Impact of Lithium Fluoride on Fluoride Evolution from Aluminium Electrolytic Cells in Maaden

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https://doi.org/10.71659/icsoba2025-al056

Abstract

The impact of lithium modified baths in electrolytic cells has been widely studied in the past, which provides a lot of guidance on the impact and extent in the electrolytic process. However, there is very limited information available from smelters operating with lithium fluoride in the bath at an amperage as high as 410 kA. Maaden is an integrated aluminium complex completely depending upon the alumina produced from its own bauxite supplied by mines located at Al-Baitha, Kingdom of Saudi Arabia. Bauxite in Maaden contains traces of lithium, which finds its way to the bath in the smelter through smelter grade alumina (SGA). The tendency of lithium to accumulate in the bath has been clearly witnessed with an increase in lithium fluoride content in the bath in the smelter. This paper is summarizing all the information available so far about the behavior of lithium modified baths on bath properties and fluoride emissions and describes our actual experience over ten years of gradual increase in LiF concentration and its impact on fluoride evolution from electrolytic cells and from Gas Treatment Centre (GTC) stacks as well.

Keywords: Aluminium electrolytic cells, Lithium fluoride (LiF), Fluoride evolution, Electrolyte.

1. Introduction

Maaden, The Saudi Arabian Mining Company is the largest fully integrated aluminium complex in Ras Al-Khair, Kingdom of Saudi Arabia, and consists of bauxite mines, an alumina refinery, an aluminium smelter and a rolling mill. The aluminium smelter commenced operation on 12 December 2012 with 720 AP37 technology reduction pots in two lines, operating at 370 kA. The potlines were upgraded with Alcoa center of excellence (ACE) 410 kA package from 2019 to increase amperage to 410 kA and gradually increasing the production to 805 kt Al/y.

Maaden Aluminum smelter was fully commissioned, and all 720 pots were in operation by July 2014 at an amperage of 370 kA, sourcing smelter grade alumina (SGA) from different locations worldwide, while the Maaden alumina refinery was still under commissioning phase. The production in the refinery started in January 2015 with calciner-1 and brought to full production by November 2016. The aluminum smelter was slowly transitioning from imported to Maaden alumina and from December 2016 Maaden became self-dependent for alumina requirement and thereby eliminating the imports.

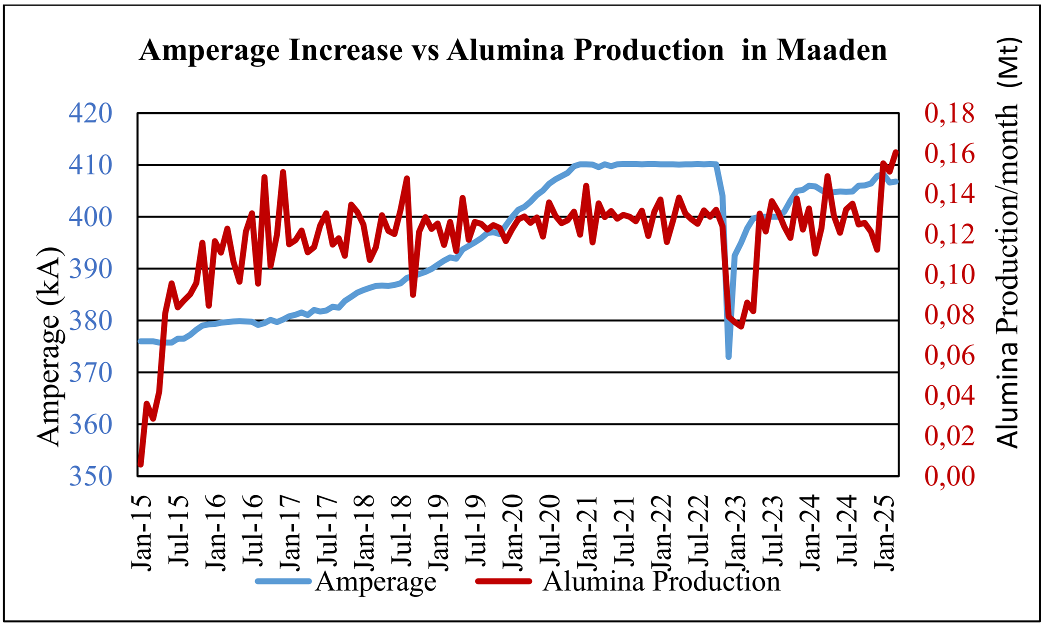

Figure 1. Increase in potline operating amperage and monthly alumina production.

2. Evolution of Bath Chemistry with Transition into Maaden SGA

The journey of increase in amperage and transition from imported to indigenous alumina were followed simultaneously. Figure 1 represents the increase in amperage in the smelter and increase in alumina production in the refinery together. Figure 2 represents the gradual change in ratio of Maaden alumina blended with imported aluminas as the production in the refinery was gradually increased.

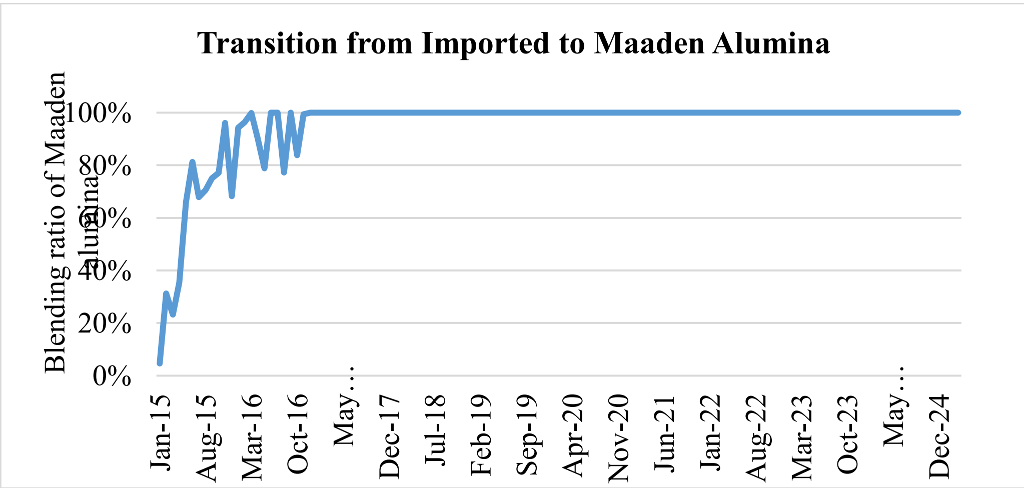

Figure 2. Transition from imported to Maaden alumina.

The bauxite for alumina refinery is sourced from Maaden Al-Baitha mines, which also contain traces of lithium in the form of lithium oxide (Li_2O). Lithium, as it enters the bath through calcined alumina, tends to accumulate in the bath unlike most other impurities, which get dissolved rapidly and ends up alloyed with the metal. Figure 3 shows the gradual increase of LiF concentration in the bath over the years since 2016. It increased to 3 % by April 2022 while the Li impurity in the metal gradually increased from 3 ppm in 2016 to 18 ppm in 2022. After that both values have decreased. The Li content in the metal shows good correlation with the content of LiF in the bath.

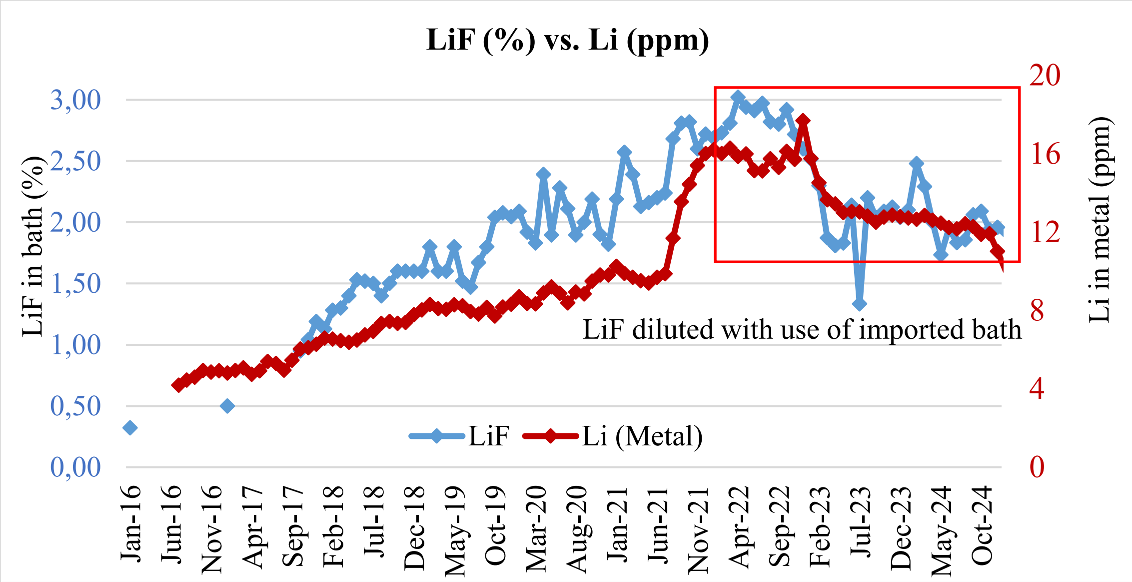

Figure 3. Increase of LiF in bath and Li in metal.

Towards the end of 2022, there was an operational disturbance in the smelter prompting the stoppage of 304 pots [1]. Pure (tapped) bath was imported from several GCC smelters to speedily restart the pots. The external tapped bath resulted in the dilution of the LiF content in the molten bath and Li in the metal. Since then, imported pure baths have continued to be used for pot start-up activities, and this has resulted in the sustained reduced level of LiF concentration in the bath.

Another unique property of Maaden alumina is its sodium oxide (Na_2O) content, which is lower by 50-60% compared to most other market suppliers. The low Na_2O content limits the bath generation and helps to retain LiF concentration in the bath, which otherwise would be diluted through bath tapped in moulds. Figure 4 represents the historical trendline of Na_2O content in alumina consumed over a period of ten years. Since mid-2017 it has been fairly constant at 1800 ± 400 ppm Na_2O in Maaden SGA.

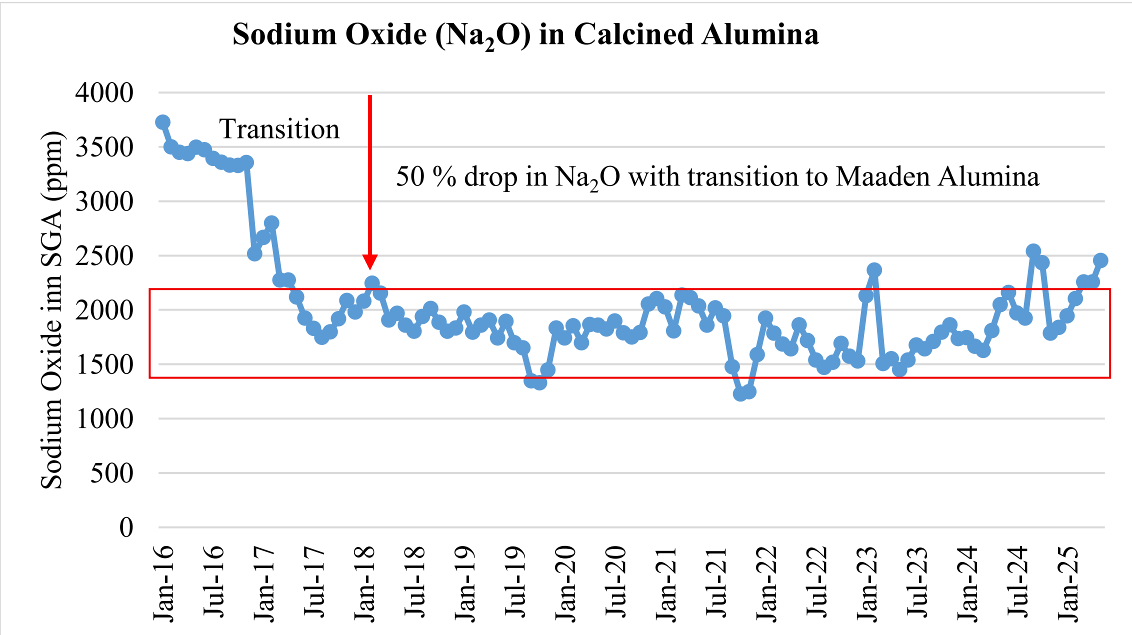

Figure 4. Sodium oxide content in Maaden SGA.

3. Impact of Lithium Fluoride on Bath Properties

Based on various research done earlier, the impact of LiF additives in the bath are summarized below.

Merits:

- The presence of LiF increases the electrical conductivity of the bath, which may help in optimizing the set target resistance of the pots with potential energy saving (lower DC kWh/t Al) and possible amperage increase and subsequent increased metal production.
- Decrease in vapour pressure of the bath. The vapour pressure of $LiAlF_4$ at 1027 °C is only 26 % of that of $NaAlF_4$ and lowers the liquidus temperature of the bath, thereby reducing fluoride evolution [2, 3].
- Increase in surface tension between bath and gas leads to decrease in bath loss into the flue gas in the form of entrainment of droplets and thereby reducing fluoride losses from the pots [2, 4].
- LiF behaves like sodium fluoride (NaF), a Lewis base when added to cryolite and tends to increase the alkalinity of the bath and increase the bath ratio [5].
- Reduces the specific consumption of aluminium fluoride (AlF_3) [5].

Demerits:

- LiF is reduced by aluminum at the cathode, leading to small amounts of Li in the metal [2].
- Increases the viscosity and density of the bath, which reduces solubility and rate of dissolution of alumina in the bath if AlF_3 concentration is kept constant [2].
- Increase in anode effect frequency [5].
- Increase in cathode resistance due to increase in alumina sludging caused by lower temperature and increased bath density [5].
- Increase in carbon dusting because LiF modified baths have smaller wetting angles with carbon material due to increased surface tension indicating better wetting properties [6].

4. Impact of LiF on Fluoride Evolution from Electrolytic Cells

With reference to the research done and correlations established earlier, gaseous fluoride evolution from pots could drop by 50 % with 2 % LiF modified bath cells [8]. This study was conducted in cells operating at 70 kA, but here it is tried to assess the same in high amperage cells at 410 kA.

Using the mathematical model published by Warren Haupin and Halvor Kvande in 1993 [7], (Figure 5) the fluoride evolution from pots were calculated with changing bath properties over a period of ten years. The annual average values were considered for all the applicable parameters as per model, keeping the CE constant at 93 %. Another set of the same calculations was done using actual current efficiency. However, the results derived from both show an insignificant difference.

Apart from LiF, there are other variables like excess AlF_3, CaF_2, Al_2O_3 and MgF_2 in the bath, Na_2O and Loss on Ignition (LOI) in alumina, bath temperature, CE in the potline, H_2 in anodes and alumina, etc., used in the model. The results derived are given in Table 1.

Fluorid evolution from pots.

Mathematical model, Warren Haupin and Halvor Kvande. TMS 1993

Pot status:	Temperatur	%AlF3 excess	%CaF2	%Al2O3	%MgF2	P_b KPa	%H2anode	LiF	LOI 0-300g	%CE	%Al2O3sek	Wore
	963.5	11.2	5.8	3.0	0	101.33	0.2	0	1	94.12	96.5	1.04

F_{GP}: Formation of HF.

F_{GB}=((2914000-1364000*Rb)/(%CE*Pb))*exp(7,4941-8401/T_kelvin)*((Wore/(25,96+1,237*Wore))+((%H2anode))^0,5)*a(AlF3)^(1/3)*a(Al2O3)^(-1/6)

30.28

F_{VP}: Volatilation of Bath.

F_{VP}=5351000/CE/Pb*(4*Pm+8*Pd+P_NaF) **11.36**

F_{EP}: Entrained bath

F_{EP}=76000*(1-Catch)/(SurfT*CE) **0.64**

Total Fluorid evolution kg/m.t. Al: 42.3

Figure 5. Fluoride evolution in pots, according to [7].

Figure 6 corresponds to the relative fluoride evolution with respect to LiF concentration in the bath, which is calculated using the Haupin and Kvande model [7]. As per the results derived from the mathematical calculations, with 1 % LiF concentration in the bath, the fluoride evolution from pots dropped by 10 %. With 2 % concentration in the bath, the fluoride evolution dropped by 23 % and with 3 % LiF concentration in the bath, the fluoride evolution dropped by 30 %.

Based on the actual measurements done by sampling at GTC inlet ducts, the average total fluoride concentration measured at the inlet of four GTCs in 2014 was 230 mg/Nm^3, which dropped to 147 mg/Nm^3 in 2024, approximately 35 % decrease at 2.1 % LiF concentration in the bath. It is important to mention here that the Na_2O content in alumina during both these tests were 4200 ppm and 1750 ppm, respectively.

Table 1. Evolution of fluorides with respect to LiF concentration in the bath calculated using the Haupin and Kvande model [7].

Year	LiF (%)	Total fluoride evolution calculated with actual CE (kg/t Al)	Drop in total fluoride evolution calculated with actual CE (%)	Total fluoride evolution calculated with constant CE (kg/t Al)	Drop in total fluoride evolution calculated with constant CE (%)
2015	0.00	42.3	Ref.	42.8	Ref.
2016	0.32	41.6	2.8 %	42.1	1.6 %
2017	0.91	37.9	11.4 %	38.4	10.3 %
2018	1.45	35.6	16.8 %	35.9	16.1 %
2019	1.75	34.6	19.2 %	34.7	18.9 %
2020	2.03	33.0	22.9 %	33.0	22.9 %
2021	2.46	31.4	26.6 %	31.4	26.6 %
2022	**2.86**	**29.6**	**30.8 %**	**30.0**	**29.9 %**
2023	2.10	32.5	24.1 %	32.4	24.3 %
2024	2.02	32.9	23.1 %	33.0	22.9 %

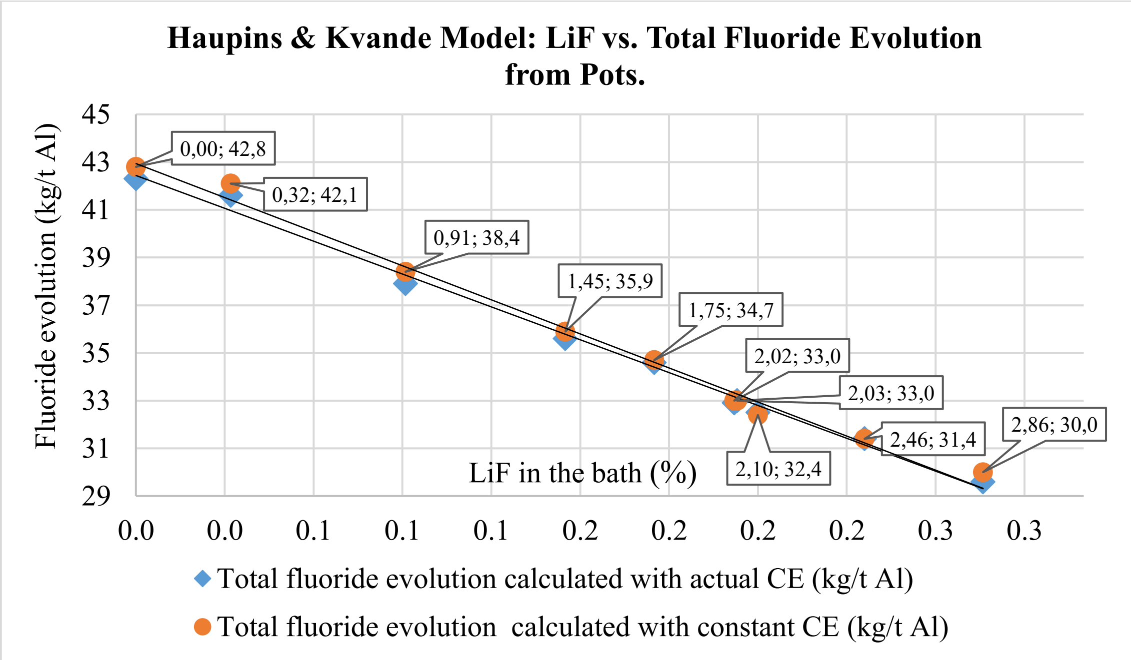

Figure 6. Relative fluoride evolution with LiF concentration in Maaden, calculated with the Haupin and Kvande model.

If the amount of excess AlF_3 is kept constant, the vapour pressure decreases due to the reduced temperature. At constant liquidus temperature, the reduced pressure is caused by the reduced excess AlF_3. In Maaden, both excess AlF_3 and temperature were reduced [2].

Operating with high excess AlF_3 causes very high cryolitic vapour pressure, which in turn results in high fluoride emissions. Increase in LiF concentration in the bath helps to reduce excess AlF_3 and gives lower bath operating temperatures. In a 180-kA Pechiney smelter, pots modified with 3 % LiF witnessed a drop in vapour pressure by 50 % [5].

- LiF increases density of the bath and reduces vapour pressure. This reduces the evolution of gaseous fluorides from the pots (Figure 7).
- Lower Na_2O in the alumina (Figure 4) reduces bath generation in the potline, thereby reducing liquid bath droplets entrained in gases and reduces the particulate fluoride concentration in gases collected in GTCs.

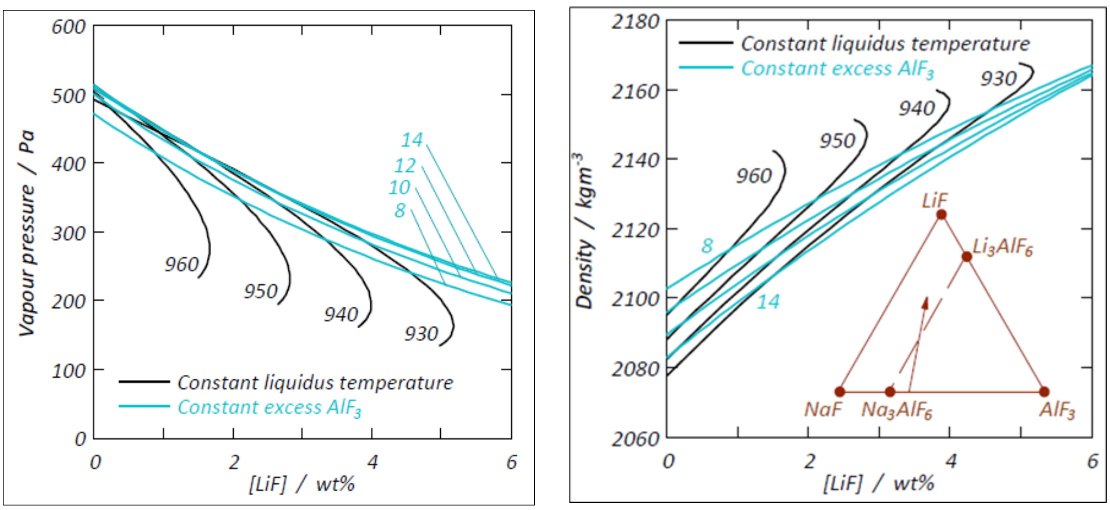

Figure 7. Vapour pressure (left) and density (right) as a function of LiF [2].

With the evolution of LiF concentration in the bath gradually over years the corresponding changes in excess AlF_3 and bath temperature set points are plotted in Figures 8 and 9, respectively. The acidity of the bath requires adjustment with an increase in LiF to avoid any drift in superheat, which can lead to high bath generation, compromise of side wall protection and increase Si level in the metal. Also, to prevent the impact on alumina dissolution rate, which may be impacted if AlF_3 is kept constant, the drop in liquidus temperature is steeper in baths with increase in LiF composition. At constant excess AlF_3, 1 % LiF will reduce the liquidus temperature by 12 °C [5].

Excess AlF_3 in the bath was reduced from 11.5 % to 9 % and bath temperature reduced from 964 °C to 957 °C, while LiF was peaking at 3 %.

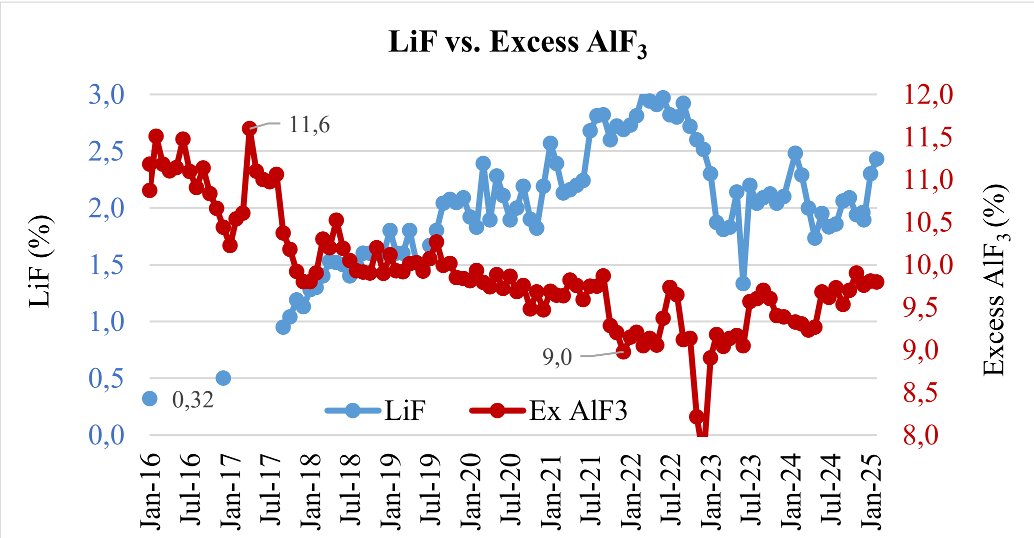

Figure 8. Reduction in excess AlF_3 with increase in LiF.

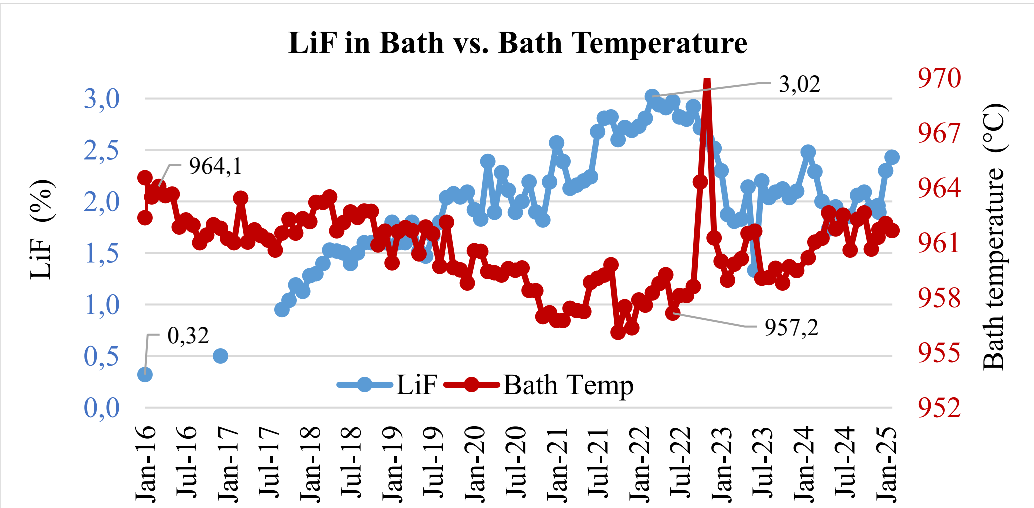

Figure 9. Reduction in bath temperature with increase in LiF.

Figure 10 (left) depicts the change in gaseous as well as particulate fluoride evolution with respect to change in bath ratio and superheat, while Figure 10 (right) depicts the impact on fluoride evolution from pots after adding 3 % LiF in bath at a constant superheat of 15 °C [2].

- The gaseous as well as particulate fluoride evolution decreases with an increase in bath ratio.
- The gaseous as well as particulate fluoride evolution decreases with a decrease in superheat.
- Significant decrease in gaseous as well as particulate fluoride evolution at 3 % LiF in bath.

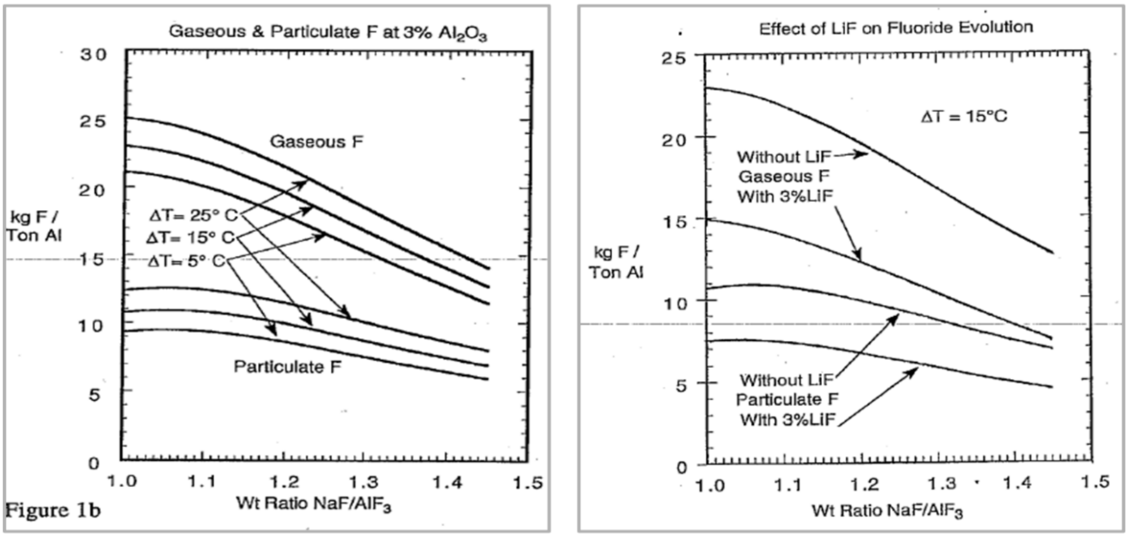

Figure 10. Fluoride evolution from pots with respect to bath ratio and superheat [7].

From Figure 11 (right), LiF has a high impact on the surface tension of the bath as compared to other additives in an acidic cryolite melt. The presence of LiF increases ionic concentrations in the melt, which leads to higher surface tension. This would lead to decreased bath loss in the flue gas in the form of entrainment of droplets. Also, the change in cryolite ratio poses a significant direct impact on the surface tension of bath. This influences the penetration of bath into the carbon lining, the separation of carbon particles from the bath, coalesce of fine aluminium droplets and dissolution rate of alumina into the cryolite. [2]

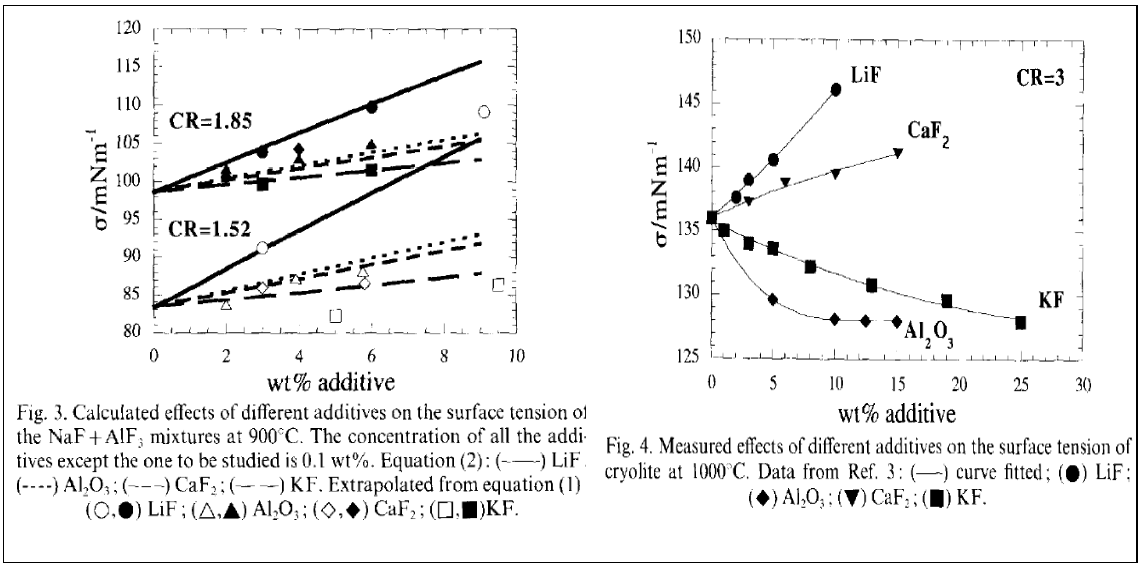

Fig. 3. Calculated effects of different additives on the surface tension of the NaF + AlF_3 mixtures at 900°C. The concentration of all the additives except the one to be studied is 0.1 wt%. Equation (2): (——) LiF (----) Al_2O_3; (– – –) CaF_2; (— —) KF. Extrapolated from equation (1) (○,●) LiF; (△,▲) Al_2O_3; (◇,◆) CaF_2; (□,■)KF.

Fig. 4. Measured effects of different additives on the surface tension of cryolite at 1000°C. Data from Ref. 3: (—) curve fitted; (●) LiF; (◆) Al_2O_3; (▼) CaF_2; (■) KF.

Figure 11. Impact of LiF and other additives on the surface tension of acidic bath [4].

With the increase in amperage from 370 kA to 410 kA, various changes adopted in potline parameters helped to reduce the surface tension of the bath, which lowered fluoride evolution from the pots.

- Increase in average metal height in pots by ~4.5 cm.
- Decrease in average bath heights in pots by ~2 cm.
- Decrease in pot operating temperatures by almost 4-5 °C.
- Decrease in excess AlF_3 composition (acidity) in the bath by ~2.5 percentage points.
- Increasing LiF concentration in the bath by ~ 2–3 %.

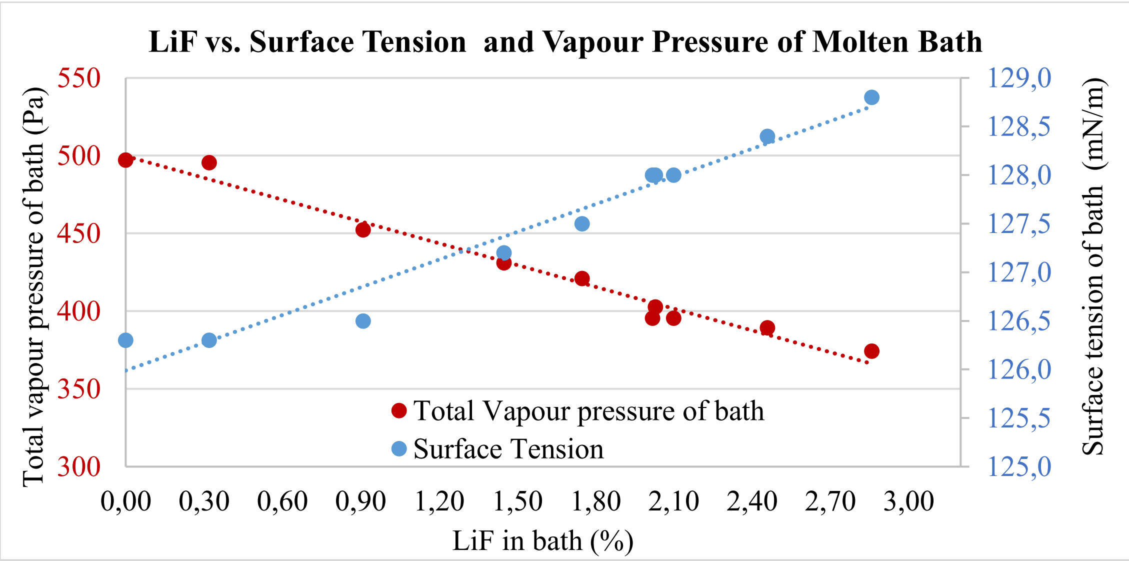

Figure 12. Relative changes in surface tension and vapour pressure with LiF in bath.

Surface tension and vapour pressure of the bath derived with Maaden operational parameters (using the Haupin-Kvande model – Figure 5) are plotted in Figure 12. It shows an increase in surface tension of molten bath by 2 % and a decrease in vapour pressure by 25 % with respect to an increase of 3 % LiF in the bath.

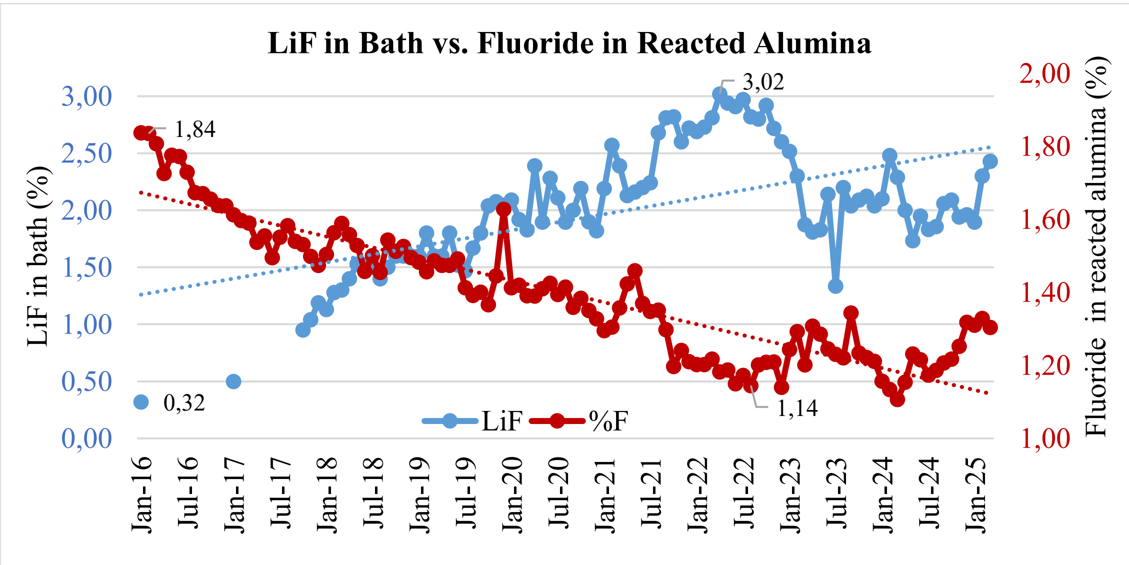

Figure 13. Relative decrease in fluorination with increase in LiF in the bath.

Figure 13 represents the gradual reduction in fluoride captured in reacted alumina in GTCs with increase in LiF concentration as an effect of drop in vapour pressure and increase in surface tension of the bath. During the period when only Maaden's alumina was used (stable Na_2O content in alumina consumed at 1800 ± 400 ppm Na_2O as shown in Figure 4), the reduction in specific consumption of AlF_3 by 2 kg/t Al from 11 kg/t Al to 9 kg/t Al when the LiF content in the bath increased from 0.7 to 3 % is evident in Figure 14.

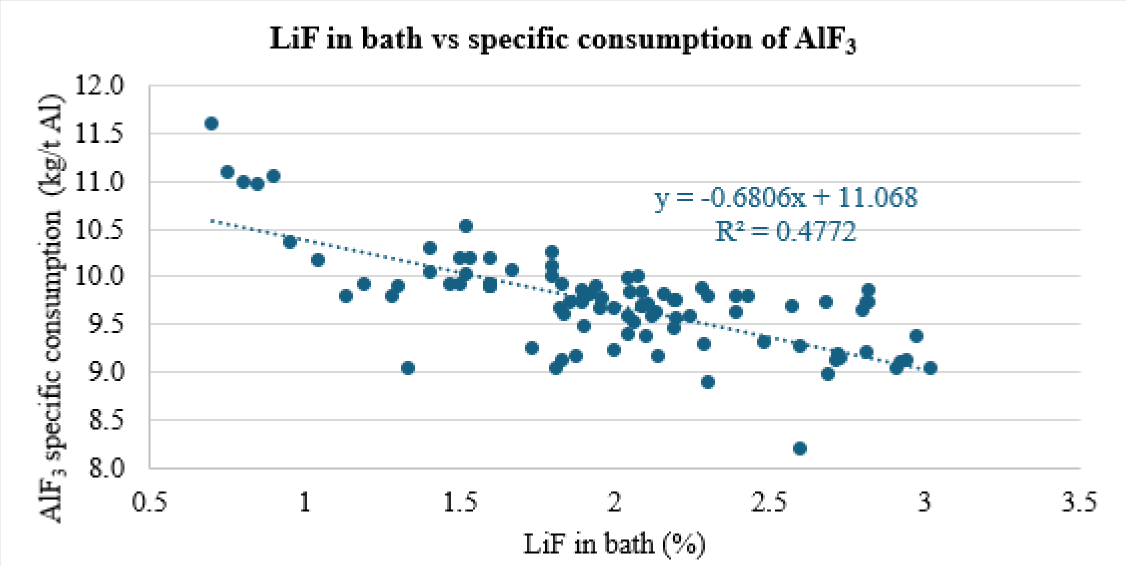

Figure 14. Relative decrease in AlF_3 consumption with increase in LiF in the bath.

An inverse correlation of LiF concentration in the bath over HF emissions from GTC stack as well as % fluoride captured in reacted alumina can be observed in Figure 15. Both experience a decreasing trend with an increase in LiF. The values used are annual average values from online HF analyzers at GTC stack and reacted alumina samples collected at GTC outlet daily.

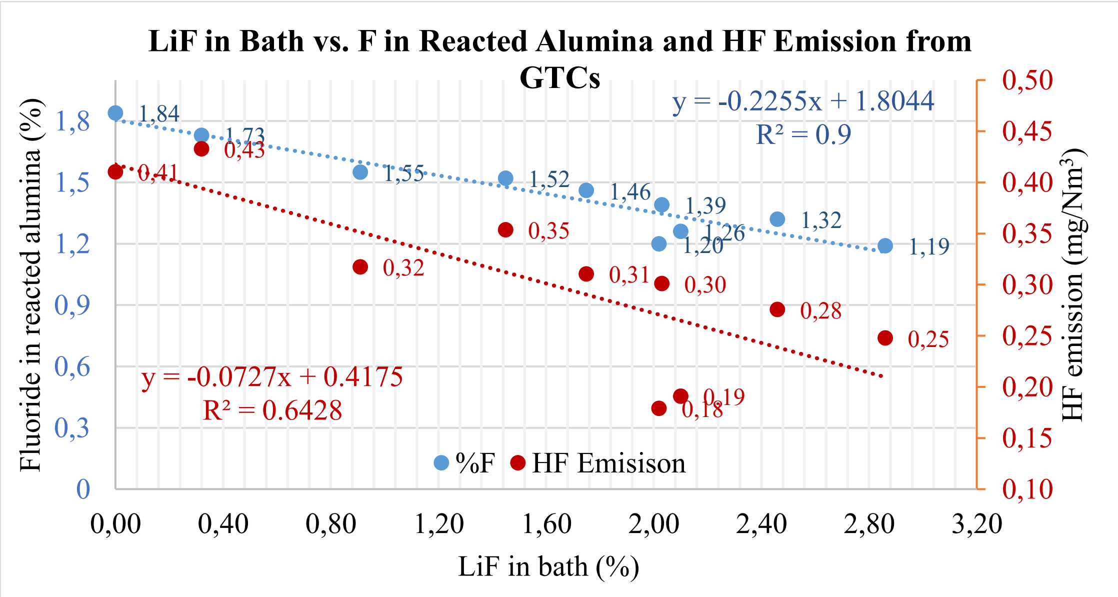

Figure 15. HF emission from GTC stack vs. fluoride capture in reacted alumina.

Maaden GTCs are installed with continuous online HF analyzers on stacks. Figure 16 signifies the annual values recorded by online analyzers, which is the average value of four GTCs. All four GTCs individually follow the same trend line. Over a period of ten years HF emissions from GTCs have been reduced by ~50 % (Figure 17). Based on the calculations done with the Haupin-Kvande model and GTC inlet sampling report, ~25 % reduction in HF emissions may be attributed by drop in fluoride evolution from pots with 2.2 % LiF concentration and ~25 % to process improvements in GTCs. The drop in pot operating temperatures had a significant impact on improving scrubbing efficiency of GTCs.

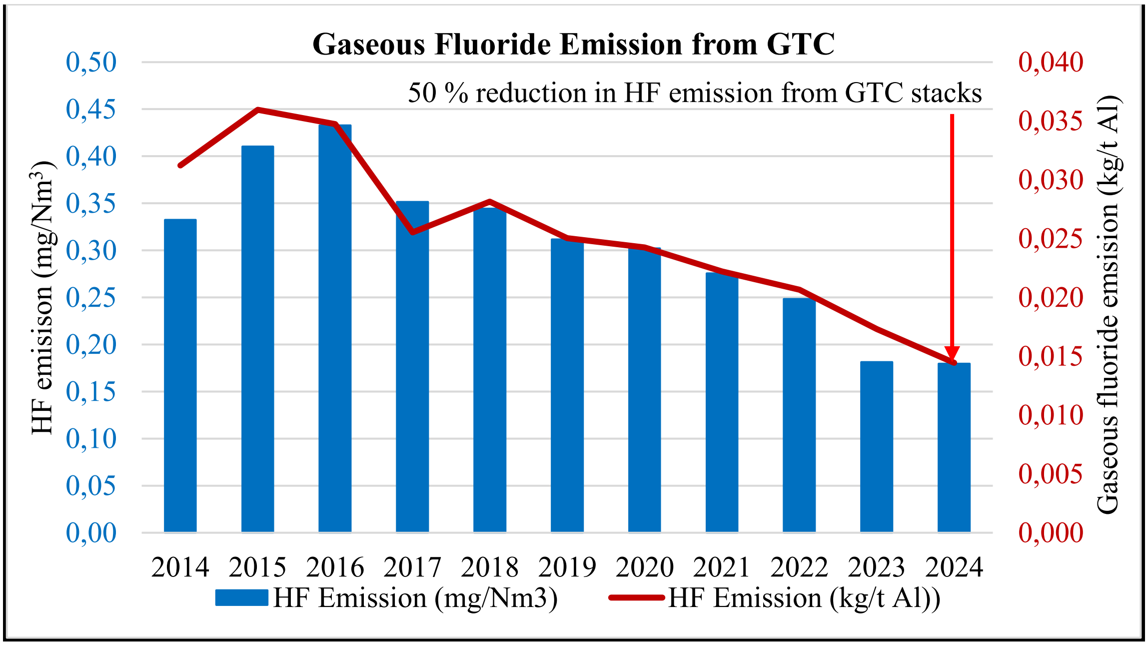

Figure 16. Annual HF emission from GTC stacks recorded by online analyzers.

5. Challenges experienced

- Alumina dusting around the feeder holes increased, which is not limited to deposition of volcanoes around the feeders typically caused by fine material, but includes the material blown away due to the pressure exerted by the exhaust fumes from the feeders as soon as the crust breaker is released.
- Corrosion on steel stubs: During the latter stages of amperage increase, a unique pattern of corrosion evolved lately around the steel stub on the spent anodes, which are not common in other smelters. (Figure 17).

Figure 17. Corroded anode stubs before and after cleaning oxidized layer.

- The hardness of anode crusts increased with LiF concentration in the bath. The hard crusts are difficult to break through by hammers installed in primary bath removal system (PBRS) and increase the breakdown of hammer tool in the rodding shop.
- With the increase in bath density, AE frequency might increase above 2.8 % LiF concentration in the bath if target bath heights are not well maintained. However, with AE frequency ~0.12 per pot/day Maaden is still the second benchmark among all AP plants operating above 400 kA with better alumina feed management and liquid level controls in place.
- Since Li is an integral component of Maaden bauxite, and the smelter is fully reliant on Maaden Alumina, diluting LiF using imported alumina is a tedious exercise for the smelter. Low Na_2O content in alumina is another bottle neck to dilute the LiF.

6. Conclusion

Over a period of ten years, with the decrease in Na_2O content in alumina from ~4000 ppm to ~1800 ppm, decrease in pot operating temperatures from 963.5 °C to 960 °C, and gradual increase in LiF concentration in the bath to 2.1 %, Maaden experienced a reduction in fluoride evolution from the cells by 25 % (calculated value), reduction in fluoride concentration at GTC inlet by 35 % (measured value) and reduction in HF emission from GTCs by 50 % (measured value by online analyzers). As per the experience and with reference to the data presented here, it is recommended that the optimum LiF concentration in the bath should not exceed 2.0-2.5 % to ensure its benefits without compromising key operating indicators such as anode effect frequency, cathode resistance and specific energy consumption. The issue of increased lithium (Li) impurity in the metal has been effectively addressed by processing all crucibles through the TAC station, successfully maintaining Li levels in the metal below 7 ppm.

7. References

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