AL35 - Low Bulk Density vs High Bulk Density Aluminium Fluoride: A Comparative Study on Flowability and Practical Applications in Aluminium Smelting

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Abstract

Aluminium fluoride (AlF_3) plays an instrumental role in primary aluminium production, acting as a flux and reducing energy consumption significantly. While high bulk density (HBD) AlF_3 is conventionally utilized, the lesser-known low bulk density (LBD) variant, produced using recycled fluorine from the fertilizer industry, represents an eco-friendly alternative. Alufluor is a global LBD producer based in Sweden. Only 13 % of the total global aluminium fluoride volumes are LBD, despite the fact that there are several sources of unutilized fluorosilicic acid in the world. This study aims to debunk misconceptions about LBD AlF_3 flowability, a critical factor for efficient material transportation and feeding to electrolysis pots. A series of flow property tests, carried out by the University of Wollongong in collaboration with Rio Tinto, demonstrated comparable flowability between Alufluor's LBD and typical HBD AlF_3 of high quality, substantiated by experiences from various smelters. Our findings advocate for broader LBD AlF_3 acceptance, presenting it as an efficient, sustainable choice with excellent flowability. The transition from HBD to LBD is seamless, as verified by several smelters, underlining the product's operational versatility and potential for sustainable aluminium production.

Keywords: Aluminium fluoride, Flowability, Sustainability, Circularity, Low bulk density.

1. Introduction

1.1 Aluminium Fluoride in Aluminium Smelting

Aluminium fluoride (AlF_3) plays a crucial role as an additive in the production of aluminium. In the Hall-Héroult process, metal aluminium is extracted from alumina through electrolysis. The liquid bath which is used in the electrolysis is Cryolites which acts as flux, stabilizing the process and lowering the temperature of the melt. AlF_3 is added to the bath to form cryolite when reacting with sodium, present as a trace element in the alumina. With the lowered melt temperature, energy consumption is reduced.

1.2 The Alufluor Process and Product

Alufluor AB is a Swedish AlF_3 producer, owned by Yara and Rio Tinto. At Alufluor, the fluorosilicic acid (FSA) process, also called wet process [1], is used to produce AlF_3. Fluorosilicic acid and aluminium tri-hydroxide (ATH) react according to:

$$H_2SiF_6 + 2\ Al(OH)_3 \rightarrow 2\ AlF_3 + SiO_2 + 4\ H_2O \quad (1)$$

The FSA raw material is a by-product from other industries, including the fertilizer industry, from where it is often deposited as waste, however in this case recovered and used to create value.

The main application of the formed AlF_3 is aluminum smelting, however the company also provides purer grades of the products used in manufacturing of optical lenses, dental fillings, surface treatment and more. The formed silica is a by-product, which is collected, treated and sold as a product to other applications, as is every by-product or waste coming from the Alufluor operations. Silica is partly recycled back to the fertilizer producers where it is added to the process to capture new fluorine as FSA, hence closing a circular process.

Around 13 % of the global production of AlF_3 is produced with the FSA process [2]. The rest is instead produced in the more common dry process, where fluorspar is used as fluorine source instead of FSA. As fluorspar is a virgin raw material in scarcity, there are obvious benefits with the recycling of fluorine to be used to produce AlF_3 with the FSA process.

1.3 Low-Bulk and High-Bulk Density Aluminum Fluoride

The AlF_3 produced using fluorosilicic acid or fluorspar as a fluorine source results in the same chemical compound, AlF_3. However, the macroscopic properties of the material differ. The FSA based variant, as in the Alufluor case, has a lower bulk density and is referred to as low bulk density (LBD) AlF_3. Conversely, the fluorspar-based variant of higher bulk density is called high bulk density (HBD).

An AlF_3 product is typically ranging between 90-97 % actual aluminium fluoride, also much connected to whether the product is HBD or LBD, where the LBD products are often in the higher concentration range and HBD in the lower. The content of impurities in the product also differs between products, with typically lower impurities present in LBD.

In the table below, typical specifications for HBD products are compared with the specification of the LBD produced by Alufluor.

Table 1. Properties of aluminium fluorides of different bulk density.

	Typical HBD	**Alufluor LBD**
Bulk density	1500 kg/m^3	800 kg/m^3
Active content	90-91 % AlF_3	97.5 % AlF_3
Purity		
Non AlF_3	9	2.5
P_2O_5 (%)	0.01-0.02	0.006
SiO_2 (%)	0.05-0.15	0.08
LOI (%)	0.5	0.6
Fluorine source	Fluorspar	Fluorosilicic acid
Function in smelter	Excellent	Excellent
Flowability/transportation	Excellent	Excellent
Particle size distribution	<45 µm 8 %	<45 µm 3 %

2. Flowability

2.1 The Importance of Flowability Properties in Aluminium Fluoride

Flowability is a fundamental property for powders, such as aluminium fluoride, which significantly influences their handling and performance in various applications. Essentially, flowability refers to the ease with which a powder flows, without clumping, caking, or jamming during handling. Particle size distribution, shape, inter-particle interactions and other intrinsic properties impact the flowability of a material. High flowability implies that the material flows freely.

When facilitating flow from bin outlets, it is crucial to prevent flowability issues such as rat holes and arching. Rat holes refer to a condition in which material forms a stable vertical hole within a funnel-flow bin. Arching is a no-flow condition in which material forms a stable arch across the bin.

2.2 Flowability Concerns in Aluminium Smelting

Flowability is important for efficient transportation and feeding of the material into the electrolysis pots. HBD products traditionally have good flowability. However, the experience with LBD products is limited among many aluminum producers, leading to a common misunderstanding that LBD aluminum fluoride products inherently exhibit poor flowability. This perception may be attributed to a few potential factors. Firstly, there might exist LBD products of inferior quality that indeed demonstrate poor flowability, causing one to erroneously associate flowability solely with bulk density. Secondly, the conventional method for measuring aluminum fluoride flowability may be misleading, suggesting that LBD products have lower flowability even when they are free-flowing, such as the material offered by Alufluor.

2.3 Measuring the Flowability

There is currently no standardized method for measuring the flowability of powders that provides a comprehensive assessment of a material's ability to flow freely. Four traditional options are commonly used, each with its own set of problems and uncertainties: (1) angle of repose, (2) flow rate through a funnel, (3) tapped density, and (4) shear cell analysis. The absence of a standard test is due to the complexity of powders and their varied applications in different systems. [3]

Suitable test methods should be selected based on the intended use and the specific information required from the tests. In the case of aluminum fluoride used in aluminum smelting and related systems, such as transportation, storage, and feeding to the pots, the relevant information sought is an understanding of the material's potential risks of sticking to surfaces, caking, or exhibiting poor flowability.

The angle of repose test is a simple method, but it has significant uncertainties, including operator technique and the choice of equipment and settings, as the method lacks standardization. While it is used in the industry to measure the flowability of aluminum fluoride, the variation in results due to uncertainties makes it less ideal for accurately assessing the actual flowability.

The flow rate through a funnel is also widely employed and is slightly more refined than the angle of repose test. However, it shares similar uncertainties. An issue with using this test in the industry is the reliance on weight, specifically measuring the time it takes for a certain mass of material to pass through the funnel. This approach is inadequate for comparing aluminum fluoride products with different bulk densities. Since LBD and HBD have different volumes for the same mass, even if LBD takes a longer time to pass through the funnel, it only reflects the lower bulk density and not the ability to flow freely. However, if volume is used as the basis of comparison, measuring the time it takes for a certain volume of LBD or HBD to pass through the funnel, valuable information about flowability can be obtained.

3. Flowability Study at the University of Wollongong

3.1 About the Study

Bulk Materials Engineering Australia, situated within the Faculty of Engineering at the University of Wollongong, carried out an investigative study on behalf of Rio Tinto Australia (project number BME2120). The research was led by DB Hastie, with Rio Tinto providing the necessary samples.

A total of four distinct aluminium fluoride products, inclusive of HBD products, underwent examination, with LBD AlF_3 from Alufluor being one of them. The study encompassed the evaluation of flow properties, the determination of mass-flow hopper geometry, and flow rate testing. For the purpose of this paper, the particular interest is to compare the Alufluor LBD product to HBD products.

3.2 Test Methods and Results

For investigating the flow properties, several tests were made. The particle size distribution was measured using a Mastersizer 2000. The mean particle size (d50) for Alufluor LBD was determined to be 98 µm, comparable to the HBD products which had an average on 93 µm. Bulk density was determined using a 500 mL cylinder, and the bulk density variation using the Jenike Compressibility Tester. Bulk density for Alufluor LBD was approximately 780 kg/m^3, compared to 1450 kg/m^3 for the HBD's, which is as expected. There were also no significant differences in compressibility levels, being 4.6 % and 3.4 % respectively between 1 to 50 kPa. All products were rated as "very low" on compressibility.

Shear tests were conducted on a Jenike-type direct shear tester. The results indicate that Alufluor LBD is expected to exhibit low cohesive strength under instantaneous storage conditions, with a minor increase observed under three-day storage conditions. Based on the shear tests, the flowability index was calculated to be 0.02 for instantaneous storage conditions and 0.06 for three-day storage conditions. These results are also comparable with the HBD products, and all products were rated as "free flowing".

Wall friction tests were conducted on a Jenike-type direct shear tester on three types of steel. Low cohesion/adhesion was evident for Alufluor LBB at low normal stress levels for the three wall materials examined, whereof black cold rolled mild steel had slightly lower friction.

The angle of repose was measured by multiple tests with a stainless steel cone with an outlet diameter of 25 mm and was found to be approximately 31,8 degrees for Alufluor, which is comparable with 31,3 degrees which was the average for the HBD products.

Figure 1. Alufluor LBD angle of repose.

Flow rates were tested with cones of 25 mm, 50 mm and 75 mm cones. As expected, for a given cone, the volumetric flowrates of the different AlF_3 samples were similar, but of course, the mass flowrate of the low bulk density Alufluor was proportionately lower than that of the current source high bulk density AlF_3 material.

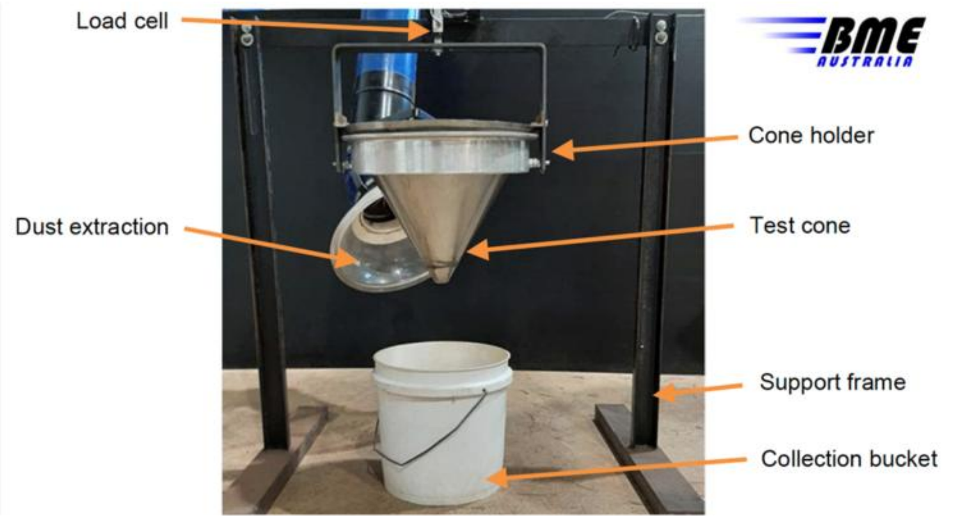

Figure 2. Flow rate test apparatus.

Table 2. Test results.

AlF_3 type	HBD	HBD	HBD	LBD
Product	**HBD A**	**HBD B**	**Average A + B**	**Alufluor**
Particle size distribution				
D10 (µm)	59.3	42.6	50.95	36.2
D50 (µm)	100.7	85.2	92.95	98.1
D90 (µm)	161.8	145.2	153.5	170.7
Moisture content as tested (%)	0.34	0.24	0.29	0.31
Loose poured bulk density (kg/m^3)				
mean of 10 measurements	1385	1517	1451	784
range	1361 ~ 1407	1498 ~ 1535		772 ~ 801
Compressibility				
compressibility over 1~50 kPa consolidation stress (%)	3.4	3.3	3.4	4.6
compressibility rating	very low	very low	very low	very low
Flowability index at consolidation stress of 10 kPa				
instantaneous	0.04	0.03	0.035	0.02
3-Days	0.055	0.05	0.053	0.06
flowability rating				
instantaneous	free flowing	free flowing	free flowing	free flowing
3-Days	free flowing	free flowing	free flowing	free flowing
Poured angle of repose (deg)	30.8	31.8	31.3	31.8
Arching index – conical mass flow hopper – instantaneous	0.04	0.04	0.04	0.04

Based on the flow property data determined, suitable critical mass-flow hopper geometry parameters were determined. Tests were made with variation of half angle and hopper outlet dimensions. The result showed that plane-flow hoppers should be considered for any mass-flow bins, and an outlet slot width greater than 0.2 m should be safe to use. To give an alternative estimation of the cohesive arching potential, the Johanson Hang-up Indicizer was used to determine Arching Indices (AI). The Arching Index is used to determine the minimum conical hopper outlet diameter needed to prevent arching in a bin or hopper. The results indicate that for the Alufluor LBD the AI = 0.04 m, which is the same level as for the HBD products.

3.3 Results from the Study

The results of instantaneous flow function tests indicate that Alufluor LBD exhibits free flowing characteristics and very low cohesive strength. The same observation is made for the 3 day storage condition, where the strength of the LBD only marginally increased. This means that it is highly likely the LBD in the condition as tested will not display an ability to form large stable cohesive arches and/or ratholes.

Under instantaneous conditions it was found that the wall friction was lowest for the black cold rolled mild steel, although differences were minor. Some very minor cohesion/adhesion was observed, and that was the same for all wall sample / product combinations.

The flowability index (FI) 0.02 for instantaneous and 0.06 for 3-day storage conditions are very low and corresponds the highest ability to flow freely.

There are no significant differences to HBD products in any of the tested parameters.

Table 3. Flowability index.

Flowability Index	Cohesive strength	Flowability
0 – 0.1	Very low cohesion	Free-flowing
0.1 – 0.25	Low cohesion	Relatively high flowing
0.25 – 0.5	Moderate cohesion	Good flow characteristics
0.5 – 0.75	High cohesion	More difficult flow characteristics
0,75 – 1	Very high cohesion	Difficult to handle
> 1	Extremely high cohesion	Extremely difficult to handle

In conclusion, both Alufluor LBD and the HBD products are characterized as very free flowing. Subsequent tests to compare bin outlet flow and flowrates show no significant difference in flowrate between the products on a volumetric basis. When considering mass as the basis, the mass flowrate of Alufluor LBD was as expected lower in proportion to the bulk density.

Thus, when comparing flowability among AlF_3 products with differing bulk densities (LBD vs HBD) using flow rate through a funnel, relying on a mass basis could yield false differences in flowability. Conversely, a volumetric basis provides an accurate comparison.

4. Experience of LBD AlF_3 in Smelters

In order to incorporate insights from practical applications of LBD in aluminium smelters, input from several companies have been solicited (anonymized in this paper). These smelters have all previously used HBD in their electrolysis processes and are either testing LBD or have made a switch from HBD to LBD fairly recently. The selected smelters also represent different technology for feeding AlF_3 to the pots.

4.1 Medium Sized Smelter in Europe

After successfully conducting a pilot scale test, a full-scale test was carried out with 300 tons of Alufluor LBD. This test occurred less than a year ago, and no issues were reported by the smelter in subsequent follow-ups.

There had been two main concerns regarding using an LBD in this plant:

- Whether the alumina and AlF_3 conveying system would be able to handle the LBD AlF_3.
- Whether there would be longer time delays before the pots receive the AlF_3 needed causing lower precision in the bath chemistry.

To test both concerns, the test has been split into two test periods. One short period for testing the conveying system and one longer for testing the pot response to the LBD AlF_3.

The conclusions from the two test periods are as follow:

- The conveying system for alumina and AlF_3 can handle the low bulk density AlF_3 from Alufluor.
- The LBD AlF_3 from Alufluor has no significant effect on the potroom operations compared to HBD.

The team at the smelter concluded that they can use the AlF_3 from Alufluor, and that they had no problems sending the material in their conveying system. The purpose of conducting the trials was to broaden the scope of potential suppliers for the future.

4.2 Small Smelter in Europe

This smaller-sized smelter, located in Europe, had been using HBD for a considerable time before attempting to switch to LBD due to a competitive purchasing process. Given the smelter's limited storage capacity for AlF_3, the transition required managing more frequent deliveries - a challenge that was effectively met.

Reflecting on the change, the smelter's team stated:

“The transition from HBD to LBD was seamless. The extracted data regarding operation-related parameters showed no significant changes. The only challenge was the need for a higher (volumetric) fluoride flow with LBD, necessitating adjustments in our supply planning.”

4.3 Large Smelter Outside Europe

A prominent aluminum company, with extensive experience using both LBD and HBD AlF_3 in their potlines, aimed to enhance flexibility in their supply strategy. As part of this initiative, they conducted experiments with mixing LBD and HBD in places where they had previously used only HBD.

The company introduced LBD into the HBD in the feeding tank and used this mixture on the same potline.

Testing various ratios of LBD and HBD have resulted in in protocol for supply shortage scenarios, where an 11 % blend of LBD is used on lines that typically operate with 100 % HBD, without necessitating any changes in operational parameters.

The company also has good experience in running some of their potlines solely with LBD products.

5. Conclusions

The study conducted at the University of Wollongong has demonstrated comparable flowability between Alufluor LBD and traditional HBD. The study encompassed a diverse array of tests aimed at elucidating the flowability properties under varying conditions and applications. In light of these findings, the common perception in the industry that LBD inherently has inferior flowability characteristics has been debunked. The flowability index of Alufluor LBD, a measure of its cohesive strength, was determined to be low, indicating that it possesses high flowability under both instantaneous and three-day storage conditions. Experience from the market indicates that poor flowability is highly connected with particle size distribution, but not to bulk density.

Regardless of smelter size, location, or the technology implemented for material feed, Alufluor LBD has exhibited exceptional performance with no recorded issues. These empirical experiences, coupled with the technical study, support a wider acceptance of LBD in aluminum smelting processes.

LBD AlF_3 presents a more sustainable alternative for aluminium production due to its recycling of fluorine from the fertilizer industry. While conventional AlF_3 production relies on mining of the scarcer fluorspar, the production of LBD AlF_3 utilizes FSA, a by-product from various industries, including the fertilizer industry. By increasing the aluminum industry's utilization of LBD AlF_3 in place of HBD AlF_3, a more circular and sustainable manufacturing process can be achieved.

6. References

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