April 16, 1946. T. A. MITCHELL 2,398,590

ELECTROLYTIC CELL

Filed Jan. 11, 1939 3 Sheets-Sheet 1

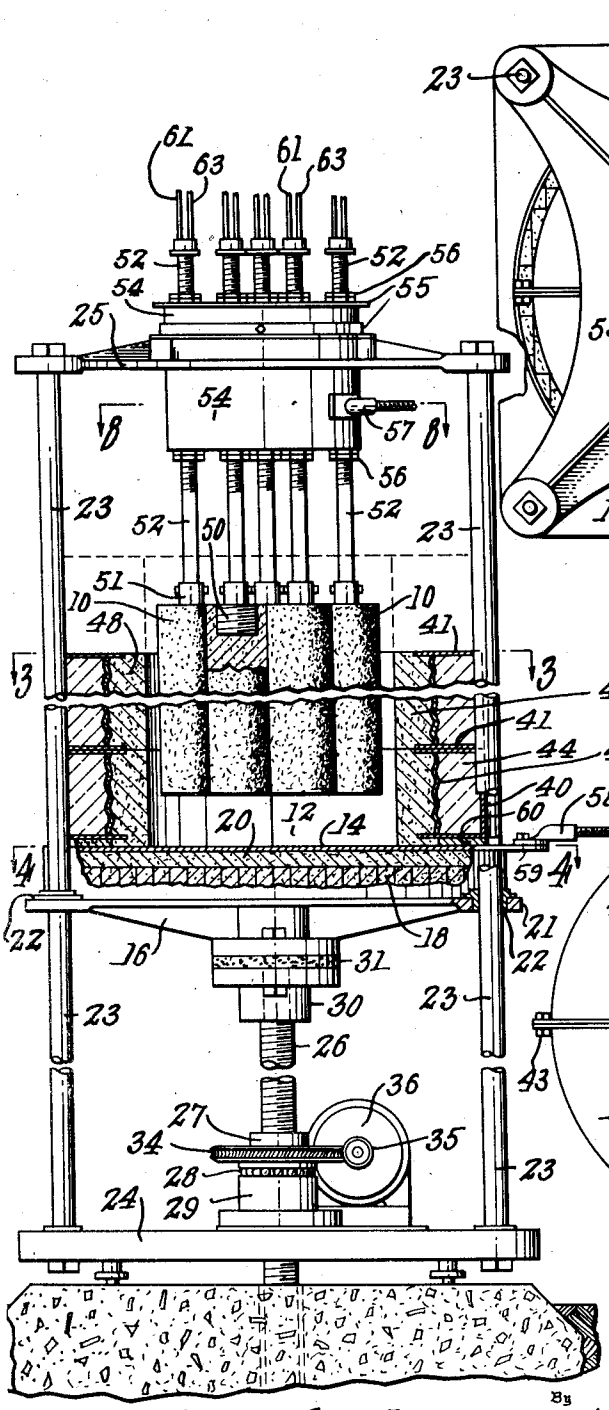


Fig. 1.

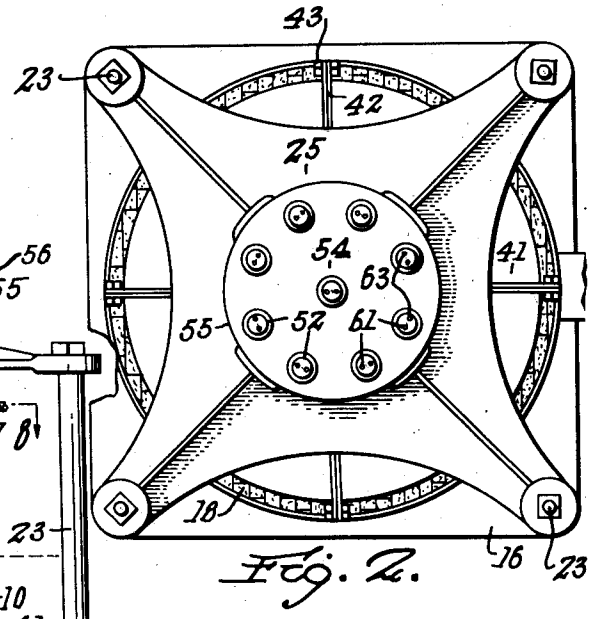


Fig. 2.

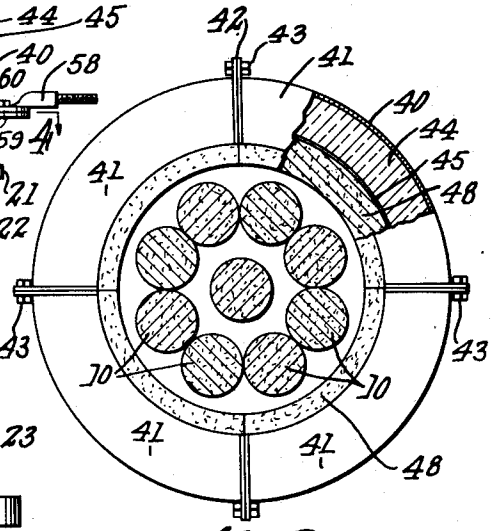


Fig. 3.

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ELECTROLYTIC CELL

Filed Jan. 11, 1939 3 Sheets-Sheet 2

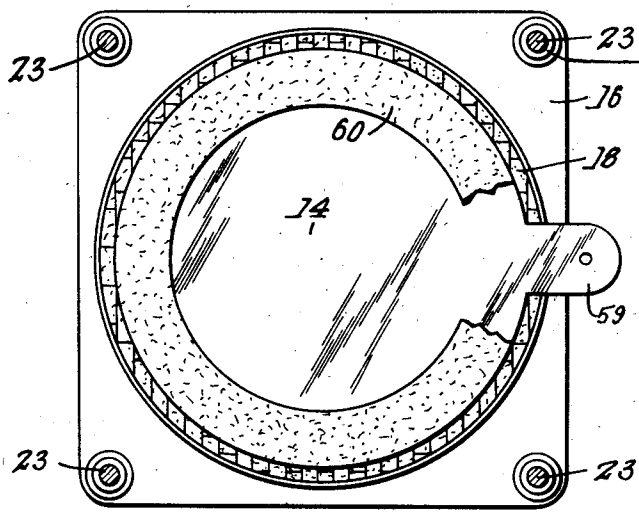


Fig. 4.

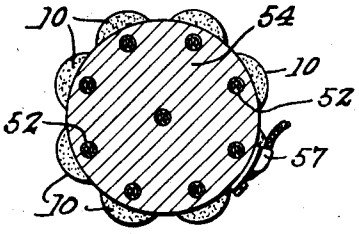


Fig. 8.

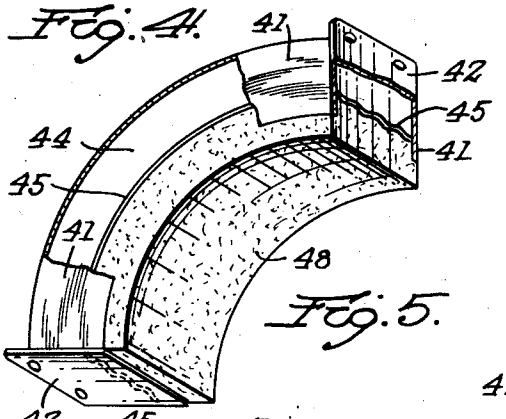


Fig. 5.

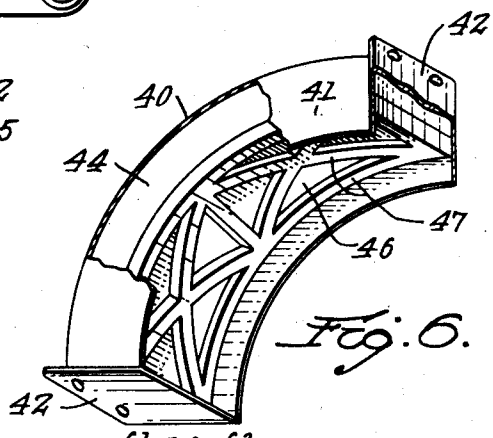


Fig. 6.

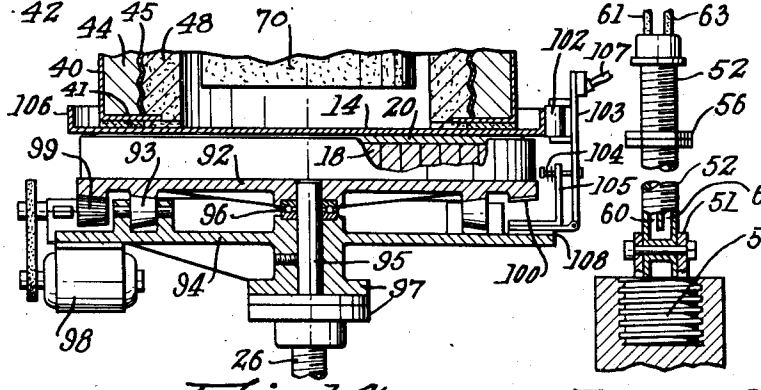


Fig. 14.

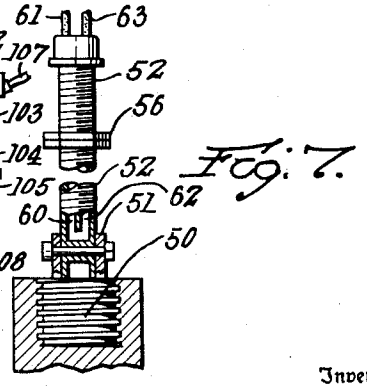


Fig. 7.

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ELECTROLYTIC CELL

Filed Jan. 11, 1939 3 Sheets-Sheet 3

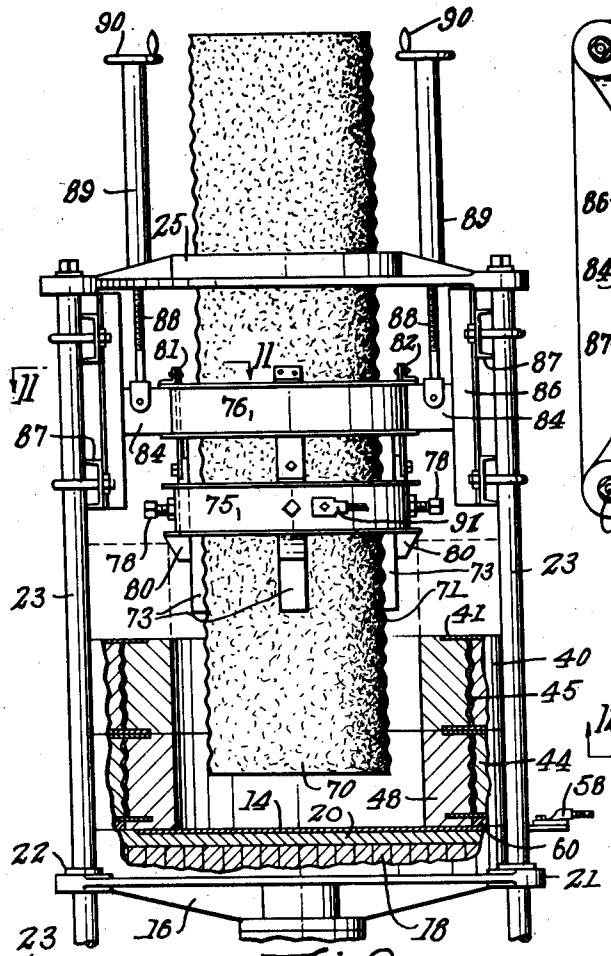


Fig. 9.

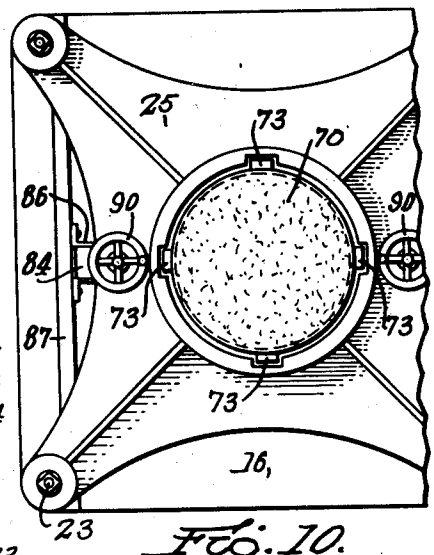


Fig. 10.

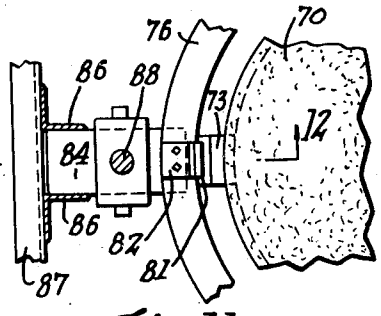


Fig. 11.

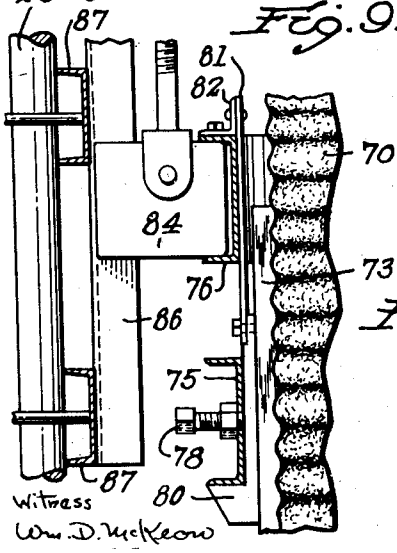


Fig. 12.

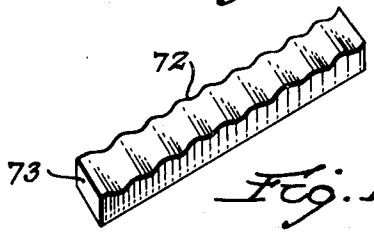


Fig. 13.

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UNITED STATES PATENT OFFICE

2,398,590

ELECTROLYTIC CELL

Thomas A. Mitchell, Torrance, Calif., assignor, by mesne assignments, to Molybdenum Corporation of America, New York, N. Y., a corporation of Delaware

Application January 11, 1939, Serial No. 250,396

1 Claim. (Cl. 204—245)

This invention relates to electrolytic cells and more particularly to a cell adapted for the production of metals by electrolytic and chemical reactions.

In accordance with my copending application filed on even date herewith, Serial No. 250,395, I have disclosed a method of making metallic manganese by the electrolysis of fused sodium fluoride or cryolite in which is dissolved the oxides of aluminum and manganese. In that process, any aluminum metal formed by electrolytic decomposition reacts to reduce manganese oxide and to cause manganese metal to be deposited, while the aluminum remains in solution.

One object of this invention is to provide a satisfactory construction of an electrolytic cell which will serve in that process for the manufacture of manganese.

A further object is to provide a cell construction which is suitable for the electrolysis of a fused bath and the production of various metals, such as manganese and ferro-manganese, depending upon the composition of the bath.

Another object is to provide a cell in which the concentration of reagents in the fused bath may be readily maintained as required.

A further object is to provide an electrolytic cell in which the electrolysis of a fused bath may be carried on for a long period of time and an ingot of the desired product will be progressively produced.

A still further object is to provide such a cell in which the constructional features are so arranged that as a reaction product ingot is produced, the anode and cathode may be maintained in their proper separated positions and the electrical control of the reaction may be readily maintained. Further objects will be apparent in the following disclosure.

Referring to the drawings which illustrate various embodiments of my invention:

Fig. 1 is a vertical section, partly broken away, of a furnace involving the use of multiple anodes;

Fig. 2 is a top plan view of the construction shown in Fig. 1;

Fig. 3 is a section on the line 3—3 of Fig. 1;

Fig. 4 is a section on the line 4—4 of Fig. 1;

Fig. 5 is an isometric view of one quadrant section of the flask which forms the cell walls, parts of the figure being broken away to show the lining material;

Fig. 6 is an isometric view of a modified form of flask sector with parts broken away and the metal oxide lining not yet applied in position;

Fig. 7 is a detail, partly broken away, showing the manner of mounting one of the carbon anodes;

Fig. 8 is a section on the line 8—8 of Fig. 1 showing the support for the carbon anodes;

Fig. 9 is a vertical section, partly broken away, corresponding with Fig. 1 which shows a single anode;

Fig. 10 is a top plan view of Fig. 9;

Fig. 11 is a detail taken on the section line 11—11 of Fig. 9;

Fig. 12 is a section on the line 12—12 of Fig. 11;

Fig. 13 is an isometric view of one of the clamping blocks used to hold the anode in position; and

Fig. 14 shows a modification of the construction of Fig. 9, whereby the cathode and cell walls are revolved relative to the anode during operation of the furnace.

In accordance with the construction shown in Fig. 1, I have provided an electrolytic and electrothermic cell comprising the set of anodes 10 of suitable material, such as carbon, movably suspended within the reaction chamber 12 over a cathode 14 of suitable material, such as a plate of copper. These parts are so arranged that an electric current may be passed through a fused bath between the electrodes and cause electrolysis of the substance therein.

A primary feature of this invention involves a construction so arranged than an ingot of the desired metal may be progressively built up on the cathode and a proper distance may be maintained between the anode 10 and the surface of that conducting material on the cathode. To satisfy this object, I propose to so mount the cathode that it may be progressively lowered as the metal product is built up thereon. In my preferred construction, the cell walls are also moved downwards with the cathode and additional sections are built up above to provide the required size of reaction chamber.

One construction involving these features is shown in Figs. 1 to 8 inclusive. As there illustrated, the cathode 14 is supported on a movable platform 16 made of an iron casting, and the cathode is thermally and electrically insulated therefrom by means of a layer of heat insulating insoluble "silocel" bricks 18, and a non-insulating board lining 20 of material sold under the trade name of "Transite," or other suitable material. The platform casting has four projecting ears 21 suitably perforated and provided with insulating bushings 22, so that the platform may slide on and be guided by a set of four rods or posts 23 projecting vertically upwards from a metal base 24 suitably supported on the floor of the furnace

room. The posts 23 are secured together at their tops by a metal frame 25 which is arranged to carry the anodes and is similarly insulated from the posts by suitable insulating bushings.

The platform 16 is supported by a screw 26 threaded into a collar 27 which is suitably mounted on ballbearings 28 carried by a hollow hub 29 mounted on the platform 24 of the framework. The upper end of the screw 26 is suitably connected to a flanged member 30 which carries the cell platform 16 and is insulated therefrom by insulation 31. The screw 26 passes downwardly through the platform 24 and into a suitable hole provided in the floor so that the cathode and cell chamber may be raised and lowered through a considerable distance as the metal ingot is built up on the cathode. The movement of the screw and platform may be effected by hand or power mechanism. As illustrated, the threaded sleeve 27 carries a gear 34 keyed thereto, and this gear is driven by a meshing gear 35 and an electric motor 36 connected therewith. This mechanism may be controlled manually by suitable rheostat and switch mechanism connected to the motor so as to move the cathode as determined by observation of the cell operation. Hence, by rotating the worm gear 34 and the threaded sleeve 27, the screw 26 may be raised or lowered as desired.

If the cell is to be used in the production of metallic manganese and the process involves the use of a fused bath of cryolite, alumina and manganese oxide, the electrolysis of the bath results in the deposition of manganese on the cathode, it being noted that any aluminum metal formed by electrolytic decomposition of the bath will react by an alumino-thermic reaction to reduce manganese oxide and cause manganese metal to be precipitated within the bath. Owing to the specific gravity of the manganese metal being higher than that of any of the other constituents of the bath, the manganese settles to the bottom of the cell and builds up an ingot on the cathode 14. The metal conducts the electric current and thus forms the cathode surface, hence by periodically or continuously lowering the cathode, the proper distance may be maintained between that cathode and the carbon anode 10.

It is necessary to maintain an adequate size of cell reaction chamber as it fills up with the manganese ingot, and from one aspect of this invention it is feasible to provide cell walls initially which are of the full required height therefor. In that case, the cell may be run continuously by merely lowering the cathode and furnace walls as the process goes on and by positioning the anodes as they are consumed, so as to maintain proper electrolytic conditions within the bath.

An important feature of this invention involves making the cell walls of removable sections which are so constructed and arranged that as the cathode is lowered the cell walls may be built up to provide the necessary electrolytic reaction chamber and thus render the process continuous until an ingot of the full dimensions permitted by the furnace structure has been made. While this wall may be made in various arrangements, I prefer that it be made of sections of such dimensions and constructional features that they may be very easily assembled on the top wall of the cell while the reaction is going on. This is accomplished by providing a set of quadrant sections of the type illustrated in Fig. 5 or Fig. 6, which are so arranged that they may be set in place and bolted together to make up an annular wall resting on the ring sections previously put into place.

I have found that if manganese oxide is fed as a powder in large quantities into the top of the cell where it slowly dissolves in the fused bath of cryolite, there is a danger of side reactions taking place between this oxide and the adjacent carbon anode, which causes the reduction of the manganese oxide and the formation of manganese carbide, and the latter is found present as a contamination in the manganese ingot built up at the bottom of the cell. It is, therefore, desirable that the manganese oxide be fed slowly to the cell as required by exhaustion of the ions in solution. This is satisfactorily accomplished by lining the cell walls with the manganese oxide and, if desired, with other reagents required in the process, such as alumina and the cryolite or other fluoride, such as sodium fluoride, used to form the solvent. Hence, I propose to so make the sectors which form the cell walls that each carries a lining of the required reagents in such quantity and arrangement that, as the process goes on, this lining may gradually dissolve into the fused bath and thus supply a large or a major portion of the reagent needed and so make it unnecessary to add any large amount of reagent material into the top of the cell.

These various constructional features are illustrated in the drawings. As shown particularly in Figs. 1, 3, 5 and 6, the sector may be a a U-shaped, arcuate, hollow, insulated wall made of an outer arcuate plate 40 and side walls 41 forming a V-shaped trough and walls 42 closing the two ends of the trough. These walls 42 project outwardly beyond the peripheral surface 40 of the sector so that the sectors may be bolted together by the bolts 43, Fig. 3. The U-shaped channel is packed with a suitable insulation material 44, such as asbestos or magnesia, and an inner arcuate steel plate 45 is then fitted into place to form an inner wall for the reaction chamber and to hold the heat insulation in position. Any other suitable construction may be provided for the purpose of insulating the cell.

The lining of reagent materials, whatever may be used, are pressed or baked into place in a position radially inwardly from the wall 45, and for convenience in holding that lining in place the sides 41 may, if desired, extend radially beyond the partition 45, as shown. Also, as an aid to holding the reagent lining in place, the wall 45 may be corrugated as shown in Figs. 1, 5 and 9. Or, it may be otherwise provided with a surface which will adhere readily to the reagent lining. For example, it may be made of an iron ribbed construction as shown in Fig. 6, wherein the plate 45 is replaced by an iron casting 46 having various shapes of cross ribs 47 thereon. The construction of Fig. 6 is otherwise the same as that of Fig 5.

The sector may be suitably lined with its reagent material in various ways. For example, the four sectors may be set up in position to form a ring and a removable circular steel shell, in sections, placed inside of the same. Then, the lining material 48 is tamped in place between that shell and the walls of the ring. The lining material may be mixed with a suitable binder to help hold it in place. If desired, it may be baked in position prior to use. Then, after the inner steel shell has been removed, the individual sectors may be set aside and mounted on the cell walls when needed. The sectors may, if desired,

be put in place on the cell, then the lining 48 tamped in place, and the baking may be accomplished by the heat from the cell during its use. This lining material may be derived from any suitable source and may include reclaimed bath and lining materials from a previous cell run.

In this type of cell, it is intended that the electrolyte be held in a fused condition and this may require a temperature between 930° to 950° C. or higher for the electrolytic formation of aluminum and manganese. The operation of the cell may be started by striking an arc between the anode 10 and the cathode 14 by suitably raising the voltage, and feeding in the bath material until a sufficiently deep pool has been formed. Thereafter, the voltage may be reduced to that required for electrolysis of the bath, which may be in the neighborhood of 6 to 8 volts, and it may be suitably regulated to provide enough heat to keep the bath molten. The ingot of manganese thus produced will be a massive solid body or formed as pellets or as a sponge of metal intermixed with bath material, depending on the temperature and the furnace operating conditions.

The anode may be made of one or more electrodes of suitable material and shape, depending on the cell shape. The anode shown in Figs. 1 and 3 comprises several cylindrical rods so suspended as to project into the fused bath. These carbon rods, which may be made of graphite as used in the electric furnace industry, may be mounted as shown particularly in Figs. 1 and 7. That is, the graphite rod is internally screw threaded at its upper end and adapted to receive a screw threaded coupling 50 of copper or other suitable metal which has an upwardly projecting split sleeve or lugs 51 bolted to the bottom closed end of a screw threaded tube 52. The tube 52 is threaded at its upper end and passes through a perforated block 54 having collars or flanges 55 arranged to prevent the block from falling through the central opening in the frame 25 in which the block is mounted. The block 54 may be hollow and water cooled if desired. It is a massive body for the purpose of receiving the electric current from the anode terminal 57 attached thereto. The cathode terminal 58 is also connected to the plate 14 by means of a lip 59 projecting outwardly from the plate. Other suitable provisions within the knowledge of one skilled in the art may be made for introducing a direct current and for insulating the cell. For example, suitable electrical insulation 60 is located between the top of the copper cathode plate 14 and the bottom of the lowermost cell wall unit, as shown particularly in Fig. 1.

The tubes 52 are suitably held in position on the block 54 by means of sets of lock nuts 56 (Fig. 7) provided for the purpose. For the purpose of cooling the tube 52, the water pipes 61 and 63 may be suitably connected to the upper ends of each of the tubes 52 and arranged to pass a stream of water downwardly through one channel 62, a suitable partition being located in the tube 52 to form these channels. Other provisions within the skill of one acquainted with electric furnace and electrolytic cell practices may, of course, be adopted for protecting the cell structure and rendering it easily operated and adjusted.

The construction shown in Figs. 9 to 13 inclusive involves the same arrangement of cathode and cell walls and mounting platform, as above described, but in this furnace there is but a single anode. This anode 70 may be a large graphite body having a corrugated outer surface 71, which is shaped and arranged to interlock with the corrugations 72 of a clamping block 73 (Fig. 13) provided for the purpose of holding the anode in place. These clamping blocks 73 are carried by two rings 75 and 76 surrounding the anode. The lower ring has a series of set screws 78 which pass through the ring and clamp against the outer surfaces of the clamping blocks 73 and so secure them tightly against the corrugated surface of the anode. The lower ring 75 is suspended from the upper ring 76 by means of a set of depending members 80 having hooked ends at their bottoms projecting outwardly beneath the lower flange of the U-shaped ring 75. A set of straps 81 support this member 80 and are secured to an angle iron 82 bolted to the top of the ring 76. The upper ring 76 is likewise supported from the upper cross frame member 25 which in turn is supported on the side posts 23. The ring 76, which does not touch the anode 70, is suspended by means of blocks 84 (Fig. 12) fitting between the top and bottom flanges of the U-shaped ring 76, and within the channel formed by the angle irons 86 suitably supported on U-shaped members 87 which in turn are supported by a clamp on the post 23. The angle irons 86 serve as guides for the sliding blocks 84 as the anode structure is raised and lowered. The blocks 84 carrying the ring 76 are suspended on two rods 88 threaded into sleeves 89 bearing on the top of the framework 25 and rotated by means of hand wheel 90 as required. The electrical connection to the anode may be made as desired, such as by means of a separate clamping device, or the anode terminal 91 may be connected to the lower ring 75 and the latter insulated from the rest of the framework by having the parts 84 or other suitable pieces made of insulating material.

The bath may be mechanically stirred by suitable mechanism, and this is preferably accomplished by the construction shown in Fig. 14, which may correspond with the structure of Figs. 1 and 9 except that the bottom of the reaction chamber is mounted on a turntable. To this end, I provide a turntable 92 mounted on rollers 93 suitably supported on a non-rotatable bottom 94. The cathode 14 and insulating materials 18 and 20 are mounted on the top of the turntable 92. A center post 95 is fixed in position on the bottom support 94 and passes centrally through the platform 92, ballbearings 96 being provided to support the center of this platform and aid in the rotation thereof. The bottom 94 corresponds with the platform 16 shown in Fig. 1 and is prevented from rotation by the vertical post 23 as there shown. The screw 26 supporting the same for vertical movement is suitably secured to the insulating hub 97. The turntable may be rotated either manually or by power mechanism, and preferably by means of a reversible electric motor 98 connected by a belt to a driving gear 99 meshing with a gear track 100 on the under side of the turntable. By this means, the cathode may be rotated continuously in either direction or oscillated periodically in opposite directions, without interference with the mechanism which lowers the cathode plate during the cell run. This motor may be controlled manually or by automatic mechanism.

The cathode connection may be made to the rotating cathode by means of a roller 102 mounted on the vertical arm 103 which in turn is pivotally mounted on the stationary platform 94. A spring

104 surrounding a bolt on the arm 103 and engaging a stationary upright member 105 tends to hold the roller 102 against a circular track 106 formed on the periphery of the cathode 14. The terminal wire 107 is fastened to the upright arm 103 so that the current passes from the roller 102 into the cathode. Suitable insulation 108 is provided between the base of the pivoted arm 103 and the platform 94 so as to prevent short circuiting the current through the framework. By this construction, the cathode serves to agitate the molten bath and to depolarize the anode by removal of the gas therefrom. It also serves to mix the bath ingredients and particularly to aid in dissolving the solid material fed to the top of the bath or that derived from the lining and to distribute it uniformly and quickly throughout the bath, and thus prevent depletion of ions and a retardation of the reactions and an increase in power consumption.

If the cell is to be operated for making manganese metal, two or more of the sector rings forming the cell wall may be put in place with their linings initially made up of manganese oxide, alumina, sodium fluoride or cryolite and a suitable binder. A mass of powdered sodium fluoride or cryolite may be placed in the bottom of the furnace and by suitably regulating the voltage and the positions of the electrodes an arc may be struck between the anode and the cathode plate. This serves to fuse the bath material, and when a sufficient depth of pool has been formed, then the voltage may be lowered to that of 6 or 8 volts and the process carried on normally for the electrolysis of the fused materials and the deposition of manganese on the cathode. Any aluminum metal which is electrolytically formed reacts with the manganese oxide present and reduces the same to the metal, and the alumina goes back into solution, and thus continues in its reactive cycle. Hence, the alumina is not materially removed from the bath. As the manganese is removed from solution, the lining 48 dissolves and thus furnishes the necessary reagent, and more may be added to the top of the bath, if desired. The electrodes will be adjusted as required to provide the necessary current flow through the molten bath, both for electrolysis and for keeping the bath fused. The temperature may be maintained partly by the exothermic reactions and if needed by occasionally raising the voltage. As the anode wears away at its lower end due to oxidation, it may be adjusted downwardly by the simple mechanism shown in the drawing. In Fig. 1 this is accomplished merely by adjusting the lock nuts 56 and moving the supporting tubes 52 downwardly. In the construction of Fig. 9, the electrode may be supported temporarily and then the blocks 73 released from their original positions and placed in new positions, after which the electrode may be lowered until it is supported on the hook like members 80 carried by the upper ring 76. As the process goes on, the lining 48 gradually dissolves, but sufficient material is introduced into the top of the furnace, if needed, to prevent all of the lining from being consumed and thus exposing the iron framework of the sectors forming the furnace wall. As the reaction proceeds, the ingot builds up and more casing sectors are placed on top of the cell wall until the limit of the mechanism has been reached.

It will now be appreciated that many equivalent parts and mechanisms may be substituted for those above described and other features may be incorporated in the construction, and that many modifications may be made within the scope of my invention. The structure is also applicable for the manufacture of other metals besides manganese, and the composition of the bath will be changed accordingly. For example, ferromanganese of low carbon content may be produced by adding a suitable iron compound, such as the fluoride or oxide of iron, to the bath in required proportions. The cell may, in general, be used for the electrolytic production of any metal which may be deposited or collected as a solid mass the same as above described, provided the fused bath is properly constituted and the electrical features of the process are suitably controlled. Hence, the above description is to be interpreted as illustrative of the invention and the principles involved therein and not as limitations on the claim appended hereto.

I claim:

A fused bath electrolytic cell for the deposition of a metal comprising a support mounted for vertical movement and for rotation about a vertical axis, a cell bottom and a side wall carried on said support which form a fluid tight cell, a cathode adjacent to the bottom of the cell, an anode removably suspended thereabove within the cell, a plurality of metal sectors removably mounted on the cell wall which are shaped and arranged to be assembled to extend the vertical height of the wall without disturbing the anode during the cell operation, means for removably securing the sectors together to form a fluid tight side wall, means for vertically lowering the cell relative to the anode and means for rotating the cell and cathode relative to the anode.

THOMAS A. MITCHELL.