Increasing Coke Impurities – Is this Really a Problem for Metal Quality?

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Abstract

Increases in the vanadium and nickel content of anode grade coke in recent years have predictably affected smelter metal quality. This has now reached the point where some smelters struggle to meet traditional metal purity specifications. New metallurgical studies have shown that metal specifications for impurities such as vanadium and nickel may be unnecessarily restrictive.

Increasing the levels of these impurities higher than the current specifications may provide opportunities to create new alloys in downstream processing. Given this, and the reality that any potential impact of these impurities on anode performance can be mitigated by maintaining adequate anode cover, there is a strong case to revise current coke and metal specifications.

Introduction

One of the most significant issues being faced by aluminium smelters is the increasing trend of higher impurity levels in its raw materials. Specifically this paper will address the issues introduced by impurities in anode grade calcined coke – but the concept can equally be applied to alumina. The real question is whether it is time to relax specifications for impurities in aluminium metal.

This paper will address the challenges faced by anode grade calcined coke suppliers, the impacts of impurities on aluminium smelter operations, studies on aluminium metal quality that indicate that higher impurities may be tolerable and in fact beneficial in many cases, and lastly review potential models to optimize smelter operations.

Anode Grade Calcined Coke Challenges

The challenges that are faced by coke suppliers have been previously reported [1], [2] and will be briefly addressed again here.

The impurity levels, specifically sulfur, nickel and vanadium, in anode grade calcined coke produced by one provider are shown in the following figures.

All of these charts illustrate the alarming trend for rising impurity levels in coke. This trend is directly a result of changing crude oil quality. In a previous paper [3], the challenges have been reported. For illustrative purposes, Table 1 provides data for

Figure 1
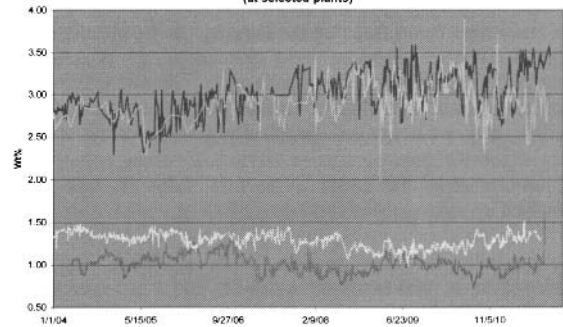Calcined Coke Sulfur
(at selected plants)

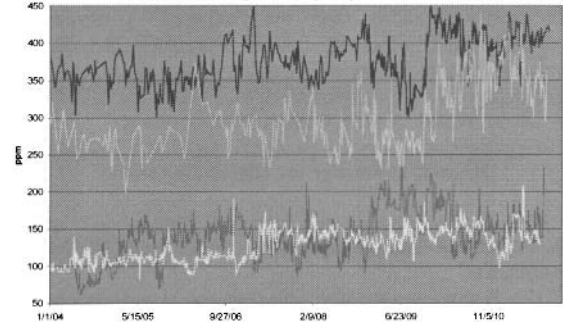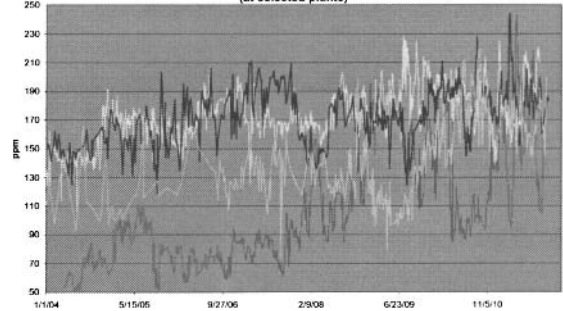Figure 2
Calcined Coke Vanadium
(at selected plants)

Figure 3
Calcined Coke Nickel
(at selected plants)

traditional crude oils used for anode coke and the present generation of crudes oils available for anode coke.

Table 1 Estimated Calcined Coke Properties from Crude Oil For a Typical Refinery			
	Calcined Coke S Wt%	Calcined Coke V ppm	Calcined Coke Ni ppm
Traditional Crude			
ANS	3.1	460	210
Brent	1.8	280	60
WTI	1.4	320	250
Present & Future Generation			
Basra	7.4	600	180
Cold Lake (Canadian Hvy)	7.2	1,080	420
Marlim	1.2	300	210
ESPO	1.9	220	220
Other crude you may want to consider			
Canadian Mixed Sweet	2.2	300	160
Green Canyon (Gulf of Me:)	5.7	1200	326
Oriente	3.6	1500	700
Hungo (WAF)	1.7	270	320

The challenges being faced by the industry can be observed from Table 1. Whilst processes exist for crude oil refineries to desulfurize/demetallize coker feedstocks, unfortunately these approaches have prohibitive capital and operating costs. In addition, they are employed specifically to improve liquid yields at the expense of coke production and in some cases, coke quality. So, unfortunately the issues evident in Table 1 need to be addressed by coke suppliers and aluminium smelters together.

The capability to treat gaseous sulfur emissions has been employed by several smelters worldwide and it is expected that the trend to install sulfur treatment equipment will continue.

We will focus the metallic impurities on here. Traditionally, coke metallic specifications have been set based more on the "typical" coke properties rather than the "required" properties for aluminium metal. Similarly, that is also likely the case for aluminium impurity levels.

Is it time to "relook" at what the true requirements are?

Impacts at Smelter for Higher Impurities

Much has been written regarding impurities from anode cokes and their impact on smelter operations, which may be broadly categorized as:
1. Positive and negative effects on anode performance.
2. Reduced cell performance, most notably current efficiency (CE).
3. As most impurities report to the cell hot metal, a significant impact is on aluminium metal purity.

Each of these categories will be looked at in terms of the potential issues for smelter performance as coke impurities increase as outlined in the previous section. The focus will be on the effect of increasing levels of the metallic impurities nickel and vanadium in cokes, as based on current projections, these are considered likely to be the most problematic.

Effect of increasing nickel and vanadium on anode performance

Numerous studies have been made on the impact of various impurities on the performance of the anode in the smelter pots [e.g. 4]. For example, sodium, calcium, and vanadium have all been widely associated with increasing the reactivity of the anode carbon to the side reactions with air (airburn) and carbon dioxide

(carboxy attack) that contribute to excess anode consumption rates. It must be noted, however, that in the case of airburn, an increase in anode air reactivity does not necessarily mean that in-cell airburn rates will increase. airburn rates are generally controlled by the access of air to the hot carbon surface, not the anode reactivity [5].

The catalytic effect of vanadium in increasing petroleum coke reactivity is generally accepted (but not universally so, e.g. see [6]). However the literature suggests the link between coke vanadium level and anode reactivity is somewhat weaker, and for reasons outlined above, the link between coke vanadium and in-cell anode airburn is at best weak. Despite this, such a relationship is often assumed, but there are little good data in the literature to quantify a correlation, especially in modern cells that generally afford good protection from air to the anodes.

In practical terms, experience has shown that protecting anodes from exposure to air will effectively control in-cell airburn. This has typically been done using anode coatings, usually aluminium spray, and/or anode cover comprising a blend of crushed bath particles and alumina applied after anode setting. Anode cover is most effective in modern cells with deep cavities that allow more complete anode protection, including immediately after setting. To be effective, however cover must be properly applied and maintained during the anode cycle. In the absence of a comprehensive study, these assertions on the dominance of anode protection, and not reactivity, in determining anode in-cell airburn will be supported by several examples (note that full details cannot be provided due to confidentiality agreements) that tend to confirm the underlying theory [5]:

- Anodes with very low vanadium levels (<10 ppm) were observed in a Chinese smelter; these anodes had air reactivity residues (ARR's) of around 98%, i.e. their air reactivity was extremely low. If reactivity was the dominant factor in controlling in-cell airburn, these reactivity results would suggest that airburn of these anodes should be very low or non-existent. In practice, when used in a reasonably modern cell with moderate quality anode cover, most of the anodes with these extremely low ARR values showed some airburn, and a significant proportion showed severe airburn attack. The extremely low anode air reactivity test results clearly did not predict anode performance.

- In plant trials of non-traditional anode cokes (NTAC's), very high vanadium cokes with proportionately high coke air reactivity values produced anodes that performed in potlines very similar to anodes made with conventional cokes, including airburn attack. Based on reactivity tests alone, these very high vanadium anodes would have been expected to be airburn disasters. In an early trial of an NTAC [7], it was concluded that high/very high vanadium coke anodes can perform perfectly adequately in potlines as long as they are properly covered in the cells.

- Over a period of more than a year, a smelter carbon plant worked diligently to increase the ARR (i.e. decrease reactivity) of their anodes using a variety of approaches. They were successful in increasing ARR by more than 10%, however in-cell airburn showed no improvement, and may have even increased during the same timeframe.

In these examples, air reactivity clearly did not drive in-cell airburn (although it may still have an effect under certain conditions), and it is considered appropriate to focus on providing

the best possible protection to anodes (i.e. optimal anode cover) as vanadium levels increase in the future. In this way, it is likely that anode performance can be maintained.

As outlined earlier, nickel levels have also increased and will continue to do so. There have been regression-based studies that concluded that nickel has a catalytic effect on air reactivity similar to vanadium. A rigorous laboratory/plant study [8] has, however shown that this is not the case. As the nickel level in cokes/anodes is nearly always highly correlated with vanadium, regression studies may falsely identify nickel as a contributor to air reactivity. Others [6] have combined nickel and vanadium in studies – this is not considered appropriate, as this will also indicate that nickel increases air reactivity. These two impurities behave quite differently in the electrolysis cells and should be considered independently. Increasing coke nickel levels will be important in terms of metal purity, but does not appear to have major implications for anode performance.

Effect of increasing nickel and vanadium on cell performance

One anode impurity, phosphorous has been linked to a decrease in cell CE [e.g. 9,10] with a mechanism involving the cyclic (re)oxidation and reduction of compounds containing the multi-valent phosphorous in the cell electrolyte.

A question not well answered in the literature is whether other multi-valent elements such as vanadium can behave in the same way as phosphorous during reduction, i.e. can vanadium also affect cell CE via a redox cycle in the bath? In one of the few publications to touch on this issue [7], a disturbingly large effect on CE was noted in a limited plant trial in small cells (7 test cells of 45kA). An increase in anode vanadium from 120 ppm to 390 ppm was associated with a reduction in CE of 0.5 – 1.0%. This is a surprisingly large CE reduction and given that the increase in vanadium experienced over the last 10 years or so does not seem to have hindered potlines achieving ever higher CE figures, the application of these small trial results to a wider scale and larger cell technologies must be questioned. It should also be noted that vanadium and phosphorous behave quite differently in the cells, with phosphorous accumulating in the bath, whereas (in simplified terms, see below for further details) vanadium will reach an equilibrium with material entering the cell escaping with the hot metal.

The effect of vanadium on cell operation would, however appear to be an area of research that warrants further work, including plant scale studies, as laboratory studies will struggle to replicate plant dynamics.

Effect of increasing nickel and vanadium on smelter metal quality

Due to the closed circuit nature of modern cells fitted with alumina dry scrubbing facilities, impurities entering cells have only limited options to where they can report. They can:
- Accumulate in the cell bath, e.g. phosphorus
- Escape in tapped hot metal
- Be lost in waste streams
- Accumulate in recycle streams around the cells.

A proportion of volatile impurities such as vanadium leave the cells via the off-gas stream, are collected on the secondary alumina in the dry scrubbers, and returned to cells. This recycle of

impurities in the off gas stream creates potential options for managing some impurities in the reduction process (Summarized in [11]). For example:
- Secondary alumina can be treated by methods such as scalping off the very fine alumina where the impurities tend to report, thereby reducing the impurity load. This high impurity, fine secondary alumina can be processed further, disposed of as a by-product, or reduced in a specific cell group to produce highly impure metal.
- Secondary alumina can be recycled to specific locations in the potlines (producing lower purity metal) while primary alumina is fed to the remainder of the potlines to produce a premium higher purity product. This partitioning approach to secondary alumina recycle has the potential to allow metal purity to be "tailor" made to meet a customer's requirements, including the ability to consistently produce higher impurity metal (together with a premium higher purity product) if this was advantageous. This approach could be enhanced by segregating anode supply of specific qualities to the cell groups producing different purity metal.

Studies on the Higher Impurity Levels on Aluminium Properties

A comprehensive study of the addition of impurities such as vanadium to the 3xxx family alloys was conducted. The work included complete characterization of physical and mechanical properties, microstructure, and transmission electron microscopy (TEM) analysis. The results of the work conducted indicate that additions of vanadium to levels well above current specification limits and equivalent to a significant increase in coke vanadium content can have neutral to positive impacts on the properties of 3xxx alloys. These results have been very encouraging in terms of utilizing higher impurity cokes without degrading metal properties; however, further work needs to be completed for specific alloys and their corresponding products. Applications in the packaging, building product and automotive sectors should be explored.

A Pathway Forward for the Industry

What has been discussed so far has been the projection that the impurities in the coke used for anode production is rising and will likely continue to do so. Also, we have proposed at that least for the packaging, building product sectors of the aluminium market, current vanadium, and nickel impurity levels should be challenged. The properties of these new alloys may allow for new applications expanding the use of aluminium.

So, it appears that accommodating the projected increase in coke impurities levels, in particular vanadium and nickel, may be possible and in fact potentially beneficial to the properties of a number of metal grades.

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