March 19, 1940. R. E. HULSE ET AL 2,194,444

FUSED SALT ELECTROLYSIS CELL

Filed July 6, 1937 2 Sheets-Sheet 1

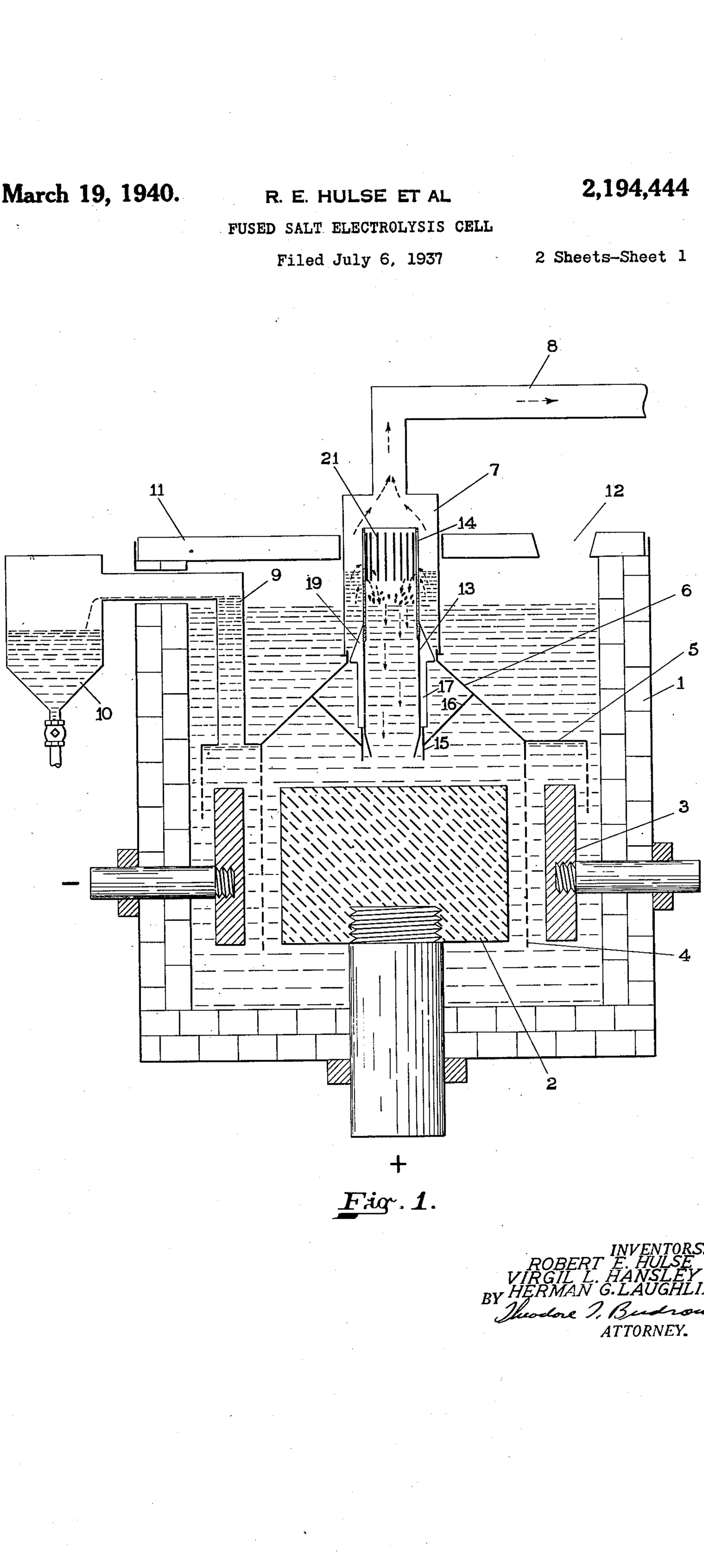

Fig. 1.

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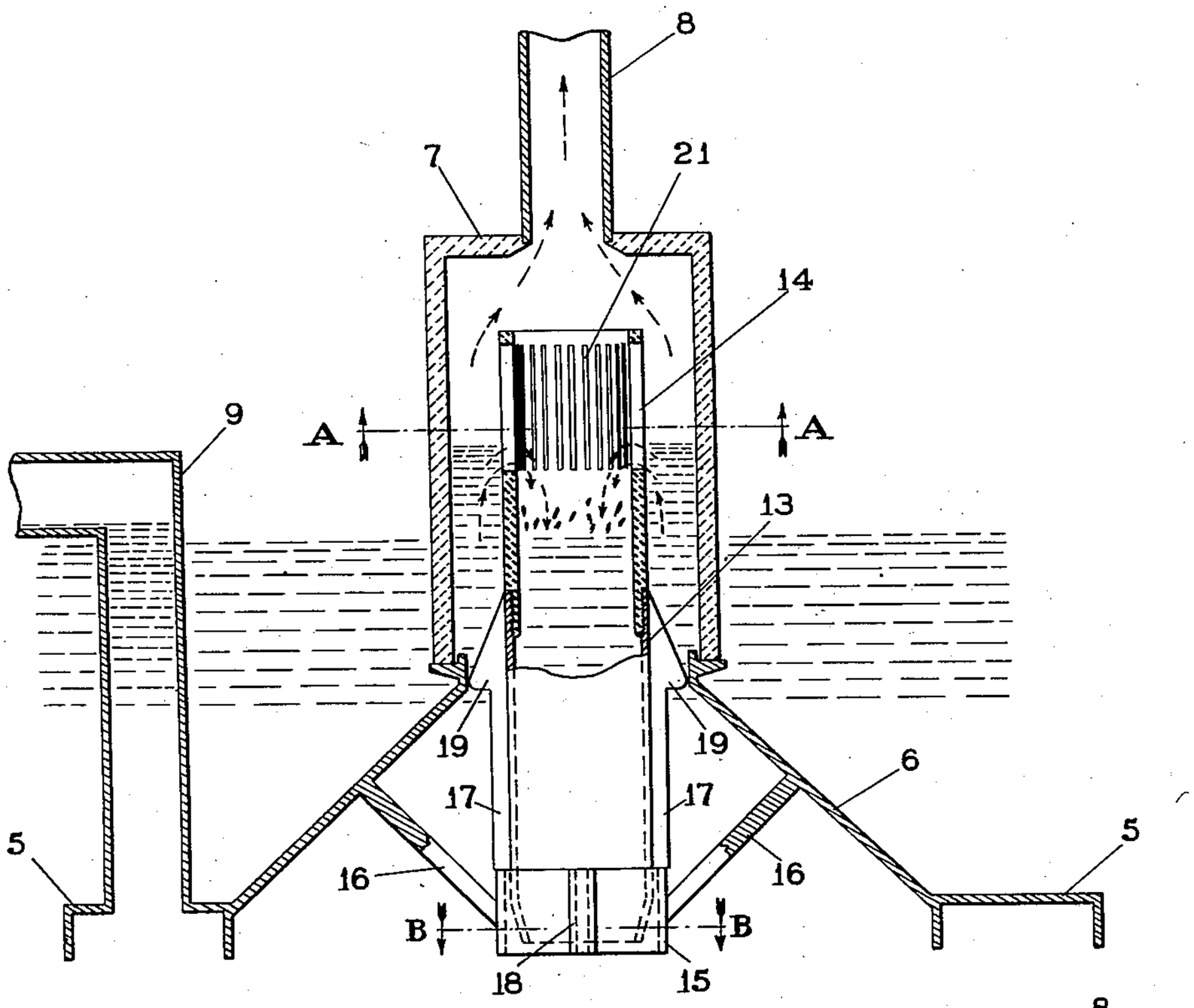

Fig. 2.

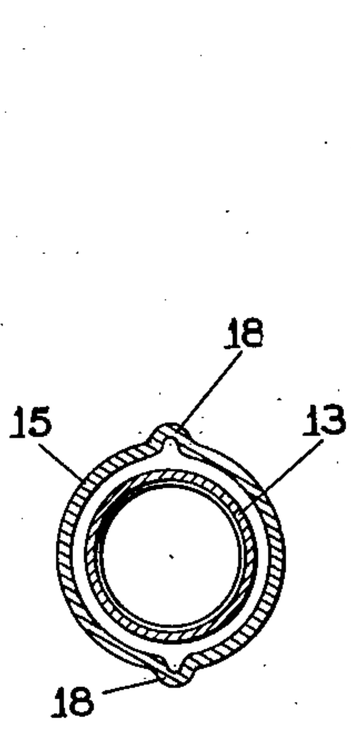

Fig. 4.

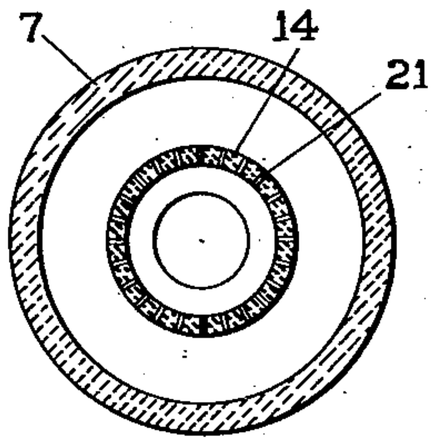

Fig. 3.

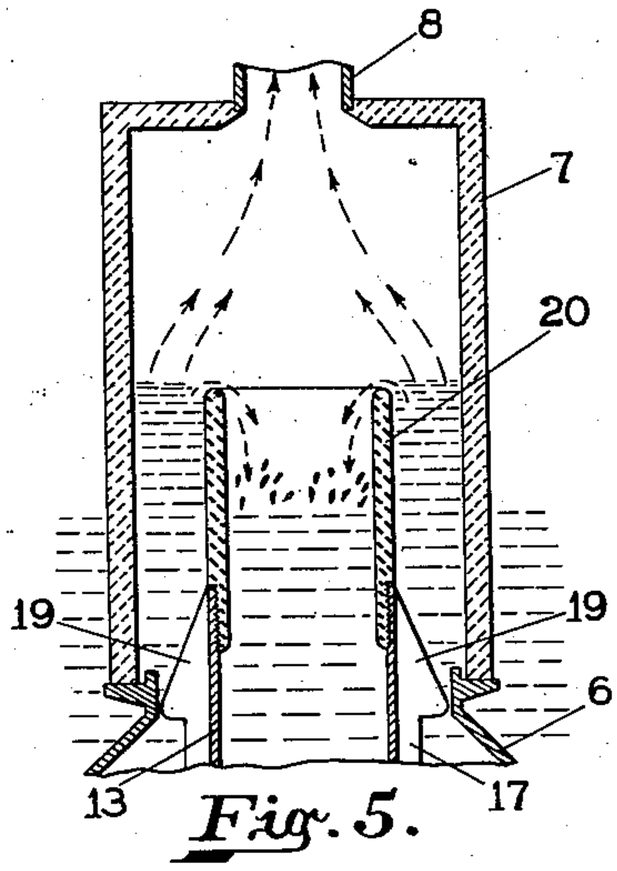

Fig. 5.

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UNITED STATES PATENT OFFICE

2,194,444

FUSED SALT ELECTROLYSIS CELL

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10 Claims. (Cl. 204—19)

This invention relates to an improvement in fused salt electrolysis cells, for example, cells used to electrolyze light metal halides to produce halogen and the corresponding metal.

In the operation of fused salt electrolysis cells, in the electrolysis of substances which evolve gaseous products at one or both electrodes, difficulty is ordinarily experienced because of more or less violent splashing of the molten salt electrolyte at the point where evolved gas leaves the electrolyte. In a large installation in which a high rate of production is obtained, the rapid evolution of gas causes a violent surface agitation of the electrolyte just below the point where the gas is collected. The resultant splashing of the electrolyte causes portions of the liquid to come into contact with the cooler upper surfaces of the gas collecting device or into the gas lead-off pipe. Most of the liquid so splashed up tends to solidify on such cooler surfaces and consequently it is necessary frequently to open the collecting device or gas lead-off pipe and clean out the solidified electrolyte. Sometimes this entails shutting down the electrolysis, which is troublesome and expensive and even when it is not necessary to stop the electrolysis operation, opening the collecting device or pipes to clean out the frozen salt causes dilution of the gas with air, thereby resulting in a more impure gaseous product and escape of the gas, which is wasteful and often hazardous to the operator.

An object of the present invention is to prevent the splashing of electrolyte in fused salt electrolysis cells in which gaseous products are obtained. A further object is to prevent the incrustation of gas collecting devices with frozen electrolyte in fused salt electrolysis cells. Another object is to provide an improved apparatus for fused salt electrolysis for the production of gaseous products. Other objects of this invention will be apparent from the following description thereof.

The above objects may be attained in accordance with the present invention by providing in a fused salt electrolysis cell a means for rapidly circulating the electrolyte in the region where gaseous products are evolved so that, at the point where gas leaves the electrolyte, the latter flows in a relatively rapid stream. More specifically, we cause the liquid electrolyte to rise together with the gaseous electrolysis product towards the surface where the gas escapes from the liquid, cause a rapid liquid flow at that point in such manner as to avoid splashing and then flow substantially gas-free liquid downwardly from the point where the gas escapes. In the practice of our invention, we preferably achieve this effect by taking advantage of the "gas-lift" effect of the ascending gas liberated from an electrode which tends to cause an upward flow of the electrolyte toward the point where the gas is discharged from the cell. To utilize this gas-lift effect, we insert in the cell suitable baffles, a down-flow tube or tubes or equivalent means so that the electrolyte lying above the point of gas formation is caused to rise by the gas-lift effect of the ascending gas bubbles and then, near the point where the gas is discharged from the cell, the liquid is caused to flow downward, for example, through one or more suitable down-flow tubes, through a region where gas evolution does not occur.

To illustrate our invention we shall describe its adaptation to a well-known type of fused salt electrolysis cell, hereinafter referred to as the "Downs cell", which is described and claimed in U. S. P. 1,501,756. The Downs cell as shown in the aforesaid patent has a centrally located graphite anode surrounded by an annular steel cathode and is ordinarily used for the electrolysis of fused alkali metal halides to produce alkali metal and halogen gas, for example, to produce sodium and chlorine. Above the annular cathode is suspended a circular trough for collecting the metal liberated at the cathode while a cone-shaped hood, surmounted by a cylindrical dome, is utilized to collect the gaseous product formed at the anode. In the normal operation of the Downs cell, the rapid evolution of halogen gas causes considerable splashing of the molten electrolyte in the dome at the top of the gas collector, which electrolyte tends to freeze on the relatively cooler walls of said dome. To prevent blocking the off-gas pipe leading from the dome, it is necessary to remove frozen salt from the dome at frequent intervals.

In adapting our invention to the Downs cell, we may insert therein a down-draft tube as illustrated by the drawings or equivalent means to cause rapid circulation of the electrolyte from the anode region towards the point of gas discharge and thence back down into the cell. Fig. 1 is a diagrammatic sectional drawing showing a Downs cell equipped with one modification of our invention. Figs. 2, 3 and 4 are sectional views showing details of the device of Fig. 1. Fig. 2 is a vertical section, while Fig. 3 is a horizontal section on plane A—A of Fig. 2 and Fig. 4 is a horizontal section on plane B—B of Fig. 2.

Fig. 5 is a vertical section showing another modification.

Referring to the drawings, a Downs cell equipped according to our invention consists of an electrolyte container 1 which is lined with a suitable refractory material, a centrally located anode 2 made of graphite, an annular cathode 3 surrounding said anode, a cylindrical diaphragm 4 made of wire gauze and suspended between the anode and cathode, inverted collecting trough 5 suspended above the cathode to collect rising alkali metal, and a conical gas collecting hood 6 surmounted by the gas collecting dome 7. The gas collecting hood 6 may be constructed of steel since it is entirely submerged in the fused salt and is thereby protected from the action of the halogen gas. Gas collecting dome 7 may be made of suitable ceramic material, to withstand the action of the halogen gas above the surface of the electrolyte. Lead-off pipe 8 is connected to the top of dome 7 to carry off the halogen gas as produced. The alkali metal collector 5 is provided with a pipe 9 through which molten alkali metal rises and is led into the receiver 10. The cell is provided with a cover 11 in which there is an opening 12 for feeding salt into the cell. The cover 11 may be omitted, if desired. Suspended within the gas collecting hood 6 and extending into the dome 7 is a down-flow pipe 13. The upper portion of pipe 13 is surmounted by graphite tube 14, near the upper end of which is a plurality of vertical, radial slots 21 extending through the walls of the graphite tube and extending vertically from a point near the end of the tube down to a point near the main level of the electrolyte in the cell. Pipe 13 is supported in this cell by means of collar 15 which in turn is supported by means of a plurality of rods 16 extending from the sides of the collar 15 and connected to the inside walls of cone 6. Two fin-shaped members or lugs 17 are welded on opposite sides of pipe 13 and the bottom ends of element 17 rest upon the upper rim of collar 15. Collar 15 as shown in cross-section in Fig. 4 is provided with two diametrically opposed semi-cylindrical protuberances 18. The size relationship between fins 17 and protuberances 18 is so arranged that when the pipe 13 is rotated on its axis so as to bring the fins 17 in alignment with protuberances 18, the fins will slide into said protuberances, whereby the pipe 13 may be lowered in the cell. At the top of fins 17 are provided stops 19 which engage with the upper edges of protuberances 18 thereby limiting the downward movement of pipe 13. In the normal operation of the device, pipe 13 rests on collar 15 in the elevated position. When desired, pipe 13 may be lowered so as to bring the graphite tube 14 below the level of the electrolyte in the cell.

In the operation of the device just described, the cell provided with the inserted pipe 13 and its attachments is operated in the usual manner. The halogen gas evolved at the anode rises upward in hood 6 on the outside of the pipe 13, little or no gas tending to enter the lower end of the pipe 13. The rapid rise of the gas in hood 6 and into dome 7 causes the liquid to rise in dome 7 some distance above the main level of the bath in the cell. The liquid spills over into pipe 13 by way of the slots in graphite tube 14 and descends back toward the electrolysis zone of the cell by way of pipe 13. The gas is separated from the liquid at the time that the liquid flow changes from an upward to a downward direction. Part of the gas escapes in the space outside of tube 14, while the remainder is disengaged from the liquid inside tube 14. The disengaged gas is led off through pipe 8. At the point where the gas is disengaged from the liquid around the periphery of tube 14, there is a rapid, and chiefly horizontal flow of liquid through slots 21 into interior of tube 14 and apparently because of the rapid flow of liquor at that point, there is substantially no splashing of the liquid in the dome 7. Hence, the apparatus may be operated for long periods of time without the necessity of cleaning frozen salt from dome 7 or pipe 8. The liquid passing through the slots in tube 14 descends by way of tube 13 into the interior of the cell.

In the above described device, in place of a slotted graphite tube 14 we may use other forms of graphite tubes at the top of pipe 13. For example, in place of the vertical slots we may use staggered horizontal slots, round holes or various other types of openings. It is also possible to carry out our invention by using a plain, unperforated graphite tube at the top of pipe 13, for example graphite tube 20 as shown in Figure 5. In the latter case, the top of the graphite tube is arranged to be a relatively short distance above the electrolyte level in the cell so as to permit the rising liquid in dome 7 to readily overflow the edges of tube 20. If desired, the edges of the upper edge of tube 20 may be provided with serrations or slots. We prefer, however, to use the slotted tube as exemplified by tube 14 of the drawings since this has proven to give the best results in comparison with other types which have been tried.

The tubes 14 and 20, as illustrated, or their equivalents are preferably made of graphite when the invention is used in a cell for the production of a corrosive gas such as chlorine. The invention is not restricted to graphite tubes, however, since metal tubes are satisfactory when the gas being collected, e. g. hydrogen, is non-corrosive to metal. Moreover, other materials, not readily corroded by the gas evolved may be utilized to from the top of the circulation tube or equivalent means.

The arrangement described above for lowering the pipe 13 by allowing the fins 17 to slide through the channels formed by protuberances 18 in collar 15 is useful when for any reason the cell temperature is temporarily lowered to such point that the upper surface of the fused electrolyte tends to freeze. For example if it becomes necessary to shut off the power from the cell for a short time, salt is likely to congeal in the upper portion of pipe 13, for example, in slots 21. This may be avoided by lowering the pipe 13 so that slots 21 are well below the electrolyte surface. To lower pipe 13, a hook or other suitable tool may be inserted through dome 7 or pipe 8 by way of an opening provided for the purpose and, for example, by engaging the tool with stops 19, pipe 13 may be rotated to allow fins 17 to slide through channels 18 in collar 15.

The invention is not restricted to the particular arrangement of supporting fins 17 and collar 15 as shown and described above. For example, the collar 15 may be formed in two semi-cylindrical parts, with two spaces or slots between each part or maybe a split ring with a single slot, through which corresponding fins or lugs on pipe 13 may pass. The stops 19 are not necessarily attached to fins 17 but may be attached directly to pipe 13. Various other modifications will be apparent to the skilled mechanic.

To those familiar with the construction and operation of fused salt electrolysis cells, it will be apparent that our invention is not restricted to the Downs type cell and further that it is not restricted to the employment of the particular device described and illustrated herein. In its broader aspect, our invention comprises providing an internal circulation of electrolyte in such manner that there is a rapid flow of electrolyte at the point where gas is disengaged from the liquid electrolyte, this flow being sufficiently rapid to overcome the tendency of the gas bubbles leaving the liquid to cause splashing and spattering. Various modifications may be employed to provide the particular type of internal bath circulation contemplated in the herein described invention. The particular means used to provide the required circulation will vary with different types of cells. In the preferred modification of the invention, a gas collecting hood is constructed beneath the electrolyte surface to bring the rising gas bubbles into a zone of restricted cross-section, thus causing a rise of liquid in said zone and providing means for rapidly flowing the liquid away at the surface of the rising liquid, either back into the lower parts of the cell or outside of the cell, preferably in a downward direction.

We claim:

1. In a fused salt electrolytic cell, a gas collecting device which comprises a gas collecting hood at least partially submerged in the electrolyte and adapted to collect gas arising from an electrode, gas outlet means connected to said hood and a substantially vertically disposed conduit located within said hood and extending from a point which is above the surface of the electrolyte outside of said hood, downwardly to a depth substantially below said surface.

2. In a fused salt electrolytic cell, a gas collecting device which comprises a gas collecting hood at least partially submerged in the electrolyte and adapted to collect gas arising from an electrode, gas outlet means connected to said hood, a substantially vertically disposed conduit located within said hood and extending downward from a point above the electrolyte surface to a substantial depth below said surface, a portion of said conduit which lies above said surface being provided with openings leading into said conduit.

3. In a fused salt electrolytic cell, a gas collecting device which comprises a gas collecting hood at least partially submerged in the electrolyte and adapted to collect gas arising from an electrode, gas outlet means connected to said hood, a substantially vertically disposed conduit located within said hood and extending downward from a point above the electrolyte surface to a substantial depth below said surface, a portion of said conduit which lies above said surface being provided with radially disposed vertical slots leading into said conduit.

4. In a fused salt electrolytic cell, a gas collecting device which comprises a conical gas collecting hood submerged in the electrolyte and adapted to collect gas arising from an electrode, a cylindrical gas collecting dome surmounting said hood; gas outlet means connected to said dome, a substantially vertically disposed conduit located within said hood and dome and extending downward from a point above the electrolyte surface to a substantial depth below said surface, a portion of said conduit which lies above said surface being provided with radially disposed vertical slots leading into said conduit.

5. In a fused salt electrolytic cell, a gas collecting device which comprises a conical gas collecting hood submerged in the electrolyte and adapted to collect gas arising from an electrode, a cylindrical gas collecting dome surmounting said hood, gas outlet means connected to said dome, a vertical, cylindrical, open tube concentric with said hood and extending from a point near the electrode at which the gas is formed upward into said dome above the main electrolyte level in the cell, a portion of said tube which lies in the gas collecting dome being provided with a plurality of openings leading into the tube.

6. In a fused salt electrolytic cell, a gas collecting device which comprises a conical gas collecting hood submerged in the electrolyte and adapted to collect gas arising from an electrode, a cylindrical gas collecting dome surmounting said hood, gas outlet means connected to said dome, a vertical, cylindrical, open tube concentric with said hood and extending from a point near the electrode at which the gas is formed upward into said dome above the main electrolyte level in the cell, a portion of said tube which lies in the gas collecting dome being provided with a plurality of vertical, radially arranged slots adapted to lead electrolyte into the tube.

7. In a fused salt electrolytic cell, a gas collecting device which comprises a conical gas collecting hood submerged in the electrolyte and adapted to collect gas arising from an electrode, a cylindrical gas collecting dome surmounting said hood, gas outlet means connected to said dome, a vertical, cylindrical, open tube concentric with said hood and extending from a point near the electrode at which the gas is formed upward into said dome above the main electrolyte level in the cell, a portion of said tube which lies in the gas collecting dome being provided with a plurality of vertical, radially arranged slots adapted to lead electrolyte into said tube, said tube being supported by means of lugs attached to the tube which rest upon the upper edge of a ring shaped member through which said tube passes, said ring-shaped member being provided with channels through which said lugs may pass when the tube is rotated to bring the lugs and channels into alignment, so as to lower the tube through said ring-shaped member.

8. In a fused salt electrolytic cell, a gas collecting device which comprises a conical gas collecting hood submerged in the electrolyte and adapted to collect gas arising from an electrode, a cylindrical gas collecting dome surmounting said hood, gas outlet means connected to said dome, a vertical, cylindrical, open tube concentric with said hood and extending from a point near the electrode at which the gas is formed upward into said dome above the main electrolyte level in the cell, a portion of said tube which lies in the gas collecting dome being provided with a plurality of vertical, radially arranged slots adapted to lead electrolyte into the tube, said tube being supported by means of lugs attached to the tube which rest upon the upper edge of a ring-shaped member through which said tube passes, said ring-shaped member being provided with channels through which said lugs may pass when the tube is rotated to bring said lugs and channels into alignment, so as to lower the tube through said ring-shaped member and said tube being provided with means for

stopping the descent of said tube at a predetermined level.

9. In a fused salt electrolytic cell, a gas collecting device which comprises a conical gas collecting hood submerged in the electrolyte and adapted to collect gas arising from an electrode, a cylindrical gas collecting dome surmounting said hood, gas outlet means connected to said dome, a vertical, cylindrical, open tube concentric with said hood and extending from a point near the electrode at which the gas is formed upward into said dome above the main electrolyte level in the cell, a portion of said tube which lies in said gas collecting dome being provided with a plurality of vertical, radially arranged slots adapted to lead electrolyte into the tube, said tube being supported by means of a pair of diametrically disposed, vertical fins, the lower ends of which fins rest upon the upper edge of a ring-shaped member through which said tube passes, said ring-shaped member being provided with channels through which said fins may pass when the tube is rotated to bring the fins and channels into alignment, so as to lower the tube through said ring-shaped member and the upper ends of said fins being provided with stop lugs adapted to engage with said ring-shaped member to limit the downward movement of said tube through said ring-shaped member.

10. A cell for fused salt electrolysis having an electrode adapted to cause gas formation located beneath the surface of the electrolyte, a gas collecting chamber located above the point of gas formation and partially submerged in the electrolyte, a conduit for flowing electrolyte, together with gas formed at said electrode, upwardly within said chamber to a point of gas disengagement located above the surface of that electrolyte which is outside said conduit and another conduit for flowing electrolyte from said point of gas disengagement downwardly within the cell back to said electrode.

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