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THE ROLE OF ELECTRODE QUALITY IN METAL PURITY

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Abstract

Anode quality excursions are well known as factors that can have substantial impact upon metal purity and the ability to produce specific metal products. But, there is more to managing anode quality, as delivered to the pot rooms, than avoiding a major excursion. In this paper the author reviews the key factors from the paste plant through the rodding shop that affect the amount of impurities that are delivered to the metal. Conclusions include a summary of sub-process and design activities that can be managed to minimize the impact of impurities to primary metal production.

Introduction

When it comes to the purity of metal from reduction cells the anodes play an important role in a number of ways beyond the impurities that are included in coke and pitch. From aggregate formulation, through mixing, forming, baking and rodding there are multiple factors that can affect metal purity especially with regard to iron and silicon content of aluminum.

Anode-to-anode consistency as assembled and delivered to the pot rooms is the key. This evokes many details in the realm of work practices and process control. Some of these may not have an obvious connection to metal purity. There are also factors that have to do with maintenance of equipment and the design of systems to separate and to isolate impurities. There may also be design considerations for the anodes themselves.

In order to manage any parameter it first must be measured. Data systems must do more than be able to only track trends. Metrics on variation can be just as important, and even more so. This may require gathering and presenting information differently.

There are also some physical properties of the anodes that can have greater impact on iron levels of metal than the chemical properties of the anodes.

The ambition of this paper is to touch upon the variety of anode related factors that can affect impurities in metal. Above average results in the pot lines and at the cast house rely upon above average attention to many of these details in the electrode plant.

Discussion

Raw Materials – It is understandable that those concerned with metal purity will focus on the levels of impurities found in anode coke and pitch. They affect the metal produced from every reduction cell.

When we examine the mass balance around iron in metal it is apparent that a significant fraction comes from the impurities contained in the anodes. Figure #1 shows an example in which 12% of all Fe in pot room metal comes from the anodes. What is not as apparent in this example is that a large fraction of the "process iron" contamination also has to do with anode properties.

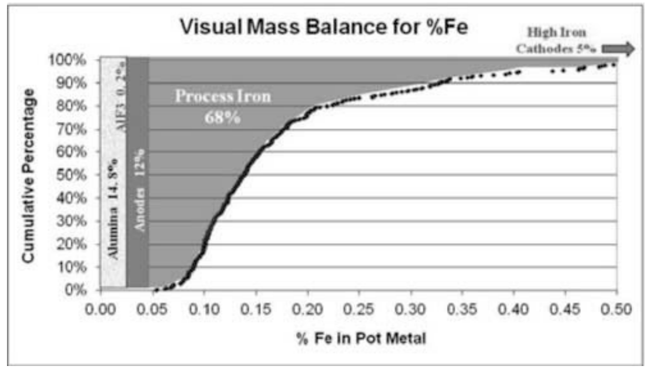

Figure 1 – Visual mass balance for Fe for a pot line

The majority of process iron comes from the castings that are used to make the mechanical and electrical connections between stubs and anodes. Tracking the amount of iron consumed each month in the rodding shop helps to illustrate the magnitude of this area of opportunity. Many tons are typically consumed annually.

Not all of this iron consumption is due to anode related factors. Attack by liquid bath and other factors also account for a large portion of "process" contamination. However, when the average thickness of anode butts change, or the variability in anode butt thickness increases, or air burning on butts increases one must examine the contributions that come from anode sub-processes.

Anode Assembly Quality – It's a matter of millimeters when it comes to spent anode thickness and the corrosive effect of bath on iron castings and steel stubs. Refer to figure #2.

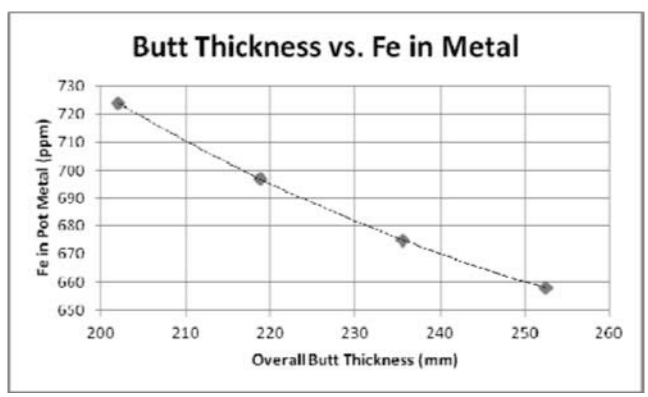

Figure 2 – Median Fe in metal vs. anode butt thickness

A change of a centimeter or more of anode butt thickness can be profound in its impact on typical iron levels in metal. This is especially true when the overall thickness is less than 175 mm.

With modern reduction cells and large, multi-stub anode assemblies the perpendicularity of the anode rod to the top surface of the anode becomes more important that it was in the days of small, single stub, anode assemblies [1]. A deviation of 1 degree away from being perfectly square from the base of an anode that is 1.5 meters long means that one end of the anode will be 26 mm lower in the bath than the other end. The outer edge of the iron casting on one stub may be 2 cm lower than the elevation of the casting on the opposite end of the same anode assembly. Nevertheless the risk of attack on cast iron by bath is amplified almost as much as if the spent anode butt were to be 2 cm thinner.

Deviations of this magnitude from may seem extreme. But, when this parameter is not routinely measured or controlled it is not unusual to find ≥15% or anode rods are 1 degree or more out of perpendicular to the top surface of the anodes. Refer to figure #3.

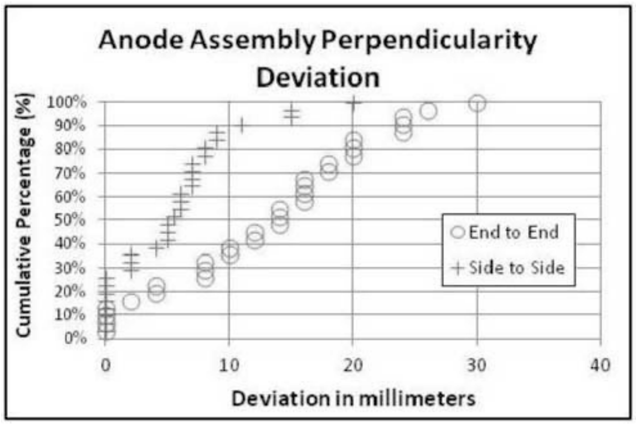

Figure 3 – Example of deviation of assemblies from perpendicular

Perpendicularity has been cited as a quality reference in order to illustrate that attention must be paid to more than just the anode blocks themselves. Many factors are important when it comes to metal purity. Electrode sub-processes including the assembly of the anode to the rod require attention to detail. This avoids adding root causes for iron to come into contact with bath and metal.

There are other obvious iron contamination concerns that have to do with anode assemblies. These include iron over-pours or splatter on the bonnets of anodes. These typically impact Fe in anode cover unless 100% are removed, usually by manual means. A thin "skin" of iron may also form during pouring against the steel stubs to fill the stub holes. This "skin" often ends up oxidizing and also finds its way into the pots via anode covering material. Then there is cast iron composition itself. It carries more than just Fe into the metal. Silicon, manganese, and phosphorus will also enter when cast iron is dissolved by bath.

Anode Properties – Even if anode surfaces are perpendicular to the anode rods the average thickness of the butts may vary. When metal purity is determined by a matter of millimeters a number of anode properties and the process control parameters that affect them come into consideration.

The baked density of anodes is an obvious concern when average butt thickness is a surrogate for metal purity. See figure #4.

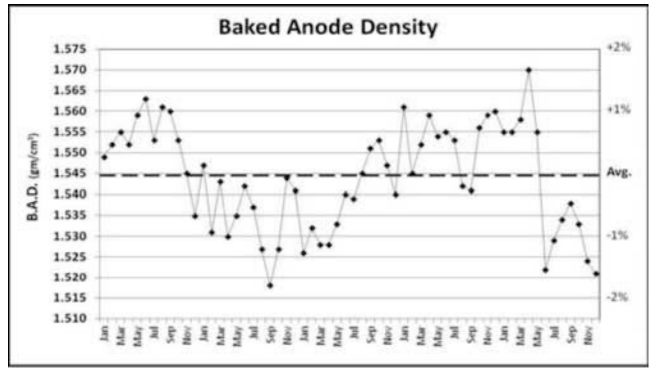

Figure 4 – Example of variation of baked anode density

A 1% change in the density of the anodes or other factors that affect the rate of consumption can change the thickness of the anode butts by 4 to 5 mm. Figure #4 shows that changes of >1% are not necessarily uncommon.

Likewise the reactivity of the anodes in CO_2 or in air can be of concern as can factors that are related to the degree of anode baking such as Real Density or L_c. All of these can change by more than a few percentage points over periods of months and all can affect individual anode butt thickness.

In real world situations any one factor, or a combination of factors may change by significant amounts. The anode setting cycle in the pot lines may not be changed in response. Ergo, metal purity becomes a response variable in such a situation. But, following shifts in average properties is only the half of it.

While average spent anode thickness matters, the thinnest anode butts and those that have exposed parts of castings via air burning will contribute the most to iron contamination. The amount of variation in key properties can be more significant than changes of a few millimeters in average anode butt thickness.

Variation in Anode Properties – The uniformity of anode butt thickness is a parameter that is not overly difficult to measure. But, it is often over-looked. It can tell a lot about variation in anode sub-processes and in pot room operating conditions.

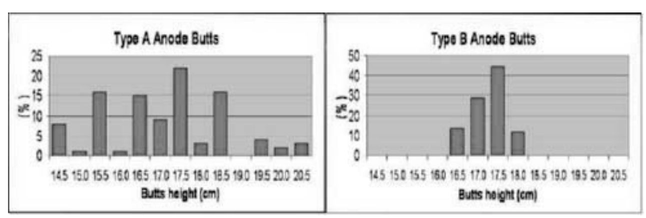

Figure 5 – Examples of variation in anode butt thickness

Figure #5 tells a story. These are butts taken from the same pot line under the same operating conditions. The anodes were from two different suppliers. The type A butt thicknesses are obviously not uniformly distributed. The range of thicknesses is +/-3 cm around the mean. The type B butts are much more uniform in thickness and encompass a range of +/-1 cm in around the mean.

Type A anodes came from an older anode plant that did not sell anodes to third parties. Type B anodes came from a new and well controlled facility that only sold anodes to third parties.

In the case study of Type A anodes there were many known issues with; coke blending, aggregate control, mixing and anode baking. The anode butt thickness distribution was multi-modal since many things were going on that all had some impact on anode consumption rates. The take-away may appear to be that purchased anodes are better than anodes that do not have to be sold to third parties.

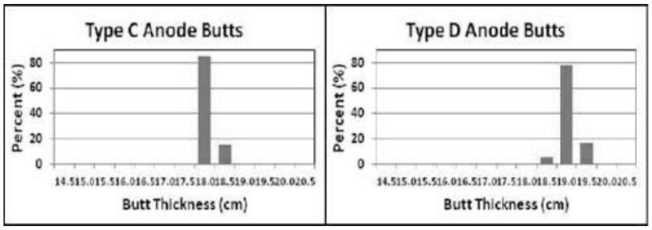

Figure 6 – Other examples of variation in anode butt thickness

Now refer to figure #6. This location makes two types of anodes for in-house use only. There are no sales to third parties. The facilities are not new, and they are well maintained. Process control is held to the highest standards through the paste plant and the anode baking furnaces. The type C and type D butts respectively encompass ranges of +/-2 and +/-4 mm around the mean values for anode butt thickness.

This location also has excellent and very predictable results with metal purity, especially with regard to iron content in metal. These results are not surprising.

The distributions for Type C and D anode butts are an order of magnitude tighter than for Type A butts. It is not uncommon in our industry to find that the range of anode butt thickness is +/-2.5 cm around the mean value. There is plenty of opportunity for improvement in this area with benefits well beyond metal purity.

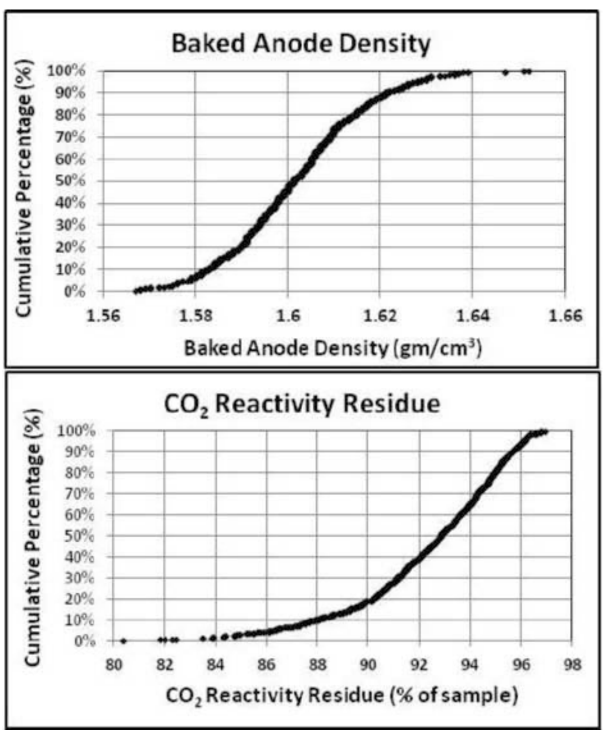

Figure 7 – Cumulative distribution examples of anode properties

The starting point for inquiry is close examination of the process data, examples of which are shown in figure #7. The parameter may be density, reactivity residue, or a host of others that relate to green and baked anode manufacturing.

Study of the entire distribution for any parameter brings the right questions into focus. Is the distribution bi-modal, or multi-modal? Why? What factors cause the upper and lower tails of the distributions to be as they are? What is necessary to obtain more uniform results, and more uniform spent anode butt thicknesses? The examples shown in figure #7 are real. The impact upon butt thicknesses and metal purity is left to the reader's imagination.

Unfortunately, conclusive links between specific anode properties and butt thickness variation metrics are left to future research.

What does not have to be left for future consideration is that parallels in the fraction of anode butts that are; quite mealy, soft, or thin have been made to the fraction of baked or green anodes that have had less than desirable characteristics.

The conclusion that begs additional research is that variations in specific anode properties do cause variations in anode butt thickness and metal purity. This is particularly so with regard to iron contamination.

Spent Anode Butts – Butts represent a significant fraction of the most anode aggregates. But, they are seldom required to pass the demanding standards that maybe set forth for other anode raw materials. This may be particularly so when they are produced and used in-house.

It is important to acknowledge that the content of Na, Ca, Fe, Si, ash and other impurities are higher in butts than in new anode assemblies. Such impurities tend to greatly concentrate in the finer butts fractions, especially in dust that is gathered during crushing of butts. Some, such as sodium and calcium also affect the reactivity of new anodes. Ultimately this affects the thickness and amount of air-burning on the next generation of anode butts.

As shown in figure #8 the iron level of butts is typically higher than that of new anode assemblies. However, the Fe content of fine butts is much higher. This is due to a number of potential contributing factors.

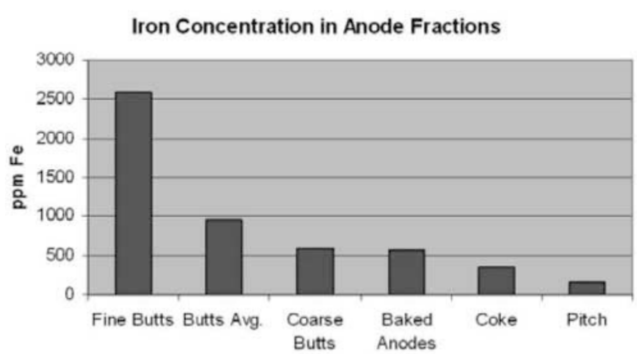

Figure 8 – Iron concentration in anode & butt fractions

Fine butts will contain bits of scale from the points of contact between the iron castings and the anodes. Iron sulfide and some forms of iron oxide formed under high temperature are not magnetic. Fortunately, these are often physically attached to particles of magnetic oxide or metal. This scale is generally quite friable and can easily be broken into small particles or even into dust. These can be quite difficult for magnetic separators to remove. With a "good" level of efficiency in removal of magnetic material being 70%, multiple passes of magnetic separation may be required to access this hard-to-get material.

Butts are often cleaned with steel shot blast of 0.4 to 1.3 mm in diameter. A sphere is the most difficult shape for magnetic separator effectiveness. Steel spheres of low mass and small diameter are particularly difficult to remove from a stream of crushed butts.

The size, or perimeter length, of castings also figure in to the steel shot equation. The voltage drop between the casting and the anode generates heat. The casting also conducts heat upwards when anode butts become thin. Conditions become favorable to air burning of a groove around the top perimeter of the castings. Without exceptionally good equipment and procedures to recover steel shot that comes to rest in these grooves the iron level of the fine butts fraction is likely to be negatively impacted. Refer to figure #9.

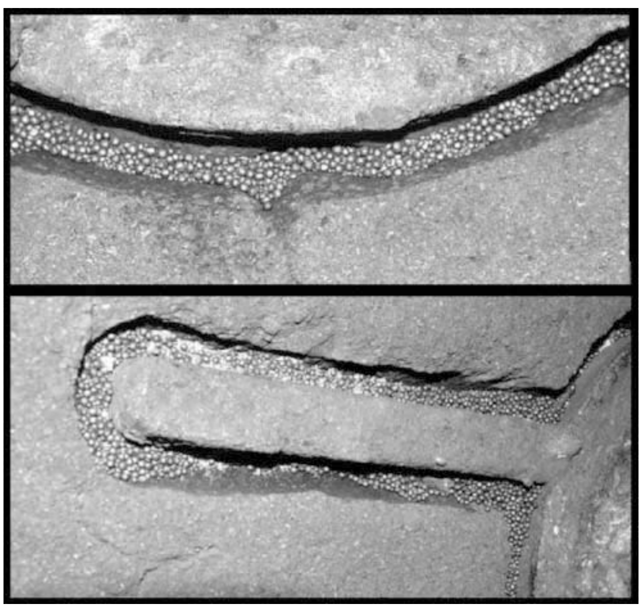

Figure 9 – Shot blast trapped in air burn grooves around castings

The other factor of concern that is also related to the perimeter of the castings is the total surface area of each casting. As flutes and extremities such as wings are added, the total area available to form oxide and sulfide scale increases. With each new cycle of anode casting thin layers of oxides and sulfides will form. The amount is in direct proportion to a few factors including the total surface area of the castings. Some fraction of this non-magnetic and mildly magnetic material then finds its way into the butts fraction, usually as fines.

Let's return to the concept of butts as a raw material that is often generated in-house. As a raw material the various fractions of butts should have certain specifications. These might include levels of; Na, Ca, Fe, Si, and ash in addition to characteristics on sizing. Control of deviations will not have the convenience of direct financial penalties, such as those applied by independent anode producers. The financial penalties will be inherent to damage caused to anode quality, the baking furnace, and even to metal purity. Thus, specifications for butts should be set and adhered to with rigor. It is one of the few components of anode impurities that manufacturers will have under their direct control going forward as properties of anode coke continue to decline.

One option that can help to significantly reduce the level of impurities in next generation anodes is to cull a certain fraction of the fine butts material [2]. This should not be used as a substitute for proper removal of shot or magnetic separation. But, at some level the very fine impurities that can not be easily removed by other means can be separated and culled. This may be limited to dust collector material. In some cases low-value, but usable end-markets have been found for butts fines fractions avoiding need for land-filling.

There are also noteworthy concerns about silicon contamination. Locations that use delayed coke to pack anodes in the baking furnaces may also recover some of this coke to anode production. This can be a large mistake if there are metal product quality concerns that are related to Si. The refractory material that flakes off refractory, mortar and insulation accumulates in the anode packing material. It normally should not be used for anode production.

Likewise there are small streams of fine coke that should never be used, such as the dust collector catch on anode bake tending cranes. As with butts, impurities tend to migrate to fine material. Dust collector catch has been measured at up to 2% Si by weight.

The Ball Mill – As noted above, butts and especially butts fines can be a significant contributor to contamination of Fe and Si to baked anode production. There is another contributor that is often at par with the contribution of butts that quite often goes unnoticed. Steel balls and the steel liners of most ball mills often contribute >120 ppm Fe to the total iron found in baked anodes.

Credible mass balance studies made internally by Alcoa and Elkem have found that it is quite common for ~50 ppm of the Fe found in pot room metal to have originated in the ball mills that are used to grind coke. Roughly 60% of this sum comes from the erosion of the steel balls themselves. The remaining 40% comes from the steel liners of the mill.

This is presumed to vary somewhat with the grade of steel used to make the balls, the fineness of the coke grind, and the percentage of fines that are used in the dry aggregate formulation.

There have been some attempts in industry to capture and remove some of this very finely ground metal. But, no standard magnetic separation equipment appears to be effective. Most attempts have fallen below 10% in removal efficiency.

If we consider a paste plant that uses coke with 150 ppm Fe in it and anode butts that include most of the butts fines or dust we could easily find that 33% of Fe in anodes comes from coke and pitch, 33% comes from butts, and the balance is from the contribution of the ball mill.

What might be done about this? The use of rubber liners for ball milling can eliminate 40% of this contributing factor. Some have reported on this technology in the literature [3]. The technology does face some challenges for it to be successful. But, it holds the potential to immediately reduce Fe to pot room metal by ~20 ppm.

Counter-Measures to Impurities – Some counter-measures are obvious and have already been specifically discussed or referred to in sections of this paper.
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In the Green Mill – Uniform aggregate control, thorough mixing and cooling of paste, uniform filling of mold boxes, rubber ball mill liners

In the Anode Bakes – Uniform baking of each anode and each pit, uniform anode heating rates, avoid use of packing material and dust in anode manufacturing

In the Rodding Shop – Perpendicularity of the anode assemblies, over-pouring of cast iron on anodes and on stubs, removal of steel shot after shot blast cabinets

In All Areas – Tracking of key properties and variation of key properties, efforts to understand and eliminate causes of special variations in properties, efforts to understand and reduce common causes of variation in properties.

There are also some design factors to take into consideration when metal purity is an important outcome. These include:

Shaping the profile of the anode bonnet to protect castings from air-burning

The design of casting including their perimeter, total surface area, and number of flutes

The design of the rodding carousel to assure perpendicularity of anode assemblies plus adequate placement of each stub to the proper place and depth

Entire systems to prevent attack of bath on stubs and castings may also be implemented. The use of stub protection collars is not uncommon in the industry. Producers of very high purity metal may employ wholesale spraying of the anode tops with an aluminum mantle. This can greatly reduce the risk of air-burning that might otherwise expose cast iron.

Conclusions

The contribution of the Electrode Plant as a whole to impurities found in pot room metal extends well beyond the impurities that arrive in anode raw materials.

The impact of butt thickness on iron contamination can be measured in millimeters of anode butt thickness. This extends to deviations that may be caused by; the perpendicularity of anode assemblies, green and baked anode factors that influence consumption rate such as density and reactivity, and the amount of air-burning that factors such as casting and anode bonnet design contribute to.

Measurement of these key parameters does not only involve following of trend information. As shown in examples included in this technical paper one must also study metrics related to process variability. This allows special causes of variation to be eliminated and common causes of variation to be better controlled using common statistical process control methodology.

An external focus on raw materials is necessary to control the input rate of impurities to pot room metal. But, many producers commonly over-look the potential that an internal focus can also reveal. Examples for managing to rigorous specifications for re-cycled anode butts and placing some focus on control of the iron contamination from ball milling or anode packing materials management have been given.

The overall summary is that Electrode Quality is much more important to metal product purity and quality than is commonly recognized. Those that have lead the way and that already excel in these areas provide hope and a pathway to those that will follow.

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