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2013 ALUMINUM KEYNOTE: IMPURITIES IN THE ALUMINUM SUPPLY CHAIN

ORGANIZER
Les Charles Edwards
Rain CII Carbon
Kingwood, TX USA

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Keynote Session

SESSION CHAIR
Les Charles Edwards
Rain CII Carbon
Kingwood, TX USA

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RAW MATERIAL IMPURITIES AND THE CHALLENGE AHEAD

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

The impurities contained in the raw materials used by the aluminum industry pose challenges that must be managed from various perspectives. These include; product quality, costs, and impact upon the work environment and areas that surround smelters. As the industry continues to grow, impurities, and changes in impurities, will take on greater meaning for process control, equipment design and selection, metal products, and environmental, health, and safety. The author provides his insights into these emerging issues.

Introduction

When it comes to impurities in aluminum, market expectations tend to become tighter as the years pass. This has been the trend since aluminum first began being traded as a commodity on the London Metals Exchange. Some regions of the primary metals world such as Australasia have migrated to even higher expectations for standard ingot purity. Refer to figure #1.

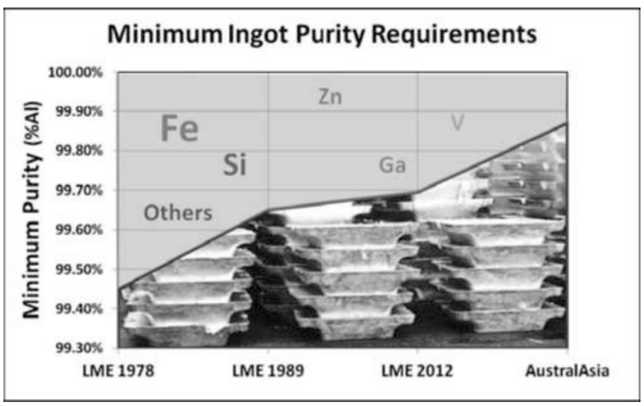

Figure 1 – Standard ingot purity requirements for the LME and the Australasian region

Primary aluminum production is anticipated to continue to grow. CRU has estimated that global primary capacity of 47.2 million metric tons in 2012 will grow to 69.4 million metric tons of capacity world wide by 2020 [1].

Regardless of the accuracy of this prediction the trend is clear. More aluminum production will place greater demand on raw material supplies. Costs of development for new raw material sources will no doubt face making some trade-offs between production capability and impurity levels that are acceptable to markets and to customers.

Discussion – Raw Materials

Greater levels of aluminum production will require new reserves of bauxite to be extracted for processing. Some is likely to include challenges in parameters like reactive silica or trace levels of elements such as manganese, chromium, and beryllium. Even so, traditional Bayer processing does not pose an impending or direct threat to higher impurities in metal. The challenges for traditional alumina processing may come from a different direction. Some smelting customers may look to alumina sourcing to offset higher impurities of SiO_2 and Fe_2O_3 in other raw materials. Pressure on alumina refineries may also become focused on parameters such as CaO and Na_2O due to smelting cost pressures. These include costly bath dilution that is driven in part by higher CaO in specific sources of coke. Then there is the cost of excess bath generation. This is driven mostly by Na_2O content that is higher than smelter consumption rates. [2]

Growth in the global alumina supply is also likely to continue to include some producers with bauxite/raw material that must pass through an acid leaching step prior to Bayer processing. Dealing with higher levels of traditional impurities such as SiO_2, Ga_2O_3, and P_2O_5 will pose some challenges. Other impurities such as Li_2O, MgO, and even residual amounts of chlorine from acid leaching may create new challenges for bath chemistry, metallic impurities, and even environment, health & safety, EHS, factors.

Conventional anode technology will require greater consumption of; petroleum coke, coal tar & petroleum based pitch, and perhaps carbon from other sources. Many primary metal producers have taken steps to adjust raw material specification limits to accommodate a changing landscape of what is available in the market. Impurities such as vanadium and nickel are already of growing concern in our industry. Refer to figure #2.

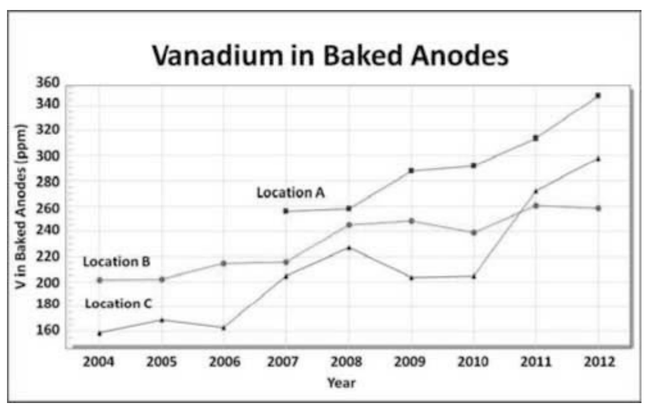

Figure 2 – Examples of trends of vanadium in baked anodes

Other impurities such as Ca and Na in coke will pose threats to anode quality and reactivity. Indirectly these have the potential to affect levels of process Fe and Si that enter reduction cells. More reactive anodes are likely to cause greater variation in butt thickness and air burning resistance. Greater variation in anode butt thickness will affect iron contamination of the metal. Greater amounts of carbon dust from more reactive anodes can cause the percentage of hot pots to increase. This ultimately concludes with greater input of Fe and Si to the metal.

Higher metal production rates will also eventually stress reserves of acid grade fluorspar that is desired by the aluminum industry for production of AlF_3. Higher levels of SiO_2 and P_2O_5 would be of greatest concern. Special levels of metal purity may then all but require AlF_3 that is produced from the fluosilicic acid process.

As the industry grows and as customer demands for purity increase there will be no lack of challenges for primary aluminum producers to face with regard to impurities in raw materials.

Discussion – Environment, Health and Safety

Impurities can also pose threats that are beyond processes and products. Some impurities of concern, such as sulfur, obviously face challenging environmental regulations. Some regions of the world have placed strong focus on employee exposure to beryllium. Others are beginning to place more focus on elements such as nickel in their emissions inventory reporting requirements.

With or without changes of %S in anodes a growing fraction of the industry has been moving towards SO_2 scrubbing. Even projects that are not being built with tail gas scrubbers are often constructing their gas treatments centers, GTCs, such that SO_2 scrubbing may be added-on later. Some consider this to only be a matter of time before it becomes a standard in the primary metals industry. Increasing levels of sulfur as an impurity in coke can only help to hasten such a change in the status quo.

Many smelters continue to focus on control of percent sulfur in anode coke as a way to manage SO_2 emissions. For many of these, especially older facilities, requirements to add tail gas scrubbers would likely cause them to become non-competitive.

Therefore, this impurity has the potential to change the standard footprint of primary aluminum production. It also may change the designs of gas treatment systems. GTCs are currently focused on their capability to capture and control total fluoride and particulate emissions with very high efficiency, often at >99.8% capture. If tail-gas scrubbing for SO_2 becomes an industry norm some trade-offs are likely that could reduce GTC costs, alumina recirculation rates, and scrubbing efficiency since small amounts of residual HF would easily be captured by wet SO_2 scrubbers.

Other sulfur related challenges are emerging. For example, there is growing focus on carbonyl-sulfide, COS, emissions in North America. COS is listed as a Hazardous Air Pollutant by US EPA. The emerging approach of regulatory agencies for COS is to place limits on the amount of sulfur in anode coke.

Some countries are placing greater interest in the levels of sulfur in alumina at least for purposes of emissions inventories. At some point certain smelters may begin to stipulate gas-calcined alumina and avoid oil-calcined product.

Beryllium is found in trace levels, >1 ppm Be, in some sources of alumina. It is a trace impurity in certain bauxite deposits. These include bauxite sources from Jamaica, The Balkan Peninsula, and some regions of China. Beryllium tends to concentrate in bath to approximately 60X its concentration in alumina [3]. It's form is most likely as the fluoride, BeF_2 and perhaps as Na_2BeF_4. Depending upon its concentration in bath and the region of the globe there may already be strict and costly regulatory requirements in place that are aimed at worker protection.

Another impurity of concern in certain regions of the globe is nickel. There is clear evidence that this trace impurity primarily reports to the metal. But, there is also evidence from a few aluminum producers that small amounts of nickel leave as fugitive emissions that are likely to be in the form of NiF_2. However, this speciation as NiF_2 is speculative, not proven.

At some smelters the mass input rate of nickel from all raw material sources is fully accounted for in aluminum production. At others, up to 30% of Ni does not report to the metal and appears to leave the pots as a fugitive emission. For example, it has been found in wet scrubber sludge. Refer to Figures #3 & #4.

The variable loss mechanism is not fully understood. It appears to be related in part to cell technology. But, increases of Ni in coke could lead to greater regulatory concern. At this time nickel is only required to be included in smelter emissions inventories, but in a growing number of countries.

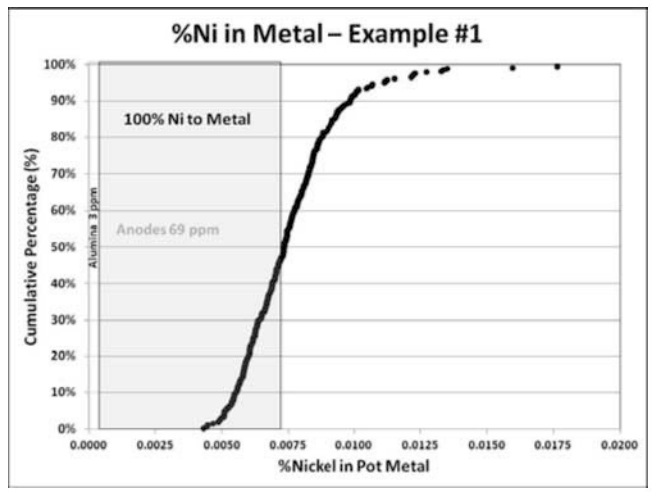

Figure 3 – Example of all Ni inputs to metal production

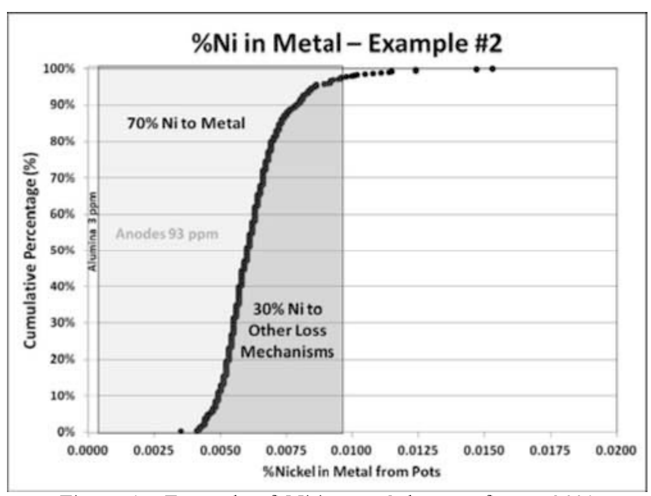

Figure 4 – Example of Ni inputs & losses of up to 30%

Discussion – Counter-Measures

Technology does exist to deal with many impurities. Some existing approaches are likely to become more prevalent in our industry as impurity levels increase. There include treatments to metal that can be made in cast house furnaces to address some metallic impurities.

For example, vanadium, titanium, and a few other trace impurities can be reduced by making additions of boron in cast house furnaces. The impurities then settle out as borides. But, without proper settling and filtering these borides may end up as fine inclusions in the metal. In some products, such as wire, inclusions can cause problems with breakage as wire is drawn.

There is a clear trend towards higher levels of vanadium in anode coke. Thus, it may not be surprising to see future modifications in cast house layouts and furnace designs to accommodate for adequate settling time, drain & clean cycles, and metal filtration. This is most likely to appear first at locations that are focused on electrical conductor products.

Increases in vanadium may also change, or limit, some aspects of smelting. As vanadium levels rise, so shall the risk of excess carbon consumption via air burning of anodes. Likewise, increases in the sodium or calcium content of anodes can increase reactivity and excess consumption. The best counter-measure for these concerns is to assure proper covering of all anodes.

To arrive to this end changes may have to be made to equipment and processes that determine the; uniformity, particle sizing, and angle of repose of anode covering material. Rotary breaker type autogenous mills may replace air-swept type mills. Handling and transport equipment may be changed as a premium becomes placed on minimal particle attrition. Even anode bonnet designs may change to better retain proper cover on top of new anodes. The alternative may be to limit or even reduce anode heights in response to higher vanadium levels in anodes.

Were gallium to become an impurity of concern, technology does exist for removal of Ga from Bayer liquor. But, it is not inexpensive. Likewise technology such as alumina leach drying and other options exist to reduce the level of Na_2O in alumina. But, again it is not inexpensive.

Higher levels of phosphorus may be addressed with strontium modification of metal in cast houses. But, there are limits on this approach depending on the product. In some cases concerns about net input rates of P_2O_5 may drive changes in; coke sources, AlF_3 sources, and may even cause some smelters to move away from certain alumina sources that are higher in P_2O_5 from being calcined with oil.

Increases in levels of iron are unlikely to drive expensive and developmental efforts to reduce Fe_2O_3 in alumina. But, it may drive some upgrades in clarification and filtration technology, especially at refineries that currently use sand filters.

The more likely counter-measure to iron for many metal products is to reduce the levels of process iron [4] that contaminates metal in reduction cells.

Increases in silicon inputs are likely to be addressed with a combination of traditional approaches. These include keeping various contaminated input streams away from the bath crusher and changing raw materials. Changing to AlF_3 sources that are low in SiO_2 content may be a cost effective approach. But, the impact will be limited with the exception of very high purity ingot.

For ultra high purity metal products only premium sources of alumina, coke, and AlF_3 which are very low in SiO_2 content are used. As baseline levels of silica increase in these raw material supplies it is quite likely that certain specialty ingot products will no longer be available from primary metal producers.

Secondary processing such as fractional crystallization or zone refining processes currently exist. Both are effective at reduction of Si, Fe, and trace impurities in metal that can not be removed by other means. These technologies may eventually be needed to fill ingot product gaps that creep in raw material impurities create.

There are fewer counter-measures for impurities to electrolytic bath. Elements such as Ca, Mg, K, Li, and Be will accumulate in bath if they enter with raw or secondary materials. The known counter-measures; control of raw material inputs, and bath dilution with electrolytic additives are the only options. There are no known technologies to concentrate and remove bath species such as CaF_2 and MgF_2 once they become a fraction of the bath.

The current threats are few and are not insurmountable. Certain sources of anodes and alumina can be very high in CaO content, or in the case of alumina, the CaO/Na_2O ratio. If these are used, management of the overall calcium mass balance for a smelter can be an effective tool.

There are emerging regulations in some regions aimed at zero land filling of dross. Care must be taken with the various impurities, including, but not limited to Mg, that can be present in this material if it is targeted as an item to be reprocessed in a smelter.

As discussed above tail-gas scrubbing appears to be the most likely outcome as regulations become tighter and as sulfur levels in coke increase. But, emerging technology may also be developed to reduce sulfur levels in coke.

Conclusions

Some of these potential threats from impurities will no doubt evolve gradually and will be dealt with by changes in processing, technology, or practices. As the proverb says; "Necessity is the mother of invention." It is apparent that as needs present themselves that technology will be developed to meet the emerging challenges or to forestall the threats.

Currently, only limited information is available in the public domain on impurities that affect the aluminum industry. It is not a topic that has been driven by the necessity to sustain operations or to service commonly produced metal products. Forums such as Plenary Sessions at annual meetings of TMS and contributions to the literature will begin to close this gap.

As discussed, changes in impurity inputs have the potential to re-shape various facets of our industry:

- Sulfur may change the common approach to exhaust gas treatment and even system designs for such treatment. In some cases requirements to treat exhaust for SO_2 emissions would drive older facilities to the point of no longer being able to compete.

- Increases in vanadium may drive changes in cast houses, bath mills, and anode cover handling systems.

- Increases in silica may drive ultra high purity ingot out of the realm of primary aluminum smelters and into secondary processing units to purify metal.

- Various changes in impurities such as iron and silicon will place greater emphasis on reduction of process contaminants from anodes, covering material, and pot lining materials. They are also likely to drive certain streams of contaminated material out of smelters and into secondary uses.

- Increases in impurities in anode coke are likely to drive counter-balanced pressure on other raw material sources such as alumina and aluminum fluoride.

- Emerging technologies for the production of alumina that begins with an acid leaching step and processes to recover various forms of dross from cast houses may broaden the pallet of impurities that require managing.

The most likely changes will be those that come from necessity. These will almost certainly drive more contributions to literature in this subject area such as this paper and the many others that are to be found in Light Metals 2013.

References

1. CRU Aluminium Long Term Market Outlook, 2012 Edition

2. Lindsay, Stephen J., "Bath Generation and Management", the proceedings of the 10th Australasian Smelting Technology Conference, Tasmania, October, 2011

3. Lindsay, Stephen J. & Dobbs, Charles L. "Beryllium in Pot Room Bath", Light Metals 2006, pp 95-100

4. Lindsay, Stephen J., "SGA Requirements in Coming Years", Light Metals 2005, pp. 117 – 122

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