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Sleppy

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[45] **Oct. 1, 1974**

[54] **NOVEL ALUMINA FEED FOR ALUMINUM CELL**

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[73] Assignee: **Aluminum Company of America**, Pittsburgh, Pa.

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[52] **U.S. Cl.** **204/67**, 204/245

[51] **Int. Cl.** **C22d 3/12**, C22d 3/02

[58] **Field of Search** 204/67, 245

[56] **References Cited**

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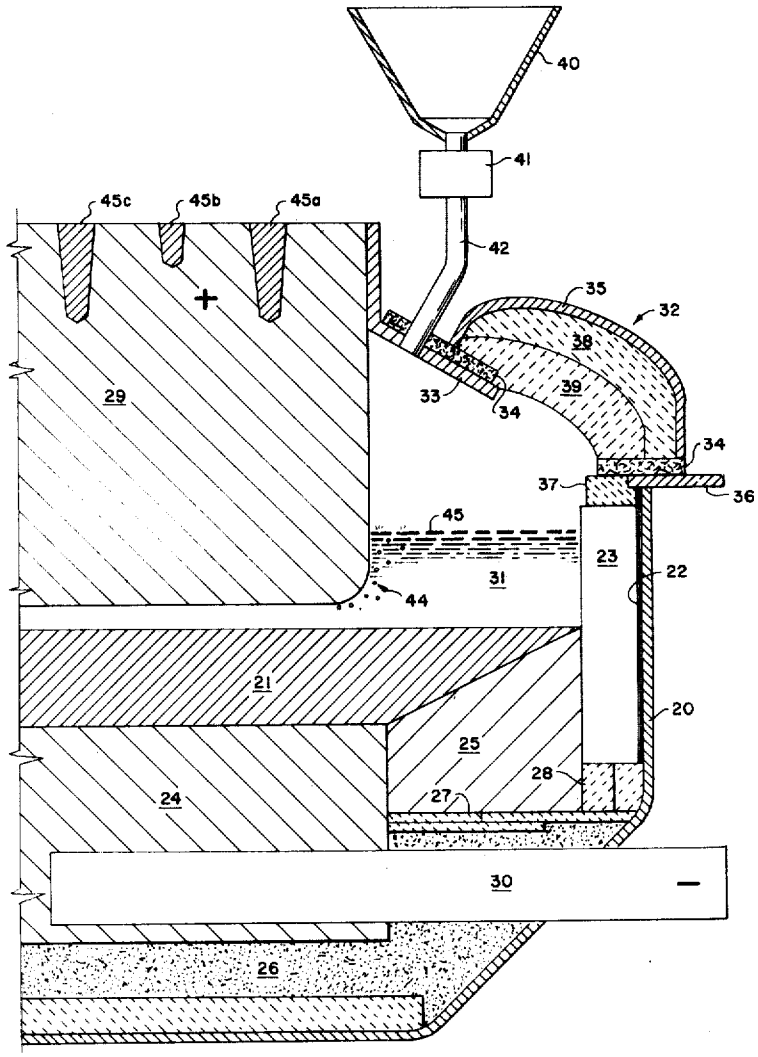
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Primary Examiner—John H. Mack
Assistant Examiner—D. R. Valentine
Attorney, Agent, or Firm—Daniel A. Sullivan, Jr.

[57] **ABSTRACT**

Use of an alumina which has a total water of 3 to 20 wt.-percent and a surface area of at least 45 m^2/g as cell feed improves the efficiency of operation of an electrolytic cell for reduction of alumina to aluminum.

8 Claims, 3 Drawing Figures



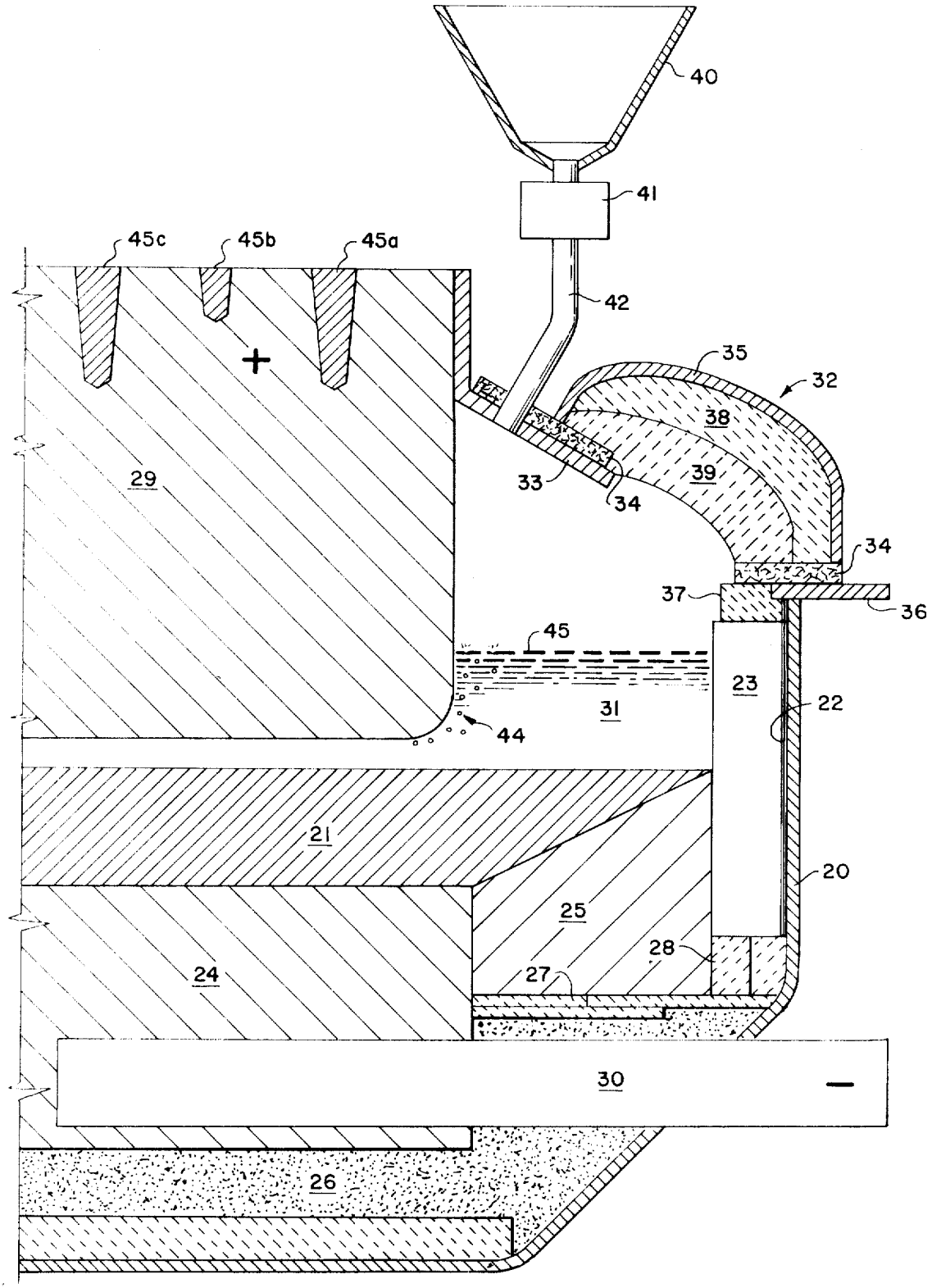
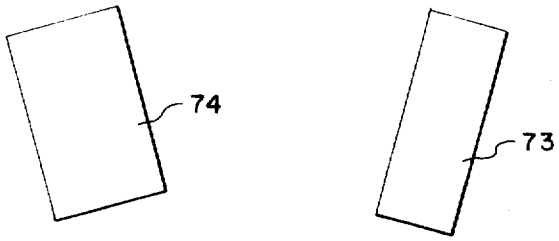

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FIG. 1



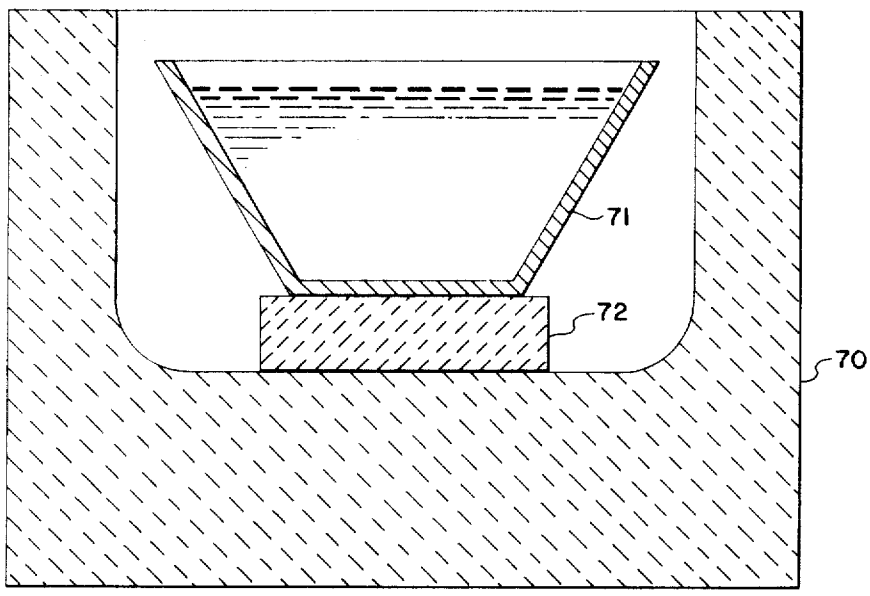


FIG. 2

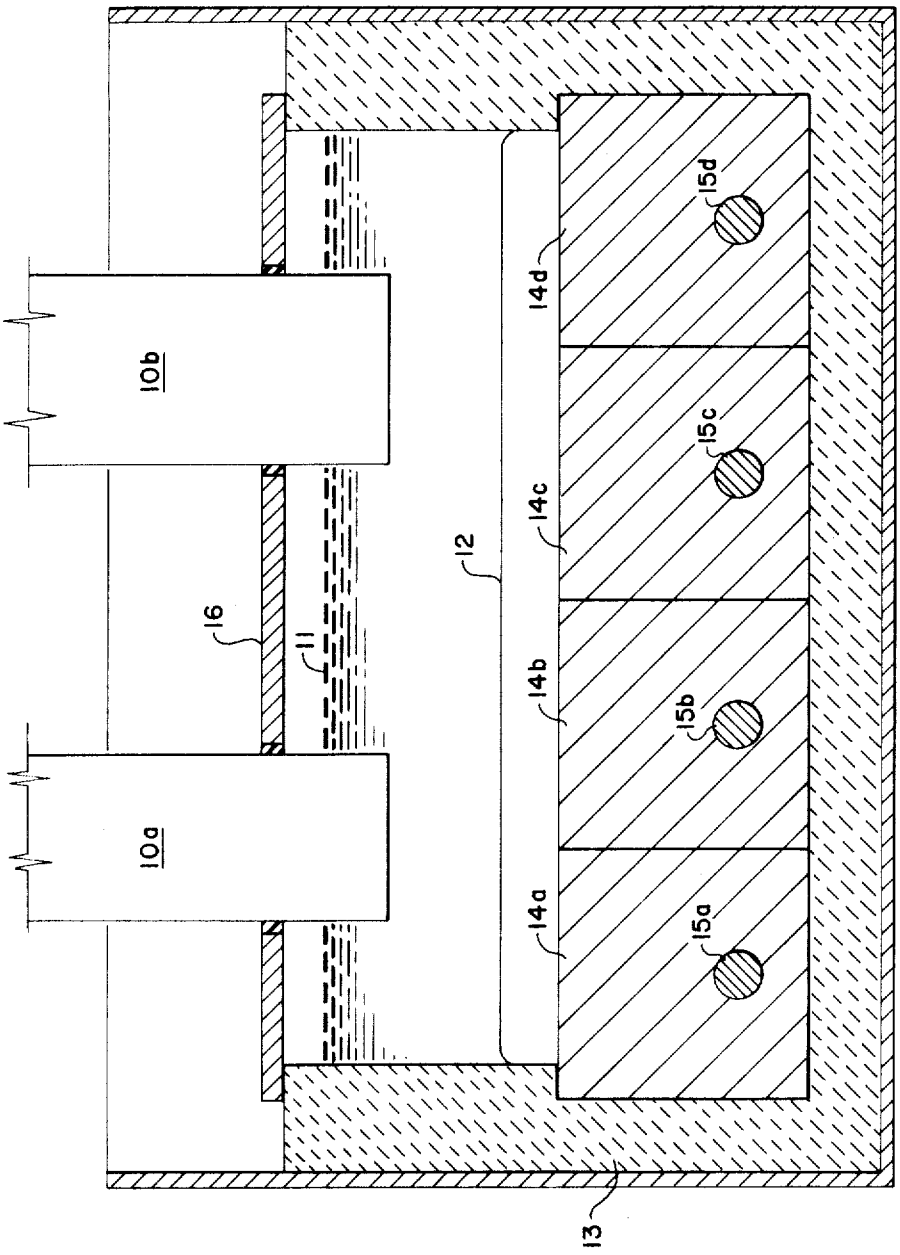


FIG. 3

NOVEL ALUMINA FEED FOR ALUMINUM CELL

BACKGROUND OF THE INVENTION

This invention relates to aluminum reduction cells. More particularly, it relates to use of alumina with characteristics differing from the alumina heretofore used as the bulk of the feed to electrolytic cells for reduction of alumina to aluminum.

U.S. Pat. No. 1,534,031 of Francis C. Frary for "Electrolytic Production of Aluminum" indicates that the rate of dissolution of alumina in molten electrolyte in a Hall cell can be an important factor in the successful electrolytic production of aluminum metal.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for the electrolytic reduction of alumina using an alumina having a hitherto unappreciated, high rate of dissolution in cryolite-base molten electrolyte.

After extended investigation, I have found that this object, as well as other objects which will become apparent in the discussion that follows, is accomplished by using as up to 100 percent of the feed alumina, preferably at least 90 percent by weight, an alumina which has a total water of from 3 to 20 weight-percent and a surface area of at least 45 meters^2 per gram (m^2/g), this alumina being fed substantially continuously, directly to the molten electrolyte of the cell. The "total water" is a measure of the water in the alumina and is defined herein as follows: Expose a sample of alumina to 100 percent humidity for several hours, then equilibrate the sample at 44 percent relative humidity, 25°C for 18 hours, then accurately weigh the sample, then ignite it to 1,100°C, then weigh again. The loss in sample weight on going from the equilibrated state at 44 percent relative humidity to the ignited state after heating at 1,100°C, divided by the sample weight at 1,100°C, and multiplied by 100 is the percent total water.

Surface area is measured by the Brunauer-Emmett-Teller method. See Stephen Brunauer, P. H. Emmett, Edward Teller, *J. of Am. Chem. Soc.*, V. 60, Pgs. 309–19, 1938.

The use of alumina of the high water content of the present invention is contrary to the commonly held view set forth at p. 34 of "The Chemical Background of the Aluminum Industry" by Pearson, published by The Royal Institute of Chemistry in 1955, that alumina used in electrolytic production of aluminum should be moisture-free.

Alumina having a total water and a surface area according to the present invention and fed substantially continuously to the electrolyte in the aluminum reduction cell is generally fed at a rate substantially equal to that at which it is consumed or converted to aluminum, that is at the rate of electrochemical reduction thereof. Within the meaning of the term "substantially continuously" as used herein, I include adding alumina continuously or in small, separate increments at frequent intervals.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevational, cross-sectional, broken-away view of a Soderberg anode type cell for use in the present invention.

FIG. 2 is a schematic, cross-sectional illustration of equipment for illustrating a principle of the present invention.

FIG. 3 is an elevational, cross-sectional view of a prebaked anode type cell for use in the present invention.

GENERAL ASPECTS OF THE INVENTION

The alumina feed to any smelting cell must dissolve in the electrolyte at a rate equal to at least the rate of electrochemical reduction so that the dissolved Al_2O_3 content of the electrolyte is not depleted. If alumina is fed to a cell more rapidly than it can be dissolved, solids then referred to as muck accumulate on the pot bottom, with attendant adverse effect upon operation of the cell. Factors that influence muck formation include the maximum Al_2O_3 solubility in the electrolyte and the solution rate of the particular alumina chosen. The method of feeding and the quantity of alumina introduced to the cell at any one time, along with the difference between cell operating temperature and the liquidus temperature of the NaF-AlF_3 electrolyte, are also important considerations with regard to muck formation.

The solubility and solution rate of alumina in NaF-AlF_3 electrolytes depends, in part, on the temperature and weight ratio of NaF/AlF_3 (bath ratio) in the fused salt bath. The maximum solubility and solution rate are found in pure molten cryolite (bath ratio 1.5:1) at elevated temperatures. As the bath ratio is lowered by addition of excess AlF_3, the temperature at which a completely liquid NaF-AlF_3 fused salt system can be maintained, the liquidus temperature, is sharply decreased. A decrease in Al_2O_3 solubility and solution rate accompany a decrease in bath ratio. Thus, while the use of low ratio fused salt mixtures as electrolytes in smelting cells permits lower temperature operations, an alumina feed with properties that improve its solution rate in the electrolyte is required. The solubility of Al_2O_3 in a given bath at a specified temperature is independent of the physical form of the Al_2O_3 charged to the electrolyte, but the solution rate of the alumina in the bath is a function of properties of the charged alumina.

The present invention makes use of the discovery that alumina having, as compared with the "metal grade alumina" conventionally used for producing aluminum metal by the electrolytic reduction of Al_2O_3 in cryolite-based electrolyte, a higher water content and a higher surface area and charged directly into contact with molten electrolyte exhibits a significantly higher solution rate. It is believed that the higher water content, and in particular a higher chemically combined water content, acts to instantaneously disperse the charged alumina through the electrolyte by the sudden release of steam as the charge comes in contact with the hot electrolyte bath. The well-dispersed particles then dissolve rapidly in the bath.

The thought of introducing the appreciable amounts of water in the alumina used in the present invention to an alumina electrolyte reduction bath may bring to mind the possibility of explosions. Thus British Pat. specification No. 274,108 of Societa Italiana di Elettrochimica for "Improvements in Processes for the Production of Aluminum in Electric Furnaces" states that it has not been possible in practice to use the hydrate or hydroxide of alumina directly on account of the more or less strong explosions produced by the material and the resultant projection of igneous liquid. Methods that have been proposed for avoiding this problem are to first agglomerate the hydrate and only

then feed it into a molten electrolyte bath; see German Pat. No. 472,006 of Feb. 21, 1929 issued to Societa Italiana di Elettrochimica in Rom for "Verfahren zur Herstellung von Aluminium." Also proposed is the charging of alumina hydrate onto the crust over a molten electrolytic bath in a Hall-Heroult cell, with introduction into the bath occurring only after dehydration has been achieved; see U.S. Pat. No. 2,464,267 of Allen M. Short for "Dehydrating Alumina in the Production of Aluminum." The practice of U.S. Pat. No. 2,464,267 is to be contrasted with that of the present invention, where an alumina of relatively high water content is added directly to molten electrolyte, rather than being allowed to rest for a period on a crust over molten electrolyte. It has been discovered that substantially continuous adding of the Al_2O_3 containing appreciable amounts of combined water does not lead to explosions. The evolved water appears only to disperse the charged Al_2O_3 rapidly to the bath, thus promoting dissolution in the bath.

The thought of purposely adding to a cell an alumina with high water content may also indicate danger of a major increase in HF evolution. It has been found that only five percent of the water on the alumina pyrohydrolyzes bath to produce HF fume.

The alumina to be used in the present invention may be fed to individual cells or to a plurality of cells in a potline. The cells may employ either prebaked anodes or anodes baked in situ, such as the Soderberg type.

Generally, calcining alumina hydrate, such as Bayer process alumina trihydrate will produce alumina for use in the present invention. In general, calcining temperatures in the range of about 300° to 1,000°C are suitable for the purpose. Apparatus and methods for heating alumina hydrate to the desired water content and surface area in kilns or by so-called "flash" heating (see U.S. Pat. No. 2,915,365 of F. Saussol; French Pat. No. 1,108,011) are well known.

Aluminas with surface areas as high as 350 m^2/g can be obtained by heating α-alumina trihydrate (gibbsite) for 1 hour at 400°C in dry air. Such materials are rapidly soluble in electrolyte baths according to the present invention.

For any alumina which is to be used as feed to the aluminum smelting cell, it is possible to run an experiment of the type set forth in Example II below, or the like, for the purpose of determining the minimum water content desirable. The water content is preferably effective for dispersing the individual particles of the alumina when the alumina is added to the electrolytic bath. If the water content is too low, steam evolution will not be effective for dispersing the particles, and a clumping of particles together will result, with resultant decrease in the effective dissolution rate of the alumina in the smelting bath. For any alumina, the most preferred particle size is 100 to 150 microns. The upper limit of water content in the alumina is not determined by the need to avoid explosions but rather by the quantity of heat that must be removed from the bath to drive off water as steam. This quantity cannot be sufficient to cause solidifcation of bath around solid alumina particles, thereby contributing to muck formation. In general, when this second criteria is satisfied, no dangerous explosions will occur according to the practice of the present invention. In general, if the water content is effective for dispersing the individual particles, it is also effective for preventing anode dusting in a sealed cell.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It is desirable that the alumina of the present invention handle and convey easily.

The properties according to the present invention that enhance the solution rate of alumina in fused NaF-AlF_3 salt systems also improve its ease of handling and serviceability in operations as in U.S. Pat. No. 3,503,184. Because the alumina used in the present invention has higher water content, less energy, as compared to the energy used in producing conventional metal grade alumina, is required to produce it from Bayer process hydrated alumina.

The alumina added to the bath according to my invention may be preheated, if desired, so long as it retains the above-mentioned total water and surface area characteristics.

Preferred properties of the alumina useful according to my invention, in addition to the 3 to 20 percent total water, include a particle size of 25–150 microns (optimum 55 to 145, i.e., below 100 mesh and above 270 mesh), and a surface area of 45–400 m^2/g.

Alumina of the above-defined properties is especially effective for producing aluminum by electrolytically decomposing Al_2O_3 to aluminum metal in an electrolyte bath between an anode and a cathodic interface formed between aluminum metal and an electrolyte bath consisting essentially of Al_2O_3, NaF, and AlF_3, and having a weight ratio NaF to AlF_3 (bath ratio) up to 1.1:1, preferably greater than 0.5:1, while maintaining said bath at an operating temperature greater than 40°C above the cryolite liquidus temperature of the bath and effective for preventing bath crusting in interfacial areas between bath and aluminum metal. The cryolite liquidus temperature is that temperature at which cryolite first begins to crystallize on cooling the bath. Preferably, when the bath ratio is equal to or less than 1.1:1, the alumina has a total water of 8 to 20 percent, more preferably 10 to 18 percent. The surface area may preferably be in the range 135 to 180 m^2/g.

For conventional cells, operating for example at 950° ± 10°C, bath ratio greater than 1.1:1, generally between 1.15:1 and 1.20:1, and ΔT not greater than 30°C, preferred alumina properties are: a surface area of 45 to 95 m^2/g, and a total water content of 3 to 7 percent.

A maximum rate of solution of alumina in a fluoride bath is obtained when heated, attrition resistant, high surface area, 8 to 20 percent total water alumina of 55–145 micron diameter (−100 mesh +270 mesh) particles is charged directly to the unfrozen surface of agitated bath at temperatures above its liquidus temperature continuously or in small separate portions, i.e., a time interval between separate portions equaling or less than 10 minutes. The phrase "small separate portions" is underlined because of its importance with regard to the ΔT at which the cell is operated. The ΔT is the difference between the operating temperature and the liquidus temperature of the NaF-AlF_3 fused salt mixture. This liquidus temperature can be lowered by addition of other salts to the bath such as CaF_2, LiF, MgF_2, etc., but for simplicity a pure NaF-AlF_3 system is visualized. Conventional smelting cells operate with ΔTs of 10°-

30°C. In conventional operations a low ΔT is desirable since the current efficiency of the cell increases as the operating temperature decreases. Because of improved control on conventional potlines the anode-cathode distance (ACD) in operating cells has been squeezed in some cases to a nominal 1-inch distance. Since the heat input to cells depends on line electrical current and internal resistance, the low ACD has enabled the lowering of ΔT to, for example, 10°C ± 5°C. While these low ΔTs are advantageous from a current and power efficiency viewpoint, they tend to increase mucking problems in the cell even when an alumina with properties that maximize its solution rate is fed to the pots. Automatic ore feeders which introduce, e.g., about 2 lb. of Al_2O_3 into the bath per increment may be used. This is a reasonably low rate of introduction of Al_2O_3 to the cell. However, if the ΔT of the bath is low, even this quantity of alumina may be so large that the heat removed from the bath to drive off water, bring the charge to temperature, and dissolve it can result in localized solidification of electrolyte. If this occurs then alumina encased in solidified bath will sink to the bottom of the cell to create muck instead of dissolving. This phenomena can lead to difficulties when, for example, 4–5 percent total water content Al_2O_3 is plugged into a pot. The term plugging refers to a method commonly used to feed Soderberg-type cells. A single plug can contain several hundred pounds of alumina. The point is, it is important to balance the size of the portion of Al_2O_3 fed to a pot at any given time against the ΔT of the cell. Low ΔT and large slugs of alumina will muck a pot, particularly when high surface area and water content aluminas are used.

A proper size distribution is advantageous with regard to ease of dissolution in a smelting cell. Alumina fines, e.g., particle size less than 44 microns (−325 mesh), tend to dust over the surface of the molten bath, agglomerate, and sink to the bottom of the cell where they contribute to mucking problems. Large particles, having diameters, e.g., greater than 150 microns (±100 mesh), also contribute to mucking problems, particularly when they are fed in large portions to pots operating with small ΔTs. The large particles acquire a layer of solidified electrolyte on contacting molten bath which causes them to sink to the pot bottom rather than rapidly dissolve. This is the same mechanism as that discussed earlier to explain muck formation in cells that receive Al_2O_3 feed in quantities too high to be accommodated by the low ΔTs. The difference is that particle sizes in excess of +100 mesh lead to muck even when ΔTs are in the vicinity of 25°C. At small ΔT, attention must likewise be paid to the heat of evaporation of the water in the alumina.

Further illustrative of the present invention are the following examples:

EXAMPLE I

The apparatus used in this example is shown in FIG. **2.** Pot furnace **70,** which was heated by electrical resistance heating, served for bringing a cryolite-base bath in a graphite crucible **71** supported on fire brick **72** to a temperature of 740°C. The nominal bath composition was 64 weight percent cryolite and 36 weight percent aluminum fluoride (AlF_3). This corresponds to a bath weight ratio $NaF/AlF_3 = 0.65$. The quantity of bath was 500 grams and 200 milliliters volume in the molten state. The bath contained 14 grams, or 2.8 weight percent, of Al_2O_3 as an impurity. At 740°C, this bath is molten (liquidus = approximately 724.5°C) and crystal clear. A 1-gram quantity of alumina having a total water of 17 percent and a surface area of 170 m^2/g was sprinkled onto the exposed, uncrusted surface of the molten bath. It had been produced by heating Bayer process alumina hydrate in the temperature range 300°–335°C. With the bath illuminated with light source **73,** the time was recorded for which no remainder of the sprinkled alumina particles could be seen in the bath through viewing tube **74.** This time was 2 minutes and 58 seconds, which equals a solution rate, in milligrams per milliliter bath-minute equal to 1.65. By way of comparison, a so-called metal-grade alumina of surface area of 40 m^2/g gave a solution rate of 0.14 milligrams per milliliter bath-minute under like conditions.

EXAMPLE II

Using the apparatus of FIG. **2** and alumina of 17 percent total water, 170 m^2/g surface area, gave, at a bath weight ratio $NaF/AlF_3 = 1.5$ and a bath temperature of 980°C, a solution rate of 16 milligrams of Al_2O_3 per milliliter of bath each minute. The solution rate measured under the same conditions for an alumina of 20 percent total water and 100 m^2/g surface area was 8 milligrams alumina per milliliter bath each minute. By way of comparison, metal-grade alumina of 30 m^2/g surface area gave under like conditions a solution rate of approximately 0.36 milligrams alumina per milliliter bath each minute.

EXAMPLE III

In a cell for the electrolytic reduction of alumina to aluminum metal, of external dimensions equaling approximately 48 inches height, 89 inches length, and 56 inches width, aluminum was produced by the electrolysis of a molten bath containing lithium fluoride at 5 weight percent, Al_2O_3 at 2 to 5 weight percent, balance NaF and AlF_3 at a weight ratio $NaF/AlF_3 = 0.8$, and having temperature levels between 850° and 950°C. The cell is shown in FIG. **3** in longitudinal, elevational cross section. Two carbon, prebake anodes **10***a* and **10***b* were suspended into electrolyte bath **11** resting on a pad of molten aluminum **12.** The molten bath and aluminum were contained laterally by refractory, nonconductive material **13.** Refractory material **13** includes a side lining in contact with the molten bath and the molten aluminum and other outwardly situated insulating material with internal structural members of, for example, steel. Refractory alumina brick and silicon carbide brick were the particular side lining materials chosen in this example. Lining the bottom of the cell were graphite blocks **14***a* through **14***d*, which were connected into the electrical system by steel bars **15***a* to **15***d*. Alumina was fed to bath **11** through a suitable port (not shown) in graphite roof **16.** Graphite roof **16** functioned to seal the bath from the air. The aluminas of Table I were used as feed.

Table I.

Alumina Properties		
Alumina No.	Surface Area m^2/g	Total Water
1	200–245	17–18
2	108–170	17–18

Table I.-Continued

Alumina Properties		
Alumina No.	Surface Area m^2/g	Total Water
3	28	2-3

The dissolution rates of both aluminas 1 and 2 were sufficient to allow cell operation without the occurrence of mucking. In contrast, the rate of solution of alumina 3 was perceptibly slower, with agglomerating prevalent, and mucking persistent.

EXAMPLE IV

Bayer-process alumina hydrate was treated in a kiln to produce kiln activated alumina suitable for use in the process of the present invention as follows. Kiln dimensions were 360 feet length and 9½ feet inner-diameter. Residence time of the material in the kiln was 1 to 1½ hours. The charged hydrate moved countercurrent to the combustion gases introduced into the lower end of the kiln. A maximum temperature of 400° to 500°C was achieved 10 to 15 feet inside the lower end of the kiln. Natural gas was burned at a rate of 6,500 cubic feet (standard temperature and pressure) per hour to produce the combustion gases. This natural gas flow rate was selected by testing the product for the desired total water. The volume ratio of air to gas was approximately 10:1. An alumina having a 12.5 percent total water was produced. Anywhere from 88 to 95 weight percent of the particles had a size greater than 325 mesh.

EXAMPLE V

Alumina having a total water of 14 percent, a surface area of 200 m^2/g, and a particle size of 100 microns (average diameter) was substantially continuously introduced as the only alumina feed at 1-2 minute intervals to a Hall-Heroult cell operating with a cryolite based electrolyte so as to maintain a bath alumina content of about 5 percent by weight and to dissolve the alumina rapidly as it was introduced. Cell current density was about 2.5 amp/in^2. The $NaF:AlF_3$ weight ratio of the bath was about 0.8, its liquidus about 725°C, and the bath temperature about 850°C. The rate of dissolution of the alumina exceeded the rate of alumina consumption by reduction to aluminum during continuous operation of the cell at a current efficiency greater than **90%** for an hour, and the rate of alumina consumption was substantially the same as the rate of alumina addition, so that the alumina in the bath was not depleted. The aluminum produced was collected. The bath composition amounted to about 63 percent Na_3AlF_6, 32 percent AlF_3 and 5 percent Al_2O_3, where percentages are by weight. Carbon consumption approached the theoretical 0.33 pounds carbon per pound aluminum produced.

EXAMPLES VI AND VII

Aluminum was produced in the cell of FIG. **1**. The maximum dimensions of the steel shell **20** in the horizontal were 18'6" × 10'2". Its maximum height was 3'9". The maximum dimensions of the molten aluminum metal pad **21** in the horizontal were 17'8" × 9'4". The electrolyte bath had the same maximum dimensions as the metal pad.

The mica mat **22** was provided between the steel shell **20** and graphite block **23** for the purpose of preventing current flow through shell **20.** Mat thicknesses of from 6 to 20 mils have been used.

The metal pad **21** of aluminum was supported on carbonaceous cathode block lining **24** and carbonaceous tamped lining **25.** The carbonaceous linings were supported on an alumina fill **26,** there being interposed between the tamped lining and the fill some quarry tile **27.** A layer of red brick **28** was provided between the graphite block **23** and quarry tile **27.**

FIG. **1** is a representative vertical section through the cell and it will be realized that, for instance, similar graphite blocks **23** would appear in other elevational sections through the cell.

The anode **29** was a Soderberg-type carbon anode. The composition charged to form this self-baking anode was 31 percent pitch of softening point equals 98°-100°C (cube-in-air method) and 69 percent petroleum coke. The coke fraction was 30 percent coarse, 16 percent intermediate, and 54 percent fine, the size distributions of the coarse, intermediate, and fine coke being given in Table II.

Table II.

Coke Size Distributions			
Tyler Sieve	Cumulative % Greater Than Sieve Size		
	Coarse	Intermediate	Fine
.371	31.1		
3	50.6		
4	66.8		
8	91.7	11	
14	97.9	48.9	
28	98.9	75.5	
48	99.1	93.5	2.4
100	99.4	98.0	10.4
200	99.7	99.0	39.7
pan	100	100	100

The cathode current was supplied through steel collector bars, such as bar **30,** to the block lining **24.** The current supply is indicated by the plus and minus signs on the anode and on collector bar **30** respectively.

The space above the bath **31** was sealed from the surrounding air by a closure **32,** including a cast iron manifold **33,** Ceraform Refractory board **34,** which is a soft (for obtaining a good seal) fibrous electrical and heat insulating board available from the Johns-Manville Co., steel shell **35,** steel plate **36,** and fire clay brick, e.g., 50 percent Al_2O_3 and 50 percent SiO_2, **37.** Within shell **35** there was provided a castable **38** serving a primarily insulative function and a castable **39,** e.g., calcium-aluminate-bonded tabular alumina, selected for its refractory properties. The particular heat transfer situation was chosen to maintain the upper surface **45** of bath **31** substantially in molten condition, i.e., free of any crusting.

Alumina is charged from hopper **40** through a fill valve and feeder assembly **41** of the type disclosed in U.S. Pat. No. 3,681,229 issued Aug. 1, 1971 to R. L. Lowe entitled "Alumina Feeder." Measured quantities of alumina are fed onto the exposed molten bath surface through Inconel-600 pipe **42.** The distance between the bottom of pipe 42 and the top of bath **31** is about 1 foot. The feeder **41** is a shot-type feeder, i.e., separate quantities of alumina are fed at timed intervals. In Examples VI and VII, two feeders **41** were used, and these fed-in alumina approximately every 5 minutes, the quantities of alumina being adjusted to main-

tain the desired alumina concentration in the bath. It takes about 1 minute to discharge the alumina increments which were about 1,500 grams. Pipe **42** is directed so as to impinge alumina onto the bath **31** where gas **44** is rising alongside the anode. This assures that the water evolved from the charged alumina protects the anode against production of carbon dust therefrom. This practice also promotes dissolution because of the bath agitation caused by the gas evolution. By charging the alumina in line with a spike row (spikes **45***a*, *b*, and *c* lie in a vertical plane parallel to the plane of FIG. **1**, which plane also contains pipe **42**) in the Soderberg anode (cracks usually occur in the anode in line with spike rows), the dissolution rate is enhanced by the increased gas evolution occurring at the cracks. Feeders **41** were operated using air as the fluidizing medium, it being recognized that this represents a small leakage of air past cover **32** to the bath.

The particular alumina used for Examples VI and VII had a total water of 16.95 percent. This alumina was 98 percent plus 325 mesh and its water content alone was sufficient to prevent anode dusting, i.e., a decomposition of the anode such that carbon particles build up in and on the bath.

The production data for Examples VI and VII are presented in Tables III to V.

Table III.

Pot Production Data

Data Name	Example No. VI	VII
Pot Days Operated	32	96
Total Lbs. Net Aluminum (Al)	35,172	110,740
lbs. Net Al/Pot-Day	1099.2	1153.5
Average % Al	99.74	99.75
Electrical Current Efficiency	92.6	90.0
Kilowatt-Hours/Lb. of Al	7.49	7.76
Anode Effects/Pot-Day	.91	1.21
Lbs. Soderberg Paste/Lb. Net Al	.56	N.M.[1]
Lbs. Cryolite Used	1850	3600
Lbs. Fluoride Used	6105	21,731
Lbs. $LiCO_3$ Used	682	1400
Anode to Cathode Distance, Inches	1.4	1.5

1. N.M. = not measured

Table IV.

Pot Electrical Data

Data Name	Example No. VI	VII
Volts/Pot	5.13	5.17
Average Ampers	66,874	72,207
Kilowatts/Pot	343.1	373.3
Ohmic Voltage Drop in Bath	1.70	1.68

Table V.

Pot-Bath Data

Data Name	Example No. VI	VII
Wt.-% CaF_2	3.11	3.17
Wt.-% Al_2O_3	4.09	4.00
Wt.-% AlF_3	48.97	45.08
Wt.-%LiF	5.61	10.165
Wt.-%NaF	38.13	36.94
Wt.-% MgF_2	.38	.28
Liquidus Temperature, °C	882	906
Calculated Wt.-Ratio NaF/AlF_3	.78	.82
Calculated Wt.-% Cryolite	63.4	61.9
Calculated Excess AlF_3	23.4	20.5
Bath Operating Temperature °C	898	922
"Eutectic" Temperature, °C	799	814
Conductivity, ohm^{-1}-$inches^{-1}$	4.87	5.67
Bath Depth, inches	8.26	7.62
Metal Depth, inches	6.02	6.25

With special reference to Table V, the excess AlF_3 indicates the quantity of AlF_3 above that present under the heading cryolite, formula $3NaF \cdot AlF_3$. In each of Examples VI and VII, Al_2O_3 would be the first substance to crystallize on going below the given liquidus temperature. The "eutectic" temperature provides an estimate of the cryolite liquidus temperature in this case. The "eutectic" temperature is determined by finding the liquidus temperature for progressively decreasing Al_2O_3 content, correspondingly increasing $NaF + AlF_3$, and constant bath ratio NaF/AlF_3 and selecting the minimum liquidus temperature on the basis of the resulting group of liquidus temperature values. The Al_2O_3 in solution is that at the particular bath operating temperature. Conductivity data is likewise for the given operating temperature.

Gases evolved from the Soderberg anode, (e.g., hydrocarbons), fluorides from the bath, and anode reaction gas, (e.g., CO_2) were vented from cover **32** through an opening (not shown) and passed through a burner to burn the hydrocarbons. Because it is difficult to provide an absolute sealing of the bath from the air using cover **32**, i.e., leads can be present in cover **32**, a pressure of 0.03 to 0.1 inches of H_2O, measured negatively from atmospheric pressure, is maintained between cover **32** and the burner in order to prevent fume leakage from the cover **32**. The burned gases were then fed to a scrubber system.

It will be understood that the above description of the present invention is susceptible to various modifications, changes, and adaptations and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

All percentages given herein are in percent by weight unless indicated otherwise.

What is claimed is:

1. A process for increasing the efficiency of smelting aluminum, comprising adding, substantially continuously, directly to a molten electrolyte in a cell for the electrolytic reduction of alumina to aluminum, an alumina which has a total water of from 3 to 20 weight percent and a surface area of at least 45 m^2/g, said alumina comprising up to 100 percent of the Al_2O_3 fed to said cell, and electrolytically reducing alumina to aluminum in said cell.

2. The process of claim **1** wherein said alumina is added in increments at intervals of up to ten minutes in amounts calculated to maintain constant alumina concentration in the electrolyte.

3. The process of claim 1 wherein said electrolyte consists essentially of NaF, AlF_3, and Al_2O_3 and has an NaF to AlF_3 weight ratio up to 1.1:1 and wherein said alumina has a total water of 8 to 20 percent.

4. The process of claim 3 wherein said alumina has a total water in the range 10 to 18 percent.

5. The process of claim 3 wherein said alumina has a surface area in the range 135 to 180 m^2/g.

6. The process of claim 1 wherein said alumina amounts to at least 50 percent by weight of the total amount of Al_2O_3 fed to the cell.

7. The process of claim 1 wherein said alumina amounts to at least 90 percent of the Al_2O_3 fed to the cell.

8. A process for increasing the efficiency of smelting aluminum, comprising adding, substantially continuously, directly to a molten electrolyte in a cell for the electrolytic reduction of alumina to aluminum, alumina having a water content effective for dispersing its individual particles upon addition thereof to said electrolyte but insufficient to cause mucking.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,839,167 Dated October 1, 1974

Inventor(s) William C. Sleppy

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 40 After "microns", change (± 100 mesh) to --(+ 100 mesh)--.

Signed and sealed this 18th day of February 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks