AL40 - Study of Gibbsite Effect on HF Emission in Aluminium Reduction Cells

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Abstract

In addition to moisture, structural water, or more accurately structural hydroxyl (Gibbsite) that is available in smelter grade alumina (SGA) and aluminum fluoride contribute to HF generation in the electrolysis cell. The hydroxyl group dissolves in molten cryolitic electrolytes and produces HF by electrochemistry. About 70-75 % of the total F emissions from aluminum reduction cells are gaseous. Even if HF and fluoride particles that emerged from the cell are effectively caught in the dry scrubber, the portion not captured will be the main source of fluoride emission out of the potrooms. Fluctuation in HF evolution from a cell can alter cell bath chemistry and increase demand of aluminum fluoride, as well as contribute to fugitive emissions of fluoride.

At Sohar Aluminium, a method to analyze gibbsite content in the alumina was developed and validated. In this paper, the impact of gibbsite in typical SGA and aluminum fluoride was quantified and potential correlations with actual results verified. This study tries to explore and isolate the impact of % gibbsite in the process parameters like fluoride adsorbed in GTC (Gas Treatment Center) and eliminate % gibbsite contribution from aluminium fluoride as part of a full study of sources of HF emissions in cells.

Keywords: Aluminium reduction cells, Fluoride emissions, structural hydroxyl, Gibbsite in smelter grade alumina, Gas treatment center.

1. Introduction

The Sohar Aluminium (SA) plant is operating AP40 cells around 400 kA with a metal production of 395 000 tons per year, a carbon plant producing baked anodes and a cast house to cast the molten aluminium into ingots and sows. Some of the molten metal is delivered to downstream customers. In addition, SA has its own 1 000 MW power plant and a port terminal.

In the aluminium industry today, smelters must rely on more than one alumina supplier. The various alumina refineries have their own technology and unique processes to produce alumina. Refineries also use different bauxites and raw materials from sources around the world. This creates certain variations in the quality of smelter grade alumina (SGA) from the suppliers. It is not uncommon that smelters experience changes in the cells process conditions when there are changes in the alumina source or in the quality [1].

The Sunndal smelter of Norsk Hydro has reported on the problems they experienced with a different alumina quality. They experienced a loss in aluminium fluoride from the bath whereby bath chemistry changed and the cryolite ratio was affected.

It is generally assumed that HF is produced by the reaction of AlF_3 in the electrolyte or as a vapor with a source of H, as shown in Figure 1, as described by Equations 1 and 2.

$$2AlF_3\text{ (g or diss)} + 3H_2O(g) \leftrightarrow 6HF(g) + Al_2O_3(\text{s or diss}) \tag{1}$$

$$3NaAlF_4(g) + 3H_2O(g) \leftrightarrow 6HF(g) + Al_2O_3(s) + Na_3AlF_6(s) \tag{2}$$

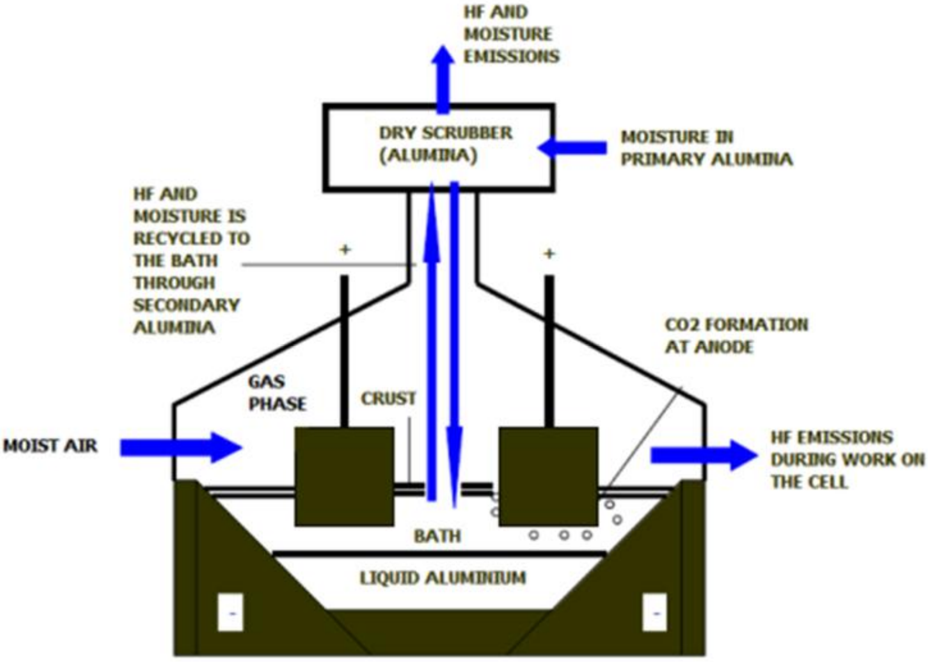

Figure 1. A principle drawing of the HF formation inside an electrolysis cell [8].

The source of H may be:
- Residual H in the anode
- Moisture in the air
- Water and hydroxyls in smelter grade alumina.

Quantification of duct HF levels in smelter studies showed that smelter grade alumina represents the largest single source of H for HF generation, Figure 2. Alumina has a strong affinity for water due to its polar surface. Moisture adsorbs on alumina in different ways [3]:
- Physisorbed water/physical adsorption of water
- Chemisorbed water
- Incorporated structural hydroxyl water in the crystal lattice.

The definition of physically adsorbed water is water that adsorbs to a surface due to relatively weak Lifschitz-van der Waals forces. This means that the water adsorbs on the surface of the molecule due to attractive interaction forces that arise from permanent and/or induced dipoles. These forces are relatively weak [4], and this type of water will mainly evaporate upon heating to 110 °C.

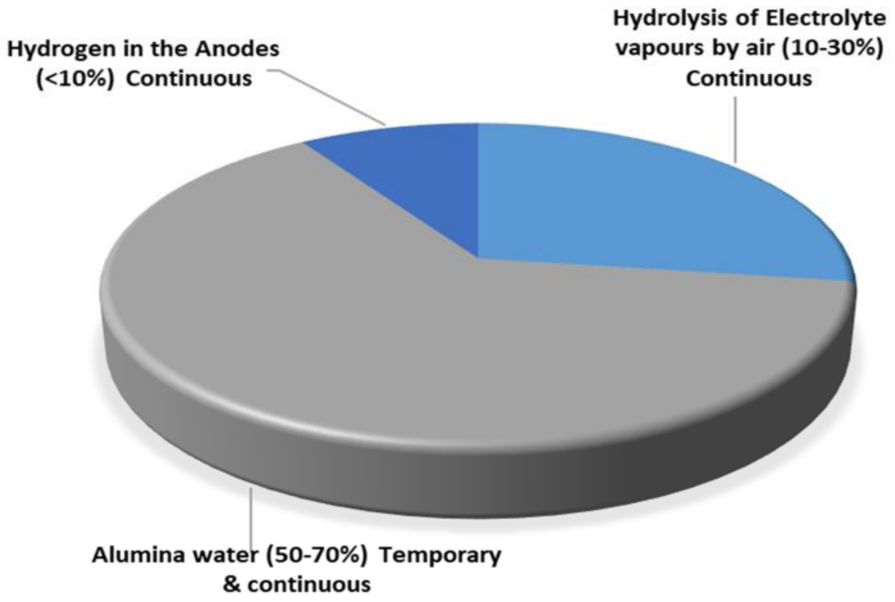

Figure 2. The relative contributions to total HF generation for the three major H sources [2].

Chemisorption can be defined as electrons being regrouped in gas molecules and on the surface of a molecule to create covalent chemical bonds. [4] and this moisture from gibbsite evaporates from approximately 220-330 ˚C and is also referred to as the LOI300.

Structural hydroxyl can be defined as OH-groups being bonded to aluminium atoms in the crystal lattice (e.g., gibbsite ($Al(OH)_3$ and boehmite (AlOOH). The structural hydroxyl has a longer residence time in the electrolyte, and will dissolve when alumina dissolves [5].

The main moisture source for HF formation has been identified as the structural hydroxyl moisture in smelter grade alumina [2, 6, 7]. Hyland et al [2] reported that smelter grade alumina has LOI (300-1000 °C) between 0.4 and 0.9. Of this total moisture, only 5-11 % is structural hydroxyl moisture. Experiments have shown that increasing structural hydroxyl moisture in the alumina increases the HF formation [2].

The extend of this study is to examine structural hydroxyl alumina present in aluminium fluoride material used in cells to maintain the cryolitic melt composition.

2. Gibbsite Phase Measurements in Smelter Grade Alumina

2.1 Identification of Hydroxyl Alumina Phase by X-Ray Diffraction

The smelter grade alumina diffractograms are shown in Figures 3; High Score Plus software was used to identify the phases and accompanying diffraction lines. Using Rietveld refinement in the Roboriet software, an effort was made to quantify the various phases. Along with other phases of (alpha and gamma) alumina, an additional peak has been found at 18.3 2-theta angle.

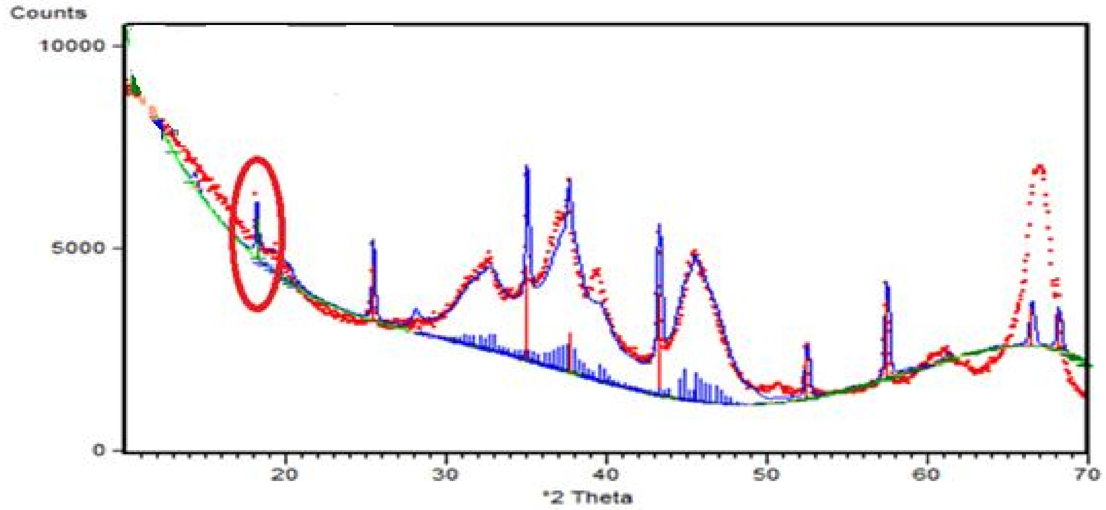

Figure 3. Identification of hydroxyl alumina phase.

2.2 Validation of Identified Hydroxyl Alumina Phase by X-Ray Diffraction

One way to isolate if a peak is hydroxyl is to calcine a sample to 500 °C and the repeat the analysis. The smelter grade alumina peak was once more scanned in the diffractogram, which was then analyzed using X-Ray Diffraction phase analysis after being calcined at 500ºC. This is shown in Figure 4. It can be seen that here we missed the peak that was shown earlier in Figure 3, and that this experiment supported the peak that was shown in Figure 3 is related to the hydroxyl group of alumina.

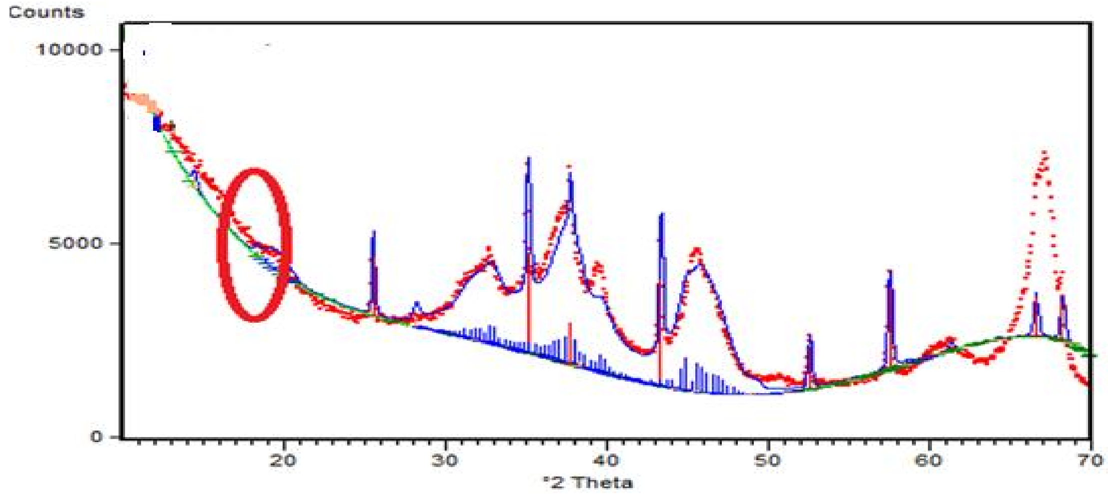

Figure 4. Identification of hydroxyl alumina phase after sample calcination at 500 °C.

2.3 Confirmation of Hydroxyl Alumina Phase Exists as Gibbsite by Standard Addition Method

The same smelter grade alumina has been mixed with 0.50 % pure analytical grade gibbsite, and it has undergone phase identification testing and refinement phase analysis to determine its exact amount. Figure 5 shows that on the same angle left side diffractogram, the phase was detected with 0.95 % gibbsite concentration (0.95 % in SGA Alumina - 0.50 % standard = 0.45 % Gibbsite). Here a 0.47 % gibbsite phase was detected in the sample that is shown in Figure 5 on the right side which was processed without any standard additions.

Minor variations in the exercises' findings brought measurement system accuracy levels on hydroxyl phase noticed with smelter grade alumina, which confirmed a peak had been detected on a specific angle connected to the gibbsite phase.

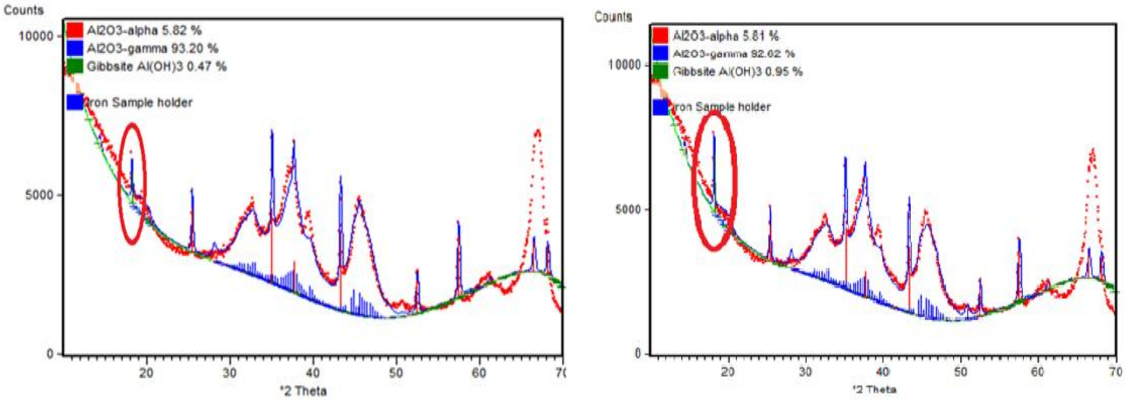

Figure 5. Confirmation that hydroxyl alumina phase exists as gibbsite.

Standard addition method validation further continued to quantify lower concentration of gibbsite phase in smelter grade alumina passed through Round Robin study (interlaboratory study), the results in Table 1 confirmed there was good accuracy achieved by this.

Table 1. Standard addition analysis method validation for low concentration of gibbsite.

Material	Normal Method		Standard Addition method	
	Standard Value	Measured Value	Standard Value	Measured Value
	Gibbsite %	Gibbsite %	Gibbsite %	Gibbsite %
Round Robin Sample	0.15	0.12	0.15 + 0.30 (STD)	0.44

The same methodology was used to quantify the gibbsite phase concentration listed in Table 2 in smelter grade alumina shipment loading point composite material received over the period of year 2022.

Table 2. Gibbsite concentration in smelter grade alumina.

Shipment Material	Supplier Name	Gibbsite (%)
19/03/2022	Supplier A	0.5
22/03/2022		0.41
28/04/2022		0.33
21/05/2022		0.48
20/06/2022		0.39
13/08/2022		0.42
06/09/2022		0.3

2.4 Gibbsite Phase in Aluminium Fluoride Material.

The introduction of the hydroxyl alumina phase to the cell and the anode's hydrogen content, which manifests as an HF emission, are often to reason for the loss of AlF_3 in the electrolyte. The existence of the gibbsite phase in one of the suppliers' AlF_3 material has been identified as a third source in addition to these two sources. Table 3 Gibbsite in Aluminium Fluoride material results listed are received from supplier X. A qualitative phase analysis is performed (see Figure 6) for both Supplier X and Y of aluminium fluoride material compared and identified Gibbsite phase only in material received from supplier X,

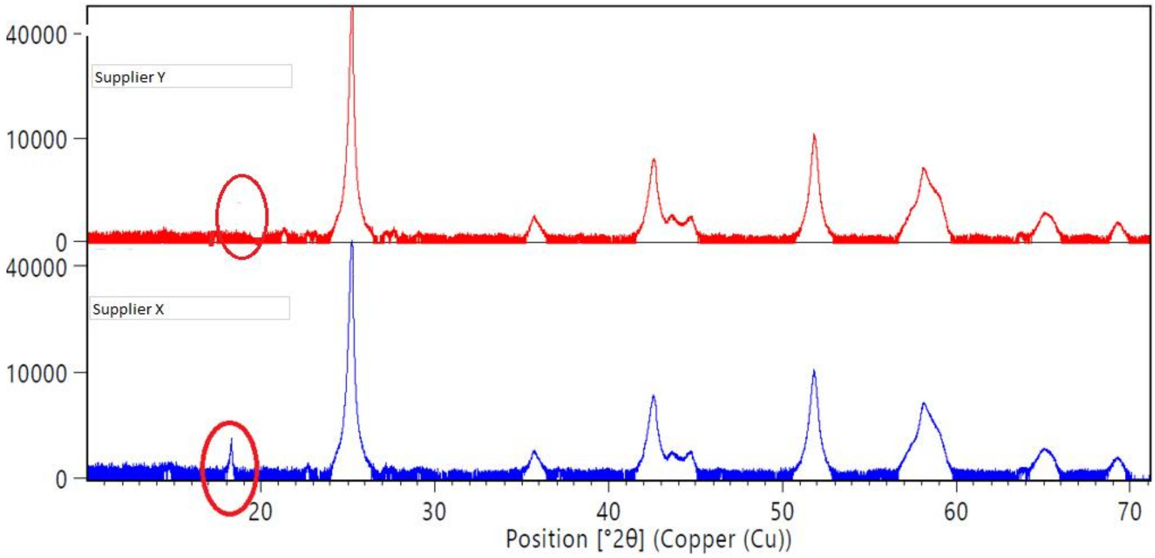

Figure 6. Diffractogram of Supplier X and Y AlF_3 material.

Table 3. Supplier X AlF_3 material Gibbsite concentration, data received from supplier.

	LOT N°	BL N°	%$Al(OH)_3$ *
Sohar Aluminium / OMAN	01/2022	216653026	0.89
	02/2022	217261631	0.93
	03/2022	217797164	1.02
	04/2022	218428898	0.92
	05/2022	219378411	0.9

*Results received from supplier, gibbsite % unable to quantify due to the unavailability of reference material.

3. Quantification of Gibbsite Effect in the Process and Emissions

3.1 Comparison of Gas Treatment Center Alumina Fluorination Level with Various SGA Gibbsite Concentrations

The study compared the levels of alumina fluorination in the gas treatment center when alumina with varying gibbsite concentrations was added. It was demonstrated by X-ray fluorescence spectrometer analysis of fluorinated alumina's fluoride percentage. The method used to quantify total fluoride combines HF, condensed cryolite vapor phase, and fine particles carried by exhaust gas. By determining the cryolitic bath phase from the difference in sodium level between SGA and gas treatment center (reacted) alumina material, the particulate (vapor phase & fine dust) fluoride participation was excluded from the total fluoride. By considering the theoretical point extra sodium that is only present in fluorinated alumina in the form of Cryolitic bath phase (considered internal bath composition), we followed internally designed algorithm equations 3 and 4.

$$CR_{(s)} = (Na_{Fl} - Na_{Fr}) * K \tag{3}$$

$$F\% \text{ in Particulate Phase} = CR_{(s)} / L \tag{4}$$

With:

$CR_{(s)}$	Cryolitic bath phase
Na_{Fr}	Wt% Na in SGA
Na_{Fl}	Wt% Na in reacted alumina
K	Constant, sodium concentration ratio in internal bath composition
L	Constant, fluoride concentration ratio in internal bath composition.

Table 4. GTC Alumina Fluorination level comparison results with SGA gibbsite %.

Month 2022	SGA Gibbsite %	HF % in GTC Alumina	Particulate F % in GTC Alumina	Total F% in GTC Alumina	Roof Emission (% deviation from target 100%)	GTC Stack Emission (% deviation from target 100%)
Feb		1.28	0.48	1.76	-6	-13
Mar		1.25	0.46	1.71	+18	-13
Apr		1.26	0.46	1.72	-6	+3
May	0.46	1.32	0.48	1.80	-25	-13
Jun	0.36	1.22	0.48	1.68	+12	+28
Jul	0.44	1.29	0.48	1.77	+10	+28
Aug	0.41	1.26	0.51	1.77	+18	-13
Sep	0.40	1.27	0.51	1.78	+10	+54
Oct	0.36	1.23	0.51	1.74	-12	-13
Nov	0.39	1.25	0.50	1.75	-17	+3

By considering stochiometric mass, theoretically 0.10 % of gibbsite is available to react with 0.07 % of fluoride in cryolitic melt. According to Table 4 in our study, 0.10 % of fluoride from cryolitic melt reacted on average with 0.10 % of gibbsite. Note that a certain set of data was selected for interpretation during a period when the process was more stable with the other contributor, which enhanced the HF emission from the cell.

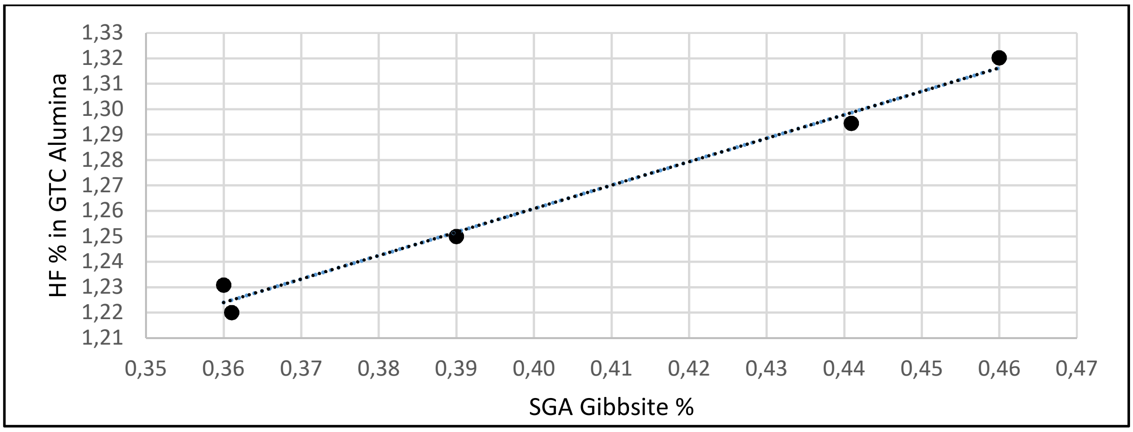

Figure 5. HF % response in GTC alumina against the SGA gibbsite concentration.

3.2 AlF_3 Demand in Cryolitic Melts

AlF_3 addition to the electrolyte serves two purposes. First, at baseline level it compensates for the additional soda content added through the alumina feed. Second, to compensate F loses from cryolitic composition over the period due to the HF emissions. In addition to this, there is also the gibbsite phase that is available in smelter grade alumina also participating AlF_3 demand. Here in

Table 5 and Figure 6 compared monthly average AlF_3 consumption compared with SGA gibbsite concentration. The period selected for the data interpretation there was gibbsite phase influence from aluminum fluoride material as well as SGA gibbsite.

Table 5. AlF_3 demand in cryolitic melt comparison with SGA and AlF_3 material gibbsite %.

Month 2022	SGA Gibbsite %	Supplier AlF_3 Gibbsite %	kg AlF_3 Demand/t Al	AlF_3 Material Density kg/m^3	Na % in SGA
Feb-22		0.89	13.93	1.52	0.28
Mar-22		0.93	13.67	1.52	0.29
Apr-22		1.02	13.45	1.51	0.28
May-22	0.46	0	13.97	1.49	0.29
Jun-22	0.36	0	12.09	1.49	0.28
Jul-22	0.44	0	12.69	1.50	0.3
Aug-22	0.41	0.92	12.73	1.52	0.29
Sep-22	0.40	0.90	12.64	1.52	0.29
Oct-22	0.36	0	12.09	1.53	0.28
Nov-22	0.39	0	12.45	1.52	0.28
Dec-22	0.15	0	11.80	1.49	0.28
Jan-23	0.10	0	11.50	1.50	0.28

** Supplier Y AlF_3 material used, * Supplier X AlF_3 material with nil gibbsite %,

Due to the additional gibbsite contribution from AlF_3 material, identifying the actual AlF_3 requirement in kg/t of Al proportionate ratio with% of SGA gibbsite had been a challenge. But Figure 6 shows that there is strong correlation in AlF_3 demand when the process sees high gibbsite % AlF_3 material (May-22 material change over period Supplier X to Y and July month high Na in SGA).

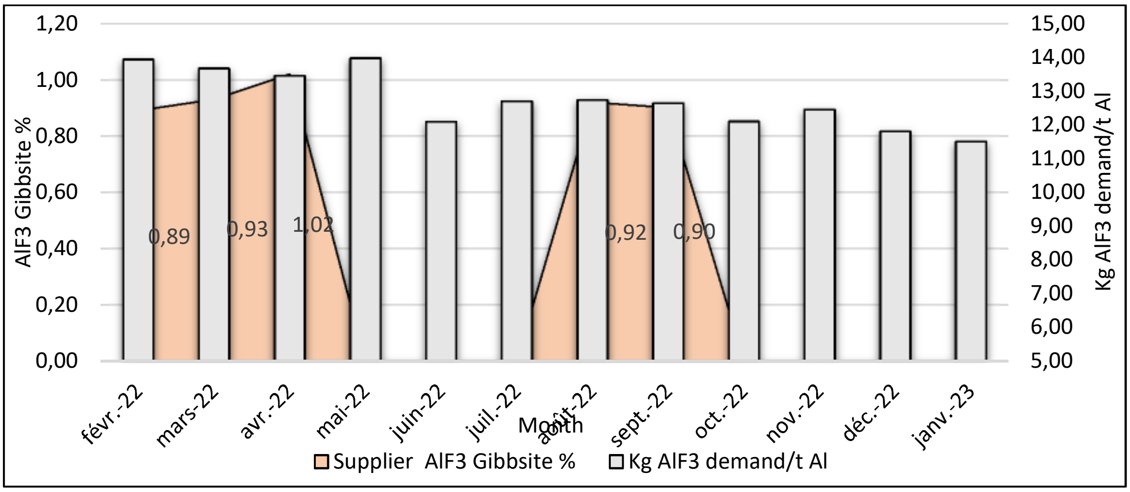

Figure 6. Chart between AlF_3 demand and Supplier X AlF_3 material gibbsite %.

Normally, the change from winter to summer has an effect on the heat balance of the cells, which can result in side wall opening and side cryolite melts, resulting in a significant demand for AlF_3. Figure 6 illustrates an increase in demand from February to May, followed by a decrease in June, when higher demand was expected and started to increase Aug and Sep the period expected low demand with high density material, this demonstrating the influence of AlF_3 material gibbsite% on AlF_3 demand kg/t Al.

4. Discussion

According to this study, the average gaseous HF emissions from aluminum reduction cells constitute 72 % of the overall fluoride % in reacted GTC alumina over the course of nine-month period average. The actual influence of the gibbsite present in SGA to the HF emission is higher than the theoretical HF generation and this discovery provides a chance to study additional hydrogen entry to the melt by the chemisorption process between gibbsite and water molecules. The correlation between gibbsite % and AlF_3 kg/t of Al demand in cryolite melt with rate variation confirms that there is a contribution from the gibbsite concentration available in both SGA and aluminum fluoride. Revealed gibbsite% in aluminium fluoride allows to narrow down the product specification to one with the least amount of gibbsite concentration.

5. Conclusions

Gibbsite present in SGA and aluminium fluoride can have direct influence in the aluminum reduction process and emissions. The quantification of gibbsite in the materials should be considered in the procurement process and should be discussed for quality purposes. Highlighted here that the quantification process is relevant. This paper increases confidence in the measuring system and the desire to have outcomes for process data interpretation.

Monitoring the gibbsite phase in aluminium fluoride material assists in notifying the supplier to improve the calcination performance to prevent feeding extra hydrogen to the cell, which will play partial role to the HF emission from the melt and influence the AlF_3 demand variation.

6. References

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