Essential Readings in Light Metals: Aluminum Reduction Technology.
Edited by Geoff Bearne, Marc Dupuis and Gary Tarcy.

ALUMINIUM FLUORIDE – A USERS GUIDE

Stephen J. Lindsay
Alcoa, Inc.; Primary Metals; 300 North Hall Road MS S-29, Alcoa, Tennessee, 37701-2516, USA
Keywords: Aluminum Fluoride, AlF_3, , Electrolytes, Excess Fluoride, TAC

Abstract

Aluminum fluoride is an important raw material that is primarily manufactured via reactions of aluminum tri-hydrate either with fluorspar or with fluosilicic acid. Impurities generally have a minor impact upon smelting processes and metal products, but there can be exceptions. Likewise there are some physical properties of concern with this raw material. In this paper the author illustrates the important factors to consider when selecting and using sources of AlF_3.

Introduction

Aluminum fluoride for commercial use in aluminum smelters is typically manufactured by two processes. The "dry" process uses fluorspar as the source of fluoride. The "wet" process uses fluosilicic acid as the fluoride source.

The predominating means of AlF_3 production is by reacting crushed fluorspar with sulfuric acid to liberate HF gas. This, in turn, is reacted with $Al_2O_3 \cdot 3H_2O$, a.k.a. gibbsite, to form AlF_3 with anhydrous calcium sulfate, $CaSO_4$, as the by-product.

The less common wet process reacts fertilizer production by-product, fluosilicic acid, H_2SiF_6, with gibbsite, $Al_2O_3 \cdot 3H_2O$, to form AlF_3 with low grade silica, SiO_2, as the by-product.

In general the process that is based on fluorspar yields a relatively dense product. It is higher in those impurities that are related to the grade of fluorspar and carry-over of sulfuric acid. The process that is based on fluosilicic acid produces a product that is relatively low in bulk density, higher in AlF_3 content, or purity, and lower in some specific impurities.

Aluminum fluoride is used as an electrolyte, or bath additive, for the purpose of maintaining a desired excess fluoride target in pot room bath. Process control is done on a cell-by-cell basis with results typically measured on a pot line basis. The quantity used can vary from 10 kg AlF_3/ton Al produced to more 50 kg AlF_3/ton [1]. More typical values for point-fed pre-bake cells fall between 13 kg AlF_3/ton and 20 kg AlF_3/ton.

Aluminum fluoride is also used in some locations as an additive to metal in crucibles before entering cast house furnaces. The process of adding AlF_3 while stirring the metal is commonly known as the TAC process, or Treatment of Aluminum in a Crucible. It is used primarily to reduce levels of Na and/or Li in the metal. The TAC process may not be used on all crucibles. The need to use it depends upon the product mix. For those crucibles that are treated, the consumption of AlF_3 can vary from 0.7 kg/ton to 1.0 kg/ton Al.

The physical and chemical properties of AlF_3 sources must be given consideration before changing from one source to another. There may be large differences in; bulk density, purity of AlF_3, and of specific impurities of concern. Customer requirements are generally not overly demanding of this raw material. But the customer requirements that regulate the use of AlF_3 in reduction cells or for treating metal can rule out certain sources.

Certificates of analysis, CoA, for AlF_3 typically include a wide array of information on the physical and chemical properties of the product. These CoA's are based on analytical methods that are not necessarily uniform. The customers and processes that consume AlF_3 are generally focused only upon a few parameters. What follows is an industrial-based summary and users guide to these parameters and observations about their importance.

Discussion

<u>Purity of Aluminum Fluoride</u>

The premier property of aluminum fluoride is its purity as a product. The average purity of commercial grades varies from just above 90% to >97%. Figure #1 shows that fluorspar-based product will vary from >90% to >92% AlF_3 by weight. Acid-based product will vary from ~95% to ~97% AlF_3 by weight.

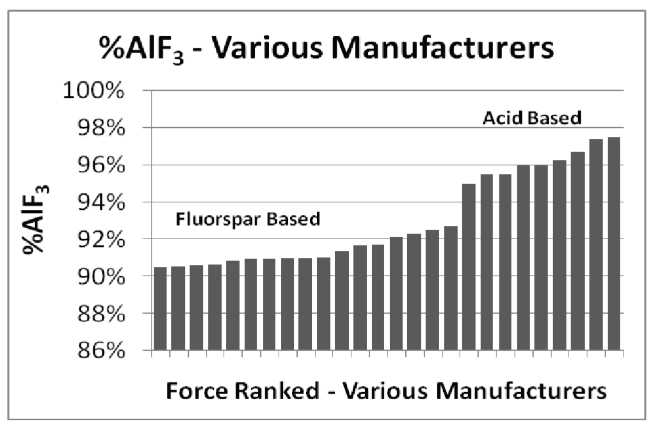

Figure 1 – Comparison of %AlF_3 in product

The major impurity found in AlF_3 is aluminum oxide, Al_2O_3. This exists in intermediate alumina phases that would be expected with calcination to approximately 600 C. If it is found at all, only small amounts of alpha phase alumina will be present. While the presence of alumina is benign to both the smelting process and the TAC process it brings no specific advantage to the product. It serves as an expensive source of alumina, but typically represents only 0.03% to 0.10% of the Al_2O_3 consumed in reduction cells.

From a technical perspective the purity is important factor in determining usage rates in smelting and in TAC applications.

Differences in purity must be included as a factor in bath chemistry control programs. It will usually be small enough to not warrant changes in AlF_3 additions to TAC processes though.

Figure #2 shows an interesting example of two sources of AlF_3. The source with the higher average purity also has approximately three times the variation in purity of the source with lower average purity.

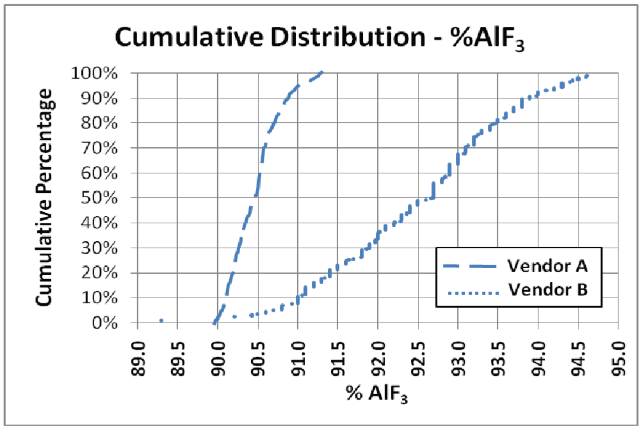

Figure 2 – Variation of $\%AlF_3$ in product of two suppliers

This raises a secondary issue that must also be considered with suppliers of AlF_3, that of variability. Obviously the preferred supplier would be one that has high average AlF_3 content and low variation from batch to batch. But, this may be a rare combination and trade-offs often come down to factors such as pricing and availability. Fortunately a variation in product purity of +/-2% will make little difference in daily additions of AlF_3 to individual cells. But it is an additional factor for the user to consider.

Understanding both the central tendencies and variations in key product properties is a responsibility that is shared both by the producers of AlF_3 and by the customers. As we will see, this is true for $\%AlF_3$ and for other properties as well.

Bulk Density

Another key parameter that is directly tied to bath chemistry control programs, inventory control, and to TAC is the loose bulk density of AlF_3.

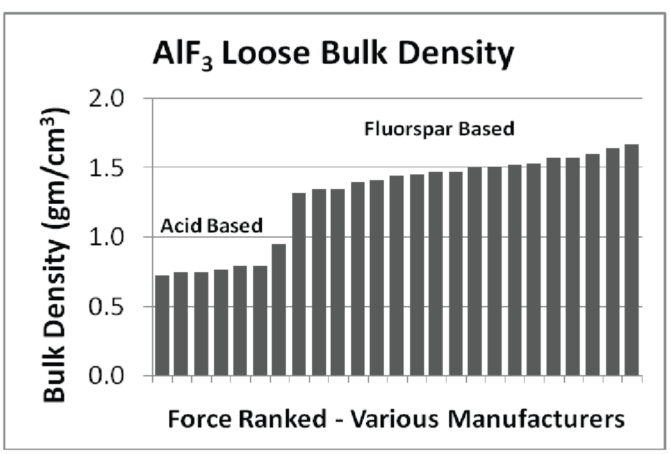

Figure 3 – Comparisons of AlF_3 bulk densities

Figure #3 shows the wide range of product bulk densities for AlF_3. Additions of AlF_3 to reduction cells and crucibles are often made on a volumetric basis. This means that differences in bulk density will need to be taken into account for distribution and dispensing of AlF_3. This is especially so when the supplier is changed from one that uses the fluorspar based process to one that uses the acid based process or vice-versa. Even a change between producers with similar manufacturing processes can cause a shift in bulk density of as much as 25%.

As with other parameters individual vendors may have significant variance in loose bulk density. An example is shown in Figure #4 showing +/- 5% variation for vendor A vs. +/-2% for vendor B. This is an additional complication in the control of bath chemistry since the combined variations in purity and density may exceed 10% for some producers.

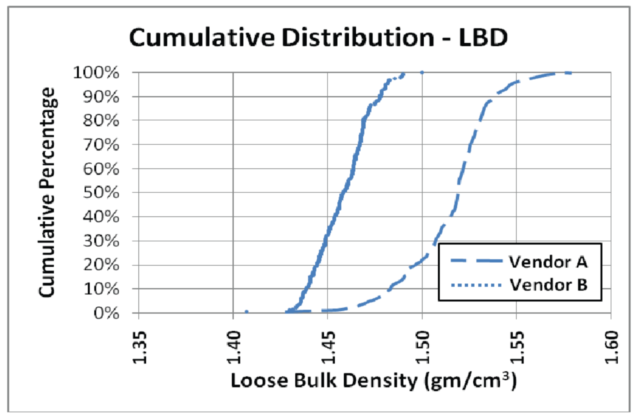

Figure 4 – Variation of density in AlF_3 of two suppliers

It is worth noting that the TAC process appears to work best with the higher density AlF_3 that is produced by the fluorspar-based process. AlF_3 from the acid-based process has been less effective in reducing Na in metal during test campaigns of limited scope.

The TAC process relies upon additions of AlF_3 to the top of a crucible filled with metal with a stirring device being lowered in place to facilitate the reactions that remove Na and Li from metal. Note the stirring device to the left shown in Figure #5.

Figure 5 – TAC process *courtesy of STAS*

Impurities - Phosphate

Arguably one of the most important impurities of concern in AlF_3 is phosphate, or P_2O_5. The concern with this impurity is related to the negative impacts that phosphorus can have on current efficiency and the metal quality of some products [2].

Since the typical consumption rate of AlF_3 is roughly 1% the consumption rate of alumina, Al_2O_3, +100 ppm, or +0.01%, of P_2O_5 in AlF_3 is roughly equal to +1 ppm of P_2O_5 in alumina [The 100:1 rule of thumb]. A comparison of many AlF_3 vendors shows a wide range of results in phosphate content in Figure #6.

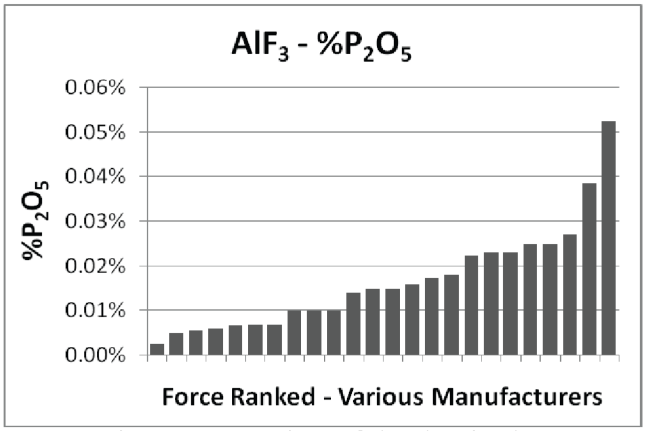

Figure 6 – Comparisons of phosphate in AlF_3

Note that producers using the acid based process are all in the lower half of the data presented above, but some producers using the fluorspar based process can also be quite low in phosphate content. This requires HF gas of high purity.

Normally, much of the difference can be ascribed to the impurities found in various grades of fluorspar. Phosphorus and silica are two common contaminants that determine the grading and the pricing of fluorspar. Fluorspar with a low level of contaminants typically has a higher market price.

However, P_2O_5 is not necessarily a problem for all aluminum producers. Phosphorus in bath is quite volatile and is easily lost to the atmosphere. Modern point-fed pre-bake cells will typically have very high capture efficiency for particulates including phosphates that are evolved from the bath. The phosphate is then returned to the pots via the dry scrubbing system. The primary loss mechanism in this system is in the form of phosphorus, P, in the metal [2].

Those locations that use side-break technology to feed pots will not be as concerned about the phosphate content of raw materials including AlF_3. Phosphate volatilization during side-break operations serves as the primary loss mechanism in these types of cells. The majority of the phosphorus escapes rapidly at very low concentrations to roof emissions. This also results in very low concentrations of phosphorus in the metal from cells that use side-break technology.

For modern point-fed cells phosphate is a concern. As with other properties it is important to know the typical content of P_2O_5 in AlF_3 and its potential for variation.

Impurities - Silica

The other impurity of great significance in AlF_3 is silica, or SiO_2. As with phosphorus, the Si content of fluorspar helps to determine its grade and its market price.

Unlike the phosphate content, the $\%SiO_2$ in AlF_3 is not strongly associated with either acid-based or fluorspar-based processing. Remember that low grade silica is the major by-product of the acid based process.

What is observed is a wide range of silica by vendor in the marketplace as is illustrated in Figure #7.

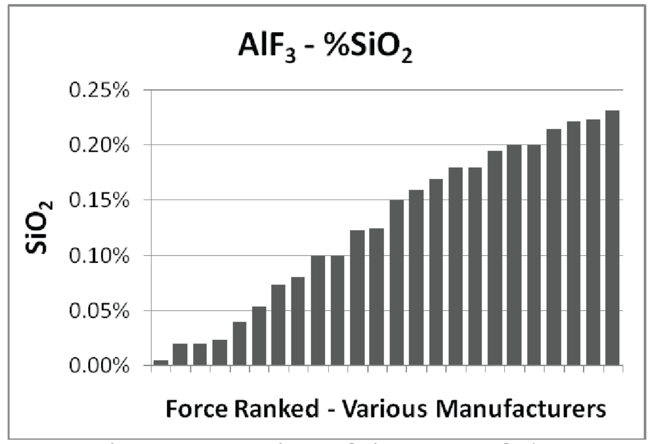

Figure 7 – Comparisons of SiO_2 content of AlF_3

Recalling the 100:1 rule of thumb for typical consumption rates of alumina with a typical SiO_2 content of 0.012% vs. aluminum fluoride with a SiO_2 content over 0.20% with one can quickly see that the contribution of SiO_2 in AlF_3 can be quite significant when performing a mass balance on silica input streams. It may exceed 15% of all process inputs. For products such as aluminum conductor rod certain sources of AlF_3 may be ruled out in favor of others.

For high purity ingot this is especially true. Since reacted or fluorinated alumina from dry scrubbing systems is not used on cells that produce high purity ingot the specific consumption rate of AlF_3 can be quite high in the range of 50 kg/mt Al. With such a high specific consumption rate many AlF_3 suppliers may be ruled out for use on high purity pot groups.

Again, understanding the central tendency and the variability of SiO_2 in a specific product may both be important to the user.

Particle Size Distribution - %-325 Mesh Size

Desirable properties of AlF_3 are often related to its content of fines, %-325 mesh, or -44 micron particle sizing. These include:

1) Flowability
2) Angle of Repose
3) Ability to be dispensed consistently
4) Dustiness

Table 1 – Factors related to particle size distribution

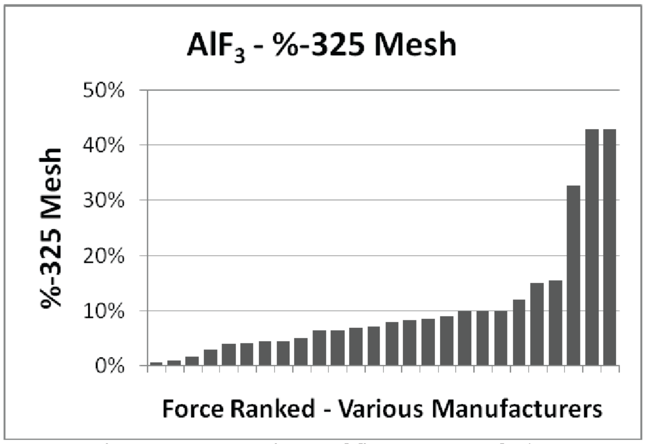

Figure 8 – Comparisons of fines content of AlF_3

AlF_3 particle sizing is controlled by the sizing of the aluminum hydrate substrate that is used. Note that a number of aluminum tri-hydrate producers will screen their product to remove fines. This is done to meet the specifications of AlF_3 producing customers. However, not all hydrate producers follow this practice. Figure #8 shows the wide range of AlF_3 product that is available in the marketplace.

There is no completely clear guideline on an acceptable level of fines content. It has a great dependence upon the means of delivery. For example, AlF_3 sources with very high fines contents may be acceptable if consumed in small, sealed bags that are placed on pots. But, in general modern cell technology and delivery systems prefer product that has ≤10% -325 mesh size.

Some smelting locations and distribution systems have been able to successfully use AlF_3 with an average of 20% -325 mesh. However, such material is not recommended as it is known to be dusty and it may also be problematic.

Concerns with particle size are linked to combinations of the four desired properties listed in Table 1. When AlF_3 is dispensed by a volumetric feeder the angle of repose and flowability of the product can have an important impact. They affect the ability to have consistent and reproducible shot sizes. These properties are typically driven by the fines content of the product.

Measuring the %-325 mesh using standard screening equipment is simple and repeatable. The consistency in measurement capability that a set of screens may also be preferred offers over the variations in the industry for flow funnel data and the lack of precision that is offered by measuring the angle of repose. This makes %-325 mesh the key product quality parameter for particle sizing of AlF_3 from the perspective of a smelting customer.

Other Properties and Impurities

Many other properties and impurities may be reported on certificates of analysis. Comparing various AlF_3 products can become confusing. In general these other parameters are less important than the five that have been discussed above. However, a few comments are offered on some of these reported properties.

Particle Sizing - The overall particle size distribution and dissolution rate of %+100 mesh material may be related to "active" and "inactive" cells [3] that have been described in the literature. However, the nature of delivery, the cell condition, and how AlF_3 is worked into the cell may be of greater importance with regard to how much AlF_3 goes to muck formation than the sizing of the AlF_3 particles.

%LOI - The %Lost on Ignition can vary widely from vendor to vendor in amount and in how it is measured. The temperature to which the sample is heated and the amount of time that it is held at that temperature both have influence over the results of the test.

Commercial grades of AlF_3 may have certificate of analysis data that references temperatures ranging from 300^0C to 600^0C at various holding times. There may also be no reference to temperature and holding time made at all. If there is one area of reporting in the AlF_3 business that cries for some standardization this is it. The most common and recommended method is to heat to 550^0C and hold one hour.

The reader should note that AlF_3 ages if it is not used immediately The %LOI will increase as months pass in storage. However, the 100:1 rule of thumb for consumption vs. alumina keeps this of being of any great concern for HF generation from the reduction cells.

%$Al_2(SO_4)_3$, %SO_4, %SO_3 or %SO_2 – The sulfur content of the product is reported in various ways. The most typical is aluminum sulfate, $Al_2(SO_4)_3$. This has little impact on the sulfur balance of a smelter, but may be needed for reporting purposes.

However, the sulfur content of AlF_3 can act as a secondary indicator of AlF_3 purity. This is in particularly true for the fluorspar based process. Residual sulfuric acid that is carried over with HF gas produced by reaction with crushed fluorspar competes with the reaction to form AlF_3 to form $Al_2(SO_4)_3$. See Figure #9 for how this is related to purity of AlF_3.

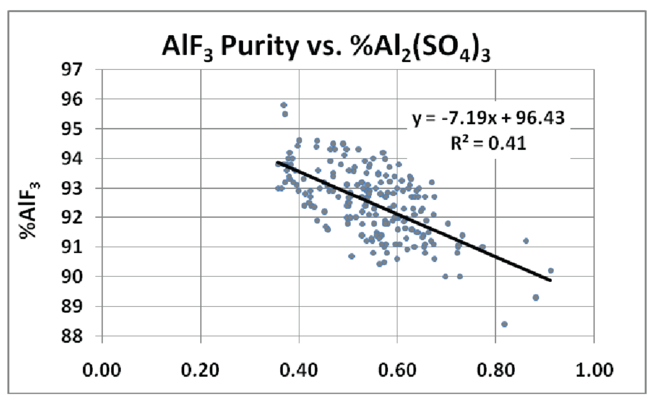

Figure 9 – Relationship between AlF_3 and $Al_2(SO_4)_3$.

%Fe_2O_3 – The iron oxide content of AlF_3 does not contribute significantly to the amount of iron in metal. Typical material will contribute about 2.5 ppm of Fe to metal and the highest levels found contribute only about 6 ppm Fe to aluminum metal.

Be (ppm) – The concentration of beryllium in AlF_3 reflects the source of aluminum tri-hydrate. It generally falls between 0.1 and 1.5 ppm. However, when the 100:1 rule of thumb is considered even the highest levels of Be found in AlF_3 are of little consequence and will contribute less than 1 ppm of Be to pot room bath. [4]

Li (ppm) – Normally the concentration of lithium in $Al_2O_3 \cdot 3H_2O$ and AlF_3 is very low, from <2 ppm, down to non-detectible levels. AlF_3 from China provides an exception to this. Levels between 100 – 150 ppm Li are often found. These levels may not be insignificant to the equilibrium concentration of LiF in pot room bath. Users are advised to check if lithium in bath is a concern.

Arsenic – A common contaminant in fluorspar is arsenic. Levels of As in AlF_3 are typically quite low. However, concentrations of arsenic in groundwater near pot room structures that have been standing for decades have been linked to low levels of As in raw materials such as AlF_3. This may be a point of interest for some customers as new technologies have been developed in Mexico to enable production of HF from high arsenic fluorspar. [5]

%Na_2O, %Na_3AlF_6, %CaO and %$CaSO_4$ – Sodium and calcium based impurities are typically not of concern to smelting clients due to the 100:1 rule of thumb.

Angle of Repose and Flowability – These properties are of concern especially with respect to the reproducibility and consistency of shot sizes of AlF_3 fed to the pot or delivered to bins on the pot. These properties are related to the particle size distribution of the product. Comments were given under the section on %-325 mesh content.

Attrition Index – When the standard Alcoa attrition index test for smelter grade alumina has been applied to AlF_3 the results have shown low to moderate levels of attrition. Since the AlF_3 at most smelters does not undergo severe forms of pneumatic transport the attrition rate is generally not a concern.

Analysis and Measurement Methods

While most AlF_3 producers have capable laboratory facilities it is important to note that common measurement standards and analytical methods have yet to be established in the AlF_3 industry.

There is an ISO Work Group that is currently addressing standards using X-ray fluorescence for determination of elements. AlF_3 is covered under standards ISO/NP 12926-1 and ISO/NP 12926-2 that are soon to be published according to Resolution #10 of the ISO meeting in Beijing.

Until industry standards are adopted analytical differences may be subtle, but for parameters that are critical, or when multiple suppliers are to be directly compared, it may be appropriate to use an independent laboratory as a referee.

As defaults for analysis of AlF_3:

ISO/NP 12926-1, ISO/NP 12926-2 and ASTM method E1621 on X-ray fluorescence are acceptable for determinations of %AlF_3, %SiO_2, %$Al_2(SO_4)_3$, %P_2O_5, %Fe_2O_3, %Na2O, and %CaO.

ASTM method E-276 on woven wire sieve screen analysis or equivalent is acceptable for determinations of %100 mesh, %150 mesh, %200 mesh, and %325 mesh.

ASTM method C323 or equivalent is acceptable for determinations of %LOI, Loss on Ignition to 550 C [held for 1 hour at 550 C], and %MOI, Moisture on Ignition to 110 C.

ASTM B212 or equivalent is acceptable for determination of Loose Bulk Density.

Conclusions

As raw materials for smelters go, the key parameters for AlF_3 are few. Product purity, density, variability, fines content, and impurities of phosphate and silica are the primary factors of concern.

Changes between suppliers and variation in product quality require consideration in both areas of application; for the control of bath chemistry and for treatment of aluminum in crucibles.

Other physical and chemical properties may be related to particular concerns. These can vary by the manufacturing process or the global region from while the raw materials originated.

The industry has yet to adopt standard measurement methods although it is getting close to having these for determination of elements. It is advisable to use a referee laboratory when making critical comparisons of key properties.

References

1. Dr. Martin Iffert, "Aluminium Smelting Cell Control and Optimisation," thesis University of New South Wales 2008, p. 10.
2. Dr. Elke William Thisthad, "Electrochemical properties of phosphorus compounds in fluoride melts" thesis Norwegian University of Science and Technology, NTNU, 2003, p. iii – v.
3. Dr. Martin Iffert, "Aluminium Smelting Cell Control and Optimisation," thesis University of New South Wales 2008, p. 135.
4. Stephen Lindsay & Charles Dobbs "Beryllium in Pot Room Bath" Light Metals 2006, pp 95-100
5. the-infoshop.com Market Research Report, abstract of "The Economics of Fluorspar" 10th Edition, 2009, http://www.the-infoshop.com/report/ros80879-econo-fluorspar.html

Acknowledgements

The author would like to acknowledge the following people for their insights and contributions:

- Andrew J. Spears, – Alcoa, Pt. Comfort and formerly of Alcoa, Ft. Meade – for insights to the processing of AlF_3 by the wet and dry processes.
- Suelyn Aschenbeck – Alcoa, Pt. Comfort – for lab analysis and analytical methods
- Dr. Neal Dando – Alcoa Technical Center – for insights and analysis of alumina phases found in AlF_3
- Richard Hamel – Alcoa, Knoxville – for assistance and contact with many producers worldwide
- Numerous contributors from the AlF_3 industry for commentary on processing, raw materials and analysis
- Merino, Dr. Margarita R. (Ph.D. – Florida State University) – for her encouragement, dedication and support.