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1,837,070	12/1931	Roth.....	204/245 X
3,294,656	12/1966	Schmitt	204/67
3,380,897	4/1968	Dewey.....	204/67 X
3,434,945	3/1969	Schmitt et al.....	204/67
3,455,795	7/1969	Boulanger et al.....	204/67

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[54] **ALUMINA FEED CONTROL**
3 Claims, 2 Drawing Figs.

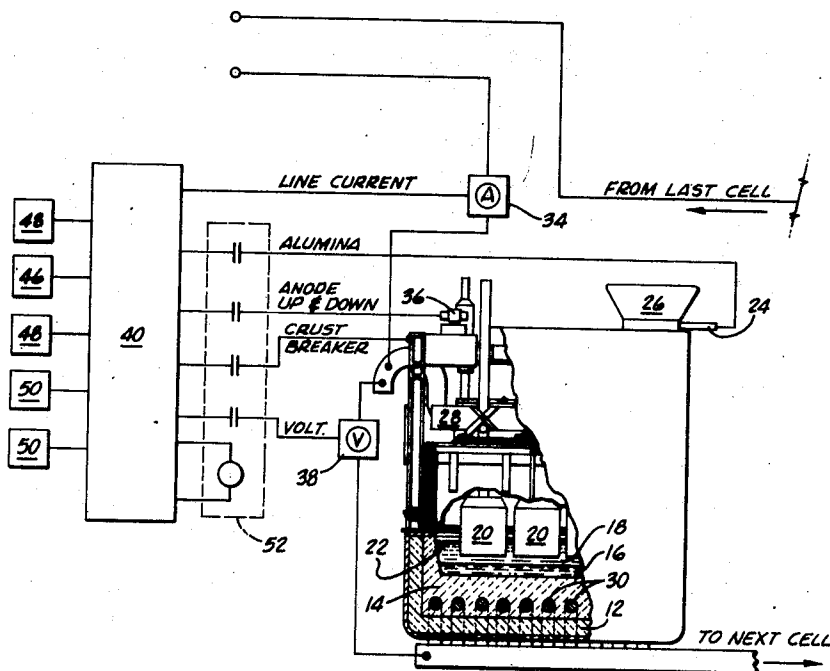
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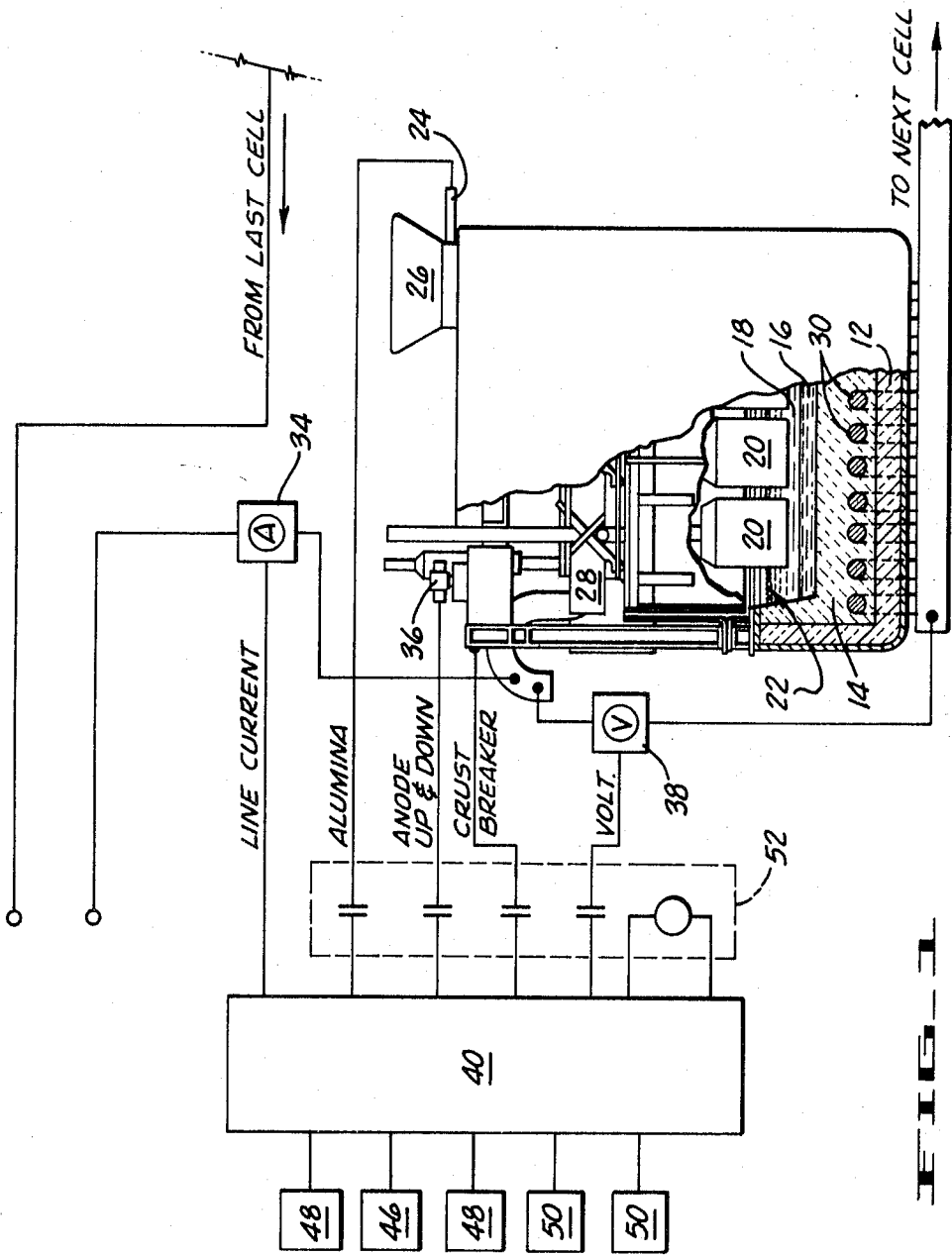
[51] Int. Cl..... **C22d 3/12**

[50] Field of Search..... **204/67,**
245, 225

[56] **References Cited**
UNITED STATES PATENTS
3,573,179 3/1971 Dirth et al..... 204/67

ABSTRACT: A method of controlling the feeding of alumina to a reduction cell for the production of aluminum. The method comprises obtaining several measurements of the voltage across the cell and current to the cell and deriving from the measurements an average resistance level for the cell which will be referred to as a base level. A smoothed resistance is derived from several sequential measurements of the voltage and current. When the smoothed resistance exceeds the base resistance level by more than an assigned limit, a controlled amount of alumina is added to the cell.





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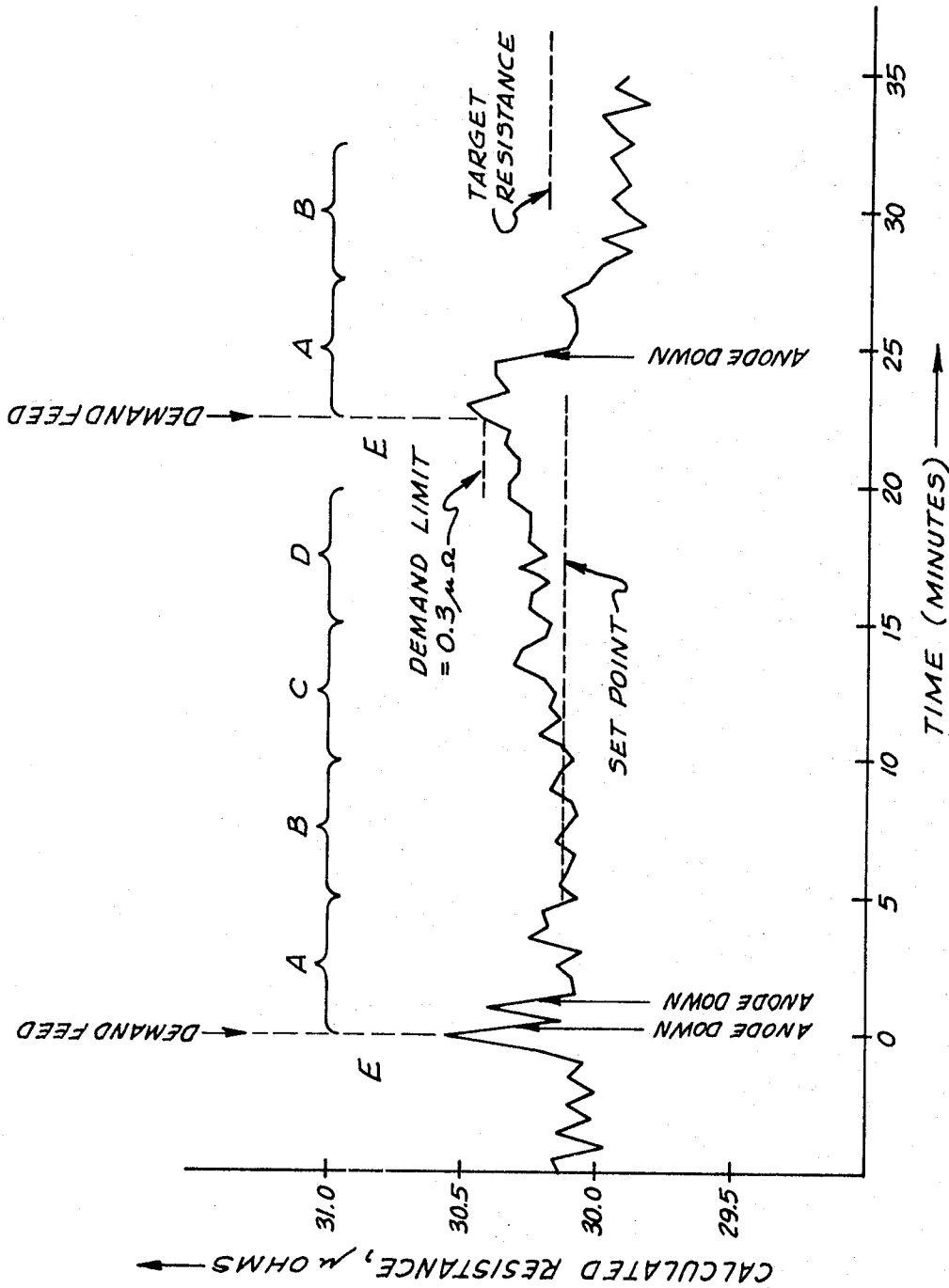


FIG. 2

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ALUMINA FEED CONTROL

BACKGROUND OF THE INVENTION

The metal aluminum is extracted from aluminum bearing compounds such as alumina (Al_2O_3) by electrolysis from a molten cell bath or electrolyte. In the production of aluminum by the conventional electrolytic process, commonly referred to as the Hall-Heroult Process, the electrolytic cell comprises in general a steel shell having disposed therein a carbon lining. The bottom of the carbon lining, together with a layer of electrolytically produced molten aluminum which collects thereon during operation, serves as the cathode. One or more consumable carbon electrodes is disposed from the top of the cell and is immersed at its lower extremity into a layer of molten electrolyte which is disposed in the cell and above the molten alumina layer. In operation, the electrolyte or bath which is basically a mixture of alumina and cryolite is charged to the cell and an electric current is passed through the cell from the anode to the cathode via the layer of molten electrolyte. The alumina is dissociated by the current so that aluminum is deposited on the liquid aluminum cathode and oxygen is liberated at the carbon anode, forming carbon monoxide and carbon dioxide gas. A crust of solidified electrolyte and alumina forms on the surface of the bath, and this is usually covered over with additional alumina.

In the conventional electrolytic process, use has been made of two types of electrolytic cells, namely that commonly referred to as a "prebake" cell and that commonly referred to as a "Soderberg" cell. With either cell, the reduction process involves precisely the same chemical reactions. The principal difference is one of structure. In the prebake cell, the carbon anodes are prebaked before being installed in the cell, while in the Soderberg, or self-baking anode cell, the anode is baked in situ, i.e., it is baked during operation of the electrolytic cell, thereby utilizing part of the heat generated by the reduction process. The instant invention is applicable to either cell.

A typical aluminum electrolytic bath used in commercial installations might have the following composition:

- 1-10 percent alumina, usually about 6 percent in conventional American practice,
- 0-10 percent aluminum trifluoride,
- 5-12 percent calcium fluoride, and
- 80-90 percent cryolite.

As the electrolysis continues, alumina is consumed in direct proportion to the metal production. As the alumina concentration in the electrolyte is reduced, a point is reached where a troublesome phenomenon known as "anode effect" occurs. The voltage drop across the cell can increase, for example, from around 4 volts to as much as 40 volts and even higher. This effect is generally attributed to too low a concentration of alumina in the reduction cell bath or electrolyte. The actual concentration of alumina in the electrolyte at which this effect occurs seems to depend upon the temperature, the composition of the electrolyte and the anode current density, but usually is somewhat below about 2 percent by weight. The occurrence of an anode effect is the signal for the addition of more alumina. The attendant does this by breaking the frozen crust on top of which he has previously distributed a layer of alumina. The addition of the alumina, accompanied by a vigorous stirring of the electrolyte, causes the anode effect to disappear, after which the electrolysis continues its normal course until the next anode effect occurs.

There are several disadvantageous results of an anode effect such that minimizing or substantially eliminating or controlling the duration of their occurrence is desirable. According to one theory, during the normal course of electrolysis, the effective surface of the anode is believed to be surrounded by gas bubbles which are constantly escaping from it. They are believed to form on the anode, break away easily, and escape from the electrolyte. Smooth evolution of gas around the anode is believed to be a sign of normal operation. The moment the anode effect occurs, according to this theory, the effective surface of the electrode is believed to be entirely sur-

rounded by a film of gas. This is believed to cover the surface of the anode and push the fused electrolyte away, producing the so-called "nonwetting" of the anode. Small arcs are thought to form between the electrolyte and the anode. Complete interruption of the current is not believed to occur, as some current is thought to be carried by these continually shifting arcs. The arcs are believed to cause local heating, volatilizing some bath material and producing sufficient gas so that the individual arcs are almost immediately broken.

New arcs are believed to form, as the bath film near the anode must necessarily be uneven in character, and momentary contacts are thought to take place between the anode and the bath. The overheating that occurs during anode effect causes excessive consumption of the anode, excessive consumption of electrolyte by volatilization, and results in a lowered yield of product. A very important result of the anode effect is a large, unproductive power consumption.

With the developing trend toward more automated cell operation, the control of alumina concentration in the bath or electrolyte through cell feeding has become quite important. In most cell control schemes, it is desired that the number and severity of anode effects be minimized without overfeeding the cell. This involves either controlling the feed rate or measuring the concentration of the alumina in the bath or electrolyte or in some way receiving an indication of incipient anode effects so that a substantially constant alumina concentration can be maintained. The prior art describes many methods which have been utilized in the past to determine the alumina concentration in the electrolyte or bath or to obtain some sort of prewarning of an oncoming anode effect. These methods include chemical analysis for the alumina concentration, either by pyrotitration techniques, caustic leach methods, gravimetric methods of analysis, volumetric methods of analysis, or by means of electrical conductivity measurements. Examination of physical properties of the electrolyte has also been utilized to some extent. The appearance of the electrolyte, both molten and solidified, has been compared with known samples; crystalline phases have been examined by microscope and X-ray diffraction, as well as in other ways. None of these prior art methods have been truly satisfactory. Those methods with high accuracy and reliability take too long to yield the desired information. Techniques which produce an answer more rapidly, tend to be rather inaccurate.

One important approach to the problem of detecting the oncoming of an anode effect is outlined in an article by McMahon, T. K., and Dirth, G. P., "Computer Control of Aluminum Reduction Cells," *Journal of Metals*, Vol. 18, No. 3, pp. 317-319, March 1966. The approach outlined therein involves measuring the total voltage drop across the cell, from collector bar of one cell to collector bar of the next, computing the total cell resistance from this and noting when the resistance starts to rise rapidly. This signifies the oncoming of an anode effect and the anode effect termination procedure is then initiated and hopefully the occurrence of an anode effect is avoided.

This procedure, theoretically, is useful in avoiding anode effects and in controlling the alumina concentration, but the resistance curve produced by the measurements suggested by McMahon et al. is quite sensitive to noise or electrical interference in the circuitry and in the cell itself. This noise or interference can sometimes result in a short, sharp temporary rise in the resistance curve which is a false indication of the oncoming of an anode effect.

The instant invention was developed against this background in the art.

SUMMARY OF THE INVENTION

It is an advantage of the instant invention that it will minimize the effect of electrical and process noise and interference on the cell resistance curve. By smoothing the curve and screening out interference the possibility of a false signal

of an incipient anode effect is minimized. Accordingly, the system will be more accurate.

It is a further advantage of the instant invention that the alumina concentration can be maintained in a range known as "lean feed," hereinafter defined.

The feed is controlled for two purposes. One is to avoid anode effects and the other, desirably, is to maintain a substantially constant alumina concentration in the cell which results in improved efficiency of the reduction process. Several measurements of the voltage drop across the cell and the current to the cell are obtained. This is normally done by connecting a suitable voltage indicating instrument between the collector bars of one cell and the collector bars of the next or between the anode and the cathode bus bars of a cell and a suitable amperage indicating instrument in series with the power supply. A resistance for the cell is derived from these measurements according to the relationship:

$$R_M = V - AI \quad (i)$$

where R_M is the resistance in ohms,
 V is the normal voltage drop across the cell in volts,
 I is the current to the cell in amperes, and
 A is the back electromotive force in volts.

The resistance level R_B for the cell will be referred to as a base level. The resistance level for the cell desirably is periodically redetermined from fresh voltage measurements and the new resistance level is used as a base level if lower in value than the previous base level. A smoothed resistance R_S is derived from several sequential measurements of the voltage and current. Smoothing techniques are well known to those skilled in the art. This may be done mathematically by determining the trend in the voltage drop and hence the resistance from these measurements and projecting what the next measurement of the voltage and hence the next value of the resistance should be, or other appropriate smoothing techniques to reduce the effect of electrical noise and static may be employed. Hence, by "smoothed" is meant any such technique, mathematical, electrical, mechanical or any combination thereof. In practice a predictor form of smoothing technique has been found to be more desirable than simple averaging. A suitable smoothing technique which can be used as a prediction has been described by Box, G. E. P., and Jenkins G. N., "Some Statistical Aspects of Adaptive Optimization and control," *The Journal of The Royal Statistical Society, Series B (Methodological)*, pp. 297-343, Vol. 24, No. 2, 1962. When the smoothed resistance R_S exceeds the base resistance level by more than an assigned limit, a controlled amount of alumina is added to the cell. This normally lowers the resistance level R_B of the cell and the cycle of operations restarts.

The procedure of always using the lowest value of the resistance as a base level makes it possible to keep the control of the alumina concentration in the lean feed range. It has been found that the alumina concentration wherein the optimum efficiency of operation of the reduction cells, as measured by the current efficiency of the cells, occurs seems to be quite close to the level at which an anode effect occurs. When an anode effect occurs, the cell reaction is believed according to one theory to change from a decomposition of alumina to a decomposition of the aluminum fluoride in the bath. Thus, the alumina concentration should be maintained by this process above the value at which the decomposition voltage for aluminum fluoride seems to be attained, the aluminum fluoride reacting to form carbon tetrafluoride with the anode, but at the same time close to it. The precise alumina concentration at which the decomposition voltage for aluminum fluoride seems to be obtained will vary somewhat from cell to cell but should always be below about 4 percent by weight. Desirably, the alumina concentration should be maintained below about 3 percent by weight. More specifically, in the normal American reduction cell, the alumina concentration should be maintained from about 2 percent to about 3 percent by weight.

Should an adjustment in the anode-cathode distance to the desired operating level be necessary, this should be done before obtaining the voltage and current measurements so that the cell resistance curve can stabilize after the anode-cathode distance adjustment before the voltage and current measurements and the resistance level determination. From this it also follows that the anode-cathode distance should desirably be maintained constant while obtaining the voltage and current measurements.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic showing of a computer controlled potentiometer.

FIG. 2 is a typical graph of predicted resistance in micro ohms versus time illustrating the principles of the instant invention.

DETAILED DESCRIPTION

The article by McMahon and Dirth mentioned above discusses the control scheme for reduction cells which is based on measuring the total resistance across the cell. The basic relationships between resistance and feed concentration discussed therein are applicable in the following discussion.

The authors thought that there were three short term variables in the total resistance; the anode-cathode distance, specific bath resistivity, and resistance of the gas film surrounding the anode. The authors felt that both the bath resistance and the film resistance were affected by the alumina concentration. However, in reality, assuming constant anode-cathode distance, the cell resistance is then determined by what may properly be described as two factors. One of these is the bath or electrolyte resistance and the other is best characterized as the back electromotive force (EMF).

The back electromotive force is not properly a pure resistance in that it involves the decomposition potential for the reaction of the alumina and the cathode gas film polarization and the anode gas film polarization as well as some other small variables. The McMahon article assumed that the decomposition potential was a constant. In reality it is not. It has been discovered that the back electromotive force builds up constantly as the alumina concentration in the electrolyte decreases. Although the factors influencing it are not precisely known, the optimum value of back EMF, that is the value that optimizes cell productivity, seems to vary from cell to cell. One can determine the optimum value of back EMF for a cell by evaluating its efficiency at various back EMF levels.

One determines an average resistance level for the cell from several measurements of the voltage drop across the cell and the current to the cell as has been discussed previously. This average resistance for the cell is referred to as a base level. This operation and the other determinations and derivations involved in the instant process may be done manually, but the process is particularly adaptable to computerization. There are many process control computers available which can be used for this. One such computer is that known in the trade as a GE/PAC 40501. This computer is specifically designed for process control and real time operation. A typical computer of this type has a core size of 12,000 24-binary bit words. It has a memory cycle speed of 5 microseconds with no bulk memory. The inputs to the computer comprise three groups of 20 digital inputs, ten groups of 16 analog inputs, one paper tape reader with the capability of 100 characters per second, and one operator console. The outputs from the computer comprise eight groups of 16 digital outputs, one paper tape punch with a capacity of 120 characters per second, and two remote console output typewriters. Using the computer the entire operation can be done much more rapidly and values can be determined and used while still representative of the cell conditions.

The average resistance level for the cell is periodically redetermined from fresh voltage and current measurements, and the new average resistance level is used as a base level if

lower in value than the previous base level. It has also been mentioned previously that a smoothed resistance is derived from several sequential measurements of the voltage and current and when the smoothed resistance exceeds the base level resistance by more than an assigned limit a controlled amount of alumina is added to the cell to bring the concentration and resistance value back into the desired range.

It has recently been found the greatest current efficiency in a reduction cell seems to occur when the cell is operating on what may be called a "lean feed." A lean feed may be defined as a quantity of alumina in the bath just sufficient to prevent the cell from going on anode effect. While the operating characteristics of the cell, such as temperature, depth of electrolyte, anode-cathode spacing, etc., may affect this value, it can be expressed in terms of decomposition (polarization) potentials. Sufficient alumina is maintained in the cell to prevent the resistance in the cell from building up until the voltage reaches the value for the decomposition of the aluminum fluoride to form carbon tetrafluoride in a reaction with the carbonaceous anode. Thus the alumina concentration must be maintained above the value at which the decomposition voltage for aluminum fluoride is attained but close to it. The allowable differential for the smoothed resistance from the base resistance level can be used to do this. A useful upper limit on concentration would seem to be about 4 percent by weight. The utilization of the lowest value of the average resistance as a base level at all times will assure that the control is on the lean side of 4 percent alumina concentration in the bath by weight. A preferred upper limit would be about 3 percent by weight, and perhaps the optimum concentration would be from 2 percent to about 3 percent by weight. Since the smoothed resistance curve is sensitive to changes in alumina concentration quite close to the anode effect concentrations, it can be used to maintain the alumina concentration in these ranges.

With reference now to FIG. 1 which shows a computer controlled potline in schematic form, it may be seen that the cell comprises first a metal shell 10, generally steel, within which is disposed in the usual manner an insulating layer 12 which can be any desired material, e.g., alumina, bauxite, clay, aluminum silicate brick, etc. Within the insulating layer 12 is disposed cell lining 14 which can be of any desired material, e.g., carbon, alumina, fused alumina, silicon carbide, silicon nitrate bonded silicon carbide, or other desired materials. Most commonly, the lining is made up of a plurality of carbon blocks or is a rammed carbon mixture or a combination of a rammed carbon mixture for the bottom of the lining with side and end walls constructed of carbon. Alternatively, the side and end walls can be constructed of blocks of silicon carbide or other suitable refractory. The lining 14 defines a chamber which contains a pool of molten aluminum 16 and a body of molten electrolyte or bath 18 as described.

Suspended from above the electrolyte and partially immersed therein are anodes 20 of the conventional carbon type and shown here as a prebaked anode. The molten electrolyte 18 is covered by a crust 22 which consists essentially of frozen electrolyte constituents and additional alumina. As alumina is consumed in the electrolyte 18, the frozen crust is broken by a suitable crust breaker, not shown, and more alumina fed into the electrolyte by the opening of ore valve 24 which causes the alumina to be fed from the feed hopper 26. The anode is connected by anode bus bar 28 to the positive pole of a source of supply of electrolyzing current. For purposes of completing the electric circuit, use is made of cathodic current-conducting elements or collector bars 30. The collector bars 30 extend through suitable openings provided in the metal shell and insulation layer with the inner ends thereof projecting into the cell lining. The outer ends of the element are connected by suitable means to the other side of the supply line.

As shown in FIG. 1, the cells are connected in series over a suitable DC current-sensing device or transducer or ammeter (I) 34 to a suitable power supply, one side of the supply being fed to the anode system of the first cell and the cathode of the

first cell being in turn connected to the anode of the second cell, etc., the cathode of the last cell being connected to the other side of the supply line. One such sensing device is that known in the trade as the Dyn/Amp DC-metering system. The cells also include suitable means for raising and lowering anodes 20 such as an air motor controlled by solenoid valves 36, a suitable crust breaker device (not shown) for each cell and the alumina ore drop previously discussed with the ore valves being operated in a suitable manner such as air operated through solenoid valves. A suitable volt meter or DC voltage isolation amplifier 38 is connected between the anode and cathode of an associated cell to provide an indication of the voltage drop across the cell. A suitable computer 40 is connected into the system, or more desirably, to minimize wiring cost, selector relays 52 are connected between the computer and the system as shown in the figure. Also operably connected to the computer 40 are operator's panels 44, tape punch 46, tape reader 48 and typewriters 50.

The process control program (system) may be generally described as a plurality of functional programs and subprograms used for monitoring, supervising and optimizing potline control. In the process scanning program which is one embodiment is scheduled to run at predetermined time intervals, the computer sequentially samples the cell voltage of all cells in the potline as provided by the isolation amplifier 38 and the line amperage as provided by the current sensing device 34. The optimum back EMF value determined in a separate background program is used in the calculation by the computer of a smoothed resistance from several sequential measurements. A separate control program updates the base level resistance and looks for deviations of the smoothed resistance from the base level in excess of an assigned limit. If the computer, in its scan of the readouts, detects that the smoothed resistance differs from the base level by more than an assigned limit a special subprogram is entered immediately and control of the particular pot which is detected to be approaching the threshold is affected by signals from the computer over the crust breaker conductor to the detected cell to break the crust and signals over the "alumina ore drop" conductors to the ore valve 24 in the detected cell to increase the alumina concentration in the molten bath. The electrolysis in the cell then continues its normal course until the cell is once more detected as approaching the predetermined threshold.

Tests were run over a period of several months in a conventional prebake anode cell of the type shown in FIG. 1. This was a commercial size cell which was operated at a normal amperage in the neighborhood of 90,000 amps and at a normal voltage drop of about 4.5 volts. The value of back EMF which provided the optimum output was predetermined to be about 1.5 volts. FIG. 2 is a portion of the cell resistance graph produced during these tests. The voltage drop across the cell and the current to the cell were measured every 5 seconds and process values were smoothed over six such measurements. A computer of the type indicated above was used to do this. Since feeding alumina to the cell upsets the cell resistance and since it is desirable to set the cell resistance by controlling the voltage, 5 minutes were set aside after each feeding of alumina to the cell as a stabilizing period for the voltage and the resistance. This allowed the alumina fed to the cell to dissolve into the electrolyte and the voltage to be adjusted as necessary (A in FIG. 2). When the cell resistance had stabilized a smoothed resistance level was calculated for a 5 minute period. This long term smoothed resistance became the base level for control decision purposes (B in FIG. 2).

Although the cell resistance normally increases gradually from this point on, it might also decrease at first and rise again. If it has a tendency to decrease this indicates that more than 4 percent alumina by weight is dissolved in the electrolyte. Hence, it is desirable to consume this excess alumina in the reactions resulting in the production of aluminum. This has a further undesirable characteristic in that it tends to delay the anode effect warning period if the base or set point resistance level is not readjusted downward. To correct this situation, a

new smoothed resistance was recalculated every 5 minutes (C & D on FIG 2); and if its value was lower than the previous set point, it became the upgraded base level.

A smoothed resistance was calculated every 30 seconds using the six scan average resistance. This allowed smoothing of the random variations in the resistance curve and also made the detection of the critical point easier. The critical or control decision point (E in FIG. 2) was reached when the smoothed resistance curve exceeded the current base resistance level by more than an assigned limit. When this occurred, a controlled amount of additional alumina was fed to the cell and the cycle restarted. As can be seen in FIG. 2, the target resistance was approximately 30.2 micro ohms and the base resistance level was approximately 30.14 micro ohms. The assigned limit was 0.3 micro ohms.

With this setup the control decision point was reached when the alumina concentration had lowered to about 2 to 2½ percent and 1 percent of alumina was added so as to increase the concentration to about 3 to 3½ percent. At stable operation, a control decision point was usually reached every 20 to 25 minutes.

This process worked very well in practice. The average alumina concentration during the test period was 3.1 percent and the anode effect frequency was reduced drastically and excellent voltage control was achieved.

While there has been shown and described hereinabove, possible embodiments of this invention, it is to be understood that the invention is not limited thereto and that various changes, alterations, and modifications can be made thereto without departing from the spirit and scope thereof as defined in the appended claims wherein:

What is claimed is:

1. A method of controlling the feeding alumina to a reduction cell having an anode adjustably movable toward and away from the cathode comprising the following steps which are carried out over a predetermined cycle for the cell:

- a. periodically measuring the voltage and current of the cell throughout the cycle,
- b. determining the cell resistance R_M from the equation

$$R_M = V - A/I \text{ where}$$

V is the measured cell voltage

I is the measured cell current, and

A is a predetermined back electromotive force

- c. determining a lowest resistance level R_B by periodically determining a base level resistance R_B by a smoothing technique from a series of R_M values determined over a first interval of time,
- d. periodically determining a resistance R_S by a smoothing technique from a series of R_M values over a second interval of time,
- e. providing comparator means for automatically comparing the R_S value with the lowest preceding R_B value during said cycle, and
- f. feeding alumina to said cell in response to said comparator means when the difference between the R_S value and the lowest R_B value exceeds a predetermined limit.

2. The method of claim 1 wherein said first interval of time is greater than said second interval of time.

3. The method of claim 1 including the step of adjusting the distance between the anode and cathode following the addition of alumina to the cell.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,625,842 Dated December 7, 1971

Inventor(s) Donald R. Bristol and Joseph G. C. Simard

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

Column 3, line 48, "level by" should be -- level R_B by --; and
Column 3, line 50, "level R_B of" should be -- level of --.

Signed and sealed this 23rd day of May 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents