

APPRAISAL OF THE OPERATION OF HORIZONTAL-STUD  
CELLS WITH THE ADDITION OF LITHIUM FLUORIDE

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Abstract

The addition of lithium fluoride to normal Hall-Heroult electrolyte (hereafter referred to as lithium electrolyte) effectively reduces the freezing point and improves the electrical conductivity of the electrolyte. Operating procedure for this process, that is, adding lithium fluoride to horizontal stud cells, at an industrial-scale operation, while intensifying current from 55KA to 60KA, is described. Analyses of lithium electrolyte and heat flow determined the optimum operating conditions for such cells. Possible decrease in fluoride emission due to lower operating temperature is also referred.

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INTRODUCTION

As the consequence of recent increasing trend in the demand for aluminum in Japan, Nippon Light Metal Company has faced the problem of increasing production while utilizing existing facilities. In order to increase production, one must

1. increase the number of operating cells,
2. intensify current,
3. improve current efficiency and/or
4. improve electrolyte composition by adding compounds, such as LiF.

In our Kambara Works, since the total line voltage has almost reached its capacity, it was natural for us to turn our attention to the lattermost means.

For the past several years, fundamental experiments on lithium electrolyte were conducted at both Research Laboratory and the Works. We were assured of the possibility of increasing current for such cells from the data of these experiments. While considering operating conditions, capacity of power facilities and availability of raw materials, 10 percent increase in current was determined to be most economically efficient. Since then, lithium electrolyte replaced the normal electrolyte in one line of horizontal stud cells (55KA) of the Works. Conditions of this line were stable and such satisfactory result was obtained in a short period after addition.

OPERATION OF LITHIUM ELECTROLYTE CELL WITH INTENSIFIED CURRENT

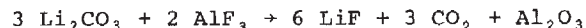
1. Procedure

a) Preparation

A month before charging  $\text{Li}_2\text{CO}_3$  into cells, sludge was removed from each cell; electrolyte composition (C.R., percentage of  $\text{CaF}_2$ ) and electrolyte and metal quantities were controlled.

b) Initial charge of  $\text{Li}_2\text{CO}_3$  to completion of current intensification

The relationship of charged  $\text{Li}_2\text{CO}_3$  to current intensification is shown in Figure 1. Economical  $\text{Li}_2\text{CO}_3$  was used to give LiF according to the following equation.



c) Transient stage to stable state of operation

High viscosity of electrolyte, sludge and anode troubles were noticeable from early stage of charging. Such resulted in increased number of sick cells, with raised or flickering voltages. Sludge in these cells were removed by controlling voltage and metal depth, adjusting C.R. and withholding  $\text{Al}_2\text{O}_3$  charge. While observing the side freeze contour, concentration of LiF was reduced from 5% to 4.5%. Thus, the number of sick cells decreased and the cells were in stable operation in one to two months after charging  $\text{Li}_2\text{CO}_3$ .

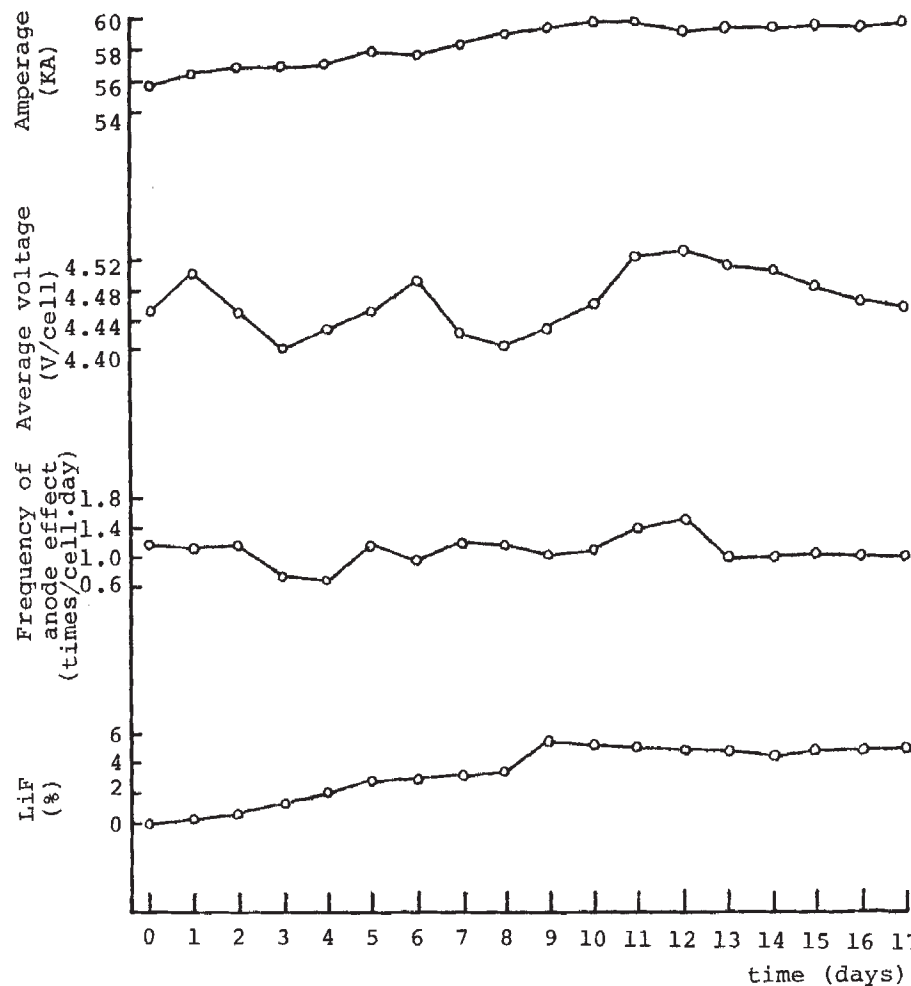


Fig.1. Variations in operating factors at the early stage of  $\text{Li}_2\text{CO}_3$  charging and intensifying current

2. Results

Table I shows differences in operating conditions of lithium electrolyte cells to that of normal electrolyte cells. Its contents are digested below.

- a) Lithium electrolyte cells were operated at approximately 10% higher amperage than normal cells. Average voltage was 0.05 V higher.

In Table II, the breakdown of cell voltage of normal Hall electrolyte and lithium electrolyte are compared.

Proportionate increases in voltage drops at bus bar, between anode bus bar and stud, and at anode are considered.

Lining resistance decreased by 9% when current was intensified. From experience, this is equivalent to 4 - 6 cm retreat of tip of bottom freeze.

Specific electrical conductivity of normal electrolyte is  $1.97 \text{ ohm}^{-1}\text{cm}^{-1}$ ; of lithium electrolyte,  $2.14 \text{ ohm}^{-1}\text{cm}^{-1}$ . This means that electrical conductivity improved by 8.5%. Consequently, anode-cathode distance is estimated to be 35.8 mm in normal electrolyte; 34.6 mm in lithium electrolyte. ACD decreased by 1 - 2 mm.

- b) Since current efficiency remained constant, production increased by approximately 10%. Accordingly, lithium electrolyte cell, though amperage was increased, maintained same current efficiency by decreasing bath temperature. This current efficiency agrees with that measured by radioactive isotope.
- c) Unit power consumption increased slightly.

Table I. Operation results of normal Hall cell and LiF cell at steady operation

	Normal Hall Cell (Average over) ( 12 months )	LiF Cell (Average over) ( 8 months )	Difference
Average amperage	54.6	59.9	+5.3
Average voltage	4.42	4.47	+0.05
Production	397.8	436.4	+38.6
Current efficiency	90.5	90.5	0
Unit consumption			
Power	KWH/ton Al	14,726	+157
Cryolite	Kg/ton Al	19.0	-4.5
AlF <sub>3</sub>	Kg/ton Al	23.5	-6.5
Anode	Kg/ton Al	528	-12
Li <sub>2</sub> CO <sub>3</sub>	Kg/ton Al	5.5	-
LiF	%	4.3	-
Cryolite ratio	%	1.43	+0.04
CaF <sub>2</sub>	%	5.0	0
Fe in metal	%	0.09	0
Si in metal	%	0.03	0
Li in metal	%	0.0033	-
Lining drop	V	0.39	0
Anode effect	times/cell·day	1.32	+0.49
Bath temperature	°C	953	-15
Freezing point	°C	927	-29
Free Al <sub>2</sub> O <sub>3</sub> in bath	%	4.2	-0.8

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Table II. Breakdown of cell voltage for normal Hall cell and LiF cell

	(unit: V)	
	<u>Normal Hall Cell</u> (54.7 KA)	<u>LiF Cell</u> (60.0 KA)
Bus bar and stud	0.197	0.213
Anode	0.525	0.575
Electrolyte	1.431	1.382
Lining drop	0.390	0.390
Decomposition, Overvoltage	1.700	1.700
Anode effect	0.120	0.140
Rack raizing	0.060	0.070
	<hr/>	<hr/>
Total	4.420	4.470

d) Unit consumptions of cryolite,  $AlF_3$  and anode carbon improved.

Amount of dust carbon in lithium electrolyte, however, was greater than that of normal electrolyte.

e) Unit consumption of  $Li_2CO_3$  was approximately 5.5 Kg/ton Al.

f) Optimum bath composition is: 4.3% LiF; 1.43 C.R.; and 5%  $CaF_2$ .

g) Fe and Si contents in molten metal are same as those of normal electrolyte. Li content is approximately 33 ppm, just after tapping, but Li forms an oxide with the atmosphere in the course of holding and this decreases the content to several ppm.

h) Frequency of anode effect increased.

Due to the decreases in bath temperature and solubility of alumina, the number of anode effect increased slightly and anode effect voltage increased.

i) While freezing point of lithium electrolyte dropped by  $30^\circ C$ , intensification of current modified this value to  $15^\circ C$ .

j) Concentration of  $Al_2O_3$ , measured between feedings, is slightly less in lithium electrolyte.

### 3. Determination of optimum operating conditions

Ready analysis of lithium electrolyte composition and close investigation of heat flow, along with careful scheduling and skillful operating, were essential for determining the optimum operating conditions.

#### a) Analysis of lithium electrolyte

X-Ray diffractometer and fluorescent analyser have been used to analyse the composition of normal electrolyte. For the lithium electrolyte, X-ray diffraction is used.

In principle, cryolite ratio and the variation of  $\text{Na}_2\text{LiAlF}_6$ ,  $\text{LiF}$  and  $\text{CaF}_2$  are correlated. Two ratios,

$$\frac{\text{NaF}}{\text{AlF}_3} \text{ (C.R.) and } \frac{(\text{NaF} + 42/26 \text{ LiF})}{\text{AlF}_3} \text{ (L.C.R.),}$$

are taken into consideration and their relationship can be expressed as:  $\text{C.R.} = \text{L.C.R.} - K(\text{LiF})$  where  $K$  is a constant (usually 0.045).

Estimation of  $\text{LiF}$  concentration can be obtained from the relationship of C.R. and L.C.R. which in turn are measured from intensities of  $\text{Na}_2\text{LiAlF}_6$  and  $\text{LiF}$ .

The equipments were specifically designed to measure cryolite ratio and are able to automatically type out intensities in digital values.

Accurate  $\text{LiF}$  concentration is directly measured by exposing powdered sample to quantometer.

#### b) Investigation of heat flow

By closely studying heat flow and estimating side freeze contour of lithium electrolyte cells, the optimum operating conditions were decided. For different situations that could be assumed to be caused by current intensification, freezing temperature of electrolyte, bath temperature and heat flow were calculated by relaxation technique. In another words, thickness of freeze, amount of heat transfer and temperature distribution were obtained from inputting condition of freeze, heat generation inside cell, ambient temperature, heat transfer coefficient of exterior surfaces of cell, heat conductivity and cell dimensions into computer.

When the current was intensified from 55KA to 60KA in cells with 4.3%  $\text{LiF}$  electrolyte, electrical conductivity improved by 8.5% and the difference between freezing and bath temperatures increased from  $12^\circ\text{C}$  to  $26^\circ\text{C}$ . The results of analysis of heat flow and comparisons of estimated freeze contour in these conditional differences are given in Table III and Figure 2, respectively

Under the conditions listed in Table III, by intensifying the current of lithium electrolyte cell, the bottom freeze somewhat retreats due to greater difference between freezing and bath temperature than that of normal electrolyte and increase in heat transfer from metal and electrolyte to cathode. The heat generated in cathode from the intensification is thought to increase proportionately to the square of amperage but the retreat of freeze withhold the increase in heat generation inside of cathode. Therefore, the heat generated in cathode decrease by 2.7 KW. Consequently, total heat

loss from cathode becomes 5.8 KW, which is equivalent to the increase in heat transfer from metal and electrolyte and the decrease in heat generation in cathode.

4. Effect on fluoride emission

The decreases of bath temperature and vapor pressure lead to the possibility of decrease in emission of fluorides. The percentage decrease in HF gas emission was detected to be in the range of 20 to 30 percent. This outcome corresponds to the result of improvement in consumption of fluorides.

CONCLUSION

1. Optimum operating conditions of a lithium electrolyte cell with intensified current were set and bath composition of this electrolyte is: 4.0 - 4.5% LiF; 1.40 - 1.45 C.R.; 5% CaF<sub>2</sub>.
2. Current efficiency remained unchanged and is 90.5%.
3. Electrical conductivity increased by 8.5% by adding Li.
4. Unit consumption of Li<sub>2</sub>CO<sub>3</sub> at steady operation is 5 - 6 Kg/ton Al.
5. Bath temperature decreased by 15°C. Consequently, unit consumptions of anode carbon and AlF<sub>3</sub> decreased; emission of HF gas was reduced by 20 - 30%.

Table III. The analysis of heat flow in normal Hall cell and LiF cell

		<u>Normal Hall Cell</u>	<u>LiF Cell</u>
Bath temperature (T <sub>B</sub> )	°C	970	955
Metal temperature (T <sub>M</sub> )	°C	965	950
Freezing point (T <sub>F</sub> )	°C	955	930
Amperage	KA	55	60
Heat output			
Total	KW	77.3	83.1
	ratio	1.0	1.08
Deck plate	KW	6.6	8.0
Shell side	KW	22.3	24.8
Shell bottom	KW	31.8	32.2
Collector bar	KW	16.6	18.0
Heat input			
Total from fluids	KW	48.7	57.2
	ratio	1.0	1.174
From bath	KW	8.3	13.1
From metal	KW	40.4	44.1
Joule heat			
Total	KW	28.6	25.9
Cathode	KW	25.5	22.2
Collector bar	KW	3.1	3.7

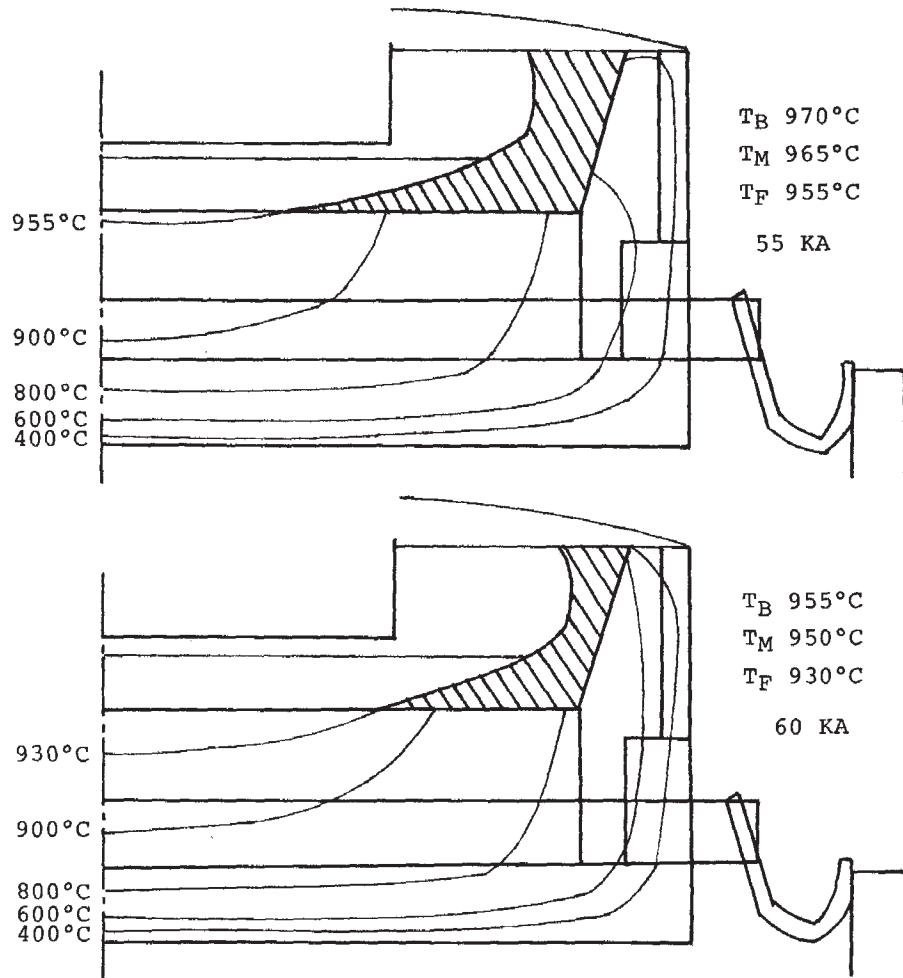


Fig.2. Comparison of estimated freeze contour between normal Hall cell and LiF cell