

CUSTOMER IMPACTS OF Na₂O AND CaO IN SMELTER GRADE ALUMINA

Stephen J. Lindsay

Alcoa, Inc.; Primary Metals; 300 N. Hall Rd. MS S-29, Alcoa, Tennessee, 37701-2516, USA

Keywords: Alumina, SGA, Na₂O, Soda, CaO, Calcia, Bath

Abstract

Two major impurities in Smelter Grade Alumina, SGA, directly impact the bath chemistry of smelting customers. Aluminum fluoride is consumed in great quantities to neutralize the impact of calcium and sodium that enter the process. Consumption solely for the neutralization of excess CaO and Na₂O generates surplus bath. The resulting cryolitic material can then only be consumed by the primary aluminum industry. In this paper the author discusses points of concern from the perspective of customers with regard to %CaO, %Na₂O, and the ratio of between %CaO and %Na₂O. Conclusions include the impact that the growth of surplus cryolitic bath will have upon producers of SGA.

Introduction

Over many decades the quantities of Na₂O and CaO in alumina have served purposes that have been beneficial to the production of primary aluminum. The typical amounts of these impurities found in SGA have provided for the losses of Na and Ca from the aluminum reduction process. They have also provided for sufficient generation of excess bath from existing aluminum smelters to support the growth of the primary aluminum industry.

Things were not always this way. In the early days of aluminum production, inexpensive sources of sodium and cryolitic bath were in high demand. At first, pure cryolite was mined from Greenland. This continued until just after the second world war. Production of synthetic cryolite and bath from electrolytes such as aluminum fluoride plus sodium carbonate followed. But, these were not inexpensive sources of bath. Thus, some aluminum producers of that era built and operated cryolite recovery plants to leach bath and alumina from spent pot liner to recover it at a lower cost.

When pot lining designs with pre-baked blocks and dry scrubbing technology emerged the need to operate cryolite leaching plants came to an end. Lower net losses of sodium to cathode residues had shifted the industry-wide mass balance such that many smelters began producing more bath than they could use. This excess either went to smelters that consumed bath or to support the needs of Greenfield or Brownfield expansion projects.

The recent migration towards high amperage cell designs, of >350 kA, constructed with graphitized cathode blocks is shifting the worldwide mass balance yet again. These improved lining materials reduce the net amount of sodium that intercalates into the cathode. As the industry continues its migration towards this technology it is expected that a much greater emphasis will be placed on levels of Na₂O and CaO in SGA. If there is no net reduction in these impurities it is estimated that metal producers will spend over US\$450 million by 2020 just for surplus bath production. This is surplus that will extend beyond the growth needs of the global aluminum industry.

Industrial Data

Alcoa, Inc. operates twenty smelters and nine alumina refineries worldwide. Na₂O content of SGA is a key parameter that is managed by all internal Customer Satisfaction Indexes, or CSIs [1]. Some CSIs also follow parameters such as %CaO or the ratio of %CaO to %Na₂O in SGA. These factors are all related to the control of bath chemistry of the reduction cells. But, over a longer-term they are also related to the amount of excess bath that smelters produce at significant expense.

As with the rest of the industry excess bath that is produced by Alcoa is consumed by other smelters internally or it serves new projects that consume this material. For the purposes of this paper Alcoa's group of smelters and refineries is considered to be a reasonable cross-section for bath generation and consumption in the global primary aluminum industry. The range of pot types in this group includes cells of slightly >100 kA to >350 kA.

In this group the typical generation rate of excess bath for cell technologies that fall between 100 kA and 230kA is from 4.2 to 5.0 kg/mt Al produced. To put this in perspective a typical pre-bake smelter of 250,000 mt/yr capacity will generate 1050 to 1250 mt of excess tapped bath per year, or about 100 mt per month.

Newer technology pre-bake pot lines operated at >350 kA have a bath generation rate that is higher, in the range of 6.5 to 7.0 kg/mt Al produced.[2] See Figure 1. A new pot line that has not yet begun its first pot relining cycle may produce as much as 10.0 kg/mt Al. These differences may seem small when we speak in terms of kilograms. But, the cumulative impact over the entire aluminum industry is significant and it is costly.

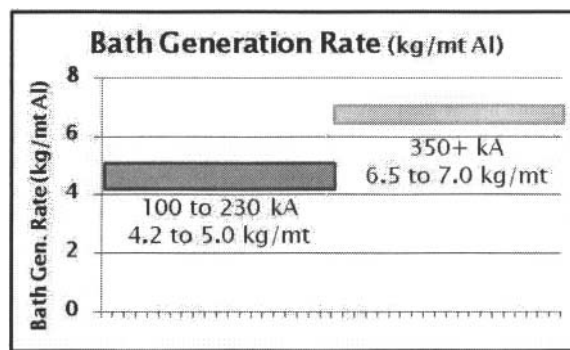


Figure 1 – Comparison of excess bath generation rates

Bath generation all starts with the introduction of alkali and alkaline earth materials, primarily as oxides and as other forms of sodium and calcium. These and some other trace impurities that accumulate in bath must be neutralized by smelters to their standard bath chemistry parameters. This bath typically takes the

form of cryolite enriched with excess aluminum fluoride, Na_3AlF_6 plus 10% to 12% excess AlF_3 by weight that also includes 4% to 7% CaF_2 . Thus, excess Na_2O , CaO , Na_2CO_3 , etc. all are neutralized by adding sufficient quantities of AlF_3 .

While the mass balance of a modern reduction cell is more complex than this simplified description, these additions of AlF_3 represent excess costs to smelters. The majority, typically 50%, is consumption of AlF_3 . By the ton, this is the most expensive raw material commonly consumed by modern smelters. Market prices fluctuate with demand, but generally fall into the range of US\$850/mt to US\$1850/mt [typical 2008 to 2011 pricing]. There are additional expenses for energy, labor, and materials that can, and often do, add up to more than US\$2000/mt for excess bath production.

While excess bath is bought and sold it is not profitable to generate. The market price for excess bath typically falls into the range of US\$150/mt to US\$300/mt. Thus, its sale recovers only a fraction of the sunken cash costs. Refer to Figure 2 to see how this compares to the typical range of generation costs.

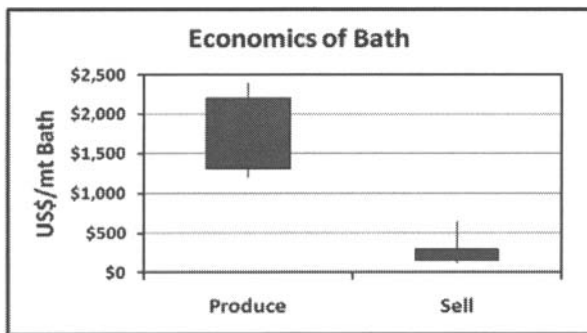


Figure 2 – Costs to produce a tonne of bath vs. its sales price

Soda and Calcia

Impurities of Na_2O and CaO are central to the generation of excess bath in pot lines. Between 20% and 50% of the CaO that enters a smelter may be in its anode coke supply. But, with rare exceptions, the majority of CaO enters with the alumina supply. However, the amount of sodium that enters smelters is an order of magnitude higher than calcia. Again, smelting grade alumina is the main source, but without exception in this case. The second most common source of sodium comes via additions of Na_2CO_3 to adjust bath chemistry targets of individual pots. Normally this is limited to cells that are new, or that are high in superheat, which is the actual bath temperature minus its liquidus temperature.

There is no doubt that our vertically integrated industry needs, uses, and wastes tremendous amounts of sodium. Caustic liquor is essential to the Bayer process. Bath, made of sodium fluoride and aluminum fluoride is essential to the Hall-Héroult reduction process. But, after serving these processes most sodium ends up in refinery residue storage areas, in spent pot liner, and in cast house dross residues serving little, if any, useful purposes.

With this in mind one might ask how much sodium is needed? With regard to excess bath generation the answer is clearly less.

Sodium intercalation into cathodes and losses with liquid metal carried into cast house furnaces are both accepted at some level. But, methods to reduce the amount of bath poured with metal into ingot furnaces are always sought. Newer generation cathode designs for high amperage cells are now exclusively based upon graphitized cathode blocks. The greater density of this material, and its crystalline rather than amorphous structure, reduces both sodium intercalation and consumption.

Both of these are positive outcomes that reduce sodium loss mechanisms. They also have the potential to reduce AlF_3 costs, provided that sodium in the raw materials to smelters can also be reduced. If it cannot, excess Na only serves to generate another industrial waste product from a global perspective, surplus bath.

As noted, the sodium mass balance of a smelter can be complex. But, a simplified rule of thumb is that with an average pot life of six years, or ~2200 days, that 0.28% to 0.32% Na_2O in SGA balances typical loss mechanisms. It also generates sufficient excess bath that provides for growth of the aluminum industry.

But, very few refineries in the world operate with % Na_2O in this range. The average is closer to 0.39% in SGA. Refer to Figure 3.

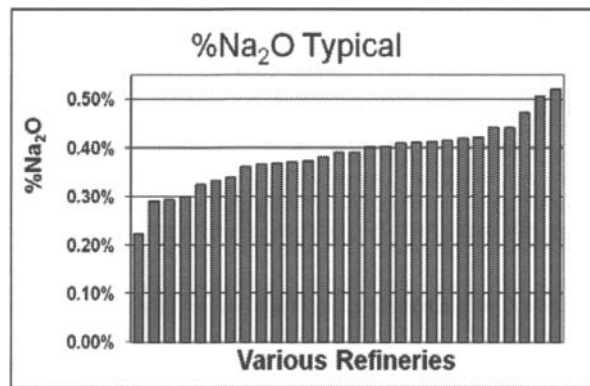


Figure 3 - % Na_2O in SGA for a sampling of refineries

When must also take into account that it is generally preferred to have a $\text{CaO}/\text{Na}_2\text{O}$ ratio of $\leq 10\%$. The data shows that issues with % CaO in SGA being above 0.030% are not as prevalent, but for some refineries a $\text{CaO}/\text{Na}_2\text{O}$ issue can emerge. Refer to Figure 4.

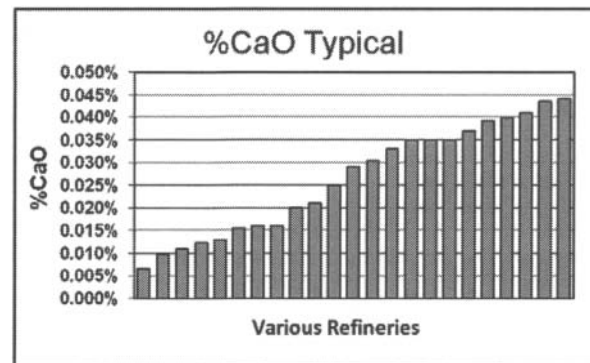


Figure 4 - % CaO in SGA for a sampling of refineries

The Role of Alumina

Technologies exist to reduce Na_2O in SGA. These include;

- 1) Washing the hydrate to remove residual soda
- 2) Raising precipitation temperature to reduce occluded soda in hydrate [3]
- 3) Modification of seeding patterns in precipitation to control the growth rate of hydrate
- 4) Alumina leach drying, ALD, to remove soda from SGA
- 5) Technologies that reduce organics in Bayer liquor

All of these are proven technologies, having been used in our industry. Almost all are also costly for refineries to implement.

The most common low-cost approach for control of the $\%\text{Na}_2\text{O}$ in SGA is to wash hydrate with hot condensate to remove and reclaim residual caustic soda. Washable soda normally accounts for less than 10% of the total Na_2O content of SGA. But, in some circumstances opportunity remains to reduce washable soda at the expense of energy to avoid excessive dilution of Bayer liquor.

Beyond good washing of hydrate, progressive actions to reduce the amount of Na_2O in SGA would very likely include increases in precipitation temperatures. Higher temperature promotes a higher diffusion rate of Na from the hydrate surface as the crystal grows.[4] A 1.0°C increase in precipitation temperature can result in as much as a 0.02% decrease of Na_2O in SGA.[5] But, higher precipitation temperatures drive the process towards formation of blocky crystals with higher attrition rates. It also lowers the liquor yield. Thus, raising precipitation temperature is similar to asking a smelter to reduce amperage loads in order to reduce its metallic impurities in aluminum.

Another approach to control the Na_2O content of hydrate during precipitation is to adjust seeding patterns to control the growth rate of particles.[6] A high growth rate increases the diffusion path of Na from the growth site. This requires more time for diffusion and traps more soda in the hydrate crystal. Slower growth rates promote a lower Na_2O content in SGA. Changes in seed concentration can therefore have a strong effect on the soda content of hydrate. Higher solids concentrations promote lower Na_2O content. This however affects other quality parameters of hydrate and alumina as well. As with many things a change that favors one outcome can negatively impact other factors.

There is also an option to use a process called ALD, or alumina leach drying, to remove Na_2O from alumina by leaching a fraction of the product stream with acid. See Figure #5. However, the process is costly in terms of both capital and operating expenses.

Many refineries have to deal with high levels of total organics in bauxite. These accumulate when bauxite has been affected by the decay of vegetation in soil above water permeable deposits and cause undesirable concentrations of humate and fulvic acid in Bayer liquor. Enhancements to reduce total organic carbon in liquor can improve a number of parameters such as liquor yield. But, they can also be effective in reducing the $\%\text{Na}_2\text{O}$ in SGA.

Clearly technology exists to reduce the Na_2O content of SGA. But the cost to producers may well exceed the benefits realized by customers. Working from the example of \$2000/mt for excess bath generation enables some sensitivity analysis. The costs associated having an excess of 0.10% Na_2O in SGA (e.g. 0.40% vs. 0.30%) equates to approximately \$5/mt Al_2O_3 . The current

costs to implement the technologies that have been referred to here may be 1.5X to 3.5X higher than the total costs of excess bath generation, and in some cases even more.

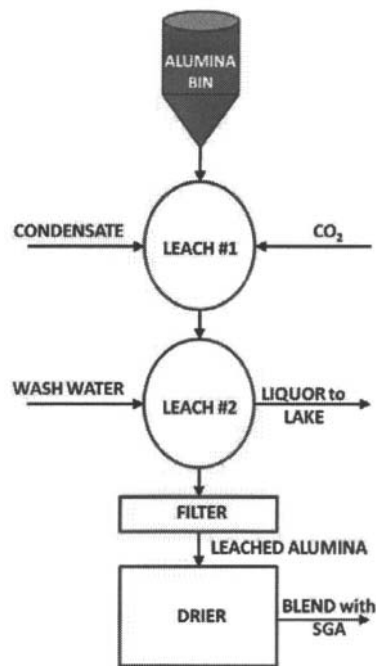


Figure 5 – A schematic of the alumina leach drying process

For many alumina refineries, especially those with low levels of Na_2O in SGA, or those with specific freight advantages, it may be difficult to justify changes to reduce soda content. Justification is more likely to become apparent during market downturns at refineries that have high levels of Na_2O in product. Other SGA producers with lower levels of soda may become preferred, or discounts on SGA with high levels of Na_2O may become demanded by the marketplace.

As noted above, alumina refineries cannot place focus only upon lowering levels of soda if levels of calcia in product are high. In some cases reductions in the $\%\text{CaO}$ in product will also be necessary to attain a $\text{CaO}/\text{Na}_2\text{O}$ ratio of 10% or less. It should also be noted that a $\text{CaO}/\text{Na}_2\text{O}$ ratio of $\leq 12\%$ may be acceptable to many modern smelters with graphitized cathode blocks and cell life that is over 2200 days.

Current Trends

Forecasts for primary aluminum production say that the industry will expand by ~20 million tonnes/yr annual capacity between 2010 and 2020. This includes the expansion of primary aluminum capacity from ~24 million mt/yr currently to ~44 million mt/yr.

Figure 6 shows how the industry has grown since the 1960s. Industry expansion has consumed an estimated 725,000 mt of bath over a fifty year period. If predicted growth is realized by 2020 another 725,000 mt of bath will have been consumed, but over a ten year period. While this may look like good news that will

relieve pressure on the %Na₂O and %CaO in SGA, it is more important to look at this by taking a broader perspective.

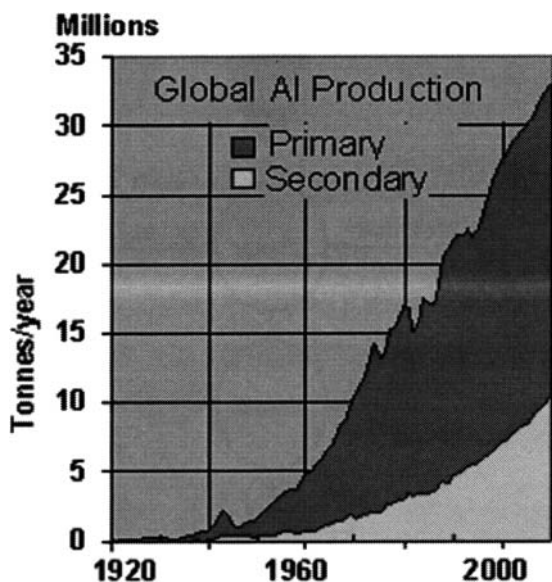


Figure 6 – History of global aluminum production [7]

Figure 7 shows a very simplified version of growth in the global surplus of bath after a level estimate of consumption serving growth of the primary aluminum industry has been taken out.

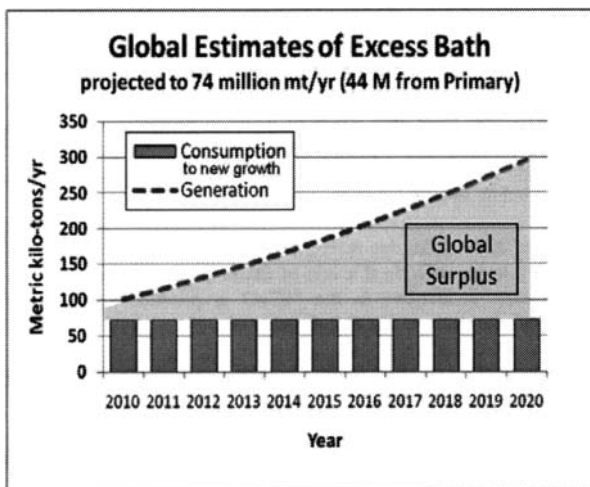


Figure 7 – Simplified projection of global bath surplus

By the end of 2020 the prediction calls for ~230,000 mt of surplus bath to have been generated in the world. The collective cost of its production by smelters may exceed US\$450 million worldwide. It is important to emphasize that this will be material for which there is no apparent use unless an alternate market for used pot room bath comes into existence.

The alternative may be to landfill this surplus material. But, a growing number of countries will not permit this. So, as the surplus of bath grows the price of it is expected to drop. This will further erode the economics around the generation of an excess ton of bath. The economic pressures that come from this can and will be expected to fall back upon alumina refineries worldwide with few exceptions.

The most likely scenario is that surplus bath with desirable properties will find wide use in the primary aluminum industry. High quality bath will support both existing operations and the growth of the industry.

As with contaminated bath that was only accessible by leaching at cryolite recovery plants, the most contaminated forms of bath, and those forms that are the most expensive to recover, are those most likely to become future industrial waste streams. Very low prices for surplus bath, and perhaps even payment by bath generators to avoid disposal costs, may drive increased consumption of bath by alternate applications. One example of this is as fluxing material in the steel industry. Other, altogether new alternatives for surplus bath may also be found as prices drop to previously unheard of levels.

Conclusions

Changes in aluminum reduction technology, and in particular in cathode block materials that support >350 kA cell designs, have reduced uptake of sodium into cathodes and ultimately in spent pot lining material. When taken in combination with highly efficient dry scrubbing technology and practices that reduce other bath loss mechanisms, a global surplus of cryolitic bath is expected over the next decade.

Examinations of the mass balance clearly show that the major inputs of both sodium and calcium are found in Smelter Grade Alumina.

Even though the drivers behind changes in surplus bath generation rates have little to do with changes in average alumina impurities, producers of aluminum metal will undoubtedly look to operators of alumina refineries to reduce levels of Na₂O and CaO in their SGA.

Technologies to do this currently exist. But, in general these alternatives cost more in capital and operating expense than the direct financial benefit that alumina customers would realize. Some approaches to reduce Na₂O content may also make particle sizing finer and reduce particle toughness, thus impacting important alumina properties and quality.

With no alternative markets for surplus cryolitic bath in existence, or on the immediate horizon, it is only the matter of a few years before consumers of SGA begin to place greater focus on reducing the content of Na₂O and CaO in product. This added focus will most likely manifest itself with those producers of SGA that have high Na₂O content, or high CaO/Na₂O ratios, during periods of alumina market downturns.

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Acknowledgements

- Bayliss, Chris & IAI – References on aluminum industry growth
- Hudson, L. Keith – Insights on Alumina Production, Alcoa, Inc.
- Travis Baroni – Editorial comments and review
- Alcoa, Inc. & Alcoa World Alumina – for support in the preparation and publication of this paper
- Merino, Dr. Margarita R. (Ph.D. – Florida State University) – for her encouragement, dedication, and support.