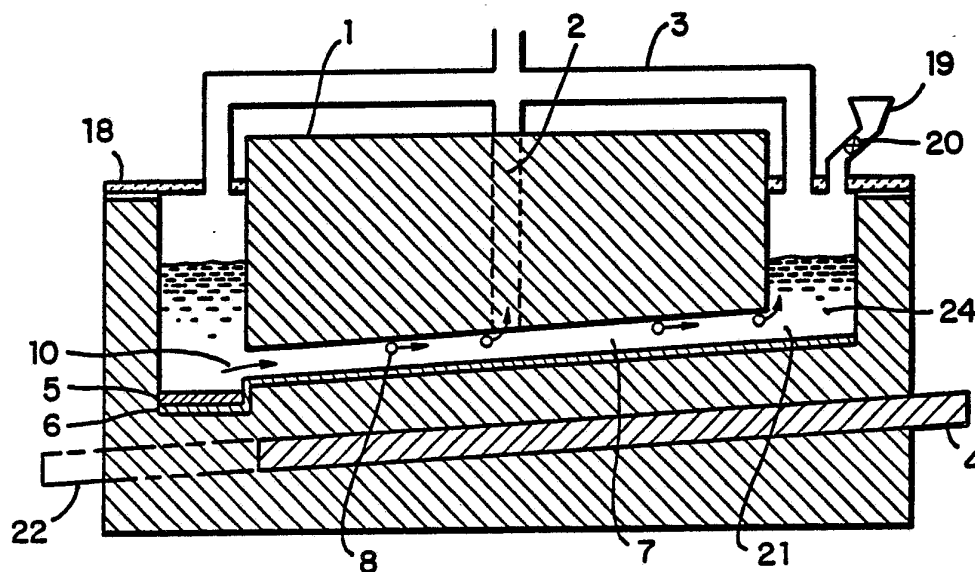




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification³ : C25C 3/08	A1	(11) International Publication Number: WO 84/ 03308 (43) International Publication Date: 30 August 1984 (30.08.84)
(21) International Application Number: PCT/US84/00075 (22) International Filing Date: 20 January 1984 (20.01.84) (31) Priority Application Number: 467,570 (32) Priority Date: 17 February 1983 (17.02.83) (33) Priority Country: US (71) Applicant: MARTIN MARIETTA CORPORATION [US/US]; 6801 Rockledge Drive, Bethesda, MD 20817 (US). (72) Inventors: BOXALL, Larry, G. ; 1210 White Mills Road, Baltimore, MD 21228 (US). GAMSON, Bernard, W. ; 11124 Hunt Club Drive, Potomac, MD 20854 (US). GREEN, John, A., S. ; 3712 Tustin Road, Ellicott City, MD 21043 (US). TRAUGOTT, Stephen, C. ; 11219 Old Carriage Road, Glen Arm, MD 21057 (US).		(74) Agents: MYLIUS, Herbert, W. et al.; Martin Marietta Corporation, 6801 Rockledge Drive, Bethesda, MD 20817 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), SU. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: LOW ENERGY ALUMINUM REDUCTION CELL WITH INDUCED BATH FLOW

**(57) Abstract**

In an electrolytic cell for the production of aluminum from alumina, having an anode-to-cathode gap of from 1 to 5 cm, the flow of electrolyte to the inter-electrode gap is induced by positioning the cathode at an inclination of from about 2 to about 15 degrees from the horizontal, and operating at an anode current density of from about 0.5 to about 3.0 A/cm². The cathode surface is a Refractory Hard Material which is wetted by aluminum.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

-1-

LOW ENERGY ALUMINUM REDUCTION
CELL WITH INDUCED BATH FLOW

Background of the Invention

5 This invention relates to a novel electrolytic cell for the manufacture of aluminum from alumina, and to the operation of such a cell. More particularly, the invention relates to an aluminum producing electrolysis cell using bath electrolyte based on sodium cryolite, wherein the problems resulting
10 from reduced anode to cathode gap distances achieved in previous drained cathode cells are demonstrated to have been overcome by inducing a particular manner of bath flow in the ACD gap, thus facilitating alumina feeding, removal of gaseous products, and enhanced drainage of product metal.
15 Operation of a test electrolysis cell has demonstrated the ability to provide a plentiful supply of dissolved alumina to the electrolysis zone even at very narrow anode to cathode spacings.

A commonly utilized electrolytic cell for the manufacture of aluminum is of the classic Hall-Heroult design,
20 utilizing carbon anodes and a substantially flat carbon-lined bottom which functions as part of the cathode system. An electrolyte is used in the production of aluminum by electrolytic reduction of alumina, which electrolyte consists primarily of molten cryolite with dissolved alumina,
25 and which may contain other materials such as fluorspar, aluminum fluoride, and other metal fluoride salts. Molten aluminum resulting from the reduction of alumina is most frequently permitted to accumulate in the bottom of the receptacle forming the electrolytic cell, as a molten metal
30 pad or pool over the carbon-lined bottom, thus forming a



-2-

liquid metal cathode. Carbon anodes extending into the receptacle, and contacting the molten electrolyte, are adjusted relative to the liquid metal cathode. Current collector bars, such as steel, are frequently embedded in the carbon-lined cell bottom, and complete the connection to the cathodic system.

While the design and sizes of Hall-Heroult electrolytic cells vary, all have a relatively low energy efficiency, ranging from about 35 to 45 percent, dependent upon cell geometry and mode of operation. Thus, while the theoretical power requirement to produce one pound of aluminum is about 2.85 kilowatt hours (kWh), in practice power usage ranges from 6 to 8.5 kWh/lb, with an industry average of about 7.5 kWh/lb. A large proportion of this discrepancy from theoretical energy consumption is the result of the voltage drop of the electrolyte between the anode and cathode. As a result, much study has gone into reduction of the anode-cathode distance (ACD). However, because the molten aluminum pad which serves as the cell cathode can become irregular and variable in thickness due to electromagnetic effects and bath circulation, past practice has required that the ACD be kept at a safe 3.5 to 6 cm to ensure relatively high current efficiencies and to prevent direct shorting between the anode and the metal pad. Such gap distances result in voltage drops from 1.4 to 2.7 volts, which is in addition to the energy required for the electrochemical reaction itself (2.1 volts, based upon enthalpy and free energy calculations). Accordingly, much effort has been directed to developing a more stable aluminum pad, so as to reduce the ACD to less than 3.5 cm, with attendant energy savings.

Refractory hard materials (RHM), such as titanium diboride, have been under study for quite some time for use as cathode surfaces in the form of tiles, but until recently, adherent RHM tiles or surface coatings have not been available. Titanium diboride is known to be conductive, as well as



-3-

possessing the unique characteristic of being wetted by molten aluminum, thus permitting formation of very thin aluminum films. The use of a very thin aluminum film draining down an inclined cathode covered with an RHM surface, to
5 replace the unstable molten aluminum pad of the prior art, has been suggested as a means to reduce the ACD, thus improving efficiency, and reducing voltage drop. However, attempts to achieve such goals in the past have failed due to the inadequacy of available RHM surfaces, and the inability to
10 overcome the difficulty of providing a sufficient supply of dissolved alumina to the narrowed ACD (as small as 1.5 cm). Thus, problems of alumina starvation occur at minimal ACD, including excessive and persistent anode effects. Overfeeding alumina to prevent these problems has resulted in deposits
15 of sludge (mucking), which can clog the cell and restrain its operation.

An alternative approach to reducing energy consumption has been to smelt aluminum from aluminum chloride rather than alumina. This process requires 30 to 40 per cent less
20 electrical power to produce aluminum than conventional electrolysis. In this process, the conventional Bayer method is utilized to convert bauxite to alumina, which is converted to aluminum chloride in a chemical plant, then smelted in an electrolytic cell. In the cell, the aluminum
25 chloride breaks down into aluminum, which is drawn off, and chlorine, which may be recycled back to the chemical plant for the production of more aluminum chloride. Such techniques utilize a flow-through reactor, having non-consumable anodes. However, the aluminum-producing cells of this
30 process are incompatible with the Hall-Heroult type cell, and cannot be retrofitted to an existing aluminum plant. Thus, the chloride process requires the capital expense of an entirely new installation. To a greater degree, the present invention permits appreciable energy savings in a
35 retrofitted plant, and obviates the need for completely new facilities.



-4-

It is against this background that the present invention was developed.

Summary of the Invention

It is an object of this invention to provide an improved
5 aluminum electrolysis cell, utilizing a bath electrolyte
based on sodium cryolite, and having improved electrical
efficiencies. It is thus a purpose of this invention to
provide a basic cell for the production of aluminum metal
from alumina which may be used in a single cell system, or
10 in a multiple cell system, to achieve construction and
operating economies.

It is an object of the present invention to provide a
cell design which provides a narrower ACD than the prior
art, and hence improved current efficiencies and voltage
15 drops, and which may be retrofitted to existing Hall cell
installations. Accordingly, an object of the present
invention is to provide an electrolysis cell with an ACD
of less than 3 cm, wherein an adequate alumina supply to the
anode-cathode gap is assured, without requiring overfeeding.
20 Additional objects of the invention are to provide an aluminum
reduction cell design providing a flow-through configuration,
and a controlled atmosphere.

These, as well as other objects, which will become more
apparent in the disclosure which follows, are achieved by
25 providing a cell in which individual process steps are separated to the greatest extent possible. A sloped solid
cathode is utilized to shape the anode, which may be either
Soderberg or pre-baked, which in concert with the proper
choice of other parameters defined herein induces such a
30 bath flow through the anode-cathode gap as to provide the
proper alumina supply to the anode, without adverse impact
on the drainage of aluminum product into a collection sump.
In one configuration, gas pumping action under the anode
causes the bath to flow through the cell, into a cell feeding



-5-

chamber, out of the cell feeding chamber, and back to the opposite side of the cell. Multiple individual cells of this nature may be combined in numerous configurations to structure the system for the physical and economic restrictions of any plant site.

Thus, the present invention relates to an electrolytic cell in which the cathode is so arranged and inclined that the anode gases induce a plentiful and sufficient flow of enriched materials between the anode and cathode, without impeding the drainage of molten aluminum to a collection sump, or disrupting the surface of the draining aluminum so as to cause lower current efficiencies. Thus, the bath is induced to flow from an enriched bath zone to a zone where the bath is somewhat depleted in alumina content. The bath may be supplied with an automatic feed of alumina in a controlled amount, to prevent either mucking or anode effects.

Brief Description of the Drawings

Figure 1 constitutes an end view of an electrolytic cell employing an inverted V cathode, or dual slope cathode configuration.

Figure 2 constitutes an end view of a cell concept of the present invention, utilizing a single slope cathode.

Figure 3 constitutes an end view of a single-slope cathode, flow-through aluminum reduction cell having external replenishment.

Figure 4 constitutes an end view of a V-shaped drained cathode cell.

Figure 5 illustrates a plan view of a single slope drained cathode cell, utilizing a continuous aluminum tapping system and a separate replenishment and mixing zone.

Figure 6 represents a plan view of a multiple cell system, utilizing a plurality of single sloped drained cathode cells in tandem.



-6-

Figure 7 represents a plan view of a single slope drained cathode cell employing partial barriers to restrict bath flow velocity.

5 Figure 8 represents a plan view of a cell having two oppositely sloped cathodes.

Figure 9(a) illustrates a side elevation view of a hydraulic analog model designed to simulate gas evolution in a sloping cathode cell.

Figure 9(b) illustrates normal bath flow in the ACD.

10 Figure 9(c) illustrates a region of reverse bath flow in the ACD, adjacent to the draining aluminum metal.

Figure 9(d) illustrates a region of turbulent and disrupted bath flow, whereby no net flow of bath material through the ACD occurs.

15 Figure 10 constitutes a graphic representation of bath flow versus cathode slope in the cell simulation model under high flow resistance conditions.

Figure 11 constitutes a graphic representation of bath flow versus cathode slope in the cell simulation model under
20 medium flow resistance conditions.

Figure 12 constitutes a graphic representation of bath flow versus cathode slope in the cell simulation model under low flow resistance conditions.

25 Figure 13 is a conceptual pump efficiency-flow resistance diagram for a drained cathode cell.

Figure 14 graphically illustrates required flow resistance in the return channel versus cathode slope.

Figure 15 constitutes a cell design parameter diagram.

30 Figure 16 is a cross section of a sloping cathode electrolysis test cell.

Figure 17 is a graphic representation of cell operational stability achieved in three test cells.

35 Figure 18 illustrates the relationship between anode-cathode polarization and cathode slope at two current densities.



-7-

Description of Preferred Embodiments

The present invention consists of utilizing a sloped, drained cathode, having a surface of titanium diboride or other similar refractory hard material, in which the slope or inclination from the horizontal is selected so as to contribute to a controlled bath motion, which bath motion is hydrodynamically dependent upon specifically identified critical parameters. The bath motion is so controlled as to induce sufficient alumina-rich bath to flow into the inter-electrode gap in the space immediately beneath the anode face to avoid any anode effects, while not interfering with the drainage of aluminum. Thus, it is possible to overcome problems of alumina feeding, such as muck formation resulting from excessive bath addition, persistent anode effects resulting from insufficient bath addition, and ledging, which interferes with bath circulation, which occur at the very low values of anode-cathode distance (ACD) made possible by the development of refractory hard metal surfaced cathodes operating without a conventional metal pad.

Success of a low energy drained cathode aluminum reduction cell concept depends on two critical components: 1) a durable RHM cathode material, and 2) the ability to control and optimize the bath flow through the narrow anode-cathode gap (ACD). Ongoing tests in production cells indicate that a material has been developed which satisfies the first requirement. Copending U.S. Patent Applications 395,343, 395,344, and 395,345, filed July 9, 1982; and applications 400,762, 400,763, 400,764, 400,765, 400,772, and 400,773, filed July 22, 1982; and others, all commonly assigned to the assignee of this application, relate to Refractory Hard Material coating compositions, application methods, and cathode structures providing durable, adherent cathode surfaces exhibiting aluminum wettability and improved electrical characteristics.



-8-

Studies using a water model to simulate hydrodynamic conditions in the ACD of a sloping cathode cell have now generated the cell design criteria necessary to satisfy the other requirement. Results from the water model have been
5 verified in a laboratory scale electrolytic cell. A number of cell designs, such as in the Kaiser-DOE sloping TiB_2 cathode tests reported under Contract DE-AC03-76CS40215, and as used in other published reports and patents, fall outside
10 our design requirements, and fail to address crucial hydrodynamic issues, the criticality of which has now been established. These design criteria include slope or inclination of the cathode surface, the ACD spacing, the resistance to bath flow in the return path, and anode current density. Only the first two of these criteria have been
15 considered in previously existing designs, reports, and patents, while the latter two criteria, and their criticality, are newly established herein.

It is well established in aluminum electrolysis that the anode face is configured by the electrolysis process to
20 be essentially parallel to the cathode. Thus, an inclined cathode causes the anode to be similarly inclined. As is also well known, there exists a plentiful gas evolution at the anode face due to the electrolysis process.

It is also well known for aluminum reduction cells of
25 conventional design, with horizontal anode and cathode faces, that gas evolved at the anode face travels sideways (laterally) outwards underneath the anode face from the center of the cell to the nearest vertically oriented vent, said vents generally comprising the vertical side faces of
30 the anode. A sloped anode may either enhance or inhibit this gas motion, depending on the direction and magnitude of the slope. A suitable cathode, and therefore anode, inclination can therefore be found to cause the anode gases to move in a desired direction. In turn, these anode gases will
35 drive, by a well known action also utilized in the design of



-9-

gas lifts and gas jet pumps, as well as bubble columns, the bath near the anode surface in the same desired direction. This drive may be supplemented and enhanced (if necessary) by other pumping action, e.g. a suitably designed pump.

5 It is well known in hydrodynamics that the flow of a fluid system is established by a balance between the fluid drive and the resistance to flow within the components of the system, and that, dependent upon the configuration, the velocity within local regions flow may be in the same direc-
10 tion but may sometimes be in the direction opposite to the direction of the fluid drive. It is a principle of the present invention to so arrange the slope, or slopes, so as to achieve that balance between buoyancy-generated bubble
15 bubbles sideways beneath horizontal anodes on the one hand, and the flow resistance on the other hand, to give a net motion of the bath to provide the required alumina supply. The local bath velocity near the anode surface is in the desired direction, i.e. the direction in which the driving
20 gas bubbles move. At the same time, the configuration is so positioned to provide bath velocities near the cathode surface in the same direction as those near the anode, yet not so large as to interfere with the drainage of aluminum at the cathode, which aluminum drainage is opposite in direction to
25 the flow of the gas bubbles driving the bath. With the source of alumina-rich bath located on a particular side of the cell, a bath flow into the space immediately beneath the anode face is achieved when this side of the anode is low with an upward slope away from this side. This slope must
30 be sufficiently large to overcome, and reverse, the flow of gas which would otherwise be toward this anode edge from the inner parts of the anode. The precise configuration and arrangement of inclinations may vary with the location of the alumina-rich bath supply. This may be on one side, on
35 both sides, or in the center of the cell, depending upon the



-10-

size of the cell and the type of anodes used (prebaked or Soderberg).

Alternative embodiments of the invention are envisioned in which the cathode (and therefore anode) inclination is
5 uniform over the width of the cell, or in which the slope is variable, in a variety of forms. These may include, for example, unequal but constant inclinations in the same directions in the two halves of a transverse cross-section of a cell, and also equal but opposite inclinations in these two
10 halves (e.g. a double slope, inverted V configuration). The concept of this invention can be applied to cells of both prebaked and/or Soderberg anode design. For example, while the inverted V configuration may be most suitable for cells whose width is covered by two prebaked anode blocks,
15 such a configuration can also be applied to a vertical stud Soderberg anode, vented in the center. An inverted V configuration would be applicable to feeding from both sides, while a V configuration would be suitable for center feeding. Similarly, a design with the slope in one direction only
20 (constant or variable) may be preferentially applied, but the invention is not restricted to a single monolithic unvented Soderberg anode fed from one side.

The choice of cathode slope for a particular application must be made compatible with other governing parameters
25 to achieve the desired hydrodynamic characteristics. These parameters are the ACD gap (i.e. the ACD spacing), anode current density, (current and anode face dimensions), and bath return resistance (i.e. the bath return channel or passageway length, depth, width, and wall material). The
30 controlled bath flow ensures a sufficient supply of alumina-rich electrolyte to the anode face for the prevention of excessive anode effects. Additional benefits are the avoidance of excessive gas accumulation in the ACD, and reduction of anode and cathode overvoltages, and minimizing of disruption
35 of flow of aluminum product.



-11-

An end view of a vertical stud Soderberg reduction cell with side feed, utilizing an inverted V cathode design with center gas exit, and collector bar, is shown in Figure 1.

The cathode surface, 6, is sloped upwardly from the cell sides toward the center of the anode, 1, where anode gas is vented through the gas vent, 2, to a collection system (not shown). Collector bars, 4, are illustrated as closely parallel to the cathode surface, 6, and being offset to clear aluminum drain sump 5.

10 The angle of the cathode surface 6 from the horizontal should be large enough to induce the desired bath flow, but not so large as to cause excessive deformation of the bubbles, or bath turbulence, in the anode-cathode space, 7, and in accordance with the limitations disclosed herein-
15 after. It has now been observed, for example, that the angle of inclination has a pronounced, and previously unreported, effect upon bubble configuration and travel. When the anode surface is tilted from the horizontal, the bubbles exhibit a more pronounced tendency towards an elongated oval
20 shape, the long axis of which is perpendicular to the direction of travel of the bubble up the anode slope. The leading edge of the bubble forms a brow, or increased thickness, as the relative speed between bubble and liquid increases. Thus, the increasingly thick leading edge may result in
25 decreased bubble driving action, due to increased resistance resulting from the effects of interfacial distortion and friction, over some range of inclination. For example, it was observed that large bubbles on the anode surface are subject to considerable distortion and resistance at an
30 anode inclination of about 15° from the horizontal. Suitable angles of inclination have been found to range from about 2 to about 15 degrees, although slightly larger or smaller angles may be acceptable for given cell conditions. A preferred slope is from about 5 degrees to about 10 degrees
35 from the horizontal, with a more preferred slope of from



-12-

about 6 to about 8 degrees. The most preferred cathode slope has been found to be about 8 degrees.

The cathode surface, 6, may be covered with an electrically conducting and aluminum wetted material, such as TiB_2 , to facilitate the formation of a thin film of aluminum (or aluminum alloy) on the cathode surface. While a titanium diboride containing surface is to be preferred, the use of other aluminum-wetted refractory hard materials (RHM), such as titanium carbide, zirconium carbide, zirconium diboride, or mixtures thereof, is also contemplated. Suitable cathode surfaces, and coating compositions for providing such cathode surfaces, are set forth in copending U.S. Patent Applications 395,343, 395,344, and 395,345, filed July 9, 1982; and applications 400,762, 400,772, and 400,773, filed July 22, 1982; and others, all commonly assigned to the assignee of this application.

The aluminum drains from the sloping surface of the cathode into a side collection drain sump, 5, thus minimizing the likelihood of back reaction, which would reduce current efficiency, and expediting tapping procedures, and making them independent of other cell operations. This thin film of draining aluminum is insensitive to induced magnetic fields, a major improvement over the use of conventional molten aluminum pads. Further, the controlled bath motion, as described, does not interfere with its drainage.

The gas bubbles, 8, moving up along the lower inclined edge of the anode, are vented as required, such that the bubbles do not get excessively large, i.e. do not cover a significant portion of the anode face, or extend excessively into the anode to cathode space. However, over-venting should be avoided in order to not seriously diminish the desired drive for bath flow in the narrow anode to cathode space. Venting may be done through a slot or slots or a pattern of vent tubes, channels, holes, etc., in the anode.



-13-

Venting holes may be made by inserting pipes just through the paste or plastic zone of a Soderberg anode, or baked into a prebaked carbon anode. It is noted that a non-uniform distribution of vents in the anode will redistribute the bath flow in the cell to compensate for bath flow non-uniformities in the cell.

Alumina may be added to the bath at hopper 19, to replenish the depleted alumina bath. Of course, other bath make-up materials may also be added simultaneously. The arrows, 10, indicate flow of the alumina rich bath through the narrow anode to cathode space, 7, induced by gas bubbles 8, while arrow 13 indicates the flow of aluminum metal, as a thin film, to drain sump 5.

Figure 2 represents an aluminum reduction cell utilizing a single sloped cathode, in end view. The single slope cathode surface, 6, enables the use of a straight collector bar, 4, permitting maintenance of a constant distance between the upper cathode surface and the collector bar. While there are some voltage reduction advantages if the collector bar extends from both sides of the cell, 22, this is not necessary if a deeper aluminum drain sump, 5, is more advantageous. The configuration of this cell permits the use of more-or-less conventional construction and installation techniques for collector bar placement. The inclination of the cathode surface, 6, must be sufficient to efficiently move gas bubbles up along the shaped anode face, and to allow aluminum to drain down the cathode surface. As illustrated, excess anode gas bubbles, 8, which might otherwise cause excessive distortion of the metal film flowing down the cathode face, may be vented through the gas vents in the anode, 2, to a gas collection system 3. Use of a mechanical bath cover, 18, ensures complete control of bath atmosphere and reduces emissions to the atmosphere. Alumina is added to the bath at the interelectrode gap outlet, 21, by means of hopper 19. An automatic control, 20, may be



-14-

utilized to accurately replenish the bath. Addition of the alumina, and other bath make-up materials, in this fashion has several advantages. First, after exiting the electrolysis zone, the bath is partially depleted of dissolved alumina, and thus provides the most ideal environment for rapid alumina dissolution. If some alumina does settle out on the bottom of the side reservoir, 24, the absence of a metal pad or metal sump to cover the settled alumina muck will facilitate its dissolution into the flowing bath. Further, the return path for the bath provides extra dissolution time and acts as a trap for any undissolved alumina in order to ensure that only muck-free bath is circulated into the ACD gap. Whereas addition of alumina to the metal drain sump side, 5, of the cell could result in the formation of muck beneath the metal in the sump, thus causing a sump overflow and a possible direct metal electrical short between anode and cathode, such is avoided in the present arrangement.

An end view of a flow-through single-slope cathode aluminum reduction cell is given in figure 3. The cathode angle, as illustrated, is sufficient to efficiently move anode gas bubbles, 8, up along the face of the shaped anode, 1, and to allow aluminum to drain down the cathode surface, 6, to the aluminum drain sump, 5, as indicated by arrow 13. Gas vents, 2, which may be required, are illustrated in the anode, and may be a slot or a pattern of vent holes. The anode itself may be of the Soderberg or prebake carbon variety. The aluminum drain sump, 5, preferably leads to a continuous tapping system, which minimizes disturbances to the cell, such as variations in pad thickness. The gas vents, 2, and unoccupied bath cavities, may advantageously be connected to a gas collection system, 3. In the flow-through cell, as illustrated, the electrolysis bath is replenished externally, and flows through bath inlet 9, in the path shown by arrows 10, through the anode-to-cathode space 7, to the bath outlet 11, at which point the electrolyte has been



-15-

partially depleted in alumina by the electrolysis.

In Figure 4, a dual sloped drained cathode, or V-shaped cathode, is illustrated. In this configuration, replenishment is provided by point feeders 27, which are shown as being
5 located at the higher end of the cathode slope, although replenishment may also occur between the illustrated prebaked anodes, 1. Flow of the aluminum metal, 13, is down the cathode surface 6 to the drain sump 5, advantageously connected to a continuous tapping system. Anode gas bubbles 8 induce
10 bath material flow 10 along the bottom face of the anodes.

Figure 5 illustrates a plan view of a single cell, incorporating a cell feeding and mixing zone. In Figure 5, the anode 1 is illustrated as having a slot gas vent, 2. The cathode surface, 6, is illustrated with the aluminum
15 drain sump, 5, feeding a continuous metal tapping system, 14. The direction of net flow of aluminum metal is shown by arrow 13, while the direction of net flow of the cryolite bath is illustrated by arrows 10. After passing between anode 1, and the cathode surface, 6, the partially depleted
20 bath flows from outlet 11 to a cell feeding and mixing area or zone, 16, wherein alumina is replenished, 12. After replenishment with alumina, the cryolite bath is recirculated in the electrolytic cell in the direction indicated by arrows 10. The drawing illustrates the use of an optional
25 magnetic bath circulation pump, 17, adjacent to bath inlet 9, although such a pump is not considered necessary under most conditions. A barrier, 15, may be positioned in return channels 28 to prevent bath backflow and disruption of circulation in designs incorporating a cell feeding and
30 replenishment zone (16).

Figure 6 illustrates a plan view of a multiple cell system, comprising four individual electrolytic cells operating in tandem. This system as illustrated incorporates a continuous aluminum tapping system, 14, providing a constant
35 aluminum level, and thus resulting in a more steady heat

~~BAD ORIGINAL~~



-16-

balance and bath level. Conventional discontinuous metal tapping could be used, but provision would have to be made to compensate for resulting changes in bath level. Such changes would necessarily include a bath surge tank, a lower level in the aluminum feeding/mixing tank, and heat balance adjustment means. As shown in Figure 5, alumina and other make-up materials may be added, 12, to a cell feeding and mixing zone, 16, and circulated through the anode-cathode gap in the direction indicated by arrows 10. The use of a magnetic circulation pump, 17, is optional. The aluminum formed drains into the aluminum drain sumps, 5, and passes in the direction indicated by arrows 13 to the continuous metal tapping system 14. Back flow of depleted bath is prevented by the presence of barriers 15.

15 An alumina feeding and dissolution system may be readily incorporated into either a single cell system or a more economical multiple cell system. A feature of the present system which enables it to be run under a controlled atmosphere is a sealed cell top, thus reducing reactor materials problems, emission control problems, and heat losses, although a sealed cell top is not required. The addition of a non-consumable anode surface to this design results in a self-contained, unattended, multiple electrolysis unit in a single vessel.

25 Figure 7 represents an aluminum reduction cell, utilizing a single slope cathode. As illustrated, the figure shows a continuous aluminum tapping system 14, to remove aluminum from the cell by way of drain sump 5. This acts to provide a constant aluminum level in the cell and also results in a more steady heat balance and bath level in the cell. An adjustable partial barrier, 25, is used to restrict, if required, the overall bath circulation velocity within the cell in return channel 28. The desired restriction can be achieved by means of barrier plates composed of a non-corrodable insulator, such as, for instance, silicon nitride.



-17-

Necessary replenishment means, while not illustrated, may be of any suitable type as previously discussed.

As previously indicated, a dual sloping cathode cell could alternatively be utilized within the scope of the present invention, having, for example, an inverted V configuration, as shown in Figure 1, or a V shape, as shown in Figure 4, whereby metal aluminum would flow downwardly to aluminum drain sumps. However, the single sloped cathode, inclined upward towards the alumina feeding side of the cell, as illustrated in Figure 2, may be considered a preferred embodiment, since this arrangement makes cleaning and other pot room servicing of the cell much simpler, as well as cell construction per se.

Figure 8, illustrating a plan view of an aluminum reduction cell utilizing dual single slope cathodes, illustrates another alternative form of the present invention. The flow of electrolyte is illustrated by arrows 10, indicating a circulation between the anode 1, and the cathode surface, 6, through a zone where replenishment, 12, takes place, and through the ACD of the adjacent anode-cathode pair, sloping in the opposite direction. The center line of the cell, 26, is conveniently the demarcation point of the two oppositely sloped cathodes. To ensure smooth and continuous circulation, barriers 15 and partial barriers 25 are present to prevent bath backflow, and to control net bath circulation flow rate, respectively. All other elements of the drawing are as previously discussed. It is to be noted that this configuration represents an alternative to the previously suggested V shape and inverted V configurations, and could suitably be used with prebaked anodes rather than Soderberg. Still another configuration, particularly suitable for prebaked anodes, has the angle of inclination for adjacent cathodes (and anode surfaces) in the same direction although at different values.



-18-

It is to be noted that although the figures fail to illustrate the presence of side ledges and/or crusts of frozen bath materials, the present invention applies as well to cells having such.

5 The pumping action of gas bubbles, directed upwards beneath a slightly inclined surface, with the liquid confined to a thin layer between the upper surface and a parallel lower one, was first demonstrated in a hydraulic analog experiment. This experiment was performed in room temperature
10 water, whose kinematic viscosity closely approximates that of molten cryolite. With a surface inclination of 2.5 degrees, and a gap between upper and lower surfaces of 2.2 centimeters, bubbles were generated on a porous upper surface by pressurization with air at a rate of gas evolution matched to
15 that of a typical high current aluminum electrolysis cell, resulting in net or average liquid velocities in the gap between the simulated anode and simulated cathode measured in the range of from 5 to 10 centimeters per second. These velocities were calculated to be more than sufficient to
20 supply alumina at a rate required for proper cell operation at normal alumina concentrations in cryolite. While in this experiment the surface inclination did not have to overcome the oppositely directed bubble forces, due to magnetic influences, for example, which would exist in an operating
25 aluminum electrolysis cell with a horizontal anode, the principle of gas-driven bath circulation was nevertheless clearly demonstrated.

The resulting bath circulation was found to be controlled by the balance between the pumping efficiency of the
30 gas bubbles in the ACD gap and the back pressure, or flow resistance, to bath circulation through the return channels. Further results and data were obtained from a 1:20 scale aluminum electrolysis cell and a hydraulic analog model.

The hydraulic analog model was constructed to simulate
35 a gas evolving anode surface (about 1.11 square meters) lo-



-19-

cated above a sloping solid cathode surface. This arrangement simulated a typical "drained cathode" aluminum reduction cell design in which the working anode is located above a sloping, drained TiB_2 cathode surface. The water model studies were performed in room temperature water. The flow patterns and velocities observed in the water model were similar to those anticipated in a full scale cell, since the observed flows had Reynolds numbers in the turbulent regime (> 5000). In this regime the flow is primarily controlled by the physical dimensions of the flow channels and not the fluid properties (e.g. viscosity). An air pressurized chamber with a bottom constructed from Alundum porous plates (about 20 micron pore diameter) was used to simulate a working anode evolving gas (e.g. CO_2). A gas velocity of 0.1778 cm/second through the porous anode plate was used to simulate an anode current density of 0.68 amps/cm² (the gas velocity was corrected for differences in temperature and hydrostatic pressure). Simulated currents up to about 1.4 amps/cm² were tested in the model.

The model design, a side elevation view of which is illustrated by Figure 9(a), simulated one half of the cell shown in Figure 1. In plan view, the model simulated the cell shown in Figure 7. The end wall at the "upper" end of the cathode corresponded to a vertical plane passing through the center slot or gas vent, 2. The figure illustrates the relationship of such parameters as ACD, BFL, \emptyset , h, h_o , lower channel width, and upper channel width (hereinafter defined), to the anode (1), the cathode surface (6), and the bath (29).

The following definitions are used to describe the parameters of the water model and commercial scale aluminum reduction cells, relative to the desired bubble flow upward under the sloping anode face:

BFL - the anode face dimension in the direction of bubble flow (BFL equals 122 cm in most tests)



-20-

BFW - the anode face dimension perpendicular to the direction of the bubble flow (BFW equals 61 cm in most model tests)

5 ACD - the perpendicular distance between the sloping anode and cathode surfaces, corresponding to numeral 7 in Figure 2 (the ACD was varied from 1 to 5 cm in the model tests)

10 Cathode slope (ϕ) - the angle between the upward sloping cathode surface and a horizontal plane (cathode slope was varied from 0 to 15 degrees in the model tests)

15 h - the vertical anode immersion depth from the liquid surface to the anode face (h varies along the BFL dimension of the anode according to the degree of cathode slope)

20 h₀ - the minimum vertical anode immersion depth, i.e. the anode immersion depth at the higher end of the cathode (h₀ equals 10 cm in most of the model tests)

20 The desired bath flow typically passes through four different types of channels or passageways, namely:

- 1) The ACD gap between the anode and cathode, where the introduction and flow of anode gas generates the force required to maintain the desired bath circulation in the cell.
- 25 2) The bath flow exits the ACD gap into an upper channel, corresponding to reservoir 24 in Figure 2, where the flow is directed to either or both sides of the anode. Most of the anode gas is expelled from the bath in this channel to provide a turbulent bath action ideal for dissolution of the alumina feed to the cell. This channel can be along the side of the cell as shown in Figures 2 and 7, or in the center of the cell as shown in Figure 1. The dimensions of the upper channel are defined as:



-21-

depth = depth of bath in the channel (h_0 + the vertical component of the ACD in the water model, which at low angles is essentially equal to ACD)

5 width = the horizontal dimension in the same direction as the bubble flow in the ACD gap

length = the horizontal dimension across the BFW of the anode plus the width of the return channel

10 3) The return channel or channels convey the bath flow from the upper channel to a corresponding lower channel located along the anode edge where the bath enters the ACD gap. Examples of the return channel are designated 28 in Figures 5 through 7. In the simplest form, and the type modeled in this study, the return channel is as shown in Figure 7, where the return channel depth or width may be varied to produce a variable flow resistance (similar to that ascribed to the partial barrier 25). In the water model and cells of a similar design, the return channel dimensions are defined as:

20 depth = the depth of bath in the channel (if the width of the channel is small and a working anode forms one or both sides of the channel, the effective channel depth is the actual depth less the ACD, since the upward flow in the adjacent ACD gap tends to stagnate a layer of similar thickness in the bottom of the return channel. This reduced return channel depth was used in the water model studies).
25 Due to the sloping cathode, the depth of the return channel increases as the



-22-

bath flows from the upper channel to the lower channel.

width = the horizontal width of the channel perpendicular to the flow in the channel.

5 length = the horizontal distance between the upper and lower channels (in the water model this was approximately equal to the BFL).

4) A lower channel completes the bath circulation loop by conveying the bath from the return channel channel or channels and distributing the bath along the anode edge where the bath enters the ACD gap. The dimensions for this channel are defined similarly to those for the upper channel. In most cell designs and the water model, the lower channel has a well, or trough, in the bottom of the channel to collect the aluminum metal as it drains off the sloping cathode. Such a well is shown in Figures 1 and 9a.

10

15

In all cases, the bath flow rate, Q , for the model and full-scale cells is defined as the total volumetric rate of bath flow entering the ACD gap from the lower channel.

20

To simulate an actual electrolysis cell and to evaluate the effect of changing specified dimensions or operating conditions, the water model was capable of being altered in various ways. Provision was made in the model to simulate the adjustable partial barriers (number 25 in Figure 7). The slope of the cathode and anode in the model was varied from 0 to 15 degrees to determine the effect of cathode slope on bath flow in the ACD gap. The ACD gap was varied from 1 to 5 cm in the water model studies. Gas flow was variable to simulate different current densities. Fluid flow in the model was observed and measured, using injections of colored dye in the ACD gap and in the return channel.

25

30

Anode shaping, or conformance, to the underlying sloping



-23-

35 cathode has been demonstrated in both laboratory electrolysis
test cells and in reports from Kaiser Aluminum and Chemical
Corporation to the Department of Energy (final report on DOE
Contract No. EY-76-C-03-1257, "Energy Savings Through the
Use of an Improved Aluminum Reduction Cell Cathode," 30
5 November 1977).

Figure 9(b) illustrates the desired flow of gas bubbles,
8, and direction of bath flow, 10, in the ACD. It is clear
from this figure that too large a velocity of bath at the
cathode surface, in the same direction as at the anode surface,
10 may interfere with drainage of metal on the cathode. Thus,
while unidirectional flow is preferable, excessive flow
velocity at the cathode surface is to be avoided. As demon-
strated in the water model, the water model studies revealed
that under certain design conditions three different undesired
15 phenomena can occur in the ACD; specifically:

- 20 ◦ Reverse flow occurred when the bath flowing upward
along the bottom of the anode reversed its flow
direction and flowed downward along the cathode
surface, as shown in Figure 9(c). Under severe reverse
flow conditions, as shown in Figure 9(d), the bath
forms multiple small eddies in the ACD and there is
no, or very little, net fresh bath entering the ACD.
Persistent anode effects result from the insufficient
supply of fresh bath in an actual electrolytic cell.
- 25 ◦ Air lock occurred when the removal of the anode
gases was too slow and the ACD became saturated with
large stagnant gas bubbles. An inadequate bath flow
results under this condition. In an operating cell
under these conditions, such gas bubbles disrupt the
30 local electrolysis reaction, increase the anode
current density in the affected areas of the anode,
and eventually lead to increased anode polarization
voltage losses, which can lead to the onset of an
anode effect.



-24-

- 35 ◦ Excessive bubble thickness occurred under certain
 conditions, extending through the bath and contact-
 ing the cathode surface. Under this condition in an
 operating cell, rapid loss of current efficiency
 will result from the rapid back reaction between
5 the CO₂ bubbles and molten aluminum metal on the
 cathode surface.

 The above phenomena and the net bath flow in the ACD
 gap and the return flow channel were studied as a function
 of cathode slope, ACD, flow resistance in the return channel,
10 and simulated anode current density. While all of the ob-
 served flow properties are consistent with and controlled by
 the general hydrodynamic principles referred to previously,
 their quantitative delineation has heretofore not been esta-
 blished.

15 The following general cell specifications were used in
 the water model and subsequent examples to illustrate the
 typical application of this invention to the design of an
 improved aluminum reduction cell with reduced energy con-
 sumption. In practice, these general cell specifications
20 would be chosen to fit the actual application and then the
 teachings of this invention would be used to provide the
 critical cell design specifications. Thermal balance and
 return on investment calculations have been performed, and
 indicate that "drained cathode" cells should preferably be
25 operated at anode current densities higher than those typic-
 ally employed in present industrial practice.



-25-

Table 1
Exemplary General Cell Specifications

Parameter	Cell Sized to	
	Water Model	Example
	Simulation	Cell I Cell II
Line current (KA)	5.05	100 300
Anode current density (A/cm ²)	0.68	0.68 2.5
Change in wt.% Al ₂ O ₃ entering and exiting ACD gap (wt.%)	0.2	0.2 0.2
BFL (cm)	122	122 122
Number of return channels	1	4 4
h _O , minimum anode immersion depth (cm)	10	10 10



-26-

The design parameters used in the water model studies are included in Table I for comparisons to real cells. The general cell design considered is that shown in Figure 1, with return channels connecting the single center upper
5 channel with the two outer lower channels at each end of the split VSS anode (each half of the cell is similar to that shown in Figure 7).

Figures 10, 11 and 12 illustrate the effect of cathode slope, ACD, and the flow resistance in the return channel, R_f , on the net bath flow in the ACD gap at a simulated anode
10 current density of 0.68 amp/cm². In these figures, the observation of reversed flow at the cathode surface is indicated by dashes. In all cases this is associated with significantly reduced net bath flow, becoming more severe as the
15 cathode slope is reduced.

Similar results have been obtained for other simulated current densities. A cell parameter design limit diagram, constructed from this data is shown in Figure 15. Detailed descriptions of the use of such a diagram for the design of
20 a cell having controlled bath flow are given in the subsequent examples.

The general features of the diagram are as follows. Flow resistance is related to return channel width, for particular operating conditions. For each return channel
25 width, a cross-plot, at a constant flow rate, of data from figures corresponding to Figures 10, 11, and 12 leads to a relationship between cathode slope and ACD which must be satisfied for a given anode current density in order to achieve a flow rate selected to be adequate to supply the
30 cell, as calculated by methods defined hereinafter. This relationship between cathode slope and ACD is represented by the curved lines in Figure 15. For each return channel width, therefore, these curved lines represent a condition at which adequate alumina supply will be achieved. These
35 lines are limited by boundary conditions defined by undesir-



-27-

able hydrodynamic conditions, as previously described.

Thus, a region forbidden by reason of excessive bubble thickness bounds the operating region at lower ACD dimensions, i.e. at the left of the parameter diagram (Figure 15).

- 5 Excessive anode (and cathode) slope, leading to excessive anode immersion depth, forms an upper boundary limit at a slope of about 15°. A preferred operating region is shown in Figure 15 as one somewhat above the appropriate curved line representative of the selected return channel width, so as to minimize the ACD while being compatible with the region marked "bubble thickness restriction". Operating within this region simultaneously assures an adequate alumina supply, through a sufficiently large Q value, and avoids an excessively large velocity of bath at the cathode surface (and thus interference with aluminum drainage), as well as excessive bubble thickness and attendant losses in current efficiency. The following examples will illustrate the construction and use of such a parameter diagram.

Example 1 - Choice of return channels dimensions

- 20 The bath flow rate, Q, (cm³/second) must be sufficient to supply the alumina required to maintain the electrolysis reaction in order to prevent anode effects in an operating cell. At a maximum of 100% current efficiency, the required minimum flow rate, Q, for a working aluminum reduction cell is given by the equation

$$I. \quad Q(\text{cm}^3/\text{second}) = (0.008) \frac{[\text{total cell current (amps)}]}{\Delta \text{wt.}\% \text{ Al}_2\text{O}_3}$$

where $\Delta \text{wt.}\% \text{ Al}_2\text{O}_3$ is the difference in the wt. % Al_2O_3 in the bath entering and exiting the ACD gap, or, Δ alumina.

- 30 The 0.008 constant is derived from the Faraday equation:

$$II. \quad 0.008 = \frac{(\text{Molecular weight of Al}_2\text{O}_3)(100)}{(\text{Faraday/mole})(\text{Faraday Constant})(\text{Bath density})}$$



-28-

For convenience, Q may also be expressed in terms of bath volume per second per unit of anode area. Thus, assuming a minimum anode current density of 0.5 A/cm^2 , and a maximum 5% depletion of the bath per passage through the ACD, i.e.

- 5 $\Delta \text{wt.}\% \text{ Al}_2\text{O}_3 = 5$, one may calculate from equation I, a minimum acceptable value of $Q = 8 \times 10^{-4} \text{ cm}^3/\text{second}/\text{cm}^2$ anode area.

Cell performance and thermal stability are enhanced by maintaining a uniform Al_2O_3 concentration throughout the bath. For the cells defined above, the calculated minimum
10 bath flow rates are 202, 4000 and 12000 $\text{cm}^3/\text{second}$ for the water model cell and example cells I and II, respectively. While the minimum Q bath flows are theoretically sufficient, in practice such low values should be exceeded to prevent operating problems (e.g., excessive anode effects, high
15 effective bath resistance and overvoltages due to excessive bubble volume in the ACD gap). Cell operating conditions will modify the bath flow to a degree (e.g., due to ledging, crusting, etc.) and hence could lead to less than theoretical bath flow rates. For these reasons, a design factor
20 of 4 to 5 has been applied to the minimum bath flow values to give preferred bath flows of 890, 20,000 and 60,000 $\text{cm}^3/\text{second}$ for the water model and example cells I and II, respectively. The water model data demonstrated a more reliable and stable bath circulation at these preferred Q
25 values than at the minimum theoretical Q values, while values of about 450, 10,000, and 30,000 $\text{cm}^3/\text{second}$ are considered suitable.

The water model data demonstrate that the flow resistance properties of the return channel are a critical component of this invention. As the return channel becomes more
30 restrictive (a result in attempting to maximize the anode area in the cell) the bath flow becomes increasingly sensitive to changes in the flow resistance properties of the return channel. Since there are many cell designs with equivalent
35 effective flow resistance properties in the return channel,



-29-

it is beneficial to construct a simplified hydraulic model to provide a generalized design criteria for the return channel. The hydraulic head loss, h_z , due to the flow resistance in the return channel is given by the well-known equation:

$$5 \quad \text{III. } h_z = \frac{2f_f L v^2}{D_{eq} g}$$

where

f_f = Fanning friction factor

v = velocity

10 L = length (approximately BFL in the water model)

D_{eq} = equivalent hydraulic diameter

g = gravitational constant.

The friction may be a composite value to reflect differences in the bottom and side surfaces of the channel. For a
15 single open channel

$$\text{IV. } D_{eq} = \frac{4(\text{cross section area})}{\text{wetted parameter}}$$

$$\text{V. } D_{eq} = \frac{2 hw}{2h + w}$$

20 where

w = width of return channel

h = depth of water at any point along the channel
(less the ACD correction in the water model)

$h = h_0 + x \sin \theta$

25 h_0 = h at upper end of the anode (i.e., minimum anode immersion depth)

x = the distance along the return channel length, from the upper channel

θ = cathode slope.

30 Since the observed velocity in the return channel varies with the changing water depth, it is preferred to use volume bath flow, which is independent of changing channel dimensions.



-30-

The volume bath flow, Q , is given by velocity times the channel cross section area, or

$$\text{VI. } Q = v h w, \text{ hence}$$

$$\text{VII. } v = \frac{Q}{hw}$$

5

The Q value used in these equations represents the net effective average Q for the channel as determined by timing the period required for injected, highly colored dye to be carried through the channel.

10 The hydraulic head loss can be written as:

$$\text{VIII. } h = K_f Q^2 R_f$$

where R_f represents a flow resistance geometry term, dependent upon the physical dimensions of the return channel, and K_f is a fluid/materials properties coefficient which is
15 less dependent upon physical scale up and can be determined in practice:

$$\text{IX. } R_f = \frac{(2h + w)L}{h^3 w^3}, \text{ and}$$

$$\text{X. } K_f = \frac{f_f}{2g}$$

20

Since the value of h varies in an inclined return channel, R_f is actually calculated as an integral function of h over the channel length L , with the width w generally remaining constant. Four of the different return channel flow resistances used
25 in the water model studies are given in Table 2.

The cell design in this invention is analogous to a pumped fluid loop where the gas bubbles in the ACD gap perform the pumping action to drive the bath around the ACD gap-return channel circuit. An analogous pump efficiency diagram
30 as shown in Figure 13 is used to describe the circulation properties of the "drained cathode" cell. Pump efficiency increases through curves 1, 2, and 3, reflecting increasing cathode slope and/or decreasing ACD. Flow resistance increases through slopes a, b, and c, reflecting increased length
35 and/or decreased cross sectional area of the return channel.



-31-

The observed flow rate through the ACD is determined by the intersection of the appropriate pump efficiency and flow resistance curves. Hence, by superimposing a vertical line on the pump diagram at the minimum flow rate required to satisfy the Al_2O_3 feeding requirement to the electrolysis reaction in the ACD, it is possible to portray the pumping/flow conditions. The abrupt change in slope in some of the pump efficiency curves at the lower flow rates is associated with reverse flow in the ACD. Table 2 illustrates the effect of the flow resistance in the return channel on the ACD flow rate at a constant cathode slope and ACD.

The low flow rate (Q) illustrates that a resistance factor of $2.7 \times 10^{-1} \text{ cm}^{-4}$ is outside of limits of this invention under the stated conditions. This is confirmed by the observed dominant reverse flow condition in the ACD. For the same stated conditions, an R_f value of $2.7 \times 10^{-2} \text{ cm}^{-4}$ is within the limits of this invention, but is too large to achieve the preferred flow of $890 \text{ cm}^3/\text{second}$ for the water model, resulting in some (slight) reverse flow. It is to be noted that slight reverse flow may, in some instances, be advantageous since it tends to improve, rather than hinder, drainage of aluminum down the cathode surface.

Scale up from the water model to a commercial aluminum reduction cell presents a number of design alternatives within the scope of this invention. The basic requirements that must be attained in production cells are:

- 1) Sufficient bath flow, Q , entering the ACD to support the electrolysis reaction. The minimum required bath flow is given by equation I:

$$I. \quad Q_{\min} (\text{cm}^3/\text{second}) = \frac{0.008 [\text{total cell current (amps)}]}{\Delta \text{wt.}\% \text{ Al}_2\text{O}_3}$$

Thus, for a 100 K amp cell with a $\Delta \text{wt.}\% \text{ Al}_2\text{O}_3$ of 0.2, the minimum bath flow is $4000 \text{ cm}^3/\text{second}$.

- 2) The hydraulic head for the gas-induced pumping



-32-

Table 2
Effect of Flow Resistance in Return Channel on the Bath

Flow Rate
 (cathode slope = 8° , ACD = 3 cm, anode area = 0.75m^2)

Flow Resistance in Return Channel	R_f (cm^{-4})	Flow Rate Q $\text{cm}^3/\text{second}$	Observed Reverse Flow in ACD
Low	1.3×10^{-3}	2375	None
Medium	6.3×10^{-3}	1720	None
High	2.7×10^{-2}	740	Slight
Excessively High	2.7×10^{-1}	165	Dominant



-33-

action (less the flow restriction losses in the ACD) is equal to that for the combined h of the return channel, upper channel and lower channel. For a given slope, ACD, current density and anode length, the h developed in the water model and the full-scale cell should be similar.

- 3) Single or multiple return channel designs with the appropriate dimensions can be used such that the desired effective flow resistance, R_f , term can be achieved. The R_f term for the cell is estimated from that for the model using the equation

$$\text{XI. } R_f (\text{cell}) = R_f (\text{model}) \times \frac{f_f (\text{model})}{f_f (\text{cell})} \left[\frac{Q (\text{model})}{Q (\text{cell})} \right]^2$$

where the change in friction factors and total cell current are taken into account. If the dimensions of the upper and lower channels are equal to or small compared to those of the return channel, the variable mass flow rate in the upper and lower channels must be included in the calculation. In most anticipated cell designs, and the water model, the dimensions of the upper and lower channels are sufficient that their small h_2 losses can be neglected compared to that for the more restrictive return channel. The effect of the flow resistance in the ACD is included in the reported net pumping efficiency data. Hence, the (R_f) cell term provides the necessary design criteria for the return channel or combined effect of multiple return channels in a full-scale cell. Since a "drained cathode" cell design could encompass multiple return channels, n , the effective value for each return channel is given by

$$\text{XII. } R_f (\text{cell channel}) = R_f (\text{model}) \frac{f_f (\text{model})}{f_f (\text{cell})} \left[\frac{n Q (\text{model})}{Q (\text{cell})} \right]^2$$

where the respective Q 's are defined above.



-34-

Now, one may calculate a value of R_f (cell) from a summation of all (n) return channels, as given by

$$\text{XIII. } \frac{1}{[R_f(\text{cell})]^{1/2}} = \sum_{i=1}^n \left(\frac{1}{[R_f(\text{cell channel } i)]^{1/2}} \right)$$

5 and for n equivalent channels,

$$\text{XIV. } R_f(\text{cell channel}) = n^2 R_f(\text{cell}),$$

wherein R_f (cell) may be calculated from the equation

$$\text{XV. } R_f(\text{cell}) = R_f(\text{model}) (6.25 \times 10^8) \left[\frac{\Delta \text{ wt. \% Al}_2\text{O}_3}{\text{cell current}} \right]^2$$

10 In Equation XV, $R_f(\text{model})$ is a geometric resistance factor having a value of from about $230 \times 10^{-3}/\text{cm}^4$ to about $0.2 \times 10^{-3}/\text{cm}^4$.

For example, if the friction factors for the water model and the example cells (as set forth in Table 1) are assumed to be equal, the preferred R_f term for each return channel is given by equation XII, and the width thereof may be calculated from the appropriate equations.

Cell Example I

$$\begin{aligned} 20 \quad R_f(\text{cell channel}) &= R_f(\text{model}) [4(890)/20000]^2 \\ R_f(\text{cell channel}) &= 0.032 R_f(\text{model}) \\ w(\text{cell channel}) &= 20 \text{ cm} \end{aligned}$$

Cell Example II

$$\begin{aligned} 25 \quad R_f(\text{cell channel}) &= R_f(\text{model}) [4(890)/60000]^2 \\ R_f(\text{cell channel}) &= 0.0035 R_f(\text{model}) \\ w(\text{cell channel}) &= 52 \text{ cm} \end{aligned}$$

The return channel widths given above are based on a design factor of 5 in the preferred bath flow (Q), and a preferred $R_f(\text{model}) = 6.2 \times 10^{-3}$ value. If the cell operations for Cell Example II were judged stable enough to reduce the bath flow design factor to 3, then the calculated $w(\text{cell channel})$ value would be reduced to 33 cm. An alternative method to reduce the calculated $w(\text{cell channel})$ value to 33 cm, without sacrificing the bath flow design



-35-

factor, is to increase the anode immersion depth by 8 cm (e.g., $h_0 = 18$ cm). These alternatives demonstrate the usefulness of the teachings of this invention in the designing of a "drained cathode" cell.

- 5 Figure 14 presents the R_f (model) values (as a function of cathode slope and ACD) required to obtain the preferred Q value of $890 \text{ cm}^3/\text{second}$ for the model. R_f values for other Q values can be extracted from the water model data such as shown in Figures 10, 11 and 12.

10 Example 2 - Choice of ACD

- Cell energy efficiency is improved by decreasing the ACD (and thus bath voltage loss) without a significant loss in current efficiency. At the larger ACD values (e.g., 4 cm or greater) there is a strong tendency for reverse flow condition to occur within the ACD gap. If this reversal becomes excessive, the net Q value will be reduced too much. Reducing the ACD values promotes the desired bath flow through the ACD gap and higher flow resistances in the return channel can be tolerated. However, at very small ACD values (about 1 cm) a secondary effect between the bubbles and the proximity of a solid cathode surface tends to slow down the desired bath flow (e.g., a result of the increased flow resistance in the ACD gap). Figures 10, 11 and 12 show that the maximum bath flow does not always occur at the minimum ACD as might be expected.

- The measured maximum bubble thickness decreased from about 1.0 cm to about 0.5 cm as the cathode slope increased from 2° to 5° , with a corresponding increase in net liquid flow rate. As the slope was increased beyond 5° , the bubble thickness was observed to remain fairly constant, and the bubbles were observed to assume the characteristic shape previously described, and to move more slowly. Changing the ACD was determined to have little effect on the observed



-36-

bubble thickness. If the bubble protrudes across a major portion of the ACD, the current efficiency will be seriously degraded by the back reaction of the CO_2 with the aluminum metal film on the cathode and the bath electrical resistivity will be greatly increased. For these reasons and practical considerations, the preferred ACD is from about 2 to about 4 cm, with a more preferred range of from about 2 to about 3 cm.

Example 3 - Choice of Cathode Slope

In all cases except when the return flow channel is highly restricted (Figure 10) or the ACD is 4 cm or greater, the bath flow, Q , exceeds the preferred $890 \text{ cm}^3/\text{second}$ value at cathode slopes greater than or equal to 5 degrees. Increasing the cathode slope helps overcome excessive reverse flow and air locking (excessively large stagnant gas bubbles) problems in the ACD gap. On the other hand, too steep an angle may disrupt the flow of molten metal on the cathode surface. Back pressure due to restrictions in the return channel can also be offset by increasing the cathode slope. Large cathode slopes, however, could produce excessive up-slope flow of bath in the ACD gap, which could interfere with the draining of aluminum from the cathode surface and cause practical problems with the large variation in depth of anode immersion in the bath. When the changes in bubble thickness described in Example 2 are also considered, the preferred cathode slope is in the range of from about 5° to about 11° , with about 8° being the most preferred slope.

Example 4 - Cell Parameter Design Limit Diagram

The construction and use of the previously described cell parameter diagram will now be set forth in detail. The parameter restrictions used to construct this diagram were as set forth in Table 3.



Table 3

Cell Parameter Restrictions

<u>Parameter</u>	<u>Restriction</u>	<u>Reason</u>
Anode length	122 cm	Size of water model
Preferred bath flow	890 cm ³ /second minimum	The Al ₂ O ₃ is depleted less than 0.2 wt.%, and there is a bath flow design factor of at least 4.4
Anode current density	0.68 A/cm ²	Assumed value, corresponding to actual plant value
Bubble thickness	50% of ACD maximum	To prevent poor current efficiency
Cathode slope	15° max.	Excessive variation in anode immersion depth from one end to other
ACD	5 cm max.	Persistent reverse flow problems, no improvements over present ACD
Return channel flow	turbulent	Maximize Al ₂ O ₃ dissolution rate

-37-



-38-

For convenience, and to help visualize the cell design, in Figure 15 the flow resistance in the return channel, R_f , has been recorded in terms of the corresponding channel width (assuming a channel length of 121 cm, an anode current density of 0.68 A/cm², a bath flow rate of at least 890 cm³/second, and a minimum channel height of $h_0 = 10.0$ cm). The most preferred set of cell design parameters for the water model under the conditions stated are:

	cathode slope	= 7.5°
10	ACD	= 2.5 cm
	R_f (return channel)	= 6.2×10^{-3} /cm ⁴
	bath flow, Q	= 890 cm ³ /second

The following ranges for the critical cell hydrodynamic flow design parameters are based on: 1) measured data and observations made in the water model simulation studies; 2) the data analysis presented; and 3) practicality considerations for scale-up to a commercial scale cell. A set of parameter ranges is given in Table 4, for the water model, which has a BFL of 122 cm, and a BFW of 61 cm. Parameters for a corresponding commercial scale aluminum reduction cell are given in Table 5.

The criteria of this invention may be applied to several types of cells, such as those shown in Figures 1 to 7. In particular, the cell may consist of an anode which traverses the width of the cell as one continuous mass. An example of this anode is shown in Figure 2 with the center vent (2) being absent and hence, the Bubble Flow Length (BFL) is approximately equal to the total anode width. This type of cell design would result in a narrow cell (about 122 cm wide anode for the most preferred case).

Another type of cell would be as shown in Figure 2 where the center vent (2) is included in the design. The center vent exhausts the bubbles accumulated under the first half of the anode traversed by the bath flow. In this case,



Table 4
Water Model Parameter Ranges

For anode current density of 0.5 to 1.2 A/cm ²				
Parameter	Range	More		Most
		Preferred	Preferred	Preferred
ACD (cm)	1.0-5.0	1.5-4.0	2.0-3.0	2.5
Cathode slope (°)	2-15	5-10	7-9	8
R _f (10 ⁻³ /cm ⁴)	230-0.20	20.0-1.0	10.0-5.0	6.2

For anode current density of 1.2 to 3.0 A/cm ²				
Parameter	Range	More		Most
		Preferred	Preferred	Preferred
ACD (cm)	1.0-5.0	1.5-4.0	2.0-3.0	2.5
Cathode slope (°)	2-15	4-10	5-8	6
R _f (10 ⁻³ /cm ⁴)	230-0.20	20.0-1.0	10.0-5.0	6.2



-40-

Table 5
Full Scale Cell Parameter Ranges

Parameter	Range	More		Most	
		Preferred	Preferred	Preferred	Preferred
BFL (cm)	15-300	30-250	60-200	122	
Anode Current Density(A/cm ²)	0.5-3.0	0.6-2.0	0.7-1.5	0.8-1.2	
ACD (cm)	1.0-5.0	1.5-4.0	2.0-3.0	2.5	
Cathode Slope (°)	2-15	5-10	6-8	8	



-41-

the BFL is defined as half of the total anode width. Venting of the anode gas is necessary to prevent excessive bubble volume accumulation in the ACD gap which can increase the voltage losses and decrease the current efficiency. In this type of cell, the total working anode width for the most preferred case would be about 244 cm, which is a more practical cell width.

In a commercial cell, it is desirable to operate at the highest anode current density possible without a loss of current efficiency (in order to minimize capital and labor costs per pound of aluminum produced). At the low ACD values used in a "drained cathode" cell, these same high current densities are advantageous to help maintain the cell heat balance. However, at high anode current densities, gas bubbles will accumulate faster and grow larger in the ACD gap than at lower current densities. Hence, to counter the detrimental effect of bubble accumulation in the ACD, the preferred BFL (anode dimension in the direction of the bubble flow) is decreased proportionally to the increase in anode current density. For example, if the anode current density is increased from 1.0 to 2.0 amps/cm², the preferred BFL should be decreased from 122 to 61 cm. For an inverted V cathode cell, the preferred cell design for the lower anode current densities is shown in Figure 1.

To increase the preferred total working anode width for higher anode current densities (greater than about 1.3 A/cm²), the concept of a vent to release the anode gas may be expanded to multiple vents to further increase the width of the anode. The vent may be present as a slot between the adjacent anode masses or a row of suitably spaced holes through the anode mass.

Still another approach is to use a cell design typified by that shown in Figure 1. In this case the center channel serves multiple purposes, such as gas venting, and as the upper channel to convey the bath exiting the ACD gap to the return channel or channels. In this case, the BFL is de-



-42-

fined as half the total working anode width, which yields a more practical size commercial cell. It is also understood that the cathode slopes shown in Figure 1 could be reversed with a central metal collection trough or well. In this latter case, the upper channels would be located along the exterior sides of the cell, as illustrated in Figure 4.

It is also possible to combine these cell design concepts into a multiple component cell comprising of many cells being interconnected by the bath and/or metal flows or a single cell cavity containing multiple adjacent units described above.

For all such cell designs, the dimensions of the return channel or channels would be calculated according to the teachings given in Example 1. The initial step is to select the desired bath flow, Q , based on the scale of the cell being designed, and then use the developed relationships to determine the appropriate flow resistance term, R_f . The hydraulic head loss equations may then be applied under the conditions stated to calculate a set of preferred return channel design options. Heat balance and other cell design and operation criteria are then used to select one of the hydraulically equivalent return channel designs. This final selection of return channel design can now be done with regard to impact on the critical bath flow.

Example 5 - Drained Cathode Test Cell

Test data from a laboratory scale aluminum reduction cell with a sloping TiB_2 cathode substantiates the use of a water model to simulate the hydrodynamics of a commercial aluminum reduction cell. A 61 cm x 122 cm x about 46 cm deep graphite box, filled with approximately 600 pounds of cryolite bath, was heated in an enclosed electric furnace. Once the bath was molten, test cathodes and anodes were lowered through a top-loading port and positioned in the cryolite bath as shown in Figure 16. Automatic Al_2O_3 feed



-43-

and anode lowering equipment permitted continuous electrolysis tests for up to 3 weeks without any interruption for anode replacement. Under all electrolysis conditions, the starting slope (usually horizontal) of the lower anode surface was converted after 1 to 5 days of electrolysis to that of the cathode surface immediately below. The unevenness of the anode face shown in Figure 16 is consistent with the bubble behavior observed in the water model. At the starting edge of the anode face in the water model (corresponding to region A in Figure 16) the bubbles tend to have a very slow and irregular movement resulting in a very non-uniform coverage of the anode surface. This would produce an uneven consumption of the anode carbon. As the bubbles move upward along the anode face, they gain speed and create a more uniform flow along the anode face. Electrolysis under this flow condition results in a more uniform consumption of the anode carbon as shown in region C of Figure 16. Visual observations of the flow patterns in the working test electrolysis cell are consistent with those observed in the water model.

20 Example 6 - Electrolysis Test Data

Cell voltage data were measured as a function of current density, ACD value and cathode slope in the electrolysis test cell described in Example 5. Reference voltage data for a conventional metal pad cathode were obtained by replacing the sloping TiB_2 cathode with a 3 cm deep aluminum pad in the electrolysis test cell. Figure 17 illustrates the dramatic reduction in cell voltage noise achieved by replacing an unstable horizontal aluminum pad with a sloping TiB_2 cathode in an aluminum reduction cell. In addition to the reduced cell voltage noise (e.g., improved cell stability), the drained cathode test cell demonstrated the following properties.

- 1) The test cell voltage trace of the drained cathode cell exhibited an absence of spikes,



-44-

- as illustrated in Figure 17, caused either by anode effects resulting from insufficient bath flow, or anode cathode shorts, resulting from turbulence in the metal pad (in turn a result of bubble thickness and excessive reverse flow). At low ACD values (e.g. less than 2 cm), a conventional cell voltage control system (through the raising and lowering of the anode), required significant operator intervention to operate a metal pad cathode test, while with the sloping TiB_2 cathode tests, little or no operator intervention was required.
- 5 2) Stable sloping cathode test runs were made at ACD values less than 1 cm.
- 10 3) The cell response to changes in the current density or ACD was rapid and decisive. The new steady-state cell voltage was achieved within about 1 minute, compared to a 15-30 minute restabilization period required for the metal pad cathode. This enables one to use simpler and more reliable cell automation techniques.
- 15 4) Bubble venting from the anode face was predominantly along the uppermost edge of the sloping anode face. When an anode with a horizontal face was placed in the cell with a sloping cathode, the initial venting of the anode gas bubbles was randomly dispersed around all four edges of the anode face. With continued electrolysis, the anode face began to conform to the cathode slope and gas bubble venting became concentrated along the uppermost edge of the sloping anode face. Only random gas bubble venting from the anode face was observed during tests using a metal pad cathode.
- 20 25 30

In addition to improved cell stability, the electrolysis test demonstrated that a significant reduction in the anode-cathode polarization voltage could be achieved through the use of a "drained cathode". Figure 18 shows the measured

35



-45-

anode-cathode polarization voltage as a function of the TiB_2 cathode slope in the test electrolysis cell. At the preferred cathode slope of 8 degrees, the test data indicates an approximate 45% reduction in the anode-cathode polarization voltage,

- 5 or an approximate 0.22 volt saving in the cell voltage in addition to that achieved by reducing the ACD. To date, this advantage of a "drained cathode" cell has not been reported in the literature.

- 10 The observed reduction in concentration polarization as a function of increasing bath flow rate (see Figure 18, and also Figure 12 as an example of the flow rate as a function of cathode slope) is consistent with electrochemical theory in stirred or flowing systems. In the laminar region, the concentration polarization voltage is proportional to the
- 15 square root of bath velocity. The measured voltages in Figure 18 do not decrease with increasing cathode slope as rapidly as predicted for laminar flow. This indicates the bath conditions in the ACD are either in the transition region or in the turbulent region where the change in concentration polarization voltage is less sensitive to bath flow
- 20 rate. The water model data confirm this hypothesis.

- The electrolysis test data for a sloping TiB_2 cathode cell compared to a horizontal metal pad cathode cell have demonstrated improved cell stability (e.g., improved current
- 25 efficiency and reduced anode effects), at reduced ACD values (i.e., to reduce cell voltage), improved cell response to changes in ACD and current (e.g., ability to use simpler and more reliable cell control automation), more localized anode gas venting (e.g., simpler fume control system), and reduced
- 30 anode-cathode polarization voltages. The asymptotic portion of the anode-cathode polarization curve at cathode slopes greater than 5 degrees in Figure 18 is consistent with the preferred cathode slope range indicated in the water model studies.

- 35 It is understood that the foregoing description of the present invention is susceptible to various modifications,



-46-

changes, and adaptations by those skilled in the art, and that the same are intended to be considered to be within the scope of the present invention, set forth by the appended claims.



- 47 -

Claims

1. A cell for the electrolytic reduction of alumina to aluminum in a cryolite bath, said cell having an electrolyte return flow resistance, R_f , of less than about $0.4/\text{cm}^4$.
2. A cell as set forth in claim 1, wherein said cell comprises an aluminum wettable cathode surface inclined from the horizontal at an angle of from about 2° to about 15° , and has an anode to cathode distance of from about 1 cm to about 5 cm.
3. A cell as set forth in claim 2, wherein said aluminum wettable cathode surface contains a Refractory Hard Material.
4. A cell as set forth in claim 3, wherein said Refractory Hard Material is titanium diboride.
5. A cell as set forth in claim 2, wherein said R_f is less than about $3 \times 10^{-2}/\text{cm}^4$.
6. A cell as set forth in claim 5, wherein said cell has an anode to cathode distance of from about 1.5 to about 4 cm.
7. A cell as set forth in claim 6, wherein R_f is less than about $3 \times 10^{-6}/\text{cm}^4$.
8. A cell for the electrolytic reduction of alumina in a cryolite bath, said cell having an electrolyte return flow resistance, R_f , of less than about $0.4/\text{cm}^4$, wherein R_f is calculated from the formula

$$R_f = R_f(\text{model}) (6.25 \times 10^8) \left[\frac{\Delta \text{ alumina}}{\text{cell current}} \right]^2$$
 wherein Δ alumina represents the weight percent depletion of alumina concentration in the bath as the bath flows through the anode to cathode gap and has a value of less than 5, the cell current is more than about 100 kiloamperes, and $R_f(\text{model})$ has a value of less than about $230 \times 10^{-3}/\text{cm}^4$.



- 48 -

- 5 9. A cell as set forth in claim 8, wherein said cell comprises an aluminum wettable cathode surface inclined from the horizontal at an angle of from about 2° to about 15°, and has an anode to cathode distance of from about 1 cm to about 5 cm.
- 10 10. A cell as set forth in claim 9, wherein said aluminum wettable cathode surface contains a Refractory Hard Material.
11. A cell as set forth in claim 10, wherein said Refractory Hard Material is titanium diboride.
12. A cell as set forth in claim 11, wherein R_f is less than about $3 \times 10^{-2}/\text{cm}^4$.
13. A cell as set forth in claim 12, wherein said anode to cathode distance is from about 1.5 cm to about 4 cm.
- 15 14. A cell as set forth in claim 13, wherein said R_f is less than about $3 \times 10^{-6}/\text{cm}^4$.
- 20 15. A cell for the electrolytic production of aluminum by electrolysis of alumina in a cryolite bath, said cell having an aluminum wettable cathode surface inclined from the horizontal at an angle of from about 2° to about 15°, an anode to cathode distance of from about 1 cm to about 5 cm, and n channels for the return flow of electrolyte, said cell characterized by the parameters h, w, and L of said return channels being so dimensioned that
- 25
$$\frac{1}{n^2} \times \frac{(2h + w)L}{h^3 w^3} \text{ is less than } 0.4/\text{cm}^4,$$
- wherein w is the width of the return channel in cm, L is the length of the return channel in cm, and h is the bath depth in cm at any given
- 30 point calculated from the relationship
- $$h = h_0 + x \sin \theta$$
- wherein h_0 is the minimum anode immersion depth, x is the measured distance from the upper channel, and θ is the cathode
- 35 inclination from the horizontal, in degrees.



- 49 -

16. A cell as set forth in claim 15 wherein said cathode surface contains a Refractory Hard Material and is inclined at an angle of from about 5° to about 10°, and said anode to cathode distance is from about 1.5 cm to about 4.0 cm.
17. A cell as set forth in claim 16 wherein said cathode surface contains TiB_2 and is inclined at an angle of from about 6° to about 8°, and said anode to cathode distance is from about 2 cm to about 3 cm.
18. An electrolytic cell for the reduction of alumina to aluminum, said cell having a Refractory Hard Material containing cathode surface inclined from the horizontal at an angle of from about 2° to about 15°, and an anode to cathode distance of from about 1 cm to about 5 cm, said slope and said anode to cathode distance being so dimensioned and so related as to limit the anode gas bubble thickness to less than 50% of said anode to cathode distance.
19. A cell as set forth in claim 18, wherein said anode to cathode distance is from about 1.5 to about 4 cm.



1/8

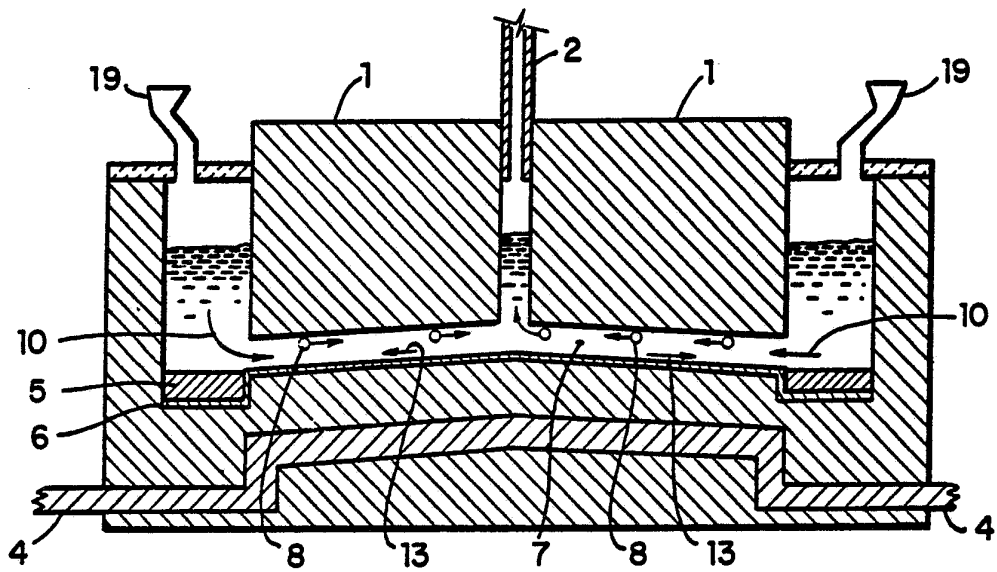


FIG. 1

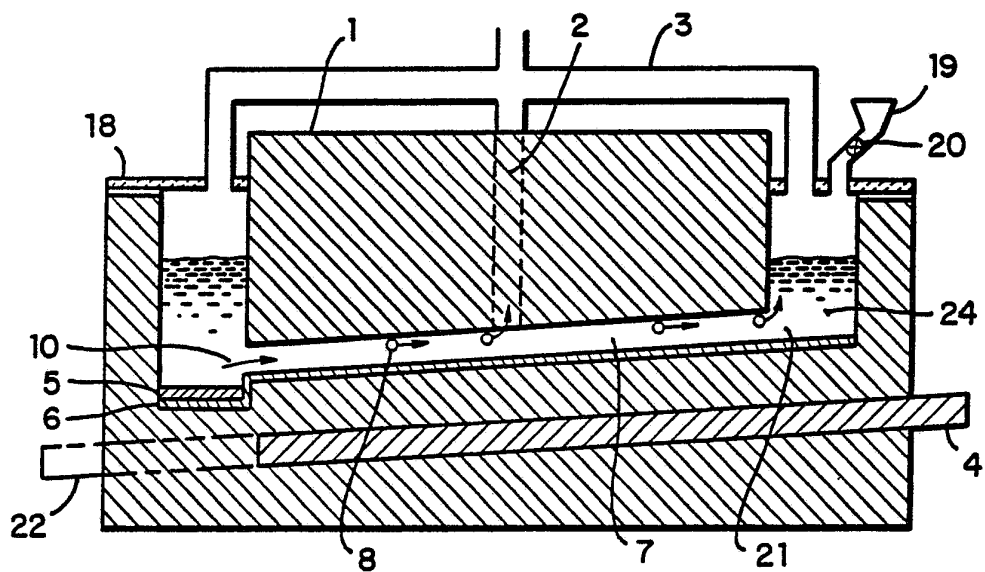


FIG. 2

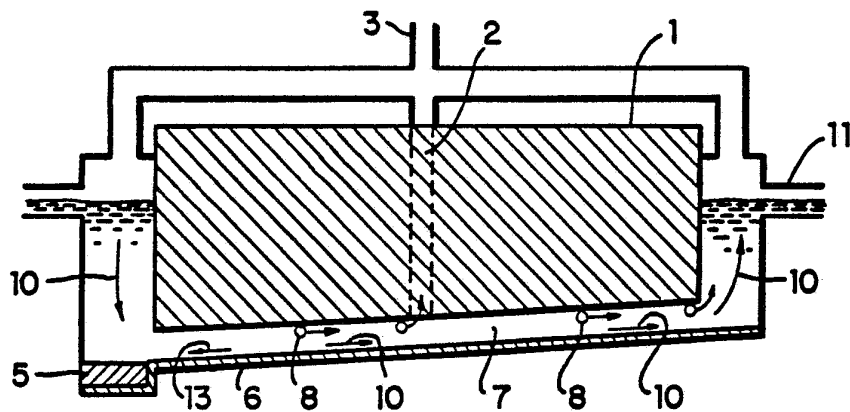


FIG. 3

2/8

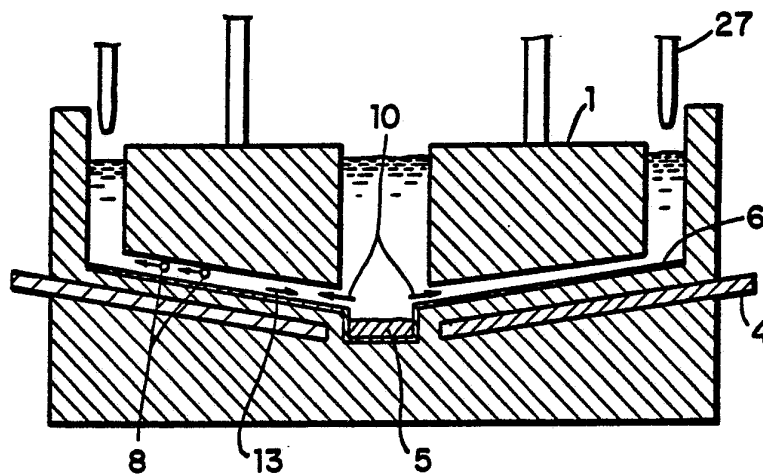


FIG. 4

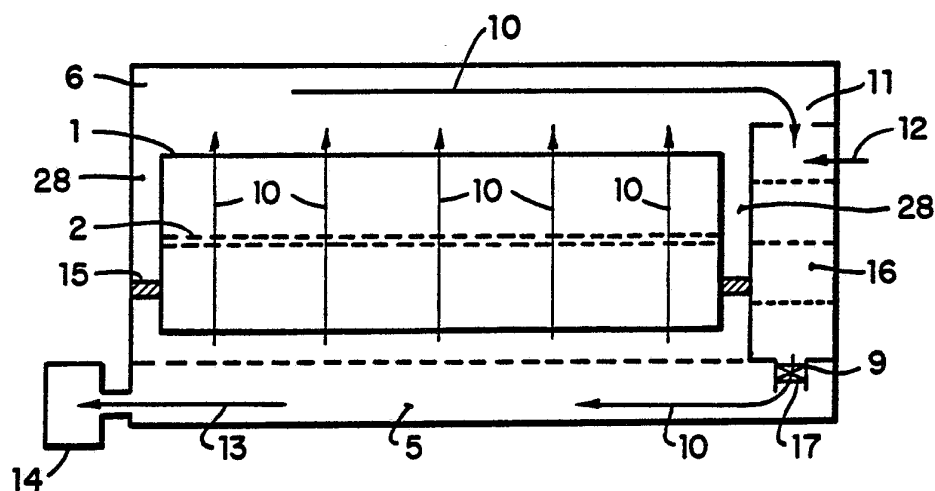


FIG. 5

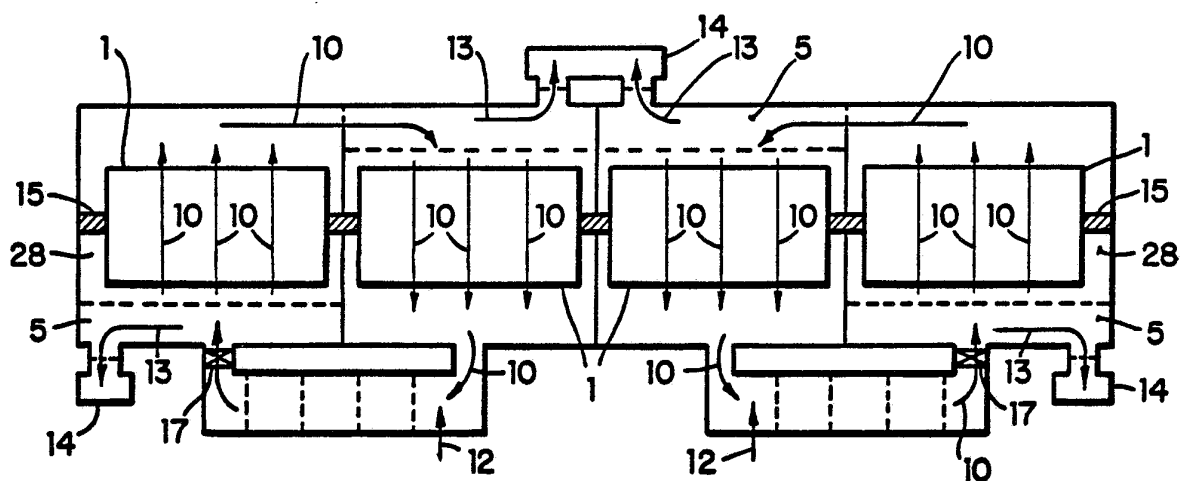


FIG. 6

5/8

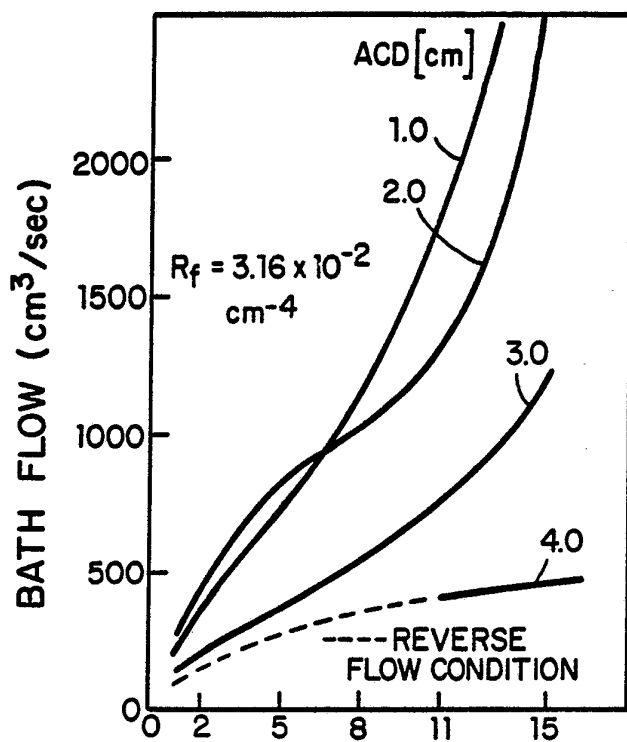


FIG. 10

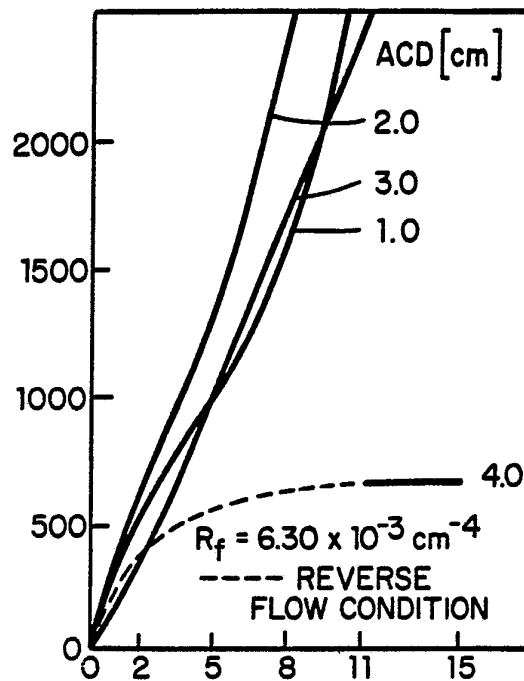


FIG. 11

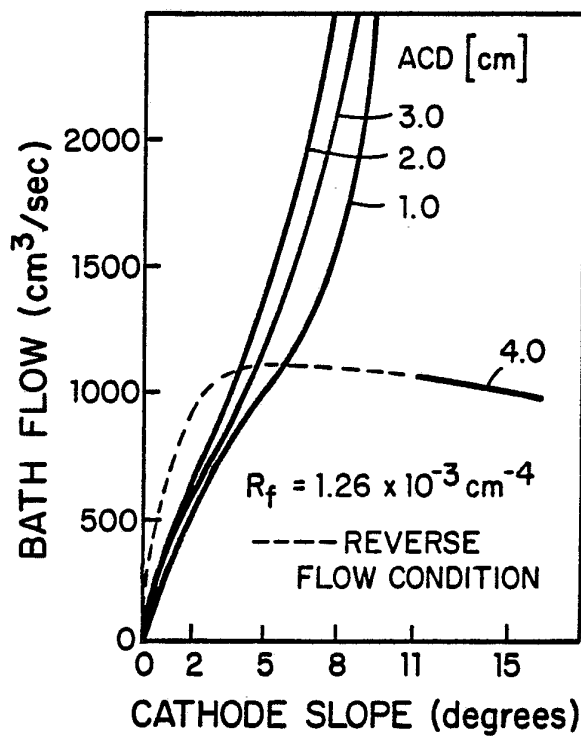


FIG. 12

6/8

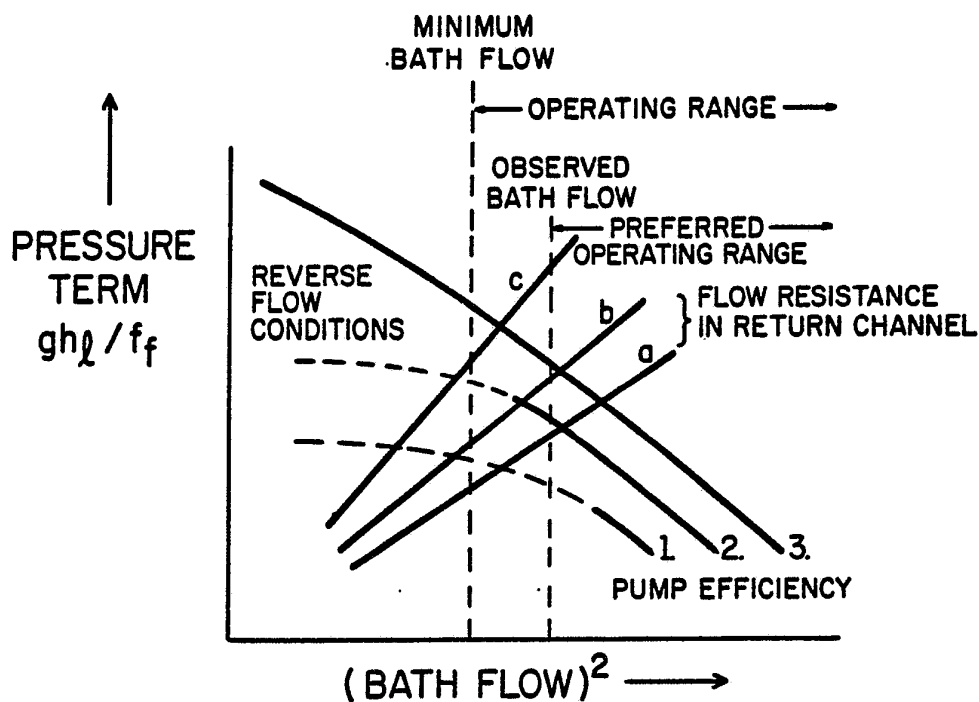


FIG. 13

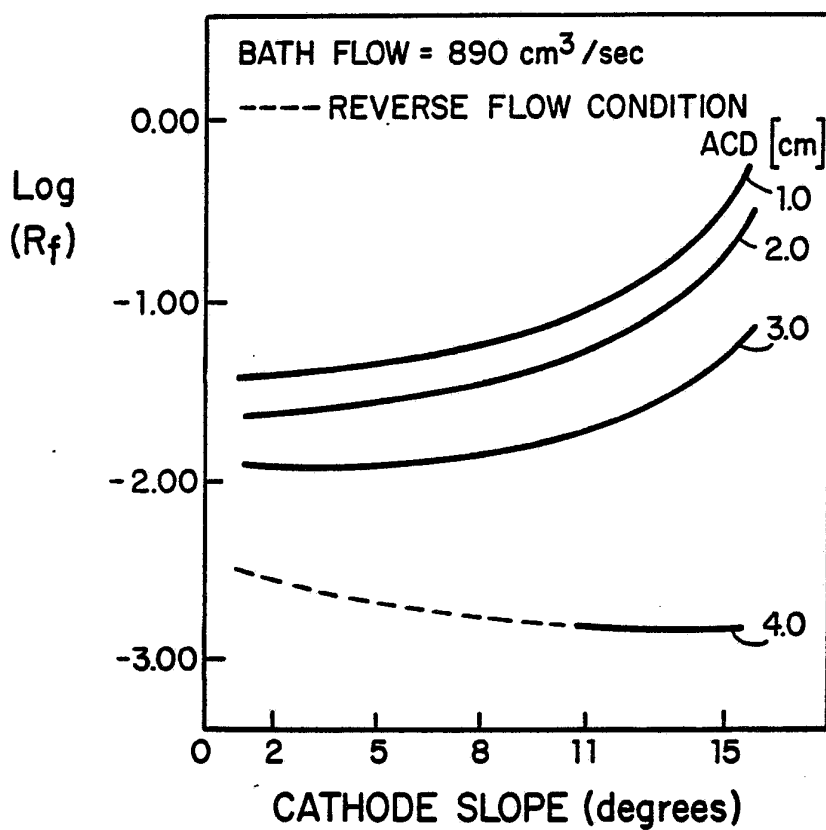


FIG. 14

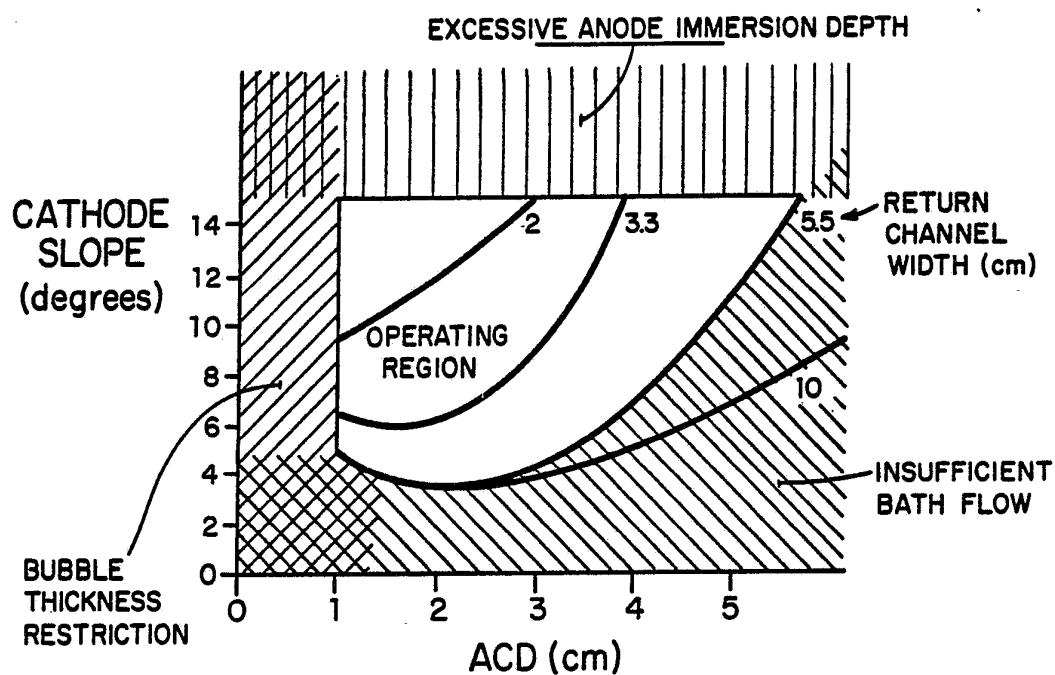


FIG. 15

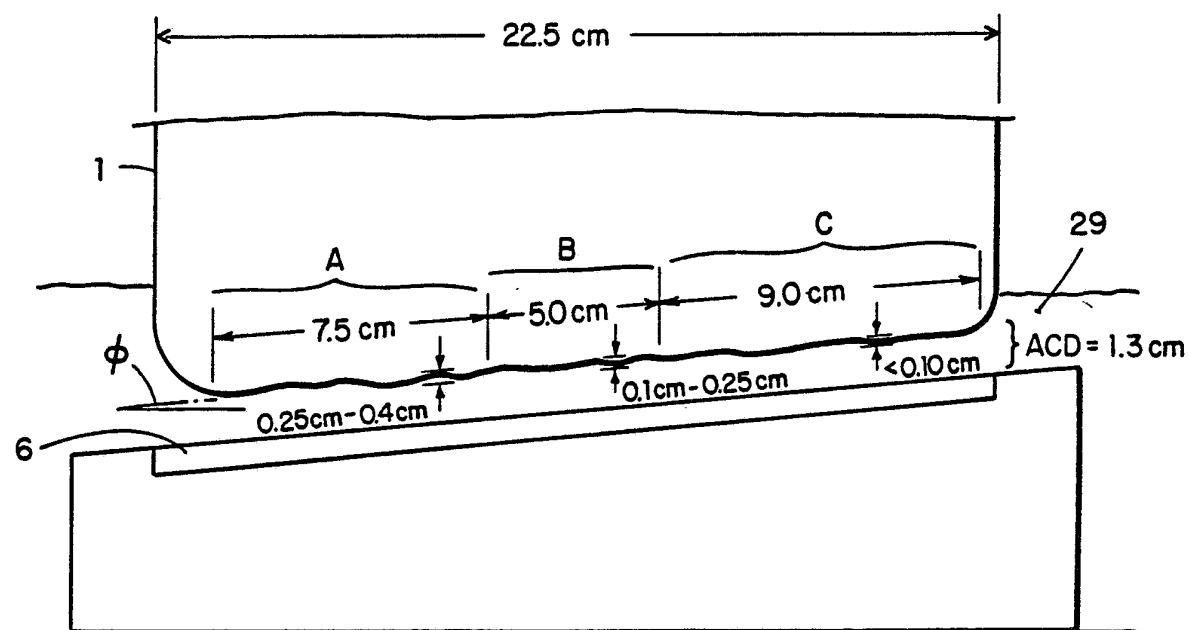


FIG. 16

8/8

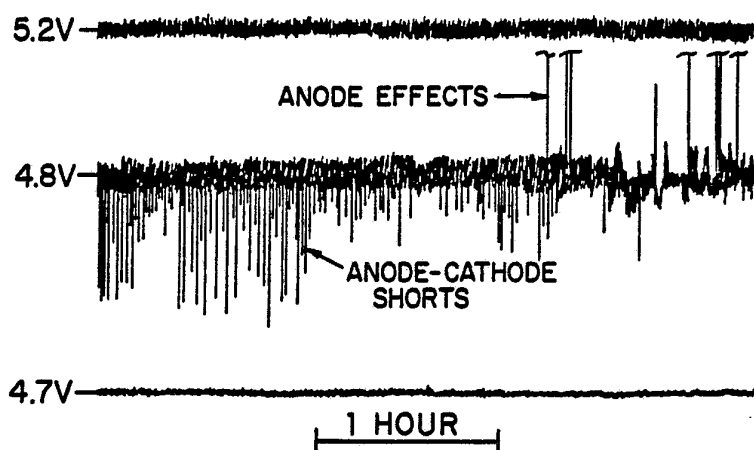
AVERAGE
CELL
VOLTAGEANODE CURRENT DENSITY = 0.68 A/cm^2

FIG. 17

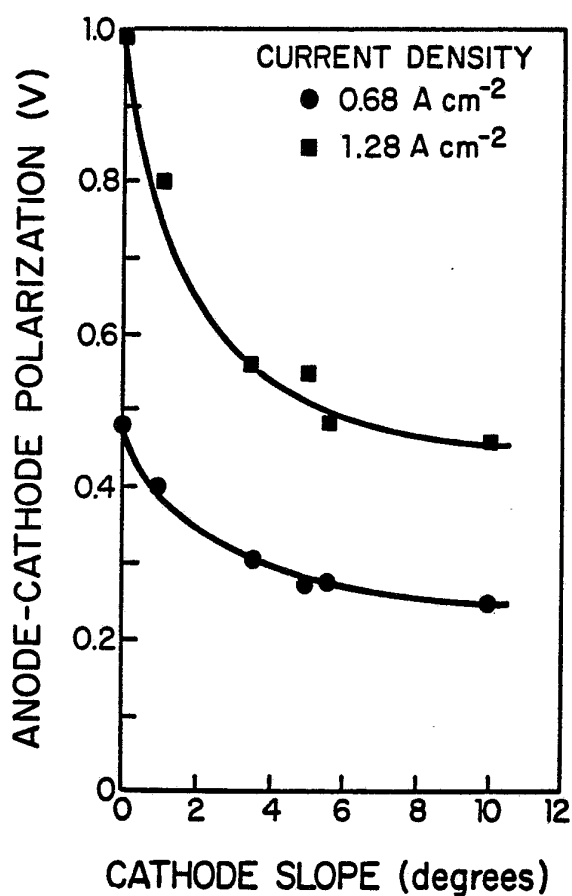


FIG. 18

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 84/00075

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC³: C 25 C 3/08

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
IPC ³	C 25 C 3

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	GB, A, 2084864 (SWISS ALUMINIUM LTD.) 16 January 1980 see figures 9,10; page 1, lines 104-114; page 4, lines 5-18; 63-103 --	1,3,4,6
Y	FR, A, 2409326 (NIPPON LIGHT METAL COMP. LTD.) 15 June 1979 see page 5, lines 23-33; figure 3 --	1,2
A	US, A, 4333813 (H. KAPLAN) 8 June 1982 see claims and figures 7,8 --	1
A	US, A, 4341611 (H. KAPLAN) 27 July 1982 see the whole document -----	1

^{*} Special categories of cited documents: ¹⁵

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹
8th June 1984

Date of Mailing of this International Search Report ²
09. 07. 84

International Searching Authority ¹
EUROPEAN PATENT OFFICE

Signature of Authorized Officer ¹⁹
G.L.M. Kruggerberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/US 84/00075 (SA 6550)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 29/06/84

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2084864	21/04/82	None	
FR-A- 2409326	15/06/79	None	
US-A- 4333813	08/06/82	None	
US-A- 4341611	27/07/82	None	

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82