July 7, 1925. 1,545,383

E. A. ASHCROFT

APPARATUS FOR ELECTROLYZING FUSED SALTS

Filed April 10, 1922 3 Sheets-Sheet 1

Fig. 2.

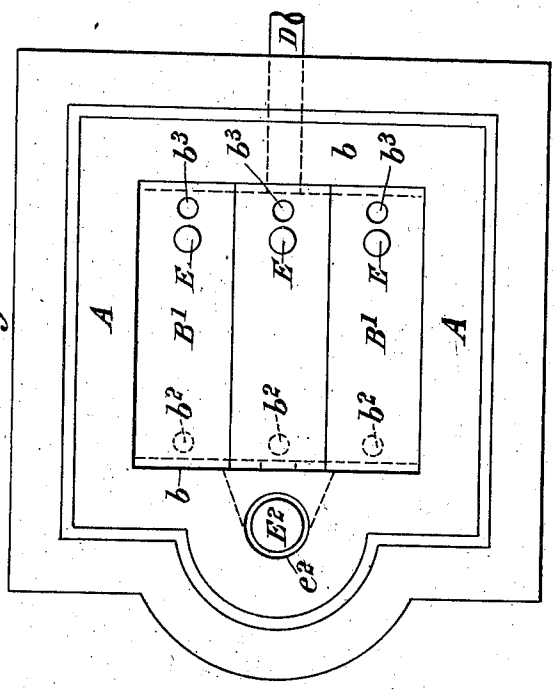
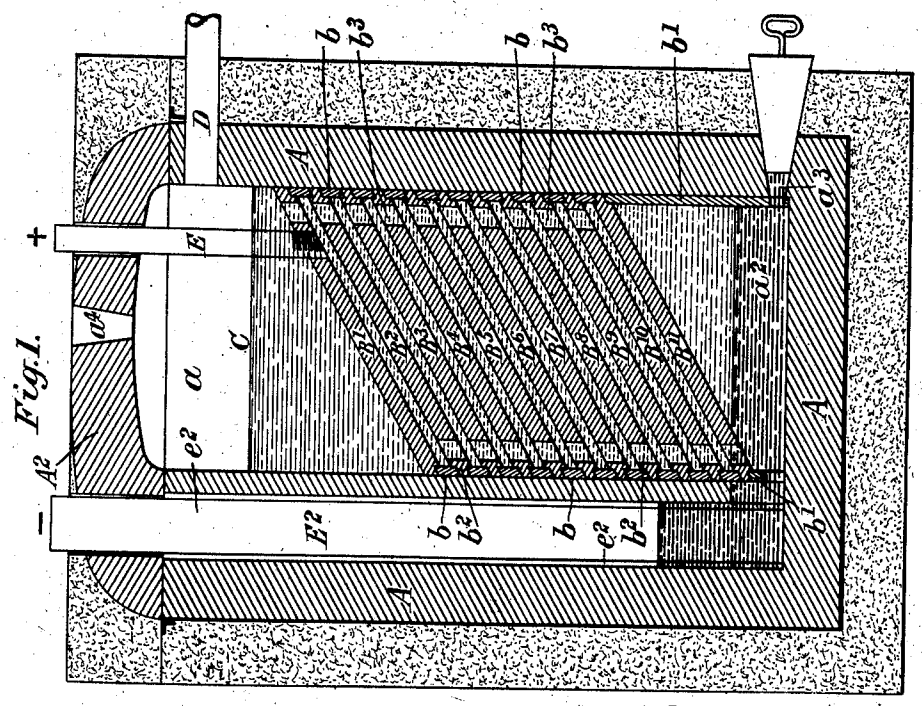


Fig. 1.



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Fig. 4.

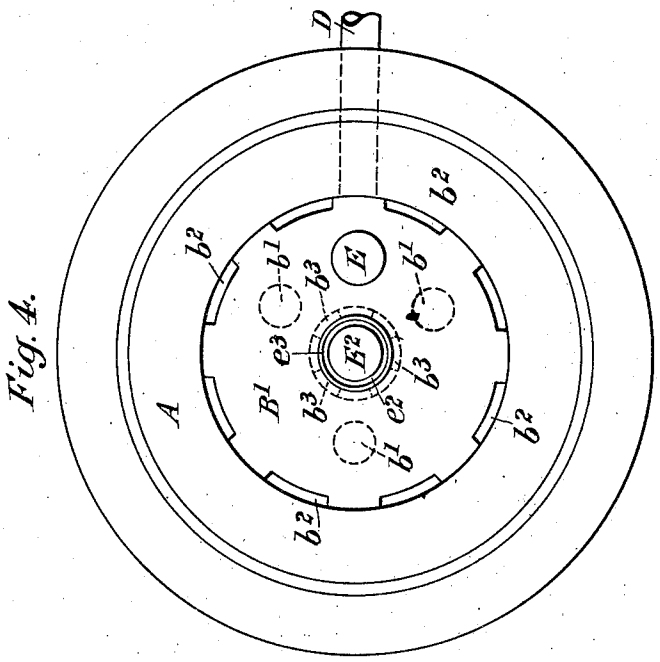
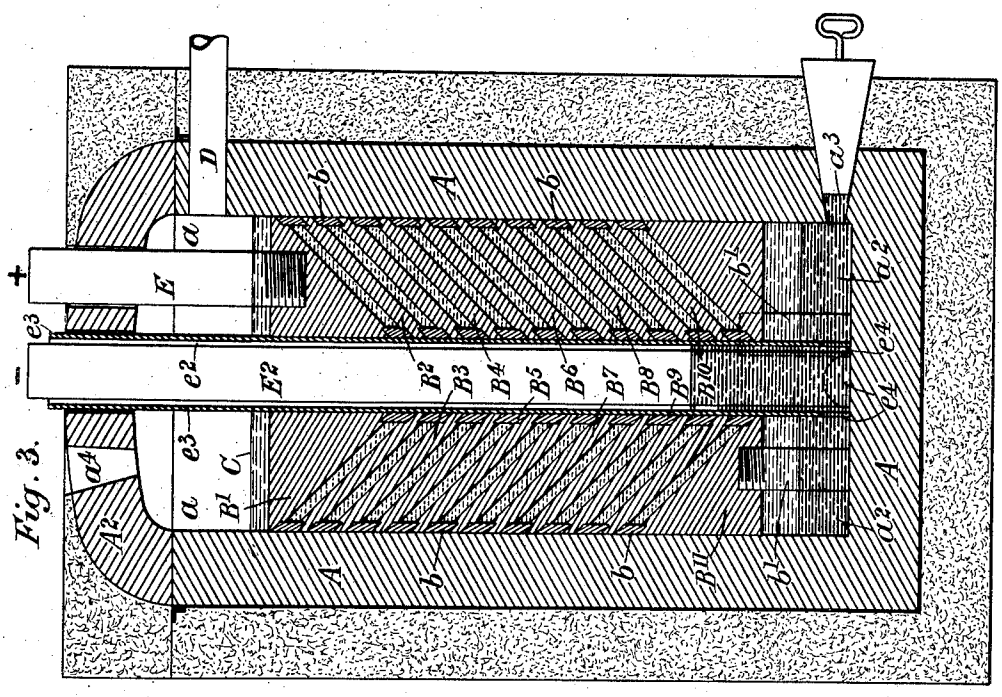


Fig. 3.



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Fig. 5.

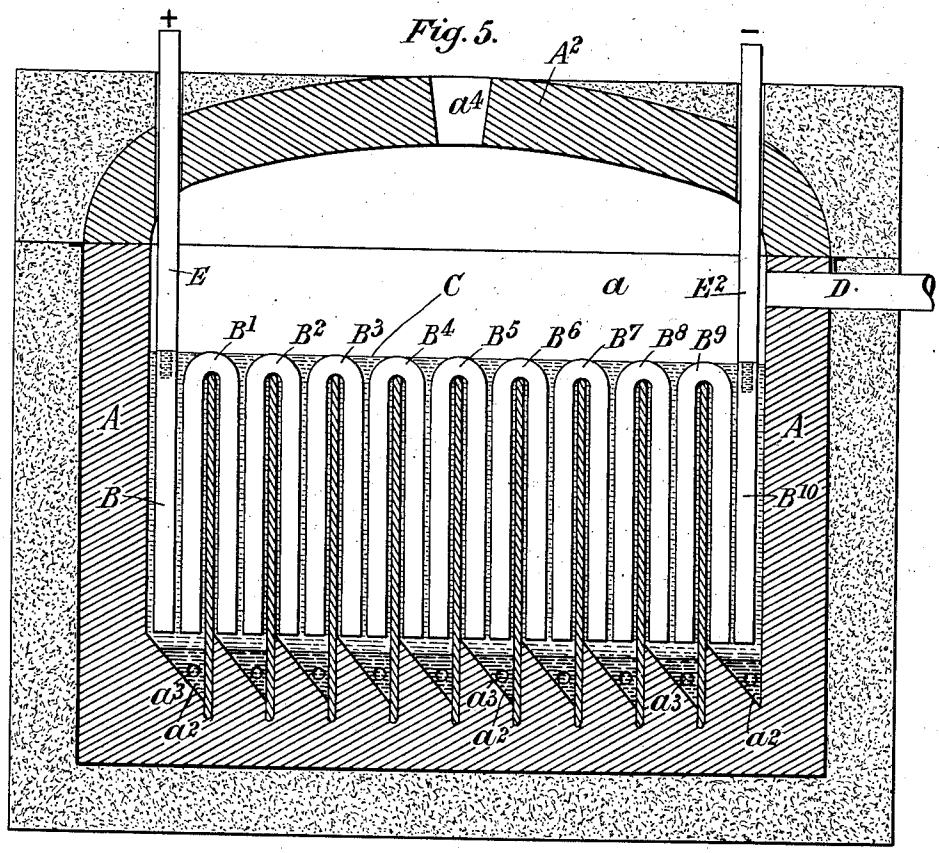
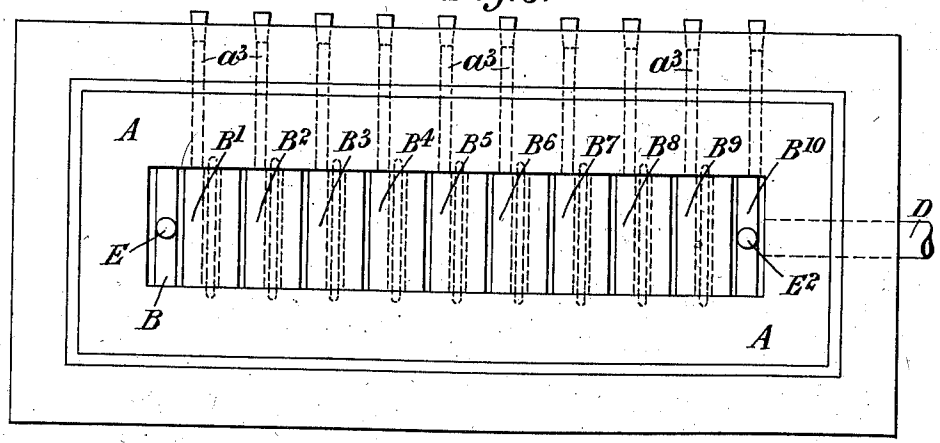


Fig. 6.



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Patented July 7, 1925. 1,545,383

UNITED STATES PATENT OFFICE.

EDGAR ARTHUR ASHCROFT, OF LONDON, ENGLAND.

APPARATUS FOR ELECTROLYZING FUSED SALTS.

Application filed April 10, 1922. Serial No. 551,306.

To all whom it may concern:

Be it known that I, EDGAR ARTHUR ASHCROFT, a subject of the King of Great Britain, residing at 32ª Liverpool Street, London, England, and at Waye, near Ashburton, South Devon, England, have invented new and useful Improved Apparatus for Electrolyzing Fused Salts, of which the following is a specification.

My invention consists in an improved apparatus for eletrolyzing fused metallic salts and recovering the metals and acid radicles therefrom, and is more especially intended for use in the electrolysis of metallic chlorides such as chloride of zinc, or chloride of lead, and the recovery of the metal and chlorine.

My invention is hereinafter described as applied to the electrolysis of zinc chloride, but I may use it for the decomposition of any other suitable salt and also for the production of alloys from mixtures of chlorides or other suitable salts.

Hitherto in the eletrolysis of fused salts separate couples have been employed, each couple consisting of an anode of carbon, or graphite, and a fused-metal cathode arranged within a container for the fused materials.

The electrolytic apparatus according to my invention consists of a multiple couple electrolyzer comprising a series of closely-spaced electrodes all to be immersed in the same body of molten electrolyte contained in a refractory and preferably heat-insulated container, only the first and last of the electrodes being connected with the electric supply conductors. The inner wall of the container surrounds, or embraces, the edges of the series of electrodes, thus preventing excessive leakage of current past the edges, and passages are provided for leading off separately the metallic and gaseous products of the electrolysis. The electrodes may if desired, be all of the same composition, for example of compressed carbon, or graphite, and any convenient number of couples may be employed, the opposed surfaces of any two adjacent electrodes and the intervening space filled with electrolyte constituting what I term a couple.

Apparatus embodying my invention is shown in the accompanying drawings in which

Fig. 1 is a vertical section through an electrolyzer;

Fig. 2 is a plan thereof with the cover removed;

Figs. 3 and 4 are views corresponding respectively to Figs. 1 and 2, but illustrating a modified construction;

Figs. 5 and 6 are also views corresponding respectively to Figs. 1 and 2, but illustrating a further modification of construction.

The accompanying drawings and description relative thereto afford examples of the apparatus constituting my invention.

Figure 1 represents in vertical section and Figure 2 in plan (with the cover removed) an electrolyzer having eleven plates or electrodes constituting between them ten electric couples of rectangular form arranged in a container also of general rectangular form. In Figure 2 each electrode is shown as consisting, for convenience, of three pieces.

The container A (which is surrounded by heat insulating material such as kieselguhr) is made of refractory non-conducting material, or consists of a metallic chamber with a refractory non-conducting lining, and the ten electric couples are formed by the electrodes B^1 to B^{11}, arranged in an inclined position one above another, there being a space a above the electrolyte in which space the chlorine collects and passes into an escape-pipe D. A reservoir a^2, at the base of the apparatus, receives the molten zinc produced, which can be removed periodically at a tap-hole a^5.

The positive conductor from any suitable source of continuous electric current is passed through a tightly packed opening in the cover A^2, and is connected with the top electrode in any convenient manner, preferably by rods E, of graphite, or other suitable material, screwed into the plates constituting the electrode. A graphite rod E^2 enters the reservoir a^2 of molten zinc and so under operating conditions makes electrical connection with the lowest electrode, the said rod E^2 passing up, through a tubular cavity, e^2, in the wall of the container A, to the upper part of the apparatus for connection to the negative pole of the electric supply. The electrodes are plates of graphite, or other suitable material, inclined preferably at a considerable angle as shown and separated by distance pieces, or rests, b of fused silica, vitreosil, obsidianite, or other hard, heat-resistant and electrically-insulat-

ing material, the supports b^1 for the lowest plate being preferably of graphite. The inner wall of the container A, closely embraces the plates B^1 to B^{11} as shown, thus providing an insulating shield to the edges of the electrodes; but holes b^2 near the lower ends of the electrodes allow the zinc to descend to the reservior a^2, and holes b^3 near the upper ends allow the chlorine gas to escape to the space a, circulation of the electrolyte C also taking place.

A closable opening a^4 in the cover of the apparatus serves for the introduction of fused zinc chloride, preferably at a temperature of about 350° to 400° C. as this prevents "fuming" of the fused salt.

The apparatus is provided with means for feeding in chloride to replace that decomposed by the current and in this manner the apparatus can be worked continuously for a long time. The fusion of the electrolyte may be maintained by means of the electric current, and external heat may be applied to the container, as hereinafter explained. The fusion may also be maintained wholly or in part by providing the apparatus with means for applying a supplementary alternating current to the first and last electrodes of the electrolyzer, such current being more economically produced than the continuous current necessary for electrolysis.

The electrolysis will set free zinc (in the instance given) on the upper surfaces of the electrodes and a corresponding weight of chlorine on the under surfaces. The zinc will flow downwards into the reservoir a^2, and the chlorine will rise to the upper part a, and they do not come again into contact after being separated by the current. Satisfactory circulation of the electrolyte throughout the apparatus is caused by the upward flow of the gas and the downward flow of the metal.

The use of a multiple-couple electrolyzer constructed in accordance with my invention results in economy of electrical energy the use of a more convenient voltage, and various advantages as regards cost of construction, working and upkeep of the apparatus. In order to understand these advantages the principles of the electrolysis of fused metallic salts generally and of zinc chloride in particular may be considered.

Theoretically the "chemical" voltage required for the decomposition of zinc chloride in a state of fusion is approximately 1.6 volts and the Faradaic yield, per ampere hour, 1,218 grams; therefore the minimum energy required to produce one kilogram of zinc is 1315 watt-hours, exclusive of that needed to keep the electrolyte in the molten condition. For technical reasons it is preferable to keep the electrolyte fused by internal electrical heating, due to extra terminal voltage or to a supplementary alternating current. It follows that efficient heat insulation is a prime factor in economy. It is necessary in all single-couple apparatus known to me to employ a high current density, and the loss of heat through the electrodes is considerable; consequently, in the best form of such single-couple apparatus, the terminal voltage per couple is believed to be approximately three times the necessary chemical voltage, and with a current efficiency of 90 per cent. The energy efficiency cannot be raised much above 30 per cent. The lower the current density employed at the electrodes, with a view to securing low terminal voltage, the more accentuated are the difficulties of practical heat conservation such difficulties being due to the increased size and inconvenient form of the apparatus designed for such a purpose. It is usually found that the economical lower limit of current density is about four, to six, amperes per square inch of electrode surface, and greater current densities have often been employed.

With my multiple-couple electrolyzer current densities of from two amperes to one ampere and even less, per square inch of electrode surface can be employed. The space between the electrodes may be reduced to half an inch, or even less, and a low terminal voltage per couple can thus be obtained. The passage of a small "leak" current through the holes and around the supports, or separators, (which are loosely placed between the ends of the electrodes and retained in position by their grooved and rabbeted formation) results in a slightly lower current efficiency than is obtainable with a single couple, but the energy so passed fulfills the useful office of maintaining the electrolyte in fusion. With such an apparatus, using only two volts per couple (that is twenty volts over the whole apparatus having ten couples), results have been obtained equivalent to a total energy efficiency of 64 per cent. of the theoretical, which is more than double the efficiency understood to be realizable by employing the hitherto known process and forms of apparatus.

But besides a saving of electrical energy, constructional advantages are obtained. Not only is the apparatus compact and simple to build and to maintain, but the important advantage of low amperage, with a corresponding reduction in the number and size of the electrical connections, results. Thus, in order to absorb the energy from a given source, it is delivered to the electrolyzers at a relatively low amperage and high voltage (instead of vice versa in the case of an installation of single-couple electrolyzers) and this permits a reduction

both in the number of apparatus employed and in the external electrical connections required.

A further advantage of my multiple-couple electrolyzer is that the chlorine is obtained in a highly concentrated condition.

A modified form of electrolyzer in accordance with my invention is shown in sectional elevation in Figure 3 and in plan, (with the cover removed) in Figure 4. The apparatus here illustrated has a circular container A, and conoidal or funnel-shaped, electrodes, inclined towards the centre, contact being made with the reservoir of zinc in the base of the apparatus by means of a central graphite rod E^2, passing through a silica tube e^3 with openings in it at e^4. The parts in these figures which correspond with those shewn in Figures 1 and 2 are marked with the same reference letters.

Another form of my electrolyzer is shown in sectional elevation and plan (with the cover removed) in Figures 5 and 6 respectively. This electrolyzer contains a number of vertical saddle-shaped electrodes, B^1 to B^9, placed over dividing partitions of refractory material. In this case the zinc gathers in the separate compartments a^2 in the lower part of the container and can be drawn off from separate outlets a^3, or from a common channel. The chlorine given off passes into the common space a above the top of the electrolyte at C and to the pipe D and thence to the required place. The electrodes B and B^{10} at each end of the container are respectively connected by the rods E and E^2 of carbon, or other suitable material, to the respective poles of the source of electricity.

Instead of these saddle-shaped electrodes, I may use graphite plates, arranged similarly side by side and supported in grooves, or the like, in the walls, or lining of the container.

It is to be understood that I do not limit my invention to the particular construction of apparatus hereinbefore described and illustrated, nor to any particular number of couples. I may employ any convenient form of container and electrodes:—for instance, I may correspondingly corrugate, or groove, the opposed faces of the electrodes in the directions of the flow of the metal and the gas.

In order to ensure heat insulation I may surround the container on all sides with a bed of non-conducting material, such as kieselguhr, and this will usually be found sufficient; but I may alternately apply external heat, derived from any cheaper source than electric energy; for instance, by means of a jacket in which superheated steam, or hot air, oil, or other fluid is circulated at a temperature sufficient to maintain the exterior of the container at about 200°–300° C., the walls of the container being constructed of a thickness suitable for this purpose.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is—

1. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, and means for establishing current flow successively through the several electrodes and interevening portions of the melt to constitute a group of electrolytic couples arranged in electrical series below the surface of the melt.

2. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, means for establishing current flow successively through the several electrodes and intervening portions of the melt to constitute a group of electrolytic couples arranged in electrical series below the surface of the melt, and means for substantially confining the flow of current to the couples in the electrolytic zone of the apparatus.

3. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, and means for establishing current flow successively through the several electrodes and intervening portions of the melt to constitute a group of electrolytic couples arranged in electrical series below the surface of the melt, together with means for leading the products of electrolytic decomposition in separate paths out of the zone of electrolysis.

4. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, and means for establishing current flow successively through the several electrodes and intervening portions of the melt to constitute a group of electrolytic couples arranged in electrical series below the surface of the melt, together with means for leading the products of electrolytic decomposition in different directions through the melt to effect a circulation of the latter.

5. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, and means for establishing current flow successively through the several electrodes and intervening portions of the melt to constitute

a group of electrolytic couples arranged in electrical series below the surface of the melt, together with means for leading the heavier products of electrolytic decomposition downward in one portion of the zone of electrolysis, and the lighter products of electrolytic decomposition upward in another portion of said zone.

6. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, and means for establishing current flow successively through the several electrodes and intervening portions of the melt to constitute a group of electrolytic couples arranged in electrical series below the surface of the melt, the active surfaces of the electrodes being arranged at an angle to the horizontal to cause a downward flow of the heavier products of electrolytic decomposition in one path, and an upward flow of the lighter products of electrolytic decomposition in a separate path.

7. In a metallurgical electrolytic apparatus having a container for a fused melt, an electrolytic couple comprising a pair of spaced electrodes adapted to receive the fused melt therebetween, the active surfaces of the electrodes being arranged at an angle to the horizontal, a passage at the upper portion of the upper electrode for the escape of gaseous products of electrolytic decomposition of the melt and a passage at the lower portion of the lower electrode for the escape of heavy products of electrolytic decomposition.

8. In a metallurgical electrolytic apparatus, a container for a fused melt, a pile of spaced electrodes immersed in the melt under operating conditions, and having their active surfaces inclined to the horizontal, the intermediate electrodes of the pile having at their upper portions passages for the upward escape through the pile of gaseous products of electrolytic decomposition, and passages at their lower portions for the downward flow through the pile of heavy metal products of electrolytic decomposition.

9. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, means for substantially confining the current to flow in series through the electrolytic couples thus established, a current supply connection to the electrode at one end of the electrode group, and a second current supply connected to the electrode at the other end of the group.

10. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, means for substantially confining the current to flow in series through the electrolytic couples thus established, a current supply connection to the electrode at one end of the electrode group, and a second current supply connection to the electrode at the other end of the group, said latter connection being established under operating conditions through a fused conductor.

11. A metallurgical electrolytic apparatus comprising a container for a fused melt, a group of closely spaced electrodes immersed in and electrically connected in series by the melt under operating conditions, means for substantially confining the current to flow in series through the electrolytic couples thus established, a well for the reception of a fused metal product of electrolytic decomposition of the melt, a current supply connection to the electrode at one end of the electrode group, and a second current supply connection to the fused metal in said well.

12. A metallurgical electrolytic apparatus comprising a closed top container for a fused melt, a pile of spaced electrodes immersed in the melt under operating conditions, current supply conductors passing through the top of the container, one of said conductors being connected to the top electrode of the pile, and the second conductor being in electrical connection with the bottom electrode of the pile, together with insulating means separating the second conductor from the upper electrodes of the pile and from the fused melt above the bottom electrode and causing substantially the entire current supply to pass in series from the top electrode to the adjacent electrode through the intervening stratum of the melt, and so on downward through the electrode pile.

13. Multiple-couple electrolyzer for fused salts, comprising a refractory container for the fused electrolyte and the gaseous and metallic products, provided with feed and discharge openings and a series of closely spaced electrodes so positioned within the container as to become immersed in the electrolyte while the electrolyzer is in operation, the container embracing the outer edges of the electrodes and only the first and last of the electrodes being connected with the external supply conductors.

14. Multiple-couple electrolyzer for fused salts, comprising a heat-insulated refractory container for the fused electrolyte and the gaseous and metallic products, provided with feed and discharge openings and a series of closely-spaced electrodes so positioned within the container as to become immersed in the electrolyte while the electro-

lyzer is in operation, the container embracing the outer edges of the electrodes and only the first and last of the electrodes being connected with the external supply conductors.

15. Multiple-couple electrolyzer for fused salts, comprising a refractory container for the fused electrolyte and the gaseous and metallic products provided with a jacket for the circulation of heating fluid, feed and discharge openings and a series of closely-spaced electrodes so positioned within the container as to become immersed in the electrolyte while the electrolyzer is in operation, the container embracing the outer edges of the electrodes and only the first and last of the electrodes being connected with the external supply conductors.

16. Multiple-couple electrolyzers for fused salts having a series of closely-spaced inclined electrodes provided with holes in their upper and lower parts for passage of the electrolyte and the products of the electrolysis, only the first and last of the electrodes being connected with the external supply conductors.

17. Multiple-couple electrolyzer for fused salts having a series of closely-spaced inclined carbon electrodes provided with holes in their upper and lower parts for passage of the electrolyte and the products of the electrolysis, only the first and last of the electrodes being connected with the external supply conductors.

18. Multiple-couple electrolyzer for fused salts having a series of closely-spaced inclined electrodes of conoidal form provided with holes in their upper and lower parts for passage of the electrolyte and the products of the electrolysis, only the first and last of the electrodes being connected with the external supply conductors.

19. Multiple-couple electrolyzer for fused salts having a series of closely spaced inclined carbon electrodes of conoidal form provided with holes in their upper and lower parts for the passage of the electrolyte and the products of the electrolysis, only the first and last of the electrodes being connected with the external supply conductors.

20. Multiple-couple electrolyzer for fused salts having a series of closely-spaced inclined carbon electrodes separated by distance-pieces of insulating, heat-resistant material and provided with holes in their upper and lower parts for passage of the electrolyte and the products of the electrolysis, only the first and last of the electrodes being connected with the external supply conductors.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

EDGAR ARTHUR ASHCROFT.

Witnesses:

G. F. TYSON,

EDWD. GEO. DAVIES.