the electrolytic separation or recovery of metals from their compounds has long been known and commercially practiced, particularly when a metal of exceptional purity has been desired or when the high market price of a metal has permitted the use of a process for its recovery that might otherwise not be commercially practicable, electrolytic processes have not, for the most part, been found to be practicable for use in extracting or separating the lower priced metals, such as iron, from their ores and compounds. Electrolytic processes have been devised and used to a limited extent for extracting iron from its ores and electrolytic processes have also been used for refining iron, but none of these processes has gone into extensive commercial use because the high cost of operation involved in each of them has made the cost of the product too high to permit competition with iron of approximately similar quality produced by other processes.

Having regard to the difficulties heretofore encountered in effecting economically the electrolytic extraction of the lower priced metals, an important object of the present invention is to provide an improved process for effecting the electrolytic extraction or recovery of metals from their ores, compounds, mixtures, alloys, scrap or waste which can be practiced as a continuous process, which will require less labor and supervision to maintain it in successful operation than processes heretofore used or conceived and in which the current consumption will be so low in proportion to the amount of metal recovered as to permit the process to be used competitively to recover such relatively inexpensive metals as iron.

Another important object of the invention is to provide apparatus which will facilitate the practice of the improved process substantially continuously and which will make easily possible the operation of the process and apparatus over long periods of time without stoppage for repair or replacement of parts or for replacement of the electrolyte.

A particular object of the invention is to effect the extraction or recovery, on a commercial scale, from their ores, compounds, mixtures, alloys, scrap or waste, of iron and other metals which

have heretofore been found to be difficult to extract electrolytically, by plating the iron or other metal to be recovered out of a solution of a salt or salts of the metal and at a cost for the iron or other metal in its marketable condition that will not only permit competition in the open market with metal of approximately the same quality produced by other processes, but also, particularly in the case of iron, will permit competition with and substitution for much less refined iron produced by other processes.

The invention aims further to produce, as an end product of the improved extraction process, iron or other metal of a quality superior to that which is the end product of existing iron refining processes and at a cost below that of the best refined iron now on the market.

With the foregoing and other objects in view, the invention aims to provide and to maintain an improved electrolyte, and particularly an electrolyte for use in the extraction of iron, which will permit the use of high current densities with correspondingly rapid electrolytic deposition of the metal to be extracted.

The invention aims further so to control the composition and condition of the electrolyte employed for the extraction of the particular metal to be extracted that continuous and uniform extraction of the metal may be obtained over long periods of operation without interruption to replace or recondition the electrolyte and without permanent contamination thereof.

An important feature of the invention is the provision of means through which successive portions of the electrolyte may be circulated outside the electrolytic zone and treated to correct any divergence from the optimum composition or condition and returned to the electrolytic zone, all as a part of a continuous circulation of the electrolyte. A further important feature of the invention is the provision, in electrolytic apparatus in which a diaphragm separates the anolyte portion of the electrolyte from the catholyte portion thereof, of means for independently circulating the anolyte portion of the electrolyte through a leaching cell and the catholyte portion of the electrolyte through a correction cell or cells, whereby the anolyte may constantly be replenished with compounds of the metal to be extracted and the condition of both parts of the electrolyte as well as the composition thereof may be kept at the optimum.

Still another important feature of the invention is the provision for reducing a less readily platable metal ion, such as the ferric ion of iron,

to a more readily platable ion, such as the ferrous ion of iron, in the electrolyte itself, whereby the process is directly applicable to the extraction of metals from compounds or mixtures in which the metals are found in their less readily platable forms.

Another important feature of the invention is the provision for adjustment of the cathode to permit the deposition thereon of relatively thick plating, thus facilitating more continuous operation and less supervision.

Other objects and important features of the invention will appear from the following description and claims when considered in connection with the accompanying drawings, in which

Figure 1 is a plan view, with some parts removed, of electrolytic apparatus suitable for practicing the novel process of the present invention and embodying novel structural features of the present invention;

Figure 2 is an end elevation of the electrolytic apparatus and of the means for supporting the cathodes and for removing them from the electrolytic cells.

Figure 3 is an isometric view, partly in section, showing the arrangement of the elements of each electrolytic cell, the electrical connections between cells and the means for supporting the elements and maintaining them in their positions in the cells;

Figure 4 is a section, on the line 4—4 of Figure 2, illustrating the arrangement of the means for introducing a reducing agent into the catholyte portion of the electrolyte in the immediate vicinity of the diaphragm;

Figure 5 is a section on the line 5—5 of Figure 1;

Figure 6 is a section of the line 6—6 of Figure 1;

Figure 7 is a section through the cathode-supporting bar and clamp;

Figure 8 is a perspective detail of a portion of the upper end of the cathode showing the tongue and hook provided on the cathode for facilitating connection to the cathode clamp, and

Figure 9 is a perspective detail showing a suitable diaphragm construction.

In the electrolytic extraction of metals from their ores, compounds or mixtures, if such extraction is to be commercially practicable, the rate of recovery of the metal, usually by plating upon the cathode of the electrolytic cell, must be such, in proportion to the current consumption, labor costs and cost of chemicals used up, as to permit competition with other processes of producing metal of approximately the same quality. In the case of the extraction of iron from its ores, compounds and mixtures, two practical difficulties have been encountered. In the first place, the electrolytes heretofore employed have been unsatisfactory, either because they were of such composition that they would not permit operation at high current densities, and therefore the rate of production was low, or the electrolyte was corrosive and difficult to handle and the metal product was of inferior quality and readily corroded. In the second place, many of the processes heretofore devised for the extraction of iron have been substantially restricted to use with ferrous compounds of iron, it being impracticable to extract iron from the ferric compounds by such processes.

The present invention aims not only to provide an improved electrolyte which will permit operation with high current densities, but also to

provide a process and apparatus which can be used either with ferrous compounds of iron or with the ferric compounds. Since iron appears in nature much more often in its ferric form than in its ferrous form, it is important that any electrolytic process for the extraction of iron be applicable to all types of iron ores.

It is not only important in a commercially practicable process for the extraction of iron from its ores, compounds and mixtures to provide an electrolyte which will permit operation with a comparatively high current density, in order to secure substantial production, but it is equally important both to maintain the electrolyte in condition to permit operation with relatively high current densities and also to keep it supplied with sufficient compound or compounds, in solution, of the iron or other metal to be extracted in order to provide for constant movement of the metal ions in substantial volume to the cathode.

These ends the present invention accomplishes by providing, in the electrolytic cell, a diaphragm separating the anolyte and catholyte portions of the electrolyte and by effecting a counterflow circulation of the two parts of the electrolyte thus defined, portions of the anolyte being caused to flow outside the electrolytic zone through a leaching cell or compartment in which the electrolyzed metal salt is replaced and portions of the catholyte being circulated through a correction cell or cells, also outside the electrolytic zone, in which it is restored to the proper hydrogen ion concentration, in which any undesirable compounds of the metal are converted into more desirable ones and in which depolarization can also be effected, if necessary. In this manner continuous operation can be maintained. Moreover, if the metal to be extracted be iron and if the iron compound leached by the anolyte be a ferrous compound, further treatment of the electrolyte will be unnecessary for relatively high capacity operation. When, however, the iron to be extracted is in the ferric form and is leached by the anolyte from the ore or other source as a solution of a ferric salt, it is important, in order to secure high capacity operation, to reduce the electrolyzed ferric ions to ferrous ions, an object which is attained by the present invention by introducing a reducing agent into the catholyte portion of the electrolyte immediately adjacent to the diaphragm so that the ferric ions are subjected to the action of the reducing agent as soon as they pass through the diaphragm.

I have found in practice that an electrolyte which will give very satisfactory results in extracting iron, either in its ferrous form or in its ferric form, from its ores, compounds or mixtures, by electroplating, is one having the following composition:

Chemical	Formula	Quantity
Ferrous sulphate.....	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	2½ lbs.
Ammonium sulphate.....	$(\text{NH}_4)_2\text{SO}_4$	1½ lbs.
Ferrous chloride.....	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	4 ozs.
Sodium sulphate.....	Na_2SO_4	4 ozs.
Ammonium chloride.....	NH_4Cl	3 ozs.
Water.....	H_2O	1 gallon.

I have further found that a satisfactory reducing agent to be employed with the above electrolyte, when extracting iron from ores, compounds or mixtures in which it appears in its ferric form, is sulfur dioxide (SO_2).

Starting with an electrolyte of the composi-

tion above given and describing the invention first as it is employed in extracting iron from an ore, compound or mixture in which it appears in its ferric form, the process may be practiced conveniently with the novel apparatus illustrated in the drawings in which a series of electrolytic cells 2 may be formed in a rectangular vat or tank 4, of the desired overall dimensions, by means of cross partitions 6. The material of which the vat or tank 4 and the cross partition 6 is made should be acid-proof, at least that part which comes in contact with the electrolyte. A suitable construction is provided by forming the main supporting structure of reinforced concrete and forming the cross partitions 6 of acid-proof bricks or other suitable material, the portions of the outside wall between the partitions being also preferably lined with some acid-proof material.

Suitable dimensions for the cells 2 for a plant of substantial commercial capacity, say, for example, 100 tons of iron per day, would be an inside distance between the partition walls 6 of 2 feet 8 inches and an overall depth of the cell of 11 feet. The other dimension of the cell will depend upon the number of cathodes, of a size conveniently to be handled, which it is desired to suspend in each cell. If the cathodes have surface dimensions of 10 feet by 10 feet and it is desired to hang three in each cell, then the lengthwise dimension of each cell would be in the neighborhood of 35 feet.

In a cell of the dimensions above given, the electrolyte is preferably maintained at a depth of about 10 feet or slightly more. In each of these cells there will be located a permanent fixed diaphragm 8, which may be of any suitable permeable material such, for example, as glass cloth. The diaphragm 8 divides each cell 2 into two compartments in one of which the anode 10 is located, the anode 10 being fixedly connected to an anode bar 11 supported on cross bars 12, and in the other of which the cathode 14 is suspended. The diaphragm also divides the electrolyte into two parts, the part 16 of the electrolyte on the anode side of the diaphragm being referred to hereinafter as the anolyte and the part 18 on the cathode side of the diaphragm being referred to hereinafter as the catholyte.

The diaphragm 8, as shown in Figure 9, may comprise panels of glass cloth 9 covering the openings in a reticulated frame 13 of Bakelite or other suitable material. The diaphragm 8 extends to the bottom of the cell 2 and also to the end walls thereof so as to form a complete partition from its top edge down and is secured in its position, it being usually unnecessary either to remove or to replace the diaphragm over long periods of time. The diaphragm may be secured, if desired, to the same cross pieces 12 to which the anodes are secured.

The anodes 10 are preferably of some form of carbon. Graphite has been found to be a satisfactory anode material for use in the extraction of iron.

The cathode plate 14 is formed of an iron sheet, preferably a sheet rolled from the electrolyte iron, and, when plated to the desired depth and removed, it will be worked up with the iron that is plated thereon. To permit the cathode sheet to be readily removed and readily replaced, special supporting means are provided which will now be described: The main cathode supporting bar 20, of substantial section and good conductivity, for example of a 3 to 4 inch square cross section and made out of some suitable material such as brass

or hard annealed copper, is suspended above the cross bars 12 by hooks 22 from an overhead carriage 24 slidable on rollers 26 on tracks 28 carried by cross supports 30 on vertical frame members 31.

Each cathode plate 14 is preferably provided with a series of integral tongues 32 on its upper edge, each of which has a turned over lip 34 to form a hook engaging the upper surface of a clamp member embracing the main cathode supporting bar 20. This clamp member, which is shaped to fit over the cathode supporting bar 20, has a long depending arm 36 on the side of the bar adjacent to the cathode 14 and a short depending arm 38 on the back side of the bar, the bar fitting tightly between these arms and the top portion 40 resting on the bar. The top members 40 of the clamps for a single cathode are connected to an iron bar 42 which serves as an armature for magnetic cathode lifting means hereinafter to be described. A yoke-shaped movable clamp member 48 embraces the stationary clamp member, is hinged thereto as shown and is provided with a recess 50 in front of the stationary clamp member into which may be driven a wedge 52 to clamp the tongue 32 and a portion of the cathode plate 14 immediately below the tongue 32 tightly against the long arm 36 of the stationary clamp member.

From the foregoing description of the means for attaching the cathode plate 14 to the main cathode supporting bar 20 it will be seen that provision is made not only for good electrical contact, but also for substantial support of the plate 14 against any tendency to swing away from the anode 10 and diaphragm 8 at its lower end as the center of gravity of the plate moves outward from a vertical plane through its connection with the bar 20 with the increase in the thickness of the plating on the cathode 14.

As the thickness of the cathode 14 increases with the plating additions thereto, it is important, in order that there may be sufficient circulation of the catholyte 18 between the cathode 14 and the diaphragm 8 to provide ferrous ions for the plating and movement thereof into plating position, that there be provision for moving the cathode 14 away from the diaphragm 8 to maintain approximately a uniform spacing of these two parts. This may be accomplished by moving the carriage 24, from which the hooks 22 are suspended, on the rollers 26 on the tracks 28. Any suitable means, such as an electric motor controlled by a hand switch (not shown), may be provided for effecting the movement of the carriage 24. Such means may be operatively attached to the carriage by means of a chain 54.

As will be seen from Figure 3, the electrodes of the successive cells are preferably connected in series and as many cells may be arranged in series as are required for the desired production or as may be suitable for producing the desired voltage drop through each cell for the total voltage drop of the circuit. Since the process is intended to be operated at high current densities, from 100 amperes per square foot of active cathode surface up, the connections between the anode of one cell and the cathode of the succeeding cell must have sufficient capacity to carry the total number of amperes to maintain such density. As shown particularly in Figure 3, a sufficient number of bus bars 56 to handle the total amperage necessary, for example 10,000 amperes or more from each anode to each cathode, will be provided. The bus bars 56 are preferably of

braided material and connect the cathode supporting bars 20 with the anode supporting bars 11.

As hereinabove suggested, not only is provision made for keeping the electrolyte in the cells 2 in movement to insure the presence, in the region of current concentration, of the metallic ions required for plating and to facilitate the movement of the ions into contact with the cathode, but the circulation is so arranged that the anolyte and catholyte move in counterflow relation to each other through the cells and that portions of each are carried outside the electrolytic zone for treatment to maintain their proper composition and condition, the anolyte being carried through a leaching cell in order to replace the metallic salts that have been decomposed and depleted of their metallic ions by the electrolysis and the catholyte being circulated through a correction cell or cells to restore its composition and condition substantially to their initial states.

As shown particularly in Figures 1 and 2 of the drawings, the circulation of the anolyte is as follows: Coming out of the leaching tank or cell 58 through the pipe 60 the replenished anolyte enters the first cell 2 of a bank of cells on the anolyte side of the diaphragm 8, the pipe 60 being arranged to discharge the replenished anolyte into the upper part of the cell 2 at this end of the bank of cells. The course of the circulation of the anolyte is then as follows:

From the other end of the first cell 2 of the bank of cells a connecting pipe 62 leads from the bottom of this first cell 2 to the top of the next cell 2. The replenished anolyte, which has entered the first cell 2 of the bank of cells, as it travels through this cell will be mixed with some of the old anolyte still in the cell and a part of this mixture will then be carried through the connecting pipe 62 into the upper part of the next cell, the connecting pipe 62 discharging this mixture into the second cell of the bank on the anolyte side of the diaphragm of that cell. At the other end of the second cell a similar connecting pipe 62 leads from the bottom of the second cell to the top of the anolyte side of the third cell and so on until the last connecting pipe 62 discharges its mixture into the anolyte side of the last cell 2 of the bank.

From the last cell 2 of the bank a discharge pipe 64 leads from the bottom of the anolyte side of this cell into the intake of a pump 66, which may be a centrifugal or other suitable pump constructed of suitable material to resist acid corrosion. This pump, driven by any suitable motor 68, forces the more or less depleted anolyte received from the last cell through a pipe 70 into the bottom of the leaching vat or cell 58 in which the ore or other source from which the metal is to be extracted is contained, thus permitting the now quite acid anolyte to leach the metal content from the ore or other metal source in the form of a salt of the acid. The anolyte forced into the leaching cell or vat 58 works its way up through the ore or other source of metal to be extracted and passes through the openings 72 in the filter compartment into the filter where any sediment forming materials contained therein are strained out before the thus replenished anolyte enters the pipe 60.

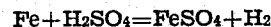
Describing now the catholyte circulation and starting with the filter chamber 74, the regenerated catholyte leaving the filter chamber 74 passes through the pipe 76 into the catholyte compartment of the first cell 2 of a bank of cells,

being conducted into this catholyte compartment near the top thereof. The catholyte in its travel through the catholyte compartment of the first cell 2 becomes mixed with the catholyte already in said compartment and a part of the mixture then passes out of the bottom of this catholyte compartment in the first cell 2 of the bank of cells through a connecting pipe 78 which conducts it into the catholyte compartment of the next cell of the bank of cells near the top of said compartment. From the bottom of the catholyte compartment of the second cell a similar connecting pipe 78 leads to the top of the catholyte compartment of the third cell of the bank of cells and so on until the catholyte or the part thereof that is to be delivered to the last cell of the bank is conducted through the last connecting pipe 78 to the catholyte compartment of the last cell 2 of the bank. From the bottom of the catholyte compartment of the last cell of the bank a pipe 80 leads to the intake of a circulating pump 82 of suitable construction, driven by a motor 84 and serving to create the catholyte circulation. The pump 82 discharges the catholyte to be corrected through a pipe 86, provided, in the first correction cell 88, with slots 90 that discharge the catholyte into the bottom part of the cell 88. The cell 88 is filled with pieces of scrap iron through which the catholyte slowly percolates.

When the catholyte leaves the catholyte compartment in the last cell 2 of the bank of cells its acidity will have been considerably increased and, when the apparatus is used for the electrolysis of iron leached from ores or other iron sources in which the iron appears in its ferric form, the catholyte will also contain some unreduced ferric iron, usually in the form of ferric sulphate. The catholyte will also contain some sulfuric acid resulting from the electrolysis. As the catholyte moves up through the scrap iron the ferric sulphate will pick up an atom of iron and be converted into ferrous sulphate in accordance with the following equation:

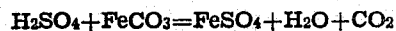


Likewise any sulfuric acid found in the catholyte will pick up iron from the iron scrap and form ferrous sulphate in accordance with the following equation:

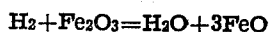


From the correction cell 88 in which the catholyte has been freed, for the most part, from its ferric iron content, it passes through openings 92 near its top into the second correction cell 94. As it enters this cell it contains very little iron in the ferric form but still has a too low hydrogen ion concentration. The purpose of the treatment in the second correction cell is to deacidify the catholyte to the required extent and also to effect such depolarization as may be necessary.

The second correction cell is filled with canvas bags containing granules or small lumps of ferrous carbonate, FeCO_3 , and iron oxide, Fe_2O_3 , in the proportion of 10 to 12 parts of ferrous carbonate to 1 part of iron oxide by weight. Here the acid content of the liquid is lowered to its necessary pH, the deacidifying and depolarizing reactions taking place in this second correction cell being represented, respectively, by the following equations:



and



the latter being the basic equation and not being intended to represent what actually takes place in the way of reactions.

The leaching cell or vat 58, like the correction cell, is provided with a filter chamber 96 through which the anolyte travels on its way to the pipe 60, after it has been replenished with metallic ions by its passage through the leaching compartment 98 in which the ore or other metal source is located. Both in the filter chamber 96 of the leaching cell or vat 58 and in the filter chamber 74 of the correction cell the filtering means may be sand. It will be understood, of course, that other arrangements for filtering the anolyte and the catholyte may be provided, such as any of the well known pressure filters.

As hereinabove suggested, when the process and apparatus of the present invention are used for the extraction of metals from their ores, compounds or mixtures in which the metals appear in their less platable forms, that is, in their higher valence forms, the invention contemplates reducing the metallic ion from its higher valence form to a lower valence form as it travels through the catholyte to the cathode. In order to insure such reduction, it is important that the reducing agent be introduced into the catholyte in close proximity to the diaphragm. As shown in Figures 2, 3 and 4, perforated pipes 100, having their perforated portions inside the cells, are connected to a manifold 102 through which the reducing agent, such for example as sulfur dioxide, SO_2 , may be supplied to the pipes 100, these pipes being located in the bottoms of the cells 2 immediately adjacent to the diaphragm 8 on the catholyte side thereof. The perforations 104 which are preferably closely spaced on the top side of the pipes, for example every $\frac{1}{4}$ " or $\frac{1}{2}$ ", may be arranged in either single or double rows as may be found desirable under the particular conditions to be met. These pipes 100 may be of any suitable acid-resisting material such as strong glass tubing.

When it is desired to remove any cathode from its cell, after it has received the desired thickness of plating, it will be seen that this can readily be done by means of an electromagnetic hoist operating on the armature bar 42 connected to the clamps which hold the cathode. As may be seen from the drawings and from the description, the cathode clamps merely rest upon the cathode bar 20 in good electrical contact therewith, thus permitting the cathode to be lifted by means of the armature bar 42 which will raise the cathode clamps up out of engagement with the cathode bar 20.

Any suitable electromagnetic hoist may be used, such as the one shown more or less diagrammatically in Figure 2, in which the magnet 106 is carried on a vertical rack 108 movable in a guide 110 on the transversely movable carriage 112 of an overhead crane, the rack 108 being movable by geared connections 114 to electrically driven hoist mechanism on the carriage 112 to lower the magnet 106 into engagement with the armature 42 of any cathode and, after energization of the magnet 106, to lift the cathode bodily out of its cell. The transversely moving carriage 112 of the overhead crane will be mounted on the usual longitudinally movable carriage 116 which extends across the entire length of the cells 2

and travels on overhead tracks 118 carried on extensions of the frame members 31.

From the foregoing description of the process and apparatus, its operation for the extraction of a metal from its ores, compounds, mixtures, scrap or waste will readily be understood. If, for example, the process and apparatus be used for the extraction of iron from a hematite ore having its iron constituent in the form of anhydrous iron oxide, Fe_2O_3 , this ore will preferably be brought to a granular or powdered state, 50 mesh or finer, and concentrated somewhat to avoid the necessity for the removal of excessive quantities of sludge from the leaching cell or vat and will then be introduced into the leaching cell or vat 58. The cells 2, the leaching cell or vat 58 and the correction cells 88 and 94 and the filter cells 74 and 96 will then be filled to the desired level with the electrolyte. With cells 2 of the dimensions hereinabove given, the electrolyte will preferably be kept at a depth of about 10 feet in each cell and the various cells are preferably so connected that the electrolyte will seek its hydrostatic level in the leaching cell 58 and in the correction cells as well as in the electrolytic cells 2, thus confining the functions of the pumps 66 and 82 primarily to circulation.

Starting with an electrolyte of the composition hereinabove given, that is, comprising ferrous sulphate, ammonium sulphate, ferrous chloride, sodium sulphate, ammonium chloride and water in the proportions hereinabove given, and having a hydrogen ion concentration to start with in the neighborhood of 6, it will be obvious that until some electrolysis takes place there will be substantially no leaching action in the cell 58 and no correction action in the correction cells.

When, however, the current is turned on and electrolysis begins to take place, migration of the metallic and acid ions of the ferrous sulphate and the ferrous chloride begins to take place. The metallic ions being in the ferrous form will readily plate out upon the iron cathode 14. The acid ions on the anolyte side of the diaphragm 8, as they move to the anode 10, will pick up hydrogen from the water of the electrolyte and release the oxygen of the water at the anode 10. There will thus be an increase of the acid content of the anolyte by the formation of sulfuric acid (H_2SO_4) and hydrochloric acid (HCl).

The pumps 66 and 82 are started, of course, as soon as the current is turned on the cells, or even before, and, as hereinabove pointed out, they cause the anolyte to move in one direction through the cell 2 and the catholyte to move in the other direction through the cell 2. To bring about sufficient turbulence in the catholyte to insure continuous presence of metallic ions between the diaphragm 8 and the cathode 14 and at the same time to assist in the movement of the metallic ions into contact with the cathode, it is desirable to provide baffle plates 120 on the sides of the cells behind the cathodes. These baffle plates 120 may be plates set at oblique angles to the side walls of the cells, successive plates being inclined in opposite directions so as to set up turbulence in the catholyte, insuring movement of the catholyte from behind the cathode to the space between the cathode and the diaphragm and also a thorough mixing of the different parts of the catholyte.

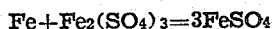
As the catholyte and anolyte move from one cell to the next under the action of the circulating pumps 82 and 66 and replenished anolyte is supplied to the first cell 2 of the bank of cells

on the anolyte side of the diaphragm 8 and corrected catholyte is supplied to said first cell 2 on the catholyte side of said cell, the acidity of the anolyte will gradually increase as it travels from cell to cell until, when it is ready to leave the last cell 2 of the bank of cells and enter the intake of the pump 66, it will have its acidity so increased that it will readily leach the iron content from the ferric oxide of the hematite in the leaching cell or vat 58 in the form of ferric salts of sulfuric and hydrochloric acids. In other words, the anolyte after passing through the leaching cell 58 will contain ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$ and ferric chloride, FeCl_3 .

When the anolyte returns to the first cell 2 of the bank of cells it will differ from the original electrolyte in that ferric sulphate has been substituted for ferrous sulphate and ferric chloride for ferrous chloride. This would cause interference with the plating, in fact no economical plating would take place in the absence of some provision for reducing the ferric ions to ferrous ions before they come into contact with the cathode. To bring this about a reducing agent is introduced into the catholyte 18 through the pipes 100. As hereinabove pointed out, an effective and suitable reducing agent for this purpose is sulfur dioxide, SO_2 , which is caused to bubble up through the catholyte 18, immediately adjacent to the diaphragm 8, as it is discharged from the openings 104 in the pipes 100.

The result of introducing the SO_2 into the catholyte immediately adjacent to the diaphragm 8 is that as the ferric ion Fe^{+++} , electrolytically dissociated from the acid ion of the ferric sulphate or ferric chloride, passes through the diaphragm 8 on its way to the cathode 14 it encounters the SO_2 travelling up the diaphragm 8 and is reduced to a ferrous ion Fe^{++} , the SO_2 being at the same time oxidized to SO_3 . The ferrous ion, if it is not reoxidized before it reaches the cathode, then plates out upon the cathode 14. The SO_3 combines with the water of the electrolyte and forms sulfuric acid H_2SO_4 , thus increasing the acidity of the catholyte.

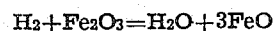
It will sometimes happen that not all of the ferric ions will be reduced to ferrous ions and that some of those which have first been reduced to ferrous ions may again be oxidized to ferric ions before reaching the cathode, with the result that there will be a gradual accumulation of ferric ions in the catholyte which must be removed in the correction cell to secure the desired efficiency of operation. These ferric ions will be found in the catholyte usually in the form of ferric sulphate as the catholyte leaves the last cell of the bank. As hereinabove pointed out, the ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, in the catholyte leaving the last cell 2 will be converted into ferrous sulphate, FeSO_4 , by picking up an atom of iron from the iron scrap in the first correction cell 88 in accordance with the equation



It will be understood that for this reaction to take place readily the iron scrap must be well cleaned and preferably acid dipped. Some of the H_2SO_4 of the catholyte will also react with the iron scrap to form FeSO_4 in accordance with the reaction $\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2$.

As the catholyte, which now has its ferric iron substantially all reduced to ferrous iron in the form of ferrous sulphate, passes from the first correction cell 88 into the second correction cell 94, it will still contain some sulphuric acid in ex-

cess of the desired amount but in this second correction cell it will come into contact with ferrous carbonate, FeCO_3 , with which it will combine to form ferrous sulphate according to the reaction $\text{H}_2\text{SO}_4 + \text{FeCO}_3 = \text{FeSO}_4 + \text{H}_2\text{O} + \text{CO}_2$. The catholyte may also contain some uncombined hydrogen from the acid reaction in the cell 88 and therefore require depolarization. In the second cell 94 this hydrogen will combine with the ferric oxide Fe_2O_3 to form ferrous oxide and water, the hydrogen acting as a reducing agent in accordance with the basic equation



When spacings of the anode 10 and cathode 14 from the diaphragm 8 are such as shown in Figure 3, in an electrolytic cell of the dimensions hereinabove set forth, and there is a potential drop of 1.5 volts through the diaphragm 8, I have found that about 3.2 volts will be required under good conditions to produce the desired ampere density but that the required voltage may increase somewhat if the diaphragms become clogged or the ferric ion content of the electrolyte becomes high. I have also found that electrolyte temperatures between 90°C . and 95°C ., with current densities of from 100 amperes per square foot of active cathode surface to 135 amperes per square foot of active cathode surface, contribute to economical operation and relatively high production.

The electrolyte hereinabove specifically described and preferably used has the following characteristics:

1. It has high conductivity and may be operated efficiently at either high or low temperatures; it is also operative with very high current densities.

2. It is stable at all temperatures up to the boiling point, it is not easily oxidized and it is therefore operative over long periods of time.

3. It is relatively non-corrosive (catholyte).

4. The cathodic polarization is low and yet there is no trouble with treeing.

5. It is comparatively difficult to contaminate.

6. Its condition and composition are easily controlled over long periods of time.

7. The metal plating on the cathode, if iron is being extracted, is white, hard and contains little occluded hydrogen. Moreover, the iron does not rust quickly when removed from the bath.

I have further found that satisfactory hydrogen ion concentrations for the catholyte in the various cells of the bank are from pH 4.5 to 6.0.

Controlling and addition agents which may be used with the preferred electrolyte of the present invention are the following:

(a) *Hydroquinone*.—If it is found necessary to use this agent it is added to the catholyte only in the proportion of from $\frac{1}{2}$ to 2 ozs. per gallon and should not be added until the bath becomes difficult to control. Its use is to keep the ferric ion concentration low, to control the oxidation of the solution and to keep corrosion of the cathode low. It acts as a reducing agent, is oxidized to quinone and reduced again by hydrogen, formed at the cathode, to hydroquinone.

(b) *Bisulphite solution*.—This solution comprises two mols of sodium or potassium bisulphite dissolved in water to which is added an aqueous solution of ferrous sulphite. This is a powerful reducing agent and may be added from time to time to the bath to control oxidation if a ferrous ore is being handled and if no sulfur dioxide is being used.

(c) If the catholyte, as it leaves the correction cell, has a pH noticeably below 5.5 its acidity may be reduced by the addition of sodium carbonate, either Na_2CO_3 or $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, added in small quantity. It should, however, not be necessary to effect continuous additions of an alkali solution to the bath because the sodium salt content would soon grow too high. If the efflux from the correction cell shows a continuous pH figure below 5.5 the SO_2 of the cathodic reduction system may be decreased and the liquid slowed slightly in its circulation through the correction cell. If decrease of the SO_2 results in too rapid accumulation of ferric ions in the catholyte this may be offset by bringing the catholyte into contact with a larger quantity of FeCO_3 in the correction cell.

(d) If the pH of the catholyte liquid as it enters the correction cell is above 4.8 it is usually desirable to reduce it, which may be done by the addition of concentrated sulfuric acid in small quantities in the influx pipe to the correction cell. It has been found that to work most efficiently the pH of the used catholyte, as it enters the correction cell, should be 4.5 or thereabout. If the pH of the catholyte, as it leaves the last electrolytic cell and enters the reduction compartment of the correction cell be above 4.5 the efficiency and speed of reduction in this compartment decreases.

Although the process and apparatus of this invention have been herein specifically described in their application to the extraction of iron from its ores, compounds, mixtures, scrap and waste, and to the refining of iron, and it has particular utility in this field because of the difficulty heretofore encountered in electrolytically extracting iron in the ferric form in which it more commonly appears, it will be understood that the process and apparatus are equally applicable to other metals which appear in different valence forms and which are more readily platable in one valence form than in the other. This will be particularly true when it is desired to plate a metal of the aforementioned type directly from a compound in which it appears in its higher valence and less platable form. For example, if it be desired to plate tin from the sodium stannate form, Na_2SnO_3 , or from its stannic sulphate form, $\text{Sn}(\text{SO}_4)_2$, this can readily be brought about by reducing the Sn^{++++} to Sn^{++} in accordance with the equation: $\text{Sn}^{++++} = \text{Sn}^{++} + 2\text{e}$.

A suitable electrolyte for use in plating tin in accordance with the process of the present invention and using, as in the treatment of iron, sulfur dioxide, SO_2 , as a reducing agent, is as follows:

Stannous sulphate SnSO_4 (saturated solution at room temperature).

NH_4SO_4 or Na_2SO_4	ozs...	8
HBF_4	oz...	1
Water.....	gal...	1

Preferred operating temperatures 75 to 95° C.
pH about 5.0.

Nickel has two valences, 2 and 3. If it is to be plated from one of its higher valence compounds, it may be reduced from its nickelic form to its nickelous form in accordance with the equation: $\text{Ni}^{++} = \text{Ni}^{+++} + \text{e}$. If, for example, nickel is to be plated directly from nickelic sulphate, $\text{Ni}_2(\text{SO}_4)_3$, with the aid of a reducing agent, such as SO_2 , a suitable electrolyte for this purpose is

NiSO_4	lbs...	2.5
$\text{Ni}(\text{NH}_2)(\text{SO}_4)_2$	lb...	.5
Na_2SO_4	lb...	.5

Boric acid.....	ozs...	2
Water.....	gal...	1

Suitable temperatures of operation for nickel plating with the above electrolyte are from room temperature to 90° C. with a pH of from 5.5 to 6.1.

However, because of the fact that tin is more commonly plated by dipping and because nickel is readily converted to its nickelous form from compounds in which it appears in its higher valence form, the process of the present invention is believed to have more commercial importance in the electrolytic extraction and refining of iron.

When the process and apparatus of the present invention are employed for the extraction of iron from its ores, compounds or mixtures and current densities, electrolyte temperatures and electrode spacings of the order of those hereinabove mentioned are employed, the resultant iron plate is substantially free from occluded hydrogen and has considerable tensile strength and ductility. If, however, it be desired to employ the process and apparatus for producing iron powder instead of iron plate of substantial tensile strength and ductility, a slightly different procedure would be followed.

To produce an iron powder by the process and apparatus of the present invention, the conditions surrounding the electrolytic extraction of the iron may be so controlled as to produce a friable plate, containing occluded hydrogen, which can readily be broken or crushed into a fine powder or the conditions may be so controlled that the electrolytically extracted iron will directly precipitate itself from the cathode in powdered form. To produce a friable plate, it is only necessary to effect the electrolytic extraction of the iron while maintaining a considerably lower electrolyte temperature and a considerably lower current density. If, for example, the temperature of the electrolyte be maintained at about 50° C. and the current density at about 50 amperes per square foot of active cathode surface, so much hydrogen will be occluded in the plating that the resultant plate will be quite friable and can readily be crushed or ground into a fine iron powder. In this case, in order to permit the friable plate to be readily stripped from the cathode, the cathode may be dipped into an alcoholic solution of paraffine to give it a thin transparent coating of paraffine to which the plate will not so tenaciously adhere.

If it be desired to cause the extracted iron to be precipitated at once in powdered form, this may be brought about by operating at very high current densities with the addition of some organic inhibitor, such as dextrose, to the electrolyte. In the latter case, the iron, instead of attaching itself to the cathode, will tend to precipitate.

When the last mentioned procedure is employed, it will be desirable, in order readily to remove the precipitated iron from the electrolyte, to provide means for trapping it, such as a canvas bag enclosing the cathode which will entrap the iron as it is precipitated from the cathode and thus permit its ready removal from the electrolyte. It will be understood that the covering of the cathode with the canvas sack for the purpose of entrapping the precipitated iron powder will increase the potential drop between the anode and the cathode and that therefore the current consumption, when this second procedure is employed for obtaining iron powder, will be considerably greater than the current consumption by the first mentioned procedure and also consid-

erably greater than when a ductile plate of considerable tensile strength is the end product. In fact, the current consumption for the direct production of precipitated iron powder will probably range in the neighborhood of double that for the production of ductile plating and more than double that for the indirect production of iron powder by first producing a friable plate. A further disadvantage of the direct method of producing an iron powder is that the resultant powder is apt to be contaminated to some extent by the decomposed organic compound employed as an inhibitor.

What is claimed as new is:

1. The process of electrolytically extracting a metal, which has two or more valences, from an ore, compound or mixture in which the metal appears in a high valence form, which consists in leaching the metal from the said ore, compound or mixture as a solution of a salt of the higher valence form, introducing the leach liquor thus obtained into the anolyte part of an electrolytic cell having suitable anodes and cathodes and having a diaphragm separating the anolyte from the catholyte, effecting an electrolytic migration of the metal ions of the higher valence from the anolyte to the catholyte and, as said metal ions move from the anolyte into the catholyte through said diaphragm, effecting the reduction of a major portion of the metal ions entering the catholyte to ions of lower valence by subjecting them to the action of sulfur dioxide directed into reactive relation thereto at the points of their entry into the catholyte.

2. A process according to claim 1 in which the reducing agent, in gaseous form, is caused to bubble up through the catholyte in a zone immediately adjacent to the diaphragm.

3. A process according to claim 1 in which portions of the catholyte are continuously withdrawn, separately from and independently of the anolyte, independently treated outside the electrolytic zone for reduction to lower valence of any still unreduced metal ions of higher valence and returned to the catholyte as a part of a continuous circulation of the catholyte.

4. A process according to claim 1 in which portions of the catholyte are continuously withdrawn, separately from and independently of the anolyte, independently treated for reduction of any still unreduced metal ions of higher valence, partly deacidified, depolarized and filtered outside the electrolytic zone and then returned to the catholyte as a part of a continuous circulation of the catholyte.

5. A process according to claim 1 in which iron in its ferric form is the metal leached from the ore, compound or mixture and in which the

reduction in the catholyte changes it to its ferrous form.

6. A process according to claim 1 in which there is added to the leach liquor, in the anolyte part of the electrolytic cell, ferrous sulphate, ammonium sulphate, ferrous chloride, sodium sulphate and ammonium chloride to produce the initial electrolyte.

7. A process according to claim 1 in which iron in its ferric form is the metal leached from the ore, compound or mixture and is reduced in the catholyte to its ferrous form and in which portions of the catholyte are continuously withdrawn, independently of and separately from the anolyte, and treated outside the electrolytic zone by causing the withdrawn catholyte to percolate through pieces of cleaned scrap iron to effect reduction of any still unreduced ferric iron content thereof to ferrous iron, and then returned to the catholyte part of the electrolytic cell as a part of a continuous circulation of the catholyte.

8. A process according to claim 1 in which portions of the catholyte are continuously withdrawn, separately from and independently of the anolyte, passed over particles of ferric oxide outside the electrolytic zone to effect depolarization of the catholyte and then returned to the catholyte part of the electrolytic zone as a part of a continuous circulation of the catholyte.

9. A process according to claim 1 in which portions of the catholyte are continuously withdrawn, separately from and independently of the anolyte, and treated outside the electrolytic zone by passing the withdrawn catholyte in succession over pieces of clean scrap iron, pieces of ferrous carbonate and pieces of ferric oxide and then returned to the catholyte part of the electrolytic cell as a part of a continuous circulation of the catholyte.

10. A process according to claim 1 in which portions of the catholyte are continuously withdrawn, separately from and independently of the anolyte, independently treated outside the electrolytic zone for reduction to lower valence of any still unreduced metal ions of higher valence and returned to the catholyte as a part of a continuous circulation of the catholyte while at the same time the more acid portions of the anolyte are continuously withdrawn, separately from and independently of the catholyte, passed through an ore, compound or mixture from which the higher valence form of the metal is to be leached, then filtered and returned to the anolyte portion of the electrolytic zone as a part of a continuous circulation of the anolyte.

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