LITHIUM-MODIFIED LOW RATIO ELECTROLYTE CHEMISTRY FOR IMPROVED PERFORMANCE IN MODERN REDUCTION CELLS

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Abstract

Modern aluminum reduction plants with large prebake reduction cells use essentially the same electrolyte chemistry, a low ratio bath containing 10 to 12 wt.% excess AlF_3. Production results from modern reduction plants demonstrate that operating with low ratio bath contributes to a higher current efficiency, typically from 94 to 96%. Lithium is used as a bath additive to improve the performance, primarily in older cells, by increasing the electrical conductivity of the molten cryolitic bath and decreasing the bath operating temperature. Plant operational results were obtained using a combined lithium-modified low ratio (LMLR) bath in modern 180 kA prebake cells. The addition of lithium within a specific composition range was found to be beneficial in decreasing the cell voltage and unit energy consumption, and resulted in a significant improvement in the cell voltage stability. However, a decrease in current efficiencies was found to occur with the increase in LiF concentration, apparently as a consequence of the corresponding decrease in AlF_3 content. The impact of the combined LMLR bath composition on electrolyte properties and cell performance is discussed.

Introduction

The electrolyte, or bath, used in industrial reduction cells is composed primarily of molten cryolite, Na_3AlF_3, which has the unique property of having a higher solubility, necessary for electrolysis, for dissolving alumina than any other fluoride compound. Other compounds, including AlF_3, CaF_2, LiF, and MgF_2, are referred to as bath additives and are added to molten cryolite to modify the physico-chemical properties in order to improve the cell performance.

By convention, the ratio of the number of moles of NaF to the number of moles of AlF_3 in cryolitic bath is defined as the cryolite molar ratio and similarly, the ratio of the wt.%. NaF to wt.% AlF_3 is the cryolite weight ratio and is more commonly referred to as the cryolite ratio or bath ratio. Because the molecular weight of sodium fluoride is one-half that of aluminum fluoride, the cryolite weight ratio is half the molar ratio. The compound cryolite containing 3 moles of NaF, (60 wt.%), and 1 mole of AlF_3, (40 wt.%), is considered neutral. Bath containing excess AlF_3 has a bath ratio lower than 1.50 and is referred to as acid bath; conversely, bath containing excess sodium fluoride has a bath ratio higher than 1.50 and is referred to as basic bath.

For cryolite:

$$\text{Cryolite Molar Ratio} = \frac{3 \text{ moles NaF}}{1 \text{ mole } AlF_3} = 3.00$$

$$\text{Cryolite Weight Ratio} = 1/2 \text{ Molar Ratio} = 1.50$$

$$\text{Cryolite Weight Ratio} = \frac{60 \text{ wt.\% NaF}}{40 \text{ wt.\% } AlF_3} = 1.50$$

Aluminum Fluoride, AlF_3, is the most commonly used bath additive in industrial reduction cells; it is considered to be a Lewis acid as it increases the acidity of cryolitic bath. AlF_3 has a direct beneficial impact on improving current efficiency in reduction cells by 1) reducing the solubility of metals dissolved in the electrolyte in equilibrium with the metal pad, 2) lowering the liquidus temperature of the cryolitic bath and consequently the bath temperature, and 3) lowering the bath density. AlF_3 has the undesirable effects of decreasing the electrical conductivity and alumina solubility of the bath.

Calcium fluoride, CaF_2, is maintained at a nominal 4-7% level in industrial baths primarily as a result of impurity in the alumina from the Bayer Process. In this range, it has the beneficial effect of lowering the freezing point of the cryolitic bath by about 12-20 degrees (1).

Other materials, such as lithium fluoride, LiF, and magnesium fluoride, MgF_2, are also used as additives for cryolitic bath in some cells, but normally only in baths containing less than 7% excess AlF_3. Combined lithium-modified low ratio bath compositions have previously been investigated, but largely as a means to achieve low temperature operations, < 900°C, in reduction cells (2,3).

Comparison of Electrolytes Used In Modern and Older-Technology Reduction Cells

Modern potlines having low anode current density, typically 0.8 A/cm², prebake reduction cells operate from 180 kA to over 300 kA with high current efficiencies, 94-96%, and low specific energy consumption, < 14 KWH/kg aluminum (4-10). These large, modern reduction cells operate efficiently because of the improvements made in the magnetic design of the electrical conductor bus components; application of state-of-the-arts hardware and software computer systems for the control and management of cell operations with alumina point feeder systems; and operating with a low ratio or high excess AlF_3 electrolyte chemistry.

Modern cells, and also most modernized prebake cells, operate with essentially the same electrolyte chemistry, a low ratio bath containing from 10 to 12% AlF_3 and 3.5-6% CaF_2. According to Wang and Peterson, an increase in current efficiency is achieved with bath containing higher excess AlF_3 due to the reduction in the equilibrium dissolution of sodium, aluminum, lithium, etc., from the liquid cathode (11,12). Consequently, the decrease in the dissolved metal species in the electrolyte results in a reduction in the reoxidation, or back reaction, between dissolved metal and anode gas, CO_2, in the electrolyte region.

To ensure good performance, reduction cells that operate with a high level of excess AlF_3 in the molten electrolyte require careful feeding of alumina with point feeders in a controlled manner and close monitoring of the cell's operational parameters, particularly the instability, by means of modern, computer systems using sophisticated software control algorithms.

Generally, the older and higher anode current density, reduction cells without these more sophisticated control systems are limited to operating with only 3 to 7% excess AlF_3 because of the difficulties encountered with 1) alumina sludging and 2) operating using too close of an a-c distance due to the higher bath resistance associated from the higher AlF_3 content. Accordingly, the metal productivity in the older-design cells is lower, in the range from 88 to 93% current efficiency.

Cell operational difficulties commonly encountered with reduction cells operating with a high excess AlF_3 content in the bath include:

- The bath operating temperature is often higher, and more variable, than desired due to rapid changes in the AlF_3 content of the electrolyte. The excess AlF_3 content in the electrolyte can change rapidly due to the sharp inflection in the phase equilibria in this high AlF_3 region.

- Higher levels of AlF_3 cause a significant decrease in the electrical conductivity of the electrolyte resulting in an increased bath voltage drop. Modern prebake cells compensate for the lower bath conductivity by using very large anodes that significantly reduce the anode current density, thus reducing both the anode overvoltage and bath voltage drop.

- Operating with high excess AlF_3 causes a very high cryolitic bath vapor pressure that, in turn, results in high fluoride emissions from cells. Modern fume recovery systems are essential for the capture and recycling of the fluorides in modern reduction plants.

Impact Of Lithium And Magnesium On Ratio Analysis

Cryolite ratio and bath ratio are terms reflecting the acid-base condition of the cryolite-AlF_3 electrolyte system used in industrial reduction cells. The acidity/basicity of bath ratio is affected by the addition of some alkali fluorides additives (13), as shown in Figure 1:

- Lithium fluoride behaves like sodium fluoride, (a Lewis base) when added to cryolite and will tend to increase the basicity of the bath and increase the bath ratio.

- Magnesium fluoride behaves as aluminum fluoride (a Lewis acid) when added to cryolite and will tend to increase the acidity of bath and decrease bath ratio.

- Calcium fluoride is a neutral additive in most cryolitic baths.

For simplification, cryolite ratio in this context is used to refer strictly to the ratio of NaF/AlF_3 for cryolitic baths not containing lithium and/or magnesium additives, except in trace amounts.

Equivalent weight ratio and bath ratio are terms used which better describes the impact of lithium and magnesium additives on the acid-base conditions of electrolytes. Cryolite ratio is numerically identical to the equivalent weight ratio for electrolytes not containing lithium or magnesium additives, but the ratios are not equal when lithium or magnesium additives are present.

Collectively, LiF and MgF_2 have empirically been found to affect equivalent weight ratio (or bath ratio) according to the following equation:

Equivalent Weight Ratio (EWR) =

$$1/2 \frac{(\% \text{ NaF} / 41.9882) - (\% \text{ MgF}_2 / 62.3088) + (\% \text{ LiF} / 25.9374)}{(\% \text{ AlF}_3 / 83.9767)}$$

The ratio, and excess AlF_3, of industrial electrolytes is determined in the analytical laboratory by either chemical or physical methods. It is generally accepted that alumina and CaF_2 do not interfere with the analysis by these methods.

Ratio values determined from the complete elemental analysis of all bath components are identical to the cryolite ratio, including baths containing lithium and/or magnesium additives, and should be used for ratio calibration standards.
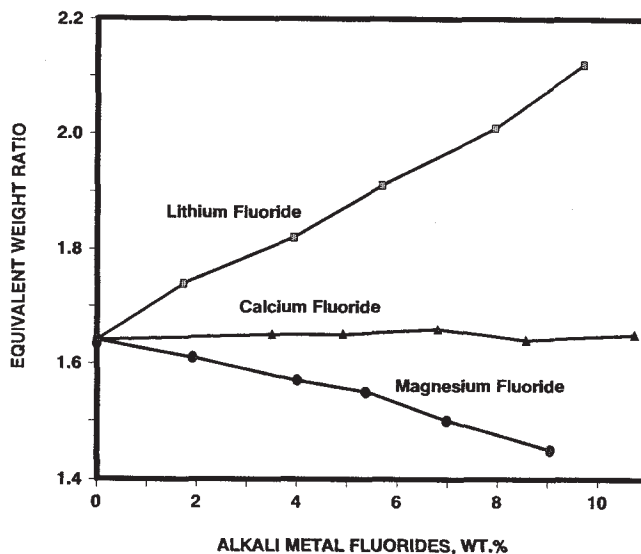

Figure 1: Addition of Alkali Metal Fluorides to Cryolitic Bath.

However, the values obtained for ratio measured by the various laboratory methods, (pH method, pyrotitration and thorium nitrate titration), are directly influenced by the addition of lithium or magnesium additives. Lithium and magnesium have a detrimental impact on the ability to determine the excess AlF_3 content in bath by the X-ray diffraction method because in addition to calcium it is necessary to measure the concentration of lithium and magnesium compounds in bath samples. In addition, calibration standards are generally obtained from electrolytes not containing lithium or magnesium additives. Therefore, it is very difficult, but not impossible, to use the X-ray diffraction method to determine the excess AlF_3 content and, therefore, the ratio of LMLR baths.

It is important to note at this point that the AlF_3 content, or ratio, in the bath of reduction cells is controlled to specific setpoints by frequent analysis and corrective additions of AlF_3 on a routine basis. Thus, the short term impact of lithium and magnesium additions on changing the acid-base condition of bath is corrected in operating reduction cells.

Previous Lithium-Modified Low Ratio Bath Plant Tests

Longon and Verin reported the first plant results for modern industrial cells operating with a combination of lithium-modified low ratio (LMLR) bath chemistry, shown in Table I (9). One Pechiney 280 kA cell was operated with various lithium levels and amperages during a nine-month test.

Table I Performance Of A Modern 280 kA Cell Using Lithium-Modified Baths

	LMLR Bath (1)	LMLR Bath (2)	LMLR Bath (3)	Low Ratio Bath (Ref.)
LiF, %	2.6	3.0	2.1	0.4
Excess AlF_3, %	7.7	9.5	12.5	12.5
Temperature, °C	953	942	937	952
Current Eff., %	91.9	94.1	95.1	95.8
Amperage, kA	281.0	284.3	285.6	281.7
kg/PD	2,080	2,156	2,186	2,174
Cell Voltage, V	4.11	4.13	4.16	4.13
KWH/MT Al	13.320	13.060	13.030	12.840

These results demonstrated the following trends for the 280 kA prebake cell operating at higher amperages with lithium modified baths compared with operating with conventional low ratio bath chemistry.

- The cell was operated at a 3-4 kA higher amperage with 2 and 3% LiF-modified baths compared with operating with low ratio bath, but at essentially the same cell voltage, 4.13 V.

- Bath temperatures were 10 to 15 degrees lower for the cell operating with 2 and 3% LiF-modified baths 2 and 3, compared with operating with low ratio bath at 952°C.

- Excess AlF_3 content was 3-4.8% lower for the cell operating with 2.6-3% LiF-modified baths 1 and 2, compared with operating with low ratio bath containing 12.5% AlF_3.

- Current efficiency was determined to be 1.7 to 3.9% lower when operating with 2.6-3% LiF-modified baths 1 and 2, compared with 95.8% operating with low ratio bath.

- Unit energy consumption was 0.22-0.45 DC KWH/MT higher for the cell operating with 2.6-3% LiF-modified baths 1 and 2, compared with 12.84 DC KWH/MT operating with low ratio bath.

It is evident from these plant test results using 2.1-3.0% LiF-modified baths in large modern 280 kA prebake cells that there was a significance decrease in the current efficiency, 1.7-3.9%, even when operating with 10-15°C lower bath temperatures. However, it should be noted that there was a corresponding 3-4.8% decrease in the AlF_3 content in these lithium modified baths compared with operating with low ratio bath.

It was concluded that the addition of lithium to these modern reduction cells could not be technically or economically justified since current efficiency exceeding 95% could be achieved without it. No comments were made regarding the operational conditions of the lithium modified cells.

Current LiF-Modified Low Ratio (LMLR) Bath Plant Tests

The electrolyte of a group of Pechiney 180 kA prebake reduction cells was modified by the introduction of 2% and 3% LiF. The results obtained from these cells was compared with results obtained when a potline of the 180 kA cells was operated for one year with conventional low ratio bath and then operated one year with a 1% LiF-modified low ratio bath.

Projected Performance

The purpose of the tests was to evaluate the changes in the specific energy consumption and technical performance of modern 180 kA prebake reduction cells operating with LMLR baths. The original projected performance targets for cells operating with 3% LiF, $MgF_2 + CaF_2 = 7.0\%$, and 1.40 bath ratio were:

Bath Temperature	=	944°C
Cell Resistance	=	12.60 μ-ohm
Cell Voltage	=	4.05
Specific Energy Consumption	=	12.806 DC KWH/kg Al

The actual average electrolyte compositions determined for the different test periods when operating with lithium modified baths and conventional low ratio bath are shown in Table II.

Table II Bath Chemistry Composition For Low Ratio Bath And LiF-Modified Baths Tests

	Low Ratio	1% LiF LMLR	2% LiF Bath	3% LiF Bath
Bath Ratio	1.15	1.19	1.31	1.36
Excess AlF_3, %	10.9	9.4	5.5	4.0
CaF_2, %	4.5	4.2	3.9	3.8
LiF, %	0.3	1.0	2.2	3.2
MgF_2, %	0.3	1.0	2.6	2.6

To maintain the bath temperature as nearly constant as possible when increasing the lithium content of the bath it was necessary to decrease the corresponding AlF_3 content of the bath. MgF_2 was added to adjust the freezing point and, thus, the bath temperature to the desired target.

The major differences in composition between the low ratio bath and lithium-modified baths other than the different levels of lithium were:

- Cells operating with lithium-modified bath had 1.5 to 6.9% lower AlF_3 content than the cells operating with conventional low ratio bath.

- The lithium-modified bath also contained from 1 to 2.6% MgF_2 in the electrolyte.

The physico-chemical properties calculated for conventional low ratio bath and the lithium-modified compositions are shown in Table III.

Table III Physico-Chemical Properties Of Low Ratio Bath
And LiF-Modified Baths

Electrolyte Properties	Low Ratio	1% LiF LMLR	2% LiF Bath	3% LiF Bath
Bath Operating Temperature, °C	956	958	953	947
Freezing Point, °C	954	948	938	937
Bath Superheat, °C	2	10	15	10
Density, g/cm	2.1213	2.1236	2.1359	2.1436
Electrical Conductivity, ohm-cm⁻¹.	2.1251	2.1809	2.2767	2.3499
Alumina Solubility, wt.%	6.2	6.2	6.0	5.6
Bath Vapor Pressure, torr	4.1	3.7	2.5	2.0
Equilibrium Metal Solubility, wt.%	0.320	0.327	0.359	0.367

Major changes in the physico-chemical properties determined for the 3% lithium-modified bath compared with low ratio bath include:

- 17°C decrease in bath freezing point, 954 to 937°C.
- 9°C decrease in bath temperature, from 956 to 947°C.
- 8°C increase in bath superheat, from 2 to 10 °C.
- 1.1% increase in bath density, from 2.1213 to 2.1436 g/cm³.
- 10.6% increase in the electrical conductivity, from 2.1251 to 2.3499 ohm-cm⁻¹.
- 9.7% decrease in maximum alumina solubility, from 6.2 to 5.6%.
- 51.2% decrease in bath vapor pressure, from 4.1 to 2.0 torr.
- 14.7% increase in metal solubility, from 0.320 to 0.367%.

The average materials consumption for the prebake cells operated with low ratio and 1% LiF-modified bath for the 12-month periods are shown in Table IV.

Table IV Materials Consumption For Low Ratio Bath
And LiF-Modified Baths

	Low Ratio	1% LiF LMLR	2% LiF Bath	3% LiF Bath
kg Fluoride/ kg Al	0.137	0.123	-	-
kg Cryolite/ kg Al	0.0010	0.0002	-	-
kg AlF₃/ kg Al	0.0230	0.0216	-	-
kg Li₂CO₃/ kg Al	0	0.0005	-	-
kg Net Carbon/ kg Al	0.400	0.405	-	-
kg Bath Tapped/PD	161	105	-	-
Metal Impurities Iron, %	0.15	0.14	-	-
Silicon, %	0.037	0.030	-	-

The major differences between the materials consumption for the one year test with 1% LiF compared with conventional low ratio bath include:

- 10.2% lower fluorine consumption
- 80% lower cryolite consumption
- 6.1% lower aluminum fluoride consumption
- 0.0005 kg Li_2CO_3/kg Al consumption
- Slightly higher carbon consumption
- Slightly lower iron and silicon impurities

Table V Performance Data For Low Ratio Bath
And LiF-Modified Baths

	Low Ratio	1% LiF LMLR	2% LiF Bath	3% LiF Bath
Months	12	12	5	3
Number Cells	240	240	18	18
Amperage, kA	181.1	181.6	180.3	179.3
Resistance, μ-ohm	14.14	13.82	12.95	13.14
Current Eff., %	94.47	94.15	93.24	91.96
Volts/Cell	4.210	4.160	3.984	4.006
KWH/kg Al DC	13.28	13.15	12.75	12.99
Instability, μ-ohm	> 0.20	0.14	0.15	0.14
Anode Effects/PD	0.15	0.18	0.23	0.22
Cathode Drop, V	0.430	0.440	0.426	0.417
Bath Tap, kg/PD	159	94	11	62

The technical results for the prebake cells operated with low ratio bath and 1%, 2% and 3% LiF-modified baths are shown in Table V. The major differences between the performance for the tests with LiF-modified bath and conventional low ratio bath include:

- Reduction in the cell voltage; -0.050 V (1% LiF); -0.226 V (2% LiF); and -0.204 V (3% LiF).

- Decrease in the cell energy consumption, -0.15 DC KWH/kg Al (1% LiF); -0.53 DC KWH/kg Al (2% LiF); and -0.29 DC KWH/kg Al (3% LiF).

- Decrease in metal production with 1 to 3% increase in LiF content and 1.5 to 6.9% decrease in the AlF_3 content, -0.32% (1% LiF); -1.23% (2% LiF); and -2.51% (3% LiF).

- Improvement in the cell stability; voltage instability factor decreased from > 0.2 to 0.144 μ-ohm.

- Increase in the anode effect frequency.

- Increase in the cathode drop, +0.009 to 0.027 V.

The combined results from the previous tests (Longon and Varin) and the current tests of lithium-modified low ratio baths shown in Figure 2 demonstrates the relationship between the decrease in current efficiency with the decrease in AlF_3 content, with LiF-modified baths.

The excess AlF_3 content in bath from cells operating with low ratio bath and 1% LiF-modified bath was determined by the x-ray diffraction method, but the pH titration method had to be used to determine the acidity of 2% and 3% LiF-modified baths.

Cell Operational Conditions

When operating with 3% LiF the pot tending operation, (anode setting, tapping, broken clads, etc.), became more difficult due to the harder and thicker crust experienced with the lower temperature operation.

Point feeder holes were often blocked by crust formation on the bath surface. The frequency of verifying and breaking open closed feeder holes had to be increased.

Because the bath crust was effectively sealed except for the point feeder holes, alumina dropped from the feeders was blown away onto the anodes by the pot gases and the anode effect frequency increased. When the ratio was lowered to 1.30 or lower, the crusts soften and operational conditions improved.

1% LiF-Modified Low Ratio Bath

A proprietary 1% LiF-modified low ratio bath composition was developed which tends to optimize the beneficial aspects, while minimizing the detrimental aspects, of a combined lithium-high excess AlF_3 bath composition (14). The technical results for the 12-month test for a potline of modern 180 kA prebake cells operating with LMLR bath compared with conventional low ratio bath, shown in Table V, indicate the following features:

- A reduction in the average cell voltage, from 4.210 V to 4.160 V.

- A reduction in the specific energy consumption, from 13.28 to 13.215 DC KWH/kg Al.

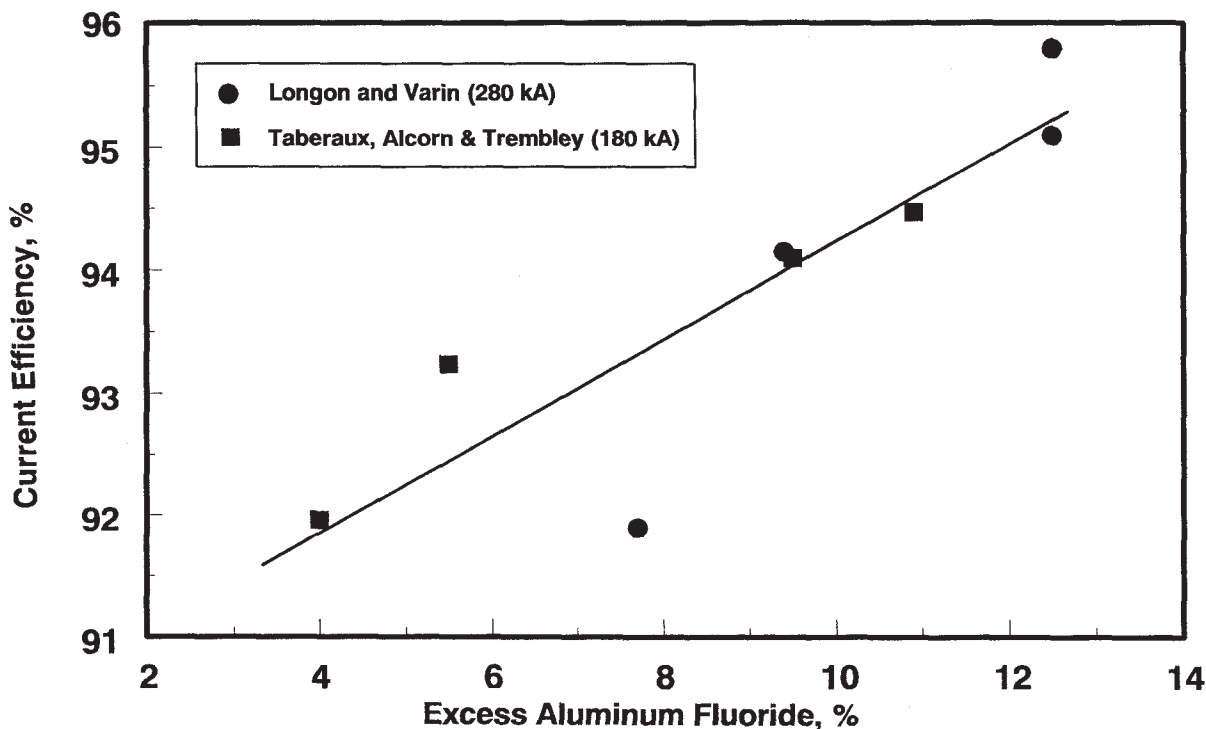- Only a small reduction in current efficiency, from 94.47 to 94.15%.

Figure 2: Change in the Current Efficiency with Aluminum Fluoride Content in the Lithium-Modified Bath Tests.

- An improvement in the cell voltage instability factor.

- A significant decrease in the bath tapped from cells, from 161 to less than 100 kg.

- A reduction in the fluoride and AlF_3 consumption.

- No significant change in cell operation conditions, for example, crust hardness, muck, cathode drop, anode effect frequency, etc.

The test proved to provide sufficient technical and economical advantages that the potline of 180 kA cells has continued to operate with 1% LiF-modified bath.

Conclusions

Lithium-modified baths can be used in modern reduction cells to provide an alternative choice for improving the operational performance depending upon the individual circumstances prevailing for individual plants; for example, the specific energy consumption can be substantially reduced during periods of increased power costs, increased resistance in cell due to material or operating conditions, increased amperage, etc., or when metal production is not the major factor.

A substantial reduction in the specific energy can be achieved when operating with 2-3% LiF content; however, the current efficiency decreased with the corresponding decrease in AlF_3 content, and operational difficulties (anode effects, mucking, cathode drops, and stopping-up of feeder holes) increased due mainly to the increase in the hardness and thickness of the crust at the lower operating bath temperatures.

A 1% LiF-modified low ratio bath composition was developed which tends to optimize the beneficial aspects, (reduction in energy consumption, improvement in stability, reduction in AlF_3 consumption, and reduction in bath tapped), while minimizing the negative aspects, (reduction in current efficiency and increase in cell operational difficulties), of a lithium-low modified bath composition.

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