

Two Perspectives on the Evolution and Future of Alumina

¹Linus M. Perander, ¹James B. Metson, ²Cornelis Klett

¹Light Metals Research Centre, The University of Auckland, New Zealand

²Outotec GmbH, Frankfurt, Germany

Alumina, Bayer process, Hall Heroult process, Emissions, Energy, Calcination

Abstract

Over the 125 year history there have been a number of step-changes in the Hall-Heroult process, despite a remarkable adherence to the original concepts of the inventors. In addition to the steady increment in scale, most noteworthy perhaps have been the introduction and impending disappearance of Soderberg technology, the introduction of magnetically compensated cell design, changes in dynamics of alumina feeding and the introduction of dry-scrubbers for HF control and fluoride recovery.

The Bayer process has also seen some significant advances, driven by the demands of energy and environmental imperatives and the steadily narrowing window of product specifications, driven in turn by refinements in the Hall-Heroult process. Demands for coarser particle size distribution, higher specific surface areas and lower attrition index have been accompanied by changes in precipitation strategy and conversion to more energy efficient stationary calcination processes.

The properties of a "typical" metallurgical alumina have thus changed. Indeed the term "alumina" is now more indicative of stoichiometry than it is of structure, and even in this, it is less than precise. In this paper we discuss how new scientific tools and insights are changing the way we define (and perhaps should specify) this material.

The History of Alumina Calcination

The early history and development of the alumina and aluminium processes and industries are summarised elsewhere [1, 2] Fundamentally these processes remain the same, although a number of technological breakthroughs and step-changes have occurred. The past 50-years in particular have fundamentally changed what a smelter demands in terms of properties and performance of the primary raw material, the alumina fed to the reduction cell. This paper addresses the impact of the calcination step in the Bayer process on the development of alumina properties and our understanding of how these properties impact on the smelter operations.

The use of dry scrubbers in the aluminium smelters started in the 1960s as a response to the rising emissions concerns, and potential fluoride losses associated with this process. The dry scrubbers make use of the high specific surface area and the reactivity of partially calcined alumina (LOI < 1 wt-%) to capture the volatile fluorides emitted from the electrolyte in the reduction cell. Around the same time as the dry scrubbers were introduced, another significant change also occurred. Traditionally, the primary raw material, alumina, was fed to the electrolysis cell periodically (often manually) and in relatively large doses. Environmental requirements to enclose the cells as much as possible and the clear process control benefits of a more

continuous way to feed the alumina resulted in the development of so called *Break and Feed* systems. The first implementation of this way of feeding was the *Bar Breaking* method. Using this method, a breaker beam is lowered to break the layer of crust (which covers the cell and anodes) and then a specified amount of alumina (determined by volume) is dumped into the cell. Along with the alumina a large amount of broken crust and cover material also enters the cell. Dissolution is slow and large amounts of undissolved alumina/crust are deposited on the surface of the cathode and gradually dissolved until the next feed cycle. The bar breaking method has given way to *Point Feeding*. Up to five of these point feeders (shot size 0.5 – 3 kg of alumina determined by volume per feeder) operate every few minutes, changing the operation from a semi-batch type to a more continuous nature [3].

As a result, particularly of these feeder changes, the demands on alumina quality have also changed. The so called *Floury Alumina* (with fine particle sizes, low specific surface areas and high alpha alumina contents) has poor flow and dissolution characteristics and has been displaced by *Sandy Alumina* (with larger particle sizes, high surface areas and low alpha alumina content). The impact of alumina properties on transport, feeding and dissolution characteristics, the ability to form a stable crust and anode cover as well as the adsorption of HF in the dry-scrubbers, have been of particular interest. Of note is the continued evolution of these properties (for example the inexorable demand for higher surface areas), at times with a limited understanding of the net process impact of such changes.

Stationary calciners, as an alternative to the Rotary Kilns were introduced in the 1950s to 60s. The gains, both in increased production volumes, reduced maintenance and in energy savings, resulted in considerable research efforts into these technologies, and as a result variations of the fluidised bed technology emerged. Today these are known as: *Circulating Fluidised Bed* (CFB), *Gas Suspension* (GS) and *Fluid Flash calciners*. For the main calciner technologies typical energy consumption, residence time, production capacity, alpha alumina content, calcination temperature and free heat transfer surface are presented in table 1. With typical production capacities between 2500 to 4000 tons per day for modern Gas Suspension or Circulating Fluidised Bed calciners, significant effort goes into minimising the downtime of these installations which has also led to other process and control improvements. Most noteworthy, however, is the reduction in energy consumption compared even to best practice Rotary Kilns.

The energy reductions can mainly be attributed to more rapid heat transfer into particles, heat recovery in the cooling stages and from the waste gas heat, resulting in common features such as the pre-heating stages and cooling stages with direct gas solid heat transfer as well as indirect heat recovery in the fluid bed coolers for both Gas Suspension and Circulating Fluidised Bed calciners. The energy consumption should however be compared to the

theoretical energy for gibbsite calcination which lies around 1.98 to 2.40 MJ kg⁻¹ for dry and moist gibbsite, respectively [4], indicating that there is still margin for improvements. With the calcination stage amounting to approximately a third of the energy consumed in the Bayer process the potential energy savings becomes significant.

Table 1. Typical energy consumptions, residence times, production capacities, alpha alumina contents, calcination temperatures and free heat transfer surface for different calciner technologies [4-8].

	Gas Suspension or Fluid Flash	Circulating Fluidised Bed	Rotary Kiln
Specific energy (MJ / kg product)	~3.0 – 3.3	~2.8 – 3.2	~4.2 – 5.5
Material residence time in the hot zone in the furnace (s)	1 - 2	180 – 300	2000 – 10000
Typical calcination temperature (°C)	1100	950	1100
Free heat transfer surface (m ² / g product)	45	0.03	0.003
Typical alpha alumina range (wt-%)	4-10	1-8	5-20
Typical production capacity (tons per day)	2700	3000	1000

Differences in the alpha alumina contents for the different technologies are directly tied to the residence times and calcination temperatures, whereas the higher free heat transfer surface for the modern calciners is related to the high gas velocities and large surface areas. It has been proposed that the heating rate during the calcination may influence the reaction pathways [9, 10], and it is therefore hardly surprising that material from rotary kilns often display different properties [11, 12]. Surprisingly limited effort has however gone into understanding how these differences arise and more specifically what impacts differences in the precursor material have on the calcination reactions and resulting product properties. The speed of the modern calciners, together with the variation of particle size and morphology, is expected to produce a structurally more disordered and heterogeneous material than those produced in rotary kilns. The disorder and co-existence of phases, often within a single particle, poses significant challenges for characterisation and understanding behaviour of these materials. It also challenges our conventional definition of what we call alumina.

The Science of Alumina Calcination

Several excellent reviews on transition alumina phase changes during the calcination of gibbsite and boehmite exist; particularly noteworthy are those of Levin et al. [13], and the overview of Wefers et al. [2]. The reactions have been found to be influenced by several parameters (such as temperature, heating rate, residence time, particle size and morphology, crystallinity, impurities and atmospheric conditions) some of which are directly related to Bayer operations [2, 9, 10, 12, 14]. Figure 1 summarizes the possible reaction pathways for gibbsite dehydroxylation. It should be pointed out that, apart from the initial decomposition to chi alumina, rho alumina or boehmite, the reactions proceed slowly; even if the energetic barriers are overcome prolonged heating is required to reach equilibrium for any of the meta-stable transition alumina forms. Thus the particles formed in modern

stationary calciners will inevitably span the diagram of reaction pathways and challenge the value of any type of quantitative phase analysis. Nevertheless such an analysis is one of the few comparative tools we have in explaining differences in alumina properties and performance.

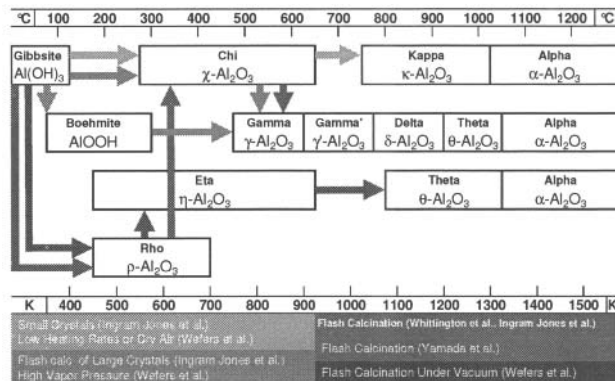


Figure 1. Thermal decomposition pathways of gibbsite, adapted from Wefers et al. [2].

High intensity, high resolution synchrotron (and neutron) diffraction data has been shown to be extremely useful in terms of monitoring gibbsite crystal growth mechanisms from Bayer liquors in-situ [15], for identifying minor crystallographic impurities [16] as well as for examining the transition aluminas and their transformation reactions [17-20]. However, for deducing information on the structures of the poorly crystalline transition alumina phases, even these techniques face some limitations [21], particularly in complex mixed phase environments such as the MGAs.

Due to the short residence times in modern calciners, deviations from the average transition alumina structures are observed. This is caused by local disorder, which results in significant peak broadening which, combined with the overlapping peaks for the transition aluminas, complicates structural analysis using traditional diffraction methods. Despite the improvements in fitting diffraction data on MGA, made possible through the works by Ashida et al. [22] and Paglia et al. [19], conventional diffraction techniques are limited by the need for crystallographic long range order. Indeed from the analysis of a typical fluid bed MGA, Ashida proposes that what we call Al₂O₃ is better described as H₂Al₁₀O₁₆ [22]. This is consistent with previous views of the structure of gamma alumina [2] and provides a clear insight into the origin of HF generation in the reduction cell as examined by Patterson et al. [23]. The hydrogen (as residual -OH groups) is a consequence of the increasing undercalcination of alumina, necessary to meet the demand for increased surface area. Thus we gain HF adsorption capacity at the scrubber, at the direct expense of an increased HF burden circulating with the cell gas.

The best practice in phase analysis is exemplified in the Rietveld refinement in figure 2 for which the diffraction data was obtained at a synchrotron source. Apart from the obvious overlap of several peaks in the diffraction pattern, the broad and diffuse peaks from the transition aluminas, the presence of additional X-ray amorphous components and the incomplete structural models for the transition aluminas, results in the discrepancies between the fitted (black) and observed (red) spectra. In the distinction

between the transition alumina phases (or forms) it is generally agreed that theta alumina is more ordered than delta alumina which again is more ordered than the gamma alumina phase [24-26], however, exactly how the transformation into the more ordered forms proceeds is still debated [2, 13, 27]. The formation of gamma – gamma' – delta and theta alumina can also be seen as waypoints on the gradual transformation into a fully ordered state (represented by the thermodynamically stable alpha alumina).

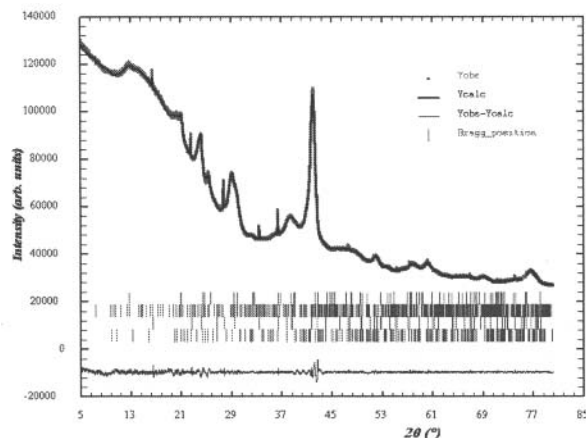


Figure 2. Synchrotron X-ray powder diffraction pattern of a CFB calcined MGA sample and resulting Rietveld refinement results. Note that the shape of the background is a result of the amorphous nature of the quartz capillary used for mounting the sample.

The move to stationary calciners has apparently swapped the historical problem of the broad distribution of residence times, and thus phase composition for individual particles, for the problem of distributions of phases within single particles due to the heat transfer constraints in these technologies. As reported elsewhere, Environmental SEM can be used to observe alpha alumina directly in cross sectioned alumina grains through the Charge Contrast phenomenon [28]. The different dielectric properties of the structurally more ordered alpha alumina, compared to the transition alumina forms, result in a contrast difference in the ESEM. This has allowed for new insights into the alumina phase distribution and phase transformation mechanisms within single particles. The results indicate that alpha alumina formation is closely tied to growth morphology, and seems to follow the same pattern as the growth rings revealed in gibbsite cross sections (figure 3). This suggests that local structure and impurities are important in the nucleation and transformation reactions and ultimately the formation and location of alpha alumina within particles.

The phase inhomogeneities between and even within particles exemplifies a wider challenge in understanding alumina behavior. The properties reported on a alumina specification sheet represent at best a heavily averaged view, where the outlier populations may be of more significance in, for example influencing alumina dissolution and flowability, than the mean value specified. The dominance of over and under calcined material in the fine particle size fraction is a good example of this [29].

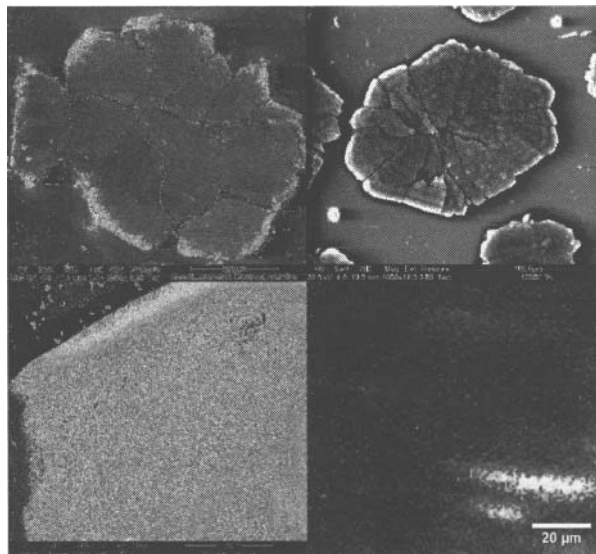


Figure 3. Top left: Alpha alumina observed around the edge of a cross sectioned GS calcined alumina particle. Top right: Alpha alumina formation in a soak calcined alumina grain following the gibbsite growth ring pattern. Bottom left: gibbsite growth rings as revealed by Environmental SEM and corresponding Na distribution (bottom right), obtained using a ToF-SIMS instrument.

The same consideration applies to specific surface area, LOI, and the rarely reported, but important, pore size distribution. As discussed more extensively elsewhere [30], the low order transition aluminas (gamma, rho, chi alumina) contain more residual hydroxyls (confirmed by LOI measurements) which inevitably results in more HF being generated upon dissolution. At the same time, the fine pore size in these under-calcined components might be expected to influence their ability to capture HF in the dry-scrubber. It seems that the narrow pores restrict access to internal porosity and readily become blocked (when HF reacts to form oxy-fluorides). This further restricts access to internal sites, thus reducing the capacity and rate of HF absorption. An example of a distinctly bi-modal pore-size distribution in a SGA sample is provided in figure 4. and corresponding HF generation and emissions data are presented and discussed in elsewhere [30].

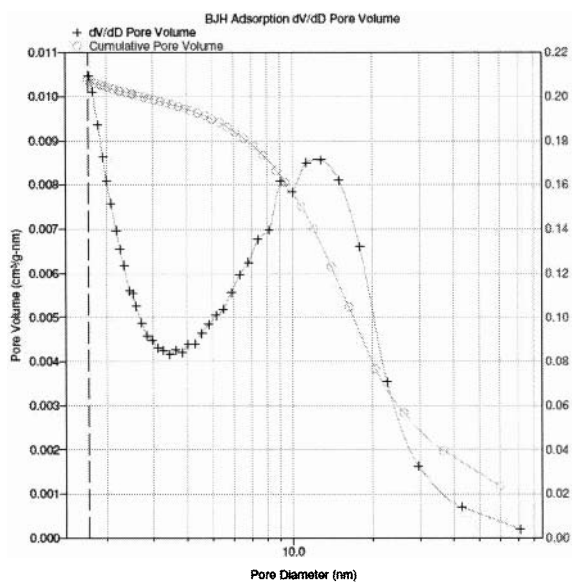


Figure 4. A sample taken from a GS calciner shows a bi-modal pore size distribution indicating the presence of under calcined components as well as over calcined material.

The Future of Alumina Calcination

With the increasing number of green- and brownfield alumina refineries it is no surprise that research today focuses primarily on production gains and energy savings through process and control improvements. Typical energy consumption is around 11.6 GJ per metric ton of Al_2O_3 . However, the broad range of energy consumption across the industry [31], indicates that there is still room for significant energy savings in a number of operations and process areas. As the higher grade bauxite reserves are being depleted the industry increasingly turns to more energy intense and difficult to process diasporic and boehmitic ores.

In the past decades alumina production volumes have increased dramatically, with calciner operating capacities up to 4000 metric tonnes per day. As a result of the push towards faster and more energy efficient, but also more abrasive, stationary calcination processes, attrition continues to receive a lot of attention [32, 33]. Many options and improvements have been developed to the calcination technologies to reduce breakage and improve product quality. Not all, but some of these improvements come with the price of higher operating costs. Thus research programmes are increasingly focusing on a better understanding of the role of the precipitation step and resulting particle morphology and gibbsite strength, for the alumina attrition behaviour during calcination and product handling. There is also a wider consensus emerging that new definitions for how attrition is defined, and indeed measured, are needed, as again the specification sheet is not always informative as to smelter experience. The next stages of this discussion should include the processes downstream of calcination in alumina handling, and also at the smelter to get a more holistic view. This informs the optimum compromise between costs, product quality and stable operation.

In the smelter surprisingly few studies systematically examine the impact of alumina quality (or properties) on operations, although the impact of alumina on HF emissions is an area of increasing

importance and interest [34]. Another critical performance criterion for the alumina is rapid dissolution in the molten cryolite based electrolyte. To achieve this, sufficient dissolution power (or superheat) is needed, but also the method, amount and frequency of the alumina additions and the quality (dissolvability) of the alumina are of importance [35-38]. The operational stability and feed strategy relies on a consistent alumina quality. However, variations between, and even within, alumina shipments is often a reality. Such variations are frequently not reflected in the specifications of the alumina, making it difficult to anticipate and make process adjustments to accommodate the raw materials variations. Typical outcomes are process fluctuations, sludge formation or other feed related instabilities and on occasion, emissions problems.

Conclusions

The alumina specification sheet currently represents a contractual quality index in terms of a number of (often historically) defined key properties. It is frequently less helpful as a predictive tool in terms of assisting process optimization and informing the smelter in terms of how the alumina is expected to behave.

This is then exacerbated by an incomplete understanding at a smelter level of how alumina properties impact on smelter performance. Good examples of this are: the impact of microstructure (particularly specific surface area and pore size distribution) or phase distribution between particle size classes on HF generation, dissolution and dry scrubbing.

These properties are primarily influenced by precipitation and calcination strategies but these relationships are complex. Most critical is the “averaging” impact of numbers reported in the specifications sheet where the outlier populations may be the dominant contributor to process fluctuations and instabilities in the smelter.

References

1. Edwards, J.D., F.C. Frary, and Z. Jeffries, *The Aluminum Industry - Aluminum and Its Production*. Chemical Engineering Series. 1930.
2. Wefers, K. and C. Misra, eds. *Oxides and Hydroxides of Aluminum*. Alcoa Technical Paper No. 19. 1987, Aluminum Company of America: Pittsburgh, PA.
3. Andrews, E.W., *A Controllable Continuous Mass-feed System for Aluminium Smelters*. PhD Thesis, The University of Auckland, New Zealand, 1998.
4. Hudson, L.K., ed. *Alumina Production*. Alcoa Research Laboratories. 1982, Aluminum Company of America: Pittsburgh, PA.
5. Jenkins, B. and C. Bertrand, *Improvements in the Design and Operation of Alumina Flash Calciners*. IFRF Combustion Journal, 2001 (November): p. 1-18.
6. Hiltunen, P., R. Bligh, C. Klett, M. Missalla, and H.-W. Schmidt, *How to achieve high availability with large calciners and avoid unforeseen downtime*. Light Metals (Warrendale, PA, United States), 2008: p. 63-68.
7. Raahauge, B.E., *Advances in gas suspension calcination technology*. Aluminium (Isernhagen, Germany), 2007. **83**(1/2): p. 40-42.
8. McIntosh, P., R. Greenhalgh, and P. Mills, *Advanced control techniques for alumina calcination rotary kilns*.

- Light Metals (Warrendale, PA, United States), 1987: p. 59-63.
9. Ingram-Jones, V.J., R.C.T. Slade, T.W. Davies, J.C. Southern, and S. Salvador, *Dehydroxylation sequences of gibbsite and boehmite: study of differences between soak and flash calcination and of particle-size effects*. Journal of Materials Chemistry, 1996. **6**(1): p. 73-9.
 10. Whittington, B. and D. Ilievski, *Determination of the gibbsite dehydration reaction pathway at conditions relevant to Bayer refineries*. Chemical Engineering Journal (Amsterdam, Netherlands), 2004. **98**(1-2): p. 89-97.
 11. Metson, J., T. Groutso, M. Hyland, and S. Powell, *Evolution of microstructure and properties of SGA with calcination of Bayer gibbsite*. Light Metals (Warrendale, PA, United States), 2006: p. 89-93.
 12. Yamada, K., T. Harato, S. Hamano, and K. Horinouchi, *Dehydration products of gibbsite by rotary kiln and fluid calciner*. Light Metals (Warrendale, PA, United States), 1984: p. 157-71.
 13. Levin, I. and D. Brandon, *Metastable alumina polymorphs: crystal structures and transition sequences*. Journal of the American Ceramic Society, 1998. **81**(8): p. 1995-2012.
 14. Bennett, I. and R. Stevens, *Calcination and phase changes in alumina*. British Ceramic Transactions, 1998. **97**(3): p. 117-125.
 15. Loh, J.S.C., A.M. Fogg, H.R. Watling, G.M. Parkinson, and D. O'Hare, *A kinetic investigation of gibbsite precipitation using in situ time resolved energy dispersive x-ray diffraction*. Physical Chemistry Chemical Physics, 2000. **2**(16): p. 3597-3604.
 16. Latella, B.A. and B.H. O'Connor, *Detection of minor crystalline phases in alumina ceramics using synchrotron radiation diffraction*. Journal of the American Ceramic Society, 1997. **80**(11): p. 2941-2944.
 17. O'Connor, B., D. Li, B.K. Gan, B. Latella, and J. Carter, *Time-resolved studies of alumina ceramics processing with neutron and synchrotron radiation data*. Advances in X-Ray Analysis, 1999. **41**: p. 659-667.
 18. Neissendorfer, F., U. Steinike, B.P. Tolochko, and M.A. Sheromov, *On the decomposition of hydrargillite investigated by synchrotron x-ray diffraction*. Nuclear Instruments & Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors, and Associated Equipment, 1987. **A261**(1-2): p. 219-20.
 19. Paglia, G., C.E. Buckley, A.L. Rohl, R.D. Hart, K. Winter, A.J. Studer, B.A. Hunter, and J.V. Hanna, *Boehmite Derived Gamma-Alumina System. 1. Structural Evolution with Temperature, with the Identification and Structural Determination of a New Transition Phase, Gamma'-Alumina*. Chemistry of Materials, 2004. **16**(2): p. 220-236.
 20. Zhou, R.S. and R.L. Snyder, *Structures and transformation mechanisms of the eta, gamma and theta transition aluminas*. Acta Crystallographica, Section B: Structural Science, 1991. **B47**(5): p. 617-30.
 21. Billinge, S.J.L. and I. Levin, *The Problem with Determining Atomic Structure at the Nanoscale*. Science (Washington, DC, United States), 2007. **316**(5824): p. 561-565.
 22. Ashida, T., J.B. Metson, and M.M. Hyland, *New approaches to phase analysis of smelter grade aluminas*. Light Metals (Warrendale, PA, United States), 2004: p. 93-96.
 23. Patterson, E.C., *Hydrogen Fluoride Emissions From Aluminium Electrolysis Cells*. PhD Thesis, The University of Auckland, New Zealand, 2002.
 24. Jayaram, V. and C.G. Levi, *The structure of delta-alumina evolved from the melt and the gamma -> delta transformation*. Acta Metallurgica, 1989. **37**(2): p. 569-78.
 25. Wilson, S.J., *The dehydration of boehmite, γ -Al(OH)₃ to γ -alumina*. Journal of Solid State Chemistry, 1979. **30**(2): p. 247-55.
 26. Wilson, S.J. and J.D.C. McConnell, *A kinetic study of the system boehmite/alumina (γ -Al(OH)₃/Al₂O₃)*. Journal of Solid State Chemistry, 1980. **34**(3): p. 315-22.
 27. Wolverson, C. and K.C. Hass, *Phase stability and structure of spinel-based transition aluminas*. Physical Review B: Condensed Matter and Materials Physics, 2001. **63**(2): p. 024102/1-024102/16.
 28. Perander, L., C. Klett, H. Wijayarane, M. Hyland, M. Stroeder, and J. Metson, *Impact of Calciner Technologies on Smelter Grade Alumina Microstructure and Properties*. in *Proceedings of the 8th International Alumina Quality Workshop*. 2008. Darwin, Australia.
 29. Perander, L.M., Z.D. Zujovic, T.F. Kemp, M.E. Smith, and J.B. Metson, *The Nature and Impacts of Fines in SGA*. Journal of Metals, 2009. **61**(11): p. 33-39.
 30. Perander, L.M., M.A. Stam, M.M. Hyland, and J.B. Metson, *Towards Redefining the Alumina Specifications Sheet – The Case of HF Emissions*. Light Metals (Warrendale, PA, United States), 2011.
 31. Henrickson, L., *The need for energy efficiency in bayer refining*. Light Metals (Warrendale, PA, United States), 2010: p. 173-178.
 32. Klett, C., M. Missalla, and R. Bligh, *Improvement of product quality in Circulating Fluidized Bed calcination*. Light Metals (Warrendale, PA, United States), 2010: p. 33-38.
 33. Wind, S., C. Jensen-Holm, and B.E. Raahauge, *Development of particle breakdown and alumina strength during calcination*. Light Metals (Warrendale, PA, United States), 2010: p. 17-24.
 34. Iffert, M., M. Kuenkel, M. Skyllas-Kazacos, and B. Welch, *Reduction of HF emissions from the trimet aluminum smelter (optimizing dry scrubber operations and its impact on process operations)*. Light Metals (Warrendale, PA, United States), 2006: p. 195-201.
 35. Dando, N., X. Wang, J. Sorensen, and W. Xu, *Impact of thermal pretreatment on alumina dissolution rate and HF evolution*. Light Metals (Warrendale, PA, United States), 2010: p. 541-546.
 36. Liu, X., S.F. George, and V.A. Wills, *Visualization of alumina dissolution in cryolitic melts*. Light Metals (Warrendale, PA, United States), 1994: p. 359-64.
 37. Østbø, P., N., *Evolution of Alpha Phase Alumina in Agglomerates upon Addition to Cryolitic Melts*. PhD Thesis, Norwegian University of Science and Technology, Trondheim, Norway, 2002.
 38. Welch, B.J. and G.I. Kuschel, *Crust and alumina powder dissolution in aluminum smelting electrolytes*. Journal of Metals, 2007. **59**(5): p. 50-54.