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Impurities

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METALLIC IMPURITIES FROM THE MINE TO METAL PRODUCTS

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Abstract

When it comes to the metallic impurities in alumina, some are of greater importance and concern than others. But, all have maximum levels that can be tolerated by downstream processes and products. This may also be true even when alumina is not the major contributor of a specific impurity, but does significantly contribute to the baseline impurity level. In this paper the author discusses various points of concern related to specific metallic impurities. Conclusions and general guidelines are offered on what acceptable levels will be to most customers of SGA.

Introduction

Certificates of Analysis, specification sheets, and summaries of typical properties for Smelter Grade Alumina, SGA, contain references to many metallic impurities. Primarily this information is either a reflection of what has occurred in nature, in the bauxite deposits, or of how the clarification and filtration areas of the Bayer plant have been configured. There are no clear distinctions, or guidelines, that relate typical or maximum levels of an impurity to its acceptability for making certain metal products.

Usually the producer gives and the client receives information on a few factors, such as levels of iron and silicon oxides, which are important to many metal products. Data on a few metallic impurities that are well above trace levels is normally included in Certificates of Analysis. These impurities may also have clear specification limits even if they are of little importance to most customers. Then there are many trace impurities that can be of significance to specific metal products, or to workplace exposure, that seldom appear on alumina specification sheets.

In some cases the metallic impurities found in SGA all but completely define the levels of that impurity to be found in the metal. This is the case with gallium or zinc. Many impurities also appear in other raw materials for aluminum smelting such as coke, aluminum fluoride, pitch, and specific electrolytes that may be added. In a few cases a metallic impurity of concern is defined more by other raw materials than by the input rate from alumina. Examples include nickel or vanadium.

The term "impurity" tends to convey a negative connotation. It is defined as something that is not desired, a pollutant, or a contaminant. Often this is an accurate assessment. But, many of the more benign impurities can act as tracers, and as such can serve positive roles in process control for aluminum production.

The definition of what is necessary, desired, useful, or acceptable for levels of impurities seldom finds its way from the mine all the way through to the metal products. The ambition behind this paper is to close some of this knowledge gap.

Discussion

Iron Oxide - There is no doubt that iron oxide content, $\%Fe_2O_3$, is the primary impurity of concern for most metal products. Using a consumption factor of 1.920 t Al_2O_3/t Al, a concentration of 100 ppm of Fe_2O_3 in alumina contributes 134 ppm of Fe to the metal produced. This is not much when one considers that the iron from alumina contributes only 10% to 20% of the total iron in the metal. But, unlike pot room process contamination factors that can vary greatly in iron impact, the iron oxide in alumina affects the metal produced from every reduction cell. The same can be said for the other large raw material input, coke to make anodes.

Consider the example shown in figure #1. This "visual mass balance" is for a group of pots that is focused on metal of good purity, less than 650 ppm Fe, or Grade P0506. By changing from an SGA source with 0.014% Fe_2O_3 to another source with 0.010% Fe_2O_3 more of the desired product can be produced.

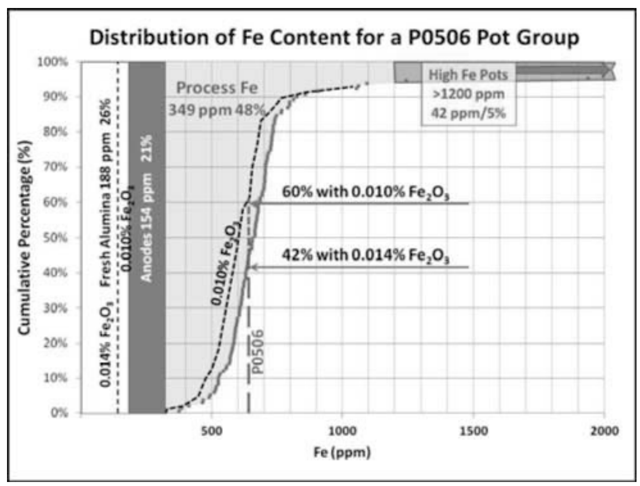

Figure 1 – Visual mass balance of iron contamination sources

Reduction of the process iron component is also a key opportunity for improvement. But, process iron is driven by factors that have greater variation than the Fe_2O_3 content of alumina. These factors include variations in total liquid levels and the thicknesses of individual anode butts.

Variation of the Fe_2O_3 content is important as well as it also affects all cells. Building upon the example given in figure #1 an alumina source with 0.012% Fe_2O_3 and low shipment-to-shipment variation may be preferred to an alumina source with 0.010% Fe_2O_3 and high variation.

In figure #2 we see such an example of a refinery that is normally quite capable of providing alumina to a producer of P0506 metal. Shipments typically average 0.009% to 0.012% Fe_2O_3. However, some individual shipments are well above this typical range.

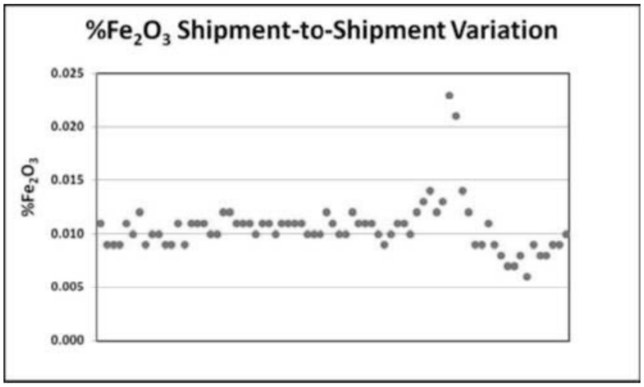

Figure 2 – Example of variation from an alumina refinery

As with other impurities, acceptable levels for metal products will be determined by more than average alumina properties [1]. They will more often depend upon the maximum level of an impurity.

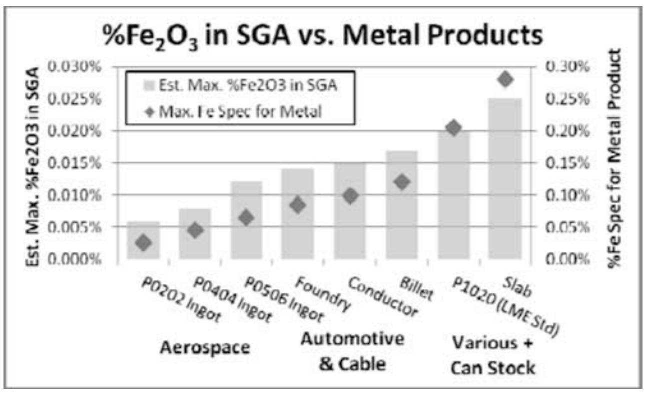

Figure 3 – General guidelines for maximum $\%Fe_2O_3$ in SGA

With this in mind the guidelines for Fe_2O_3 in SGA is shown in figure #3. These are not product specification limits. They are general summaries of what aluminum producers will typically seek out for % Fe_2O_3 in SGA in order to produce substantial amounts of the metal products listed.

Silica – The SiO_2 content of alumina is also important for metal products. Silica enters with alumina, anodes, and AlF_3. However, only few metal products rely upon low silica levels. These are primarily limited to conductor products and to pure metal grades that are suitable for aerospace. Refer to figure #4. The majority of aluminum smelters in the world, perhaps more than 75%, will have no product specific limitations on the SiO_2 content of SGA. Note that a concentration of 100 ppm of SiO_2 in alumina contributes 90 ppm Si in metal produced.

Silicon contamination in metal has a significant negative impact on its electrical conductivity [2]. It is not as harmful at the part per million level as many other metallic impurities. However, Si is typically found in greater concentration than all other metallic impurities except iron. Silicon also detracts from fracture and fatigue resistance that are required for aerospace products.

As with iron, both the typical and maximum content of SiO_2 in SGA will be of concern. Production of conductor rod and pure metal grades for aerospace can not tolerate spikes in impurities. When such events occur it can be quite disruptive to the ability to produce these products at all.

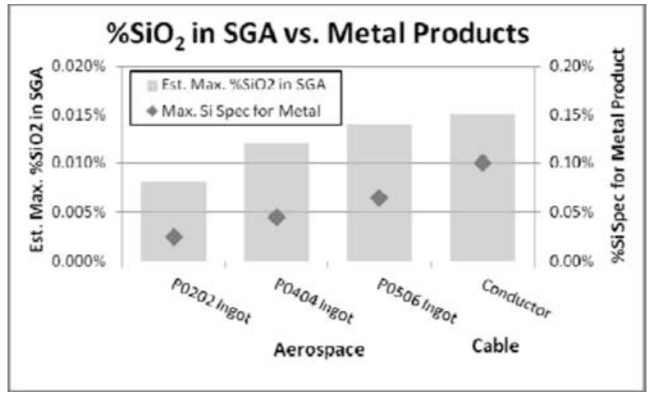

Figure 4 – General guidelines for maximum $\%SiO_2$ in SGA

Gallium Oxide – Ga_2O_3 appears on the Certificates of Analysis of many refineries. In many cases a maximum specification limit is included. Typically 0.006% to 0.014% Ga_2O_3 is found in western world SGA. A level of 100 ppm of Ga_2O_3 in alumina contributes 143 ppm Ga to the metal. Since the maximum of 0.014% Ga_2O_3 equates to 200 ppm Ga in metal gallium is of little consequence to the vast majority of metal products.

With the exception of 0.02% Ga maximum for P0202 metal used for specific applications in aerospace and electronics typical levels of Ga_2O_3 in SGA is not a concern for all but the highest purity metal products.

Gallium can play a useful role as a trace contaminant. Alumina is essentially the only source of Ga to the metal. Following the average level of Ga in metal can help aluminum producers to be accurately track changes between various alumina sources over time. Tracking trace metal "finger prints" can also provide insight on how alumina flows and blends in large storage silos. Therefore the presence of trace impurities is not always detrimental.

Titanium Dioxide – TiO_2 also appears on Certificates of Analysis and often has a maximum guaranteed specification. A level of 10 ppm TiO_2 in alumina contributes 11.5 ppm of Ti to the metal. Ti also enters with anode coke.

Titanium detracts from electrical conductivity. There are also a variety of metal products that fall subject to "combo-specs". These are sums, or combinations of, %Ti+%V+%Cr+%Mn or of %Ti+%V in metal. Even though Ti is an element of concern one must also consider that TiB_2 is commonly added as a grain refiner for many metal products including conductor products.

If levels of Ti become too high, wafers of boron are added to precipitate it out. The removal process is efficient, but borides take time to settle. This reduces metal furnace throughput rates.

With levels of 10 to 40 ppm TiO_2 in western world SGA, less Ti input is preferable. However, since TiB_2 is often added, typical levels is TiO_2 in SGA are seldom of concern. In some cases, Ti can also serve as a trace element, like gallium for pot room metal.

Vanadium Pentoxide – V_2O_5 also appears on many Certificates of Analysis. A level of 10 ppm V_2O_5 in alumina contributes 10.75 ppm of V to metal. However, vanadium enters primarily with anode coke. Increasing V in coke is beginning to place greater emphasis on all vanadium that enters the smelting process.

V_2O_5 content of SGA is generally below 10 ppm with gas calcined product. This contributes <11 ppm V to metal products. V_2O_5 content is often higher than 10 ppm when oil is used for calcination. Peak values of 0.0025% V_2O_5 contribute 27 ppm of vanadium to metal products. See figure #5.

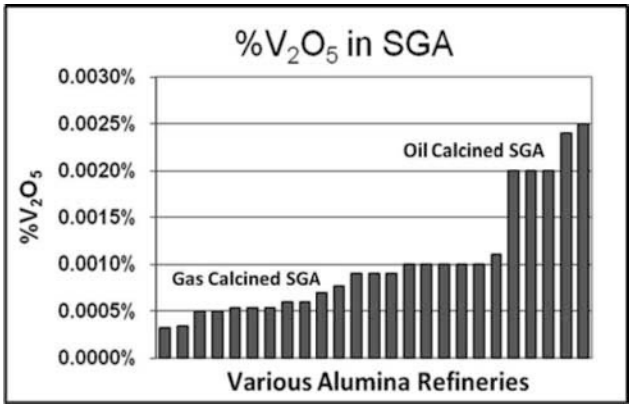

Figure 5 – V_2O_5 levels in SGA

Anode coke sources that are high in vanadium content may contribute 150 to more than 200 ppm V to metal products. Very good sources of coke will contribute >50 ppm of V to metal. Obviously, anode coke is clearly the raw material of concern.

As with titanium, vanadium detracts from electrical conductivity and as noted above, there are a variety of metal products that fall subject to "combo-specs". These are sums, or combinations of, %Ti+%V+%Cr+%Mn or %Ti+%V in metal.

If levels of V are high, wafers of boron can be added to precipitate it out. The removal process for vanadium is also quite efficient, but can reduce the metal throughput rate of a furnace.

With rising levels of vanadium in anode coke supplies, lower levels of V_2O_5 in world SGA are preferable. However, few metal producers will be as concerned about the vanadium content of their SGA as they will with the %V in their anode coke.

Zinc Oxide – ZnO appears above trace levels in only a few specific sources of bauxite. Bauxite from Jamaica, the Balkan Peninsula, parts of China, and Minas Gerais, Brazil has elevated levels of zinc that also appear in SGA. Refer to figure #6.

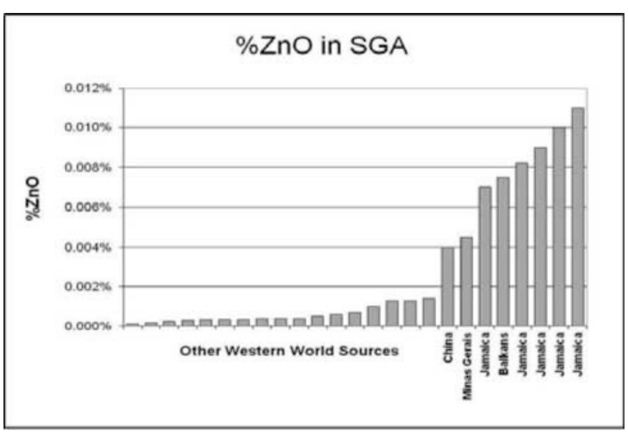

Figure 6 – ZnO levels in SGA

A level of 100 ppm ZnO in alumina contributes 154 ppm of Zn to metal. Alumina is essentially the only input source for Zn to aluminum. The primary metal product of concern is extrusion billet, especially that which is used for "bright" applications such as auto trim and venetian blinds. Zinc causes the surface of metal to have a spangled appearance, not unlike that of galvanized steel, but with much smaller grains.

Typically, the specification for such metal products is a maximum of 0.02% Zn. Since essentially all of the Zn that reports to metal comes from SGA all alumina sources that are shown in figure #6 appear to be acceptable.

While this is technically correct, the expectations of some customers such as the automotive industry are for the highest level of quality. In such cases, with other factors being equal, metal producers with higher levels of Zn in product may not enjoy the status of being a preferred supplier. Alumina producers with <50 ppm ZnO in product may be preferred over those with higher levels of ZnO for consumers that produce extrusion billet.

As noted with gallium and titanium, zinc can also serve as an excellent finger-print tracer element.

Manganese Oxide – MnO occasionally appears on Certificates of Analysis. A level of 10 ppm MnO in SGA contributes 14.9 ppm of Mn to metal. Levels of MnO in SGA seldom exceed 20 ppm. Manganese also enters the smelting process with pitch and coke. But, these sources usually account for a few ppm of Mn to Al.

Manganese strongly detracts from electrical conductivity. See figure #7. As with vanadium and titanium a variety of metal products fall subject to combination-specifications that include Mn. These are sums of %Ti+%V+%Cr+%Mn in metal. Unlike, V and Ti, Mn is not able to be precipitated out by using boron wafer additions.

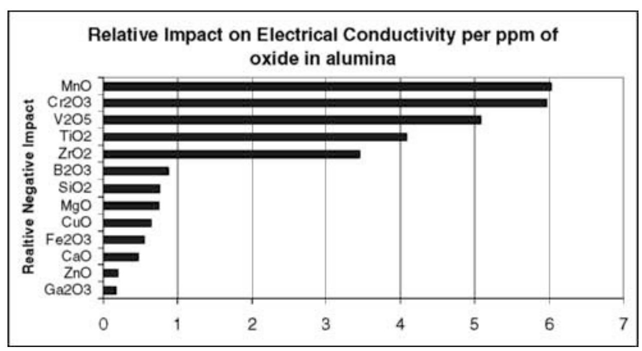

Figure 7 – Impact of Mn and other impurities upon conductivity

Like zinc, manganese is another of metallic contaminant that has more to do with the impurities found in the bauxite deposits than any other factor. Bauxite from Jamaica and the Balkan Peninsula is particularly high in Mn. Refer to figure #8.

Producers of conductor products prefer to have low levels, $\leq$5 ppm, of MnO in SGA, or <7.5 ppm in metal. But, Mn is only one of many factors that affect conductivity. If other SGA impurities, such as SiO_2 are low, a level of <10 ppm MnO may not be problematic. Levels >12 ppm MnO begin to close the door on acceptability for conductor and some "combo-spec" products.

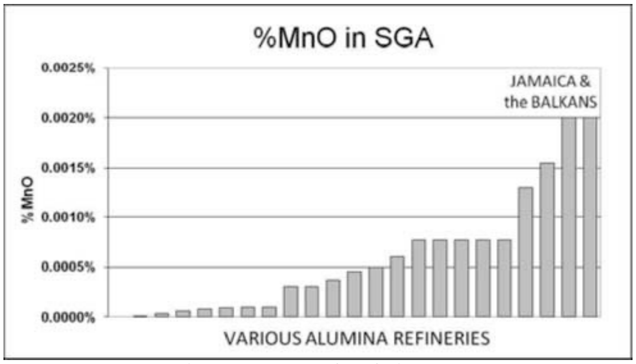

Figure 8 – MnO levels in SGA

Since MnO content is bauxite specific, and Mn input to metal is primarily from SGA, it can also act as a good finger-print tracer.

Other Metallic Oxides – Levels of Cr_2O_3, ZrO_2 and CuO are also of concern for conductor products. However, they are seldom specified on Certificates of Analysis. Data on typical levels also may not be available, even upon request. These trace elements are also bauxite deposit specific, and all primarily enter with the alumina. Levels of 10 ppm Cr_2O_3, ZrO_2, or CuO in SGA contribute 13.1 ppm of Cr, 14.2 ppm of Zr or 15.3 ppm of Cu to aluminum.

Producers of conductor products can generally accept ≤5 ppm of Cr_2O_3. Levels of >7 ppm begin to close the door on acceptability. This also begins to occur at levels of >14 ppm for ZrO2, and of >15 ppm for CuO. Note that Cr also appears in the Combo-Specs that are noted in the sections on vanadium and manganese

NiO may also be of some concern for very specific metal products. But, as with vanadium, the primary input of Ni to metal is from anode coke. NiO in SGA is seldom an item of interest.

Combination Specifications – There have been a few references to "Combo-Specs" in the sections above. These are the sums of either the %Ti+%V+%Cr+%Mn or %Ti+%V in metal.

For a few specific cast products the sum of Ti+V+Cr+Mn can not exceed 150 ppm. Other cast products, including conductor products, require this sum to be below 250 ppm.

The sum of Ti+V may be limited to 0.02% for a number of fairly common metal products. But, this may be as low as 30 ppm for some specific metal products. In such cases boron is commonly added to precipitate out both Ti and V.

This is a key point. Note that alumina and other raw material suppliers cannot depend upon cast houses to add boron to reduce impurities. Such treatment constrains the throughput capacity of the cast house by adding time for borides to settle out. It may also create quality issues for products such as lithographic sheet where small inclusions in the metal cause major product quality issues.

Combo-specs have rarely come up as a limitation on SGA sourcing. But, SGA producers from Jamaica, the Balkan Peninsula, and a few other geographic regions may begin to run into this issue as anode coke quality continues to increase in vanadium content. This would of particularly concern for those alumina refineries that also use oil for calcination.

Beryllium Oxide – Like zinc, manganese, and other trace impurities the beryllium content of SGA depends upon the bauxite source. High levels have been found in bauxite from certain regions of China, the Balkan Peninsula, and Jamaica. These often translate into ≥1.0 of Be in SGA, occasionally exceeding 5 ppm.

Levels of between 0.1 and 0.5 ppm Be can be found in other alumina sources from a wider, but limited, array of global bauxite reserves.

While the beryllium content of aluminum is often of concern it generally has to be added to the metal or be present in scrap aluminum to be in any metal products. The BeO in SGA reports to the bath that is used in smelters [3]. Bath is primarily a mixture of NaF and AlF_3 salts in molten form. But, alkaline earth metals that enter the bath generally remain there. Beryllium is thought to form BeF_2 and Na_2BeF_4.

Be from alumina is essentially the only input source to aluminum smelters. The exception is with bath that has come from other smelters that have used SGA that was relatively high in beryllium.

Beryllium concentrates in the bath to approximately 60X the input concentration of Be in alumina. Exposure of personnel to high concentrations of Be in any form has become a health concern in the United States, Quebec, parts of Europe, and Brazil.

A specific limit has not been set for acceptable levels of Be in alumina by the industry or any government agency. But, some smelting customers will closely examine any source of SGA that is relatively high in beryllium content. Fortunately, most alumina sources in the world are ≤0.3 ppm. Relatively few are higher than this, and these are generally above 1.0 ppm Be.

Other Impurities – There are other metallic impurities that are worthy of note including Na_2O and Li_2O. There are also non-metallic impurities of concern such as CaO and P_2O_5 that are not included in the scope of this technical paper.

Published literature contains quite a bit of information on the Soda and Calcia content of SGA [4,5]. The primary concern for customers is that having too much of either, or both, can become a rather expensive way to generate excess bath that has a market value well below its production cost. Consumers with good reduction cell life, pot life, may prefer to have Na_2O levels new the balance of their net consumption of soda. This often translates into 0.28% to 0.32% Na_2O in product with a CaO/Na_2O ratio of 10% or less. Most SGA producers currently are not capable of such low levels of Na_2O and CaO.

There are volumes that have been written on P_2O_5 [6]. It will suffice to say that phosphate may enter with organics found in the bauxite or, like vanadium, with the oil used for calcination. Smelters prefer levels of <10 ppm.

Lithium oxide is generally at trace levels in most western sources of alumina. But, it can be quite high, 100 to 150 ppm, in certain Mediterranean sources [7] and some Chinese sources that start with an acid extraction process of mined raw materials. Similar concerns with non-traditional impurities will exist with some new processes that have been proposed. These often begin with acid extraction of aluminous clay, Nepheline, or crushed stone to recover a variety of mineral resources including alumina.

Issues Ahead – When it comes to the issues related to impurities that are ahead for SGA producers there are generally not large gaps in product quality that must be addressed with great urgency. The challenges are likely to creep up upon the alumina industry. Keeping pace with these trends will require broad knowledge about the needs of downstream consumers and metal products.

For example, increases in vanadium levels in anode coke may drive a harder look at levels of titanium, manganese, or chromium in SGA. Higher levels of calcia in non-traditional anode coke sources are already beginning to change the rules of thumb for CaO/Na_2O ratios. As impurities of; iron, silica, vanadium, nickel, and others continue to increase this is quite likely to create greater focus on specific impurities in alumina, especially in long market conditions.

The pressures are more likely to come in the form of tighter control on key and traditional metallic impurities such as SiO_2 and Fe_2O_3 in SGA. Customer-based short-lists of unacceptable SGA producers may come to have more to do with maximum, or peak, levels of specific impurities than with average properties.

These short-lists may also begin to include alumina sources that have higher beryllium content as regulations on the aluminum industry change.

Since metallic impurities are generally reflections of what has either; occurred in nature, or in clarification and filtration the areas of product quality focus for refineries will be limited. Capital improvements in the areas of de-silification or filtration may be driven by the threat of erosion of the existing customer-base. Improvements in process control and product stability will be a more commonly taken approach to reduce maximum levels of impurities and to improve product quality.

Conclusions

In conclusion there are a few key points to consider with regard to metallic impurities in SGA.

Iron and silica levels, including shipment maximum levels will continue to dominate the focus of metallic impurities in SGA.

A few impurities that are commonly listed on Certificates of Analysis for SGA have little meaning to most customers.

A host of trace impurities detract from electrical conductivity for a narrow, but important range of metal products. Many of these do not regularly appear on Certificates of Analysis for SGA. In some cases information on typical levels is not readily available, even upon request.

Changes in other raw materials used by aluminum producers are quite likely to drive greater attention to metallic impurity levels in alumina.

Certain regions of the globe have high levels of a variety of impurities in bauxite. These can challenge the ability to use SGA produced from it to make certain metal products. Issues with emerging health regulations that are related to beryllium may also limit use of certain SGA sources.

Non-traditional processes of alumina extraction from various forms of clay and stone will undoubtedly broaden the spectrum of metallic and other impurities of concern.

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