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**ELECTRODE TECHNOLOGY for
ALUMINIUM PRODUCTION**

**Carbon Materials for
Anode and Cathode**

SESSION CHAIR

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EVOLUTION OF ANODE GRADE COKE QUALITY

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Abstract

The petroleum refining industry has historically categorized petroleum cokes as fuel, anode, or needle grade cokes. The term “anode grade coke” has been used as a broad definition by the aluminum industry to describe delayed coke with a sponge structure containing relatively low levels of metals like vanadium (typically <400ppm) and low to moderate levels of sulfur (0.5-4.0%). These classifications are less relevant today due to the much wider range of cokes used in anode blends. This paper will present a review of the growing range of coke qualities used in anode blends. Shortages of traditional quality anode coke are driving calciners and anode producers to use cokes with a much wider range of properties. Cokes previously regarded as unsuitable for anode production are being used routinely in blends at varying levels and this trend will continue. Examples are given on how smelters are dealing with changing coke quality.

Introduction

At the 2009 TMS Meeting, a joint Reduction/Electrode Technology session titled “Coping with Changes in Coke Quality” was held. Papers presented at this session were published in the 2009 Light Metals proceedings [1]. The purpose of the session was to highlight changes in coke quality and how the aluminum industry might respond. Since 2009, global aluminum production has increased by around 10 million tons and is forecast to reach about 46m t/yr by the end of 2011 and about 61m t/yr by 2016.

This increase in aluminum production has raised the demand for calcined petroleum coke (CPC). The calcining industry is struggling to source enough green petroleum coke (GPC) of the quality required to meet this demand. Historically, GPC used by calciners for anode applications has been referred to as “anode grade GPC.” Anode grade GPC is generally regarded as coke with a sponge structure having a sulfur level between 0.5-4.0%, vanadium level of 50-400ppm, and nickel level of 50-250ppm.

This definition is no longer relevant and the calcining industry is using a much broader range of GPC qualities in anode blends today. This paper will provide an update on the range of GPC qualities being used and how some of Rio Tinto Alcan’s smelters are responding and adapting to these changes.

Review of Changes in the Petroleum Refining Industry

The overwhelming drivers of the change in anode grade GPC availability and quality are crude and refining economics. GPC is produced at refineries that operate delayed cokers and the crude blends used by the refinery dictate the quality of the GPC. Refineries that run heavy, sour crudes (higher specific gravity and higher sulfur levels) produce coke with higher sulfur and metal (Ni & V) levels [2]. An unfortunate trend in crude oil quality is that it is becoming heavier and more sour.

Light, sweet crudes are easier to refine and give a higher yield of liquid fuels, but the supply is limited. Light sweet crude sells at a premium to heavy sour crude and the difference can be as much as US\$15-20/barrel. To process the cheaper crudes, refineries have gotten more complex and they require more hydrogen to remove sulfur and produce more fuel precursors. Once refineries are built with this capability, there is a large economic incentive to optimize crude supplies. Dixon [3] gives a good example of crude optimization and the impact on coke quality.

Sulfur and Metals Content

A consequence of today’s refining economics is that many high sulfur anode cokes have increased in sulfur and vanadium. Figure 1 shows the change in vanadium level of a coke produced in the US Gulf. In 2000, the coke had a V level of 200-300ppm. Today, it is higher and more variable as a result of crude changes.

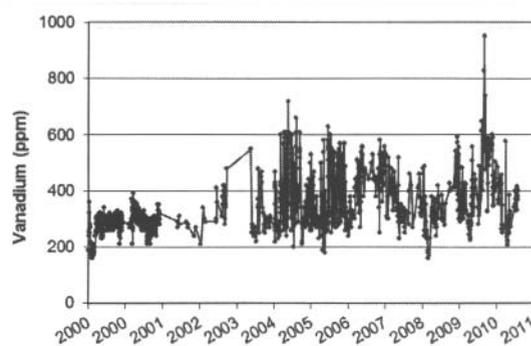


Figure 1: Change in V for one US Gulf Anode Coke

Figure 2 shows a more recent example of a high S anode coke produced in the Midwest of the US. The refinery changed a small portion of its crude blend and added ~7% of a Canadian, heavy sour crude. The economics of the change were compelling and the V level increased by 130ppm and the S level by 0.6%.

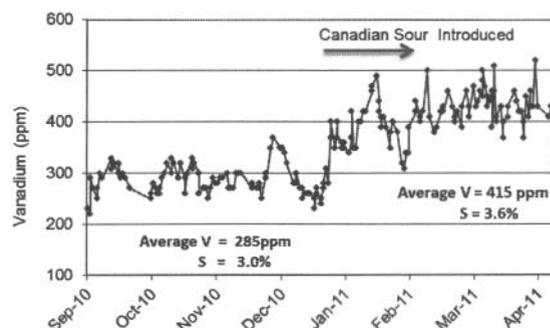


Figure 2: Change in V Level for Midwest Anode Coke

The above phenomenon is global and has been underway for some time [4]. The trend of increasing sulfur and metals levels in high sulfur cokes is compounded by a general lack of low sulfur coke. The availability of low sulfur, low metals coke is now a critical problem for the industry. The trends in crude oil production and refining do not support any significant growth in low sulfur coke production. However, the industry needs more of this coke to offset the rising sulfur and metals levels in other cokes.

GPC Quality Changes

Today, calciners are using a much wider range of GPC qualities in anode blends. The most obvious difference is the greater range of sulfur and vanadium levels. Figure 3 illustrates this and shows the range of S and V levels in GPC used by Rain CII in the US in anode blends in 2000 compared to 2011. The size of each circle is proportional to the volume of coke and the center points are the S and V levels.

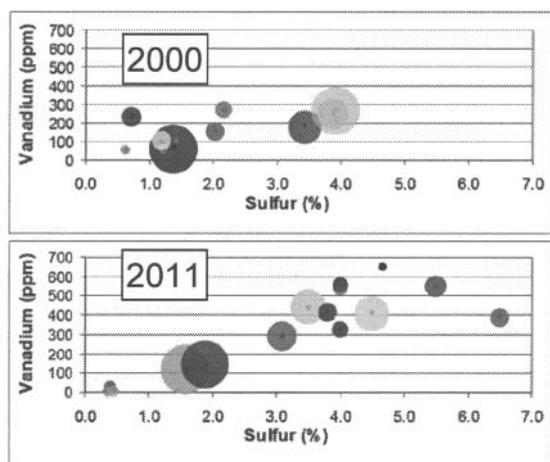


Figure 3: S and V Level of GPC Sources in 2000 & 2011

Some of the cokes shown in Figure 3 cannot be referred to as “anode grade GPC” using the definition given earlier in this paper. Some people use terms like Traditional Anode Coke (TAC) and Non-Traditional Anode Coke (NTAC) but this terminology can be confusing. In this paper, the higher S and V level cokes will simply be referred to as “marginal quality” cokes.

The difference in quality goes beyond V and S differences as shown in Table 1. All the cokes in Table 1 are used in anode blends today and although the range of qualities is broad, it is comparable to those reported with Russia cokes [5]. Cokes A-F have been used as anode cokes for over 30 years. The sulfur and vanadium level of cokes D and E have changed significantly over time and these are the cokes shown in Figure 1 and 2. The next two cokes, G and H have been used in anode grade coke blends for at least 15 years and they are also regarded as good quality anode cokes, albeit with higher impurity levels. Cokes I-K have been introduced in anode blends in the last two years and are good examples of marginal quality cokes.

Some cokes have higher VM (volatile matter) contents and HGI’s (Hardgrove Grindability Index) span a much wider range. A lower HGI means the coke is harder. A coke with a high VM content and high HGI is softer and typically finer in particle size which

creates problems during calcining and is less desirable for anode applications.

Table 1: GPC Quality

	S (%)	V (ppm)	Ni (ppm)	Fe (ppm)	Ca (ppm)	VM (%)	HGI
Coke A	1.64	121	188	140	32	10.6	92
Coke B	1.96	132	169	132	40	11.6	95
Coke C	2.95	269	147	214	29	11.7	94
Coke D	4.53	372	152	127	115	11.9	92
Coke E	3.46	420	201	276	63	10.6	85
Coke F	3.80	440	210	150	40	10.7	56
Coke G	4.13	566	289	120	36	11.3	81
Coke H	3.53	360	162	368	50	13.0	96
Coke I	5.58	554	233	328	54	9.9	35
Coke J	6.49	428	143	193	23	12.9	94
Coke K	4.10	581	199	217	78	13.5	110

Green Coke VM Content

Another undesirable trend in GPC quality is a steady increase in VM content. Higher VM coke arises when a refinery increases the throughput rate in the delayed coker for economic and process reasons. Higher feed rates are often achieved by reducing the coker cycle time and they make it more difficult to maintain coker furnace outlet temperatures. Both of these factors reduce the coking severity and increase the VM in the coke. Figure 4 shows the weighted average VM of cokes used by Rain CII since 2002.

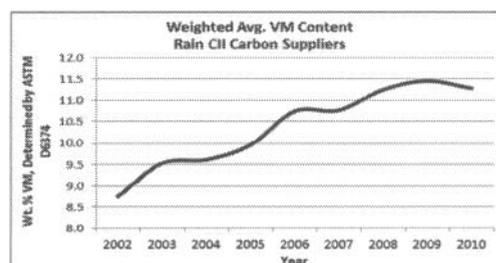


Figure 4: Trend in Average VM Content

In addition to being more difficult to calcine, higher VM GPC leads to more porosity in CPC and a lower VBD. The VBD trend at three rotary kiln calciners using a wide range of cokes over the last 10 years is shown in Figure 5. Results are shown for samples prepared to 8x14 mesh (1.18-2.36mm) but the trends are similar for samples prepared to other sizes. Shaft calciners deal much better with high VM cokes [6].

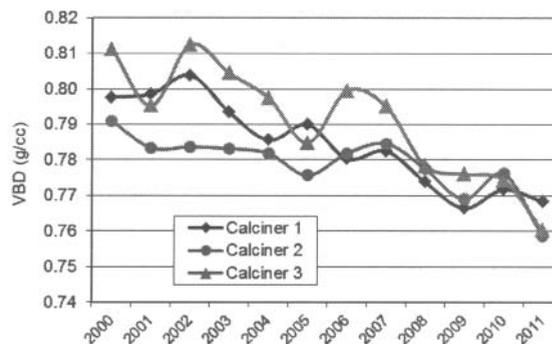


Figure 5: Coke VBD Trend (8x14 Mesh)

Coke Structure and Texture

Another difference, not obvious in Table 1, is coke structure. Historically, the aluminum industry has used CPC with a “sponge” structure. The three common structural forms of coke produced in a delayed coker are: needle, sponge and shot. Needle coke looks similar to sponge coke in terms of porosity but it has a layered structure which is generally referred to as an “anisotropic” structure or texture. Needle coke is a premium product used in graphite electrodes for electric arc furnaces. It has a low sulfur content (<0.5%) and a low CTE (coefficient of thermal expansion).

Shot coke has a very different physical form to needle coke and sponge coke and has been well described previously [7]. When samples of these coke types are examined under an optical microscope using polarized light, the structures or textures look very different [8]. Shot coke has a very fine texture referred to as an “isotropic” texture. It is quite different to the layered texture in needle coke as shown in Figure 6.

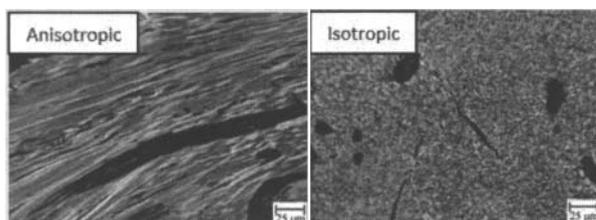


Figure 6: Anisotropic needle coke and isotropic shot coke

Coke I in Table 1 has a very isotropic texture but it is not shot coke. A scanning electron microscope image of the particles is shown in Figure 7 alongside shot coke. Coke I is very unusual in this respect and quite unique.

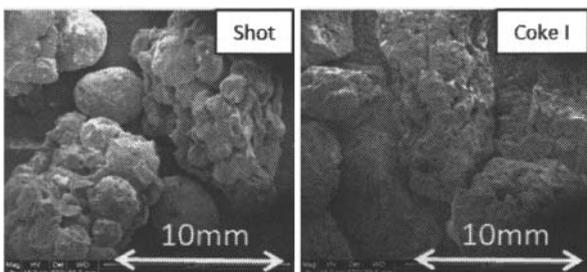


Figure 7: Shot coke and Coke I

Fuel Grade vs. Anode Grade

In addition to classifying cokes as needle, sponge and shot, another classification in common use is needle grade, anode grade and fuel grade. The difference between needle coke and the other grades is obvious but there is no longer a clear distinction between anode and fuel grade coke. Any coke used in fuel applications (e.g. power generation, gasification or in cement kilns) is broadly classified as fuel grade coke. Fuel grade coke is usually higher in sulfur and vanadium but can have a sponge or a shot structure. Fuel grade coke is typically classified by sulfur level and HGI; lower HGI values imply a higher shot content. Cokes I-K have

historically been used in fuel applications but today, they are used in both fuel and anode applications.

Coke Real Densities

Although it is not shot coke, Coke I shares many characteristics with shot coke. After calcination, the coke shows the following properties relative to sponge coke: it is harder; it has a higher CTE; it has a higher bulk density and a lower macro-porosity; it has a higher micro-porosity and an unusually low real density. Figure 8 shows the real density (RD) versus temperature relationship for several of the cokes in Table 1.

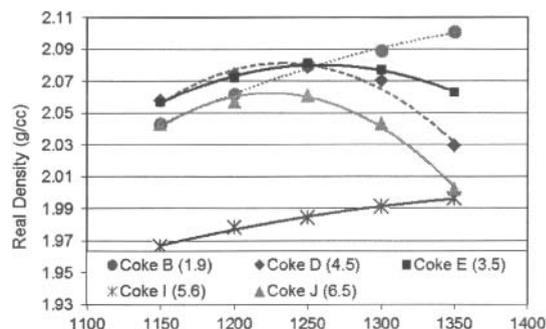


Figure 8: Temperature vs. Real Density Data

Most low sulfur (<3%) sponge cokes (e.g. coke B) show a steady increase in RD as the calcination temperature is increased. Isotropic cokes show a much lower RD at a given temperature and only a small increase with temperature. This is a consequence of their fine texture and high degree of cross-linking. The result is a dense, high strength structure with low macro-porosity but a higher level of micro-porosity. This micro-porosity is not removed when the sample is ground to -75 micron for the RD test.

The pore size distribution curves in Figure 9 were generated with a high pressure mercury porosimeter. The micro-porosity of coke I is evident below a pore size of ~0.01µm. The lower level of macro-porosity in the 1-100 µm range for coke I relative to the two sponge cokes, coke B and coke E, is also evident.

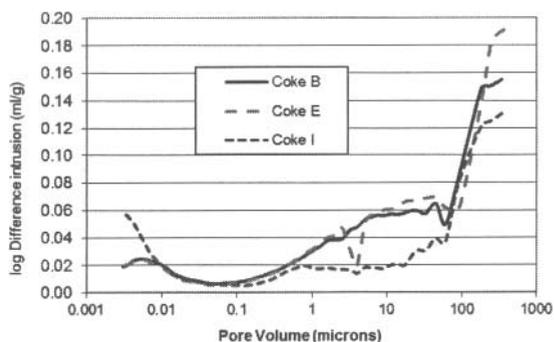


Figure 9: Mercury Intrusion Porosimetry Results

Another phenomenon evident from Figure 8 is the reduction in RD that occurs with high sulfur cokes when the calcination temperature is raised above 1250°C. This is due to thermal desulfurization which has been described previously [9]. The implications of this are as follows. When high sulfur cokes are used in blends with isotropic cokes, it can be difficult to achieve

high RD levels ($>2.06 \text{ g/cm}^3$). It is not possible to raise the average RD of such a blend by raising the temperature. The RD of the isotropic cokes stays low and the RD of the high sulfur cokes drops due to desulfurization as shown for cokes D, E and J in Figure 8.

Desulfurization is undesirable and negatively affects coke properties. Calcining at a lower average temperature avoids this problem and “under-calcined” coke (UCC) can be beneficial to anode performance [10]. Rio Tinto Alcan adopts this strategy at several smelters. In addition to reducing the risk of desulfurization during calcination, UCC also results in less anode CO_2 dusting.

Using RD to monitor the level of calcination can be misleading when using high sulfur cokes and isotropic cokes. Two alternative tests are the coke Lc test and specific electrical resistivity test. Both tests are unaffected by desulfurization and are less sensitive to coke structure. Lc data for the cokes in Figure 8 is shown in Figure 10. All cokes show a linear response to temperature which makes it easier to judge calcination levels.

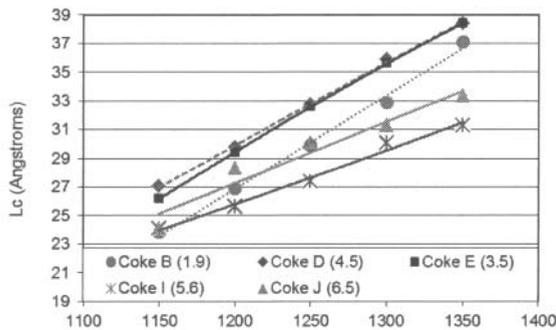


Figure 10: Coke Lc vs Temperature Data

Implications of Changes in Coke Quality

The impact of coke quality changes on selected Rio Tinto Alcan smelters using some of the Rain CII cokes presented above is discussed below.

Susceptibility To Anode Cracking

Anode CTE increases with increasing concentration of isotropic coke [8] and this can increase the risk of anode cracking. Anticipating a rise in the concentration of isotropic coke, Rio Tinto Alcan performed a lab study in 2009 on reducing the susceptibility of anode cracking. The cracking risk of anodes can be reduced by using a higher grain/sand (G/S) ratio in the aggregate [11].

Anodes were manufactured with different concentrations of the highly isotropic coke I and different G/S ratios. Following an approach described in [12], the resistance to crack initiation and propagation was determined. The results can be summarized as follows. With increasing concentration of coke I, the anodes became more susceptible to crack initiation and propagation, Figure 11. At low concentrations of coke I (0 and 15%), increasing the G/S ratio slightly increased the resistance to crack propagation. However, at the same time, crack initiation was facilitated. Nevertheless, the values remained in an acceptable range. The situation was different for anodes made with 30% coke I. Here, increasing the G/S ratio strongly increased the resistance

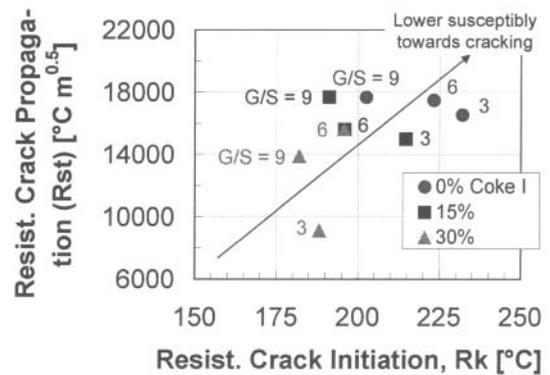


Figure 11 Impact of the concentration of isotropic coke and G/S ratio on the susceptibility to anode cracking

to crack propagation without affecting crack initiation. Thus, at elevated concentrations of isotropic coke, using a high G/S ratio makes anodes less susceptible to cracking.

During the last several years, Rio Tinto Alcan’s paste plants increased their G/S ratios. Furthermore, anode slots were introduced, which also makes anodes more resistant to cracking. Thus, Rio Tinto Alcan had confidence that a certain concentration of isotropic coke could be tolerated in anode blends.

The concentration of isotropic coke in green and calcined coke sources is regularly analyzed. In routine analyses, a simplified method similar to the one described in [8] is used. The concentration of isotropic textures varies considerably. Most sources contain 5–15 % isotropic textures. However, some sources have considerably higher concentrations, such as coke I which is represented by the far right point in Figure 12.

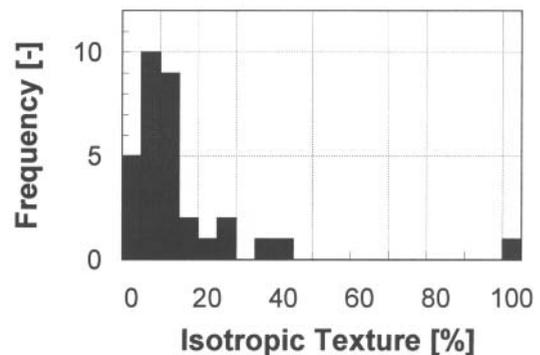


Figure 12: Concentration of isotropic textures in 32 green and calcined coke sources analyzed by Rio Tinto Alcan

The concentration of isotropic textures in some coke sources is also highly variable. This is shown in Figure 13 for green coke F. The refinery producing this coke historically operated with a stable crude blend but it now changes crude blends on a regular basis which causes the coke quality to vary. Coke F is a significant Rio Tinto Alcan green coke source. Quality changes in this coke strongly influence the quality of the overall blends at some Rio Tinto Alcan paste plants. At the end of 2010, when coke

F contained ~60 % of isotropic textures, the blend at the Alma smelter contained ~20 % isotropic textures. During this period, neither a significant increase in anode CTE, nor an increase in anode problems (including cracking) was observed, Figure 14. In 2008, however, the smelter experienced an anode crisis, which was not associated with isotropic coke.

Due to a power failure, a P155 pot line at the Latterière smelter had to be shut down in July 2010. The pot line was restarted in the following three months with anodes from the Grande-Baie smelter without significant problems. At this time, the Grande-Baie blend contained ~23% isotropic coke. In summary, Rio Tinto Alcan's experience is that ~20 % isotropic coke can be tolerated in anodes.

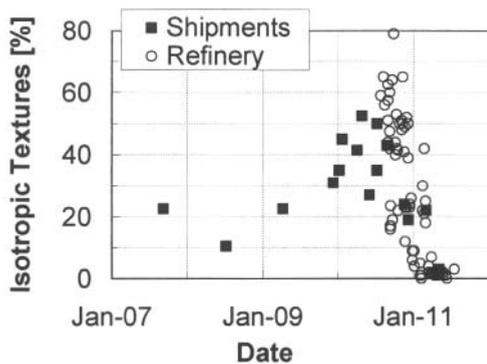


Figure 13: Concentration of isotropic textures in a Rio Tinto Alcan green coke source (Coke F)

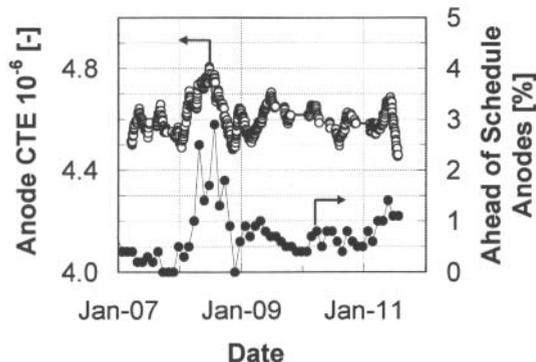


Figure 14: Anode CTE and portion of anodes changed ahead of schedule at Rio Tinto Alcan's Alma smelter

Anode Density

Anode density is generally believed to correlate with coke bulk density [13]. Decreasing coke bulk density puts pressure on paste plants that have to increase or at least maintain anode densities. Consequently, considerable work has been done on increasing anode density which has offset the impact of decreasing coke density.

As an example, the trends in coke VBD and baked anode density (BAD) at Rio Tinto Alcan's Grande-Baie smelter are presented in Figure 15. During the last five years, the VBD has been quite variable and, on average, decreased slightly. In spite of this it was

possible to increase the BAD and keep the variation small. The BAD increase in late 2007 was due to the installation of a so-called "coke separator." This equipment separates coke according to its bulk density. Low-density particles are milled and used in the fines fractions, whereas high-density particles are used in the coarse and medium fractions [14]. The coke separator also decreased the BAD variability, especially when the coke VBD changed strongly. In addition to the coke separator, several continuous improvement projects focused on the BAD [15].

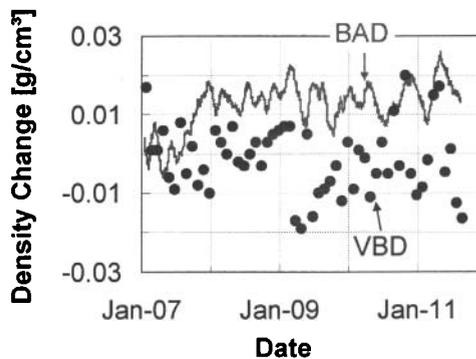


Figure 15: Change in coke VBD and BAD at Grande-Baie

SO₂ Emissions

The SO₂ emissions at smelters are driven by the coke sulfur content. As the sulfur level of some of Rio Tinto Alcan's cokes has increased, compliance with environmental limits has been achieved by procuring low sulfur cokes for blending. However, some low sulfur cokes have low VBD's. The ability to produce anodes with a reasonable BAD even with blends containing low-VBD coke allows Rio Tinto Alcan to use such cokes.

Technology does exist to scrub SO₂ from potroom gases and some smelters do this already. It is very expensive to retrofit however, and is typically not a viable solution for a smelter facing a sulfur increase in their CPC supply.

Metal Purity

Most of the trace metal impurities in coke such as vanadium and nickel report to the aluminum. Increasing V and Ni levels therefore presents a challenge for maintaining metal purity specifications. This can be mitigated by blending in low metals cokes but this approach only works if there is a readily available supply of low sulfur/low metals coke which is not the case today.

Another solution to this problem is to remove impurities from the aluminum metal. The technology to remove vanadium from metal for electrical applications exists and is widely used. The limits for V removal are not well known however and there is no equivalent technology for removing impurities such as nickel. Another approach which is attracting growing interest, is the possibility of relaxing some metal purity specifications [16].

Anode Oxidation

Another potential concern for smelters with rising V levels is anode airburn. Vanadium is a catalyst for the ignition and burning of carbon in air. This is not a significant problem for modern cell designs where anodes can be well-covered. As long as oxygen access is limited, airburn can be controlled. It can be more

problematic to keep anodes well-covered in older cell designs and cover practices and operator consistency plays a key role.

Outlook

The trend towards greater use of heavy, sour crudes will continue and the situation with anode grade coke availability is not expected to improve. One of the most significant problems today is the lack of low sulfur coke. Since 2008, North America has lost over 0.5 million tons of low sulfur anode grade coke. A good example is the loss of ~300,000 tons of Western Yorktown coke after the refinery was shut down for economic reasons in 2009.

The world is already short of low sulfur coke and as demand from the aluminum industry grows, it is hard to see where enough low sulfur coke will come from in the future. As existing supplies of high sulfur anode GPC get higher in S and V, the need for more low S coke to counteract these changes increases. Most of the marginal quality cokes are even higher in S and V.

Brazil is expected to produce additional low S coke in the future. Some forecasts estimate additional production of 3-5 million tons by 2020. Several new refineries are planned and these will use the Marlim crude that produces a good low S (<1%) coke. One of the challenges however, is competition from the Brazilian steel industry which already uses ~30% of Brazil's low S coke as a substitute for imported metallurgical coke.

China also produces significant quantities of low S GPC but as their appetite for petroleum fuels increases, they are importing more heavy sour crude. This is already having an impact on sulfur and vanadium levels in GPC in some regions.

One implication of the lack of low sulfur coke is an increase in price. This is already occurring and low sulfur GPC now commands a substantial premium price relative to high sulfur GPC. Anode grade GPC prices increased significantly in 2007-2008, decreased during the 2009 recession, and have increased again substantially since 2010. This is driving up smelter carbon costs. Carbon costs have been in the range of 7-8% of total smelter costs historically but this is now increasing to levels above 10%.

These developments present both a challenge and an opportunity for the aluminum industry. The short supply of low sulfur GPC means this product will continue to attract a price premium which is passed onto the smelters. Smelters that can utilize coke with higher S and V levels will be able to procure lower cost CPC in the future.

Conclusions

This paper has shown that the definition of anode grade GPC is less relevant in a world where marginal quality GPC is being used in anode coke blends. If a marginal quality coke is being used in an anode blend, should it be classified as an anode grade coke?

The range of GPC qualities used today may surprise some readers. A key learning from this is that anode quality and performance is probably more robust than we think. Past beliefs about which GPC can and cannot be used in anode blends is being challenged. Many different cokes are already being used successfully including highly isotropic cokes. A logical extension of this would

say that shot coke can be used in anode blends as well. A significant advantage of using cokes like this is that they are readily available and cheaper than higher quality GPC.

In a world of rapidly increasing carbon costs, the use of cheaper alternatives becomes more attractive. Most of these cheaper alternatives come with higher sulfur, vanadium and nickel and in some cases, more isotropic structures. This is the biggest challenge the industry will face. There is no shortage of GPC; the world produced ~123m tons in 2011. The calcining industry only uses about 25% of the GPC produced and as long as smelters can adapt to higher sulfur and metals levels, there is more than enough GPC for any conceivable increase in global aluminum production.

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