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Anode Raw Materials

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IMPURITY LEVEL DISTRIBUTION IN GPC AND CPC AND IMPACT ON ANODE PROPERTIES

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Abstract

Aluminum smelter specifications for trace metal impurities in calcined petroleum coke (CPC) are based on a bulk analysis of the coke. Recent experience shows that it is important to understand the distribution of impurities when considering new sources of green petroleum coke (GPC). Most GPC sources have a uniform distribution of impurities like vanadium, iron, silicon and calcium throughout the particle size range but some sources show a concentration of iron, silicon and calcium in the fines fraction. The paper presents a review of the origin and distribution of impurities in GPC and the results of an investigation into the root cause of elevated calcium levels in a GPC source used in an anode-grade CPC blend. High levels of calcium in the fines fraction of the CPC had a significant negative effect on anode CO_2 reactivities. The paper highlights the need to be cautious when using new GPC sources.

Introduction

Blending different green petroleum coke (GPC) sources is a common practice for coke calciners. Sourcing low and high sulfur GPC with varying levels of vanadium (V), nickel (Ni) and other impurities allows a calciner to produce calcined petroleum coke (CPC) with a wide range of specifications to meet customer requirements. In 2012, Rain CII sourced GPC from 16 different refineries for production of anode grade CPC for its six US based anode grade calciners. Most were sourced from North America but some low sulfur GPC was imported from Asia (predominantly China) and Europe. Each calciner typically uses 4-6 different GPC sources throughout the year to produce customer shipments.

Automatic samplers are used to take representative samples when CPC is loaded onto vessels to ensure the shipment sample accurately reflects the average quality. A minimum of 30 samples are taken for every 1000 tons of product loaded. Samples are composited together and a final shipment sample is generated by taking a representative split using equipment like rotary splitters and riffle splitters. A chemical analysis of the final bulk sample is undertaken using the ASTM D6376 XRF method after grinding the sample to -200 mesh (-75µm). This ensures that all particle sizes are properly represented in the final analysis.

In 2012, one of Rain CII's aluminum smelting customers experienced a problem with a CPC shipment that gave significantly elevated anode CO_2 reactivities. CO_2 reactivity dust (CRD) levels measured by the ISO 12988-1 method increased from typical levels of 1-2% to 4-9%. The CPC shipment met the customer specifications based on the usual analysis of the final shipment sample as shown in Table 1. Production of anodes was stopped however, until the shipment quality was investigated in more detail. The shipment sample was separated into different particle size fractions and the -1mm fines fraction showed elevated levels of calcium (Ca) and silicon (Si) relative to the bulk sample as shown in Table 1.

Table 1: Shipment CPC Quality and Specifications

Parameter	Shipment	-1mm Fines	Specification
Ash (%)	0.1	0.1	0.3
Sulfur (%)	2.76	2.6	2.8
Vanadium (ppm)	300	280	300
Nickel (ppm)	220	220	250
Iron (ppm)	160	190	300
Sodium (ppm)	80	70	150
Calcium (ppm)	180	330	200
Silicon (ppm)	140	225	300
CO_2 Reactivity (%)	13	-	15

The root cause of the problem was traced to a low-sulfur (S) GPC used in the blend at a level of 9%. A detailed investigation showed elevated levels of Ca, Si and iron (Fe) in the fines fraction of the coke. Coupled with particle size segregation during vessel loading and unloading, a disproportionate amount of the higher Ca fines ended up in the binder matrix of anodes produced with the coke causing the increase in anode CO_2 reactivities. Although the coke CO_2 reactivity appeared to comfortably meet the specification, the ISO 12981-1 test is carried out on a 12x16 mesh (1.0-1.4mm) sample and would therefore not show the impact of elevated Ca levels in the -1mm size fraction.

The concentration of impurities like Fe, Si and Ca in the fines fraction of cokes has received little attention in the past but it has been reported in at least one other paper [1]. No explanation was given for the root cause or the form of the contaminants in this reference. The objective of this paper is to provide a more detailed analysis of the impurity distribution in GPC and to describe the origin and form of these impurities. The paper will make the point that care that needs to be taken when evaluating and selecting new supplies of GPC and CPC.

Identification of Impurity Level Problem

A breakdown of the chemical analysis by particle size for the low S GPC mentioned above is shown in Table 2. An analysis of the +1mm and -1mm material is provided first followed by a more detailed breakdown in the bottom half of the table. The weight % of material in each size range is also shown.

Table 2: Chemical Analysis of Chinese Low Sulfur GPC

Size Fraction	Wt %	V ppm	Ni ppm	S %	Fe ppm	Ca ppm	Si ppm	Na ppm
Coarse (+1 mm)	61%	43	483	0.46	184	545	114	37
Fines (-1mm)	39%	43	411	0.48	605	860	702	45
+4mm	38%	20	505	0.36	192	516	104	35
2-4mm	10%	83	452	0.61	170	582	95	40
1-2mm	13%	90	438	0.66	170	608	158	41
0.25-1mm	25%	44	438	0.48	308	699	357	60
-0.25mm	14%	53	395	0.52	1048	910	895	61

The concentrations of V, Ni, S and sodium (Na) showed relatively little difference between the coarsest and finest size fractions. Differences in Fe, Ca and Si were more significant and the finest particle size material (-0.25mm), shows Fe, Ca and Si levels of ~1000, 900 and 900ppm respectively versus average levels of ~185, 550 and 115ppm respectively in the +1mm material.

Several other quality parameters for this GPC also stand out relative to most other GPC sources used by Rain CII. The Ni level is very high for such a low S coke whereas the V level is relatively low. High Ni levels are usually associated with high V levels but the V:Ni ratio of this coke is very unusual. The Ca level is also very high, even in the coarsest particle size fractions and the coke is relatively fine with a -1mm content of 39%.

Once the above analysis was completed, similar data was generated for a much wider range of GPC's (16 in total). For brevity, results are shown only for the +1mm and -1mm fractions of 10 cokes in Table 3. This breakdown is sufficient to highlight differences in contaminant levels between fine and coarse coke.

Table 3: Chemical Analysis Differences in GPC

	Ni	Fe	V	Ca	S %	Si	Na
Coke A +1 mm	483	**184**	43	**545**	0.46	**114**	37
-1mm	411	**605**	44	**860**	0.48	**702**	45
Coke B +1mm	304	**145**	5	214	0.32	**91**	29
-1mm	296	**288**	8	285	0.32	**220**	45
Coke C +1mm	285	177	12	45	0.43	167	65
-1mm	267	184	24	51	0.50	156	59
Coke D +1 mm	168	149	112	43	1.50	45	61
-1mm	162	213	108	65	1.49	49	66
Coke E +1mm	154	142	137	40	2.17	332	79
-1mm	145	148	131	64	2.15	356	71
Coke F +1mm	144	**214**	277	34	2.86	36	80
-1mm	139	**344**	273	66	2.87	44	87
Coke G +1mm	234	214	588	33	3.67	77	101
-1mm	218	206	555	92	3.59	96	114
Coke H +1mm	159	106	404	35	5.34	69	118
-1mm	146	162	374	49	5.34	88	117
Coke I +1mm	234	**334**	531	61	5.39	147	118
-1mm	227	**452**	524	85	5.43	195	131
Coke J +1mm	208	**320**	471	**118**	3.45	**258**	84
-1mm	188	**451**	440	**400**	3.63	**874**	110

Significant differences in contaminant levels are highlighted and there are relatively few of these. Coke A is the low S Chinese coke shown in Table 2 and Coke B is another low S Chinese coke. Most of the other cokes (except coke C) are sourced from North America. Of the 16 different cokes examined, only Cokes A and J showed significantly elevated contaminant levels in the fines fraction for three different elements (Fe, Si and Ca). Coke J is a US fuel-grade coke whereas all the other cokes are anode grade cokes. Coke B shows elevated levels of Fe and Si and a slightly higher level for Ca. Cokes F and I show higher Fe levels.

Source of Contamination in Fines Fraction

Given the magnitude of the problem created when coke A was used in an anode blend, further work was done to determine the source of the contamination. Early speculation was that the green coke had been contaminated by dust or other foreign material during storage. Green coke is typically stored outside in piles prior to export from China. If the export volume is large (>15,000

MT), these piles can sit on the ground for some time while the coke is accumulating.

As a first step, samples of the fines fraction from coke A were examined with an SEM (scanning electron microscope) fitted with EDS (energy dispersion spectroscopy). Polished cross-sections were also prepared after mounting in epoxy resin. Coarse particles (+4 mm) from the coke were examined in a similar manner.

The SEM analysis showed very clearly that the fines fraction was contaminated with discrete particles of species like iron oxide, calcite, potassium and sodium feldspars ($K/NaAlSi_3O_8$), quartz, spinels [$(Mg,Fe)(Al,Cr)_2O_4$] and other common minerals. Figure 1 shows a particle of iron oxide amongst the coke fines. It is not possible to differentiate the contaminants using secondary electron imaging but it is very clear using backscattered imaging which provides good atomic number contrast. The particle size of the contaminants ranged from ~10-50μm. Figure 2 shows a polished section of fines with a K-feldspar and quartz particle.
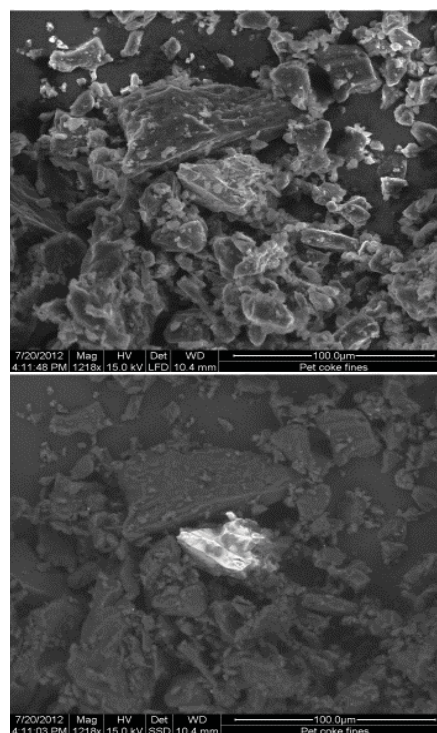

Figure 1: Coke fines: Secondary electron image (top) and backscattered image (bottom) showing bright Fe_2O_3 particle.

Figure 2: Polished cross-section showing K-feldspar and quartz

When polished cross-sections of coarse coke particles were examined, the same type of contaminant particles were observed inside the coarse particles but the average size was smaller – typically 1-10µm in size. Figure 3 shows fine grained inclusions along a grain boundary within a coarse particle. In addition to the polished cross-sections, coarse particles were also fractured to examine internal fracture surfaces. Figure 4 shows fine alumino-silicate particles along one of the freshly fractured surfaces.
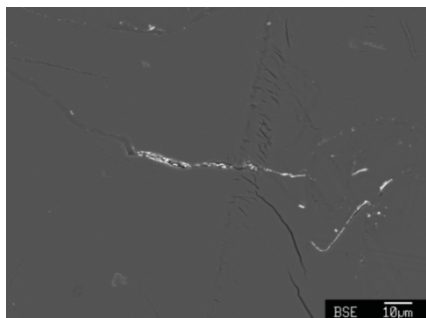

Figure 3: Fine-grained fluoro-apatite inclusions along grain boundary in coarse particle (polished section)
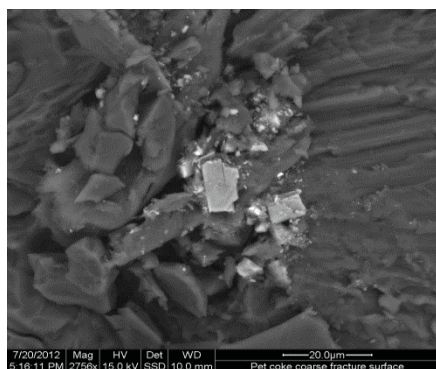

Figure 4: Alumino-silicate particles inside coarse particle.

Fine particle size clusters of calcite ($CaCO_3$) particles ranging in size from 100nm to several microns were also commonly observed along fracture surfaces of coarse coke particles as shown in Figure 5. The top left figure is a low magnification image and progressively higher magnification images of the same region are shown in the top right and bottom photos in Figure 5.

The results from the coarse coke particles are significant and suggest that at least some, if not all, of the contaminant particles were present in the feed to the delayed coker. Post production contamination of the coke from dust and other sources would not explain the presence of contaminant particles and inclusions within larger coke particles.

In the final step of this work, an electron probe micro-analyzer (EPMA) was used to undertake a quantitative analysis of trace element concentrations in the bulk carbon phase of polished cross sections of coarse coke particles. Cokes A, E and J were analyzed like this and the results are shown in Table 4. Coke J was included because it showed similar contamination in the fines fraction to coke A. The V level was also much higher. Each concentration represents the average of ~100 individual analyses.
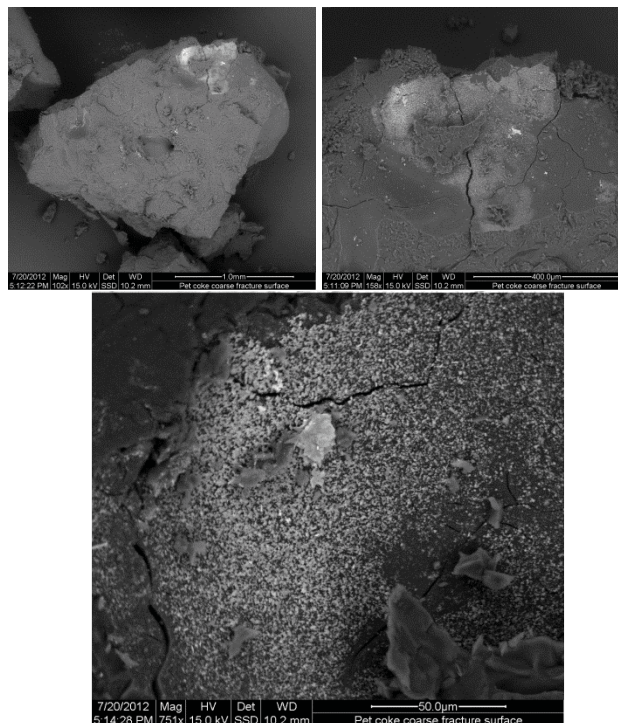

Figure 5: Successively higher magnification shot of fracture surface in coke showing fine grained calcite crystals

Table 4: Quantitative EMPA Results

	Coke A	Coke E	Coke J
S (%)	0.40	1.5	2.5
V (ppm)	19	93	324
Ni (ppm)	590	143	139
Ca (ppm)	427	16	22
Fe (ppm)	166	72	122
Si (ppm)	20	36	56
Na (ppm)	7	10	2
Al (ppm)	12	35	73

The S, V and Ni levels in the matrix of cokes A, E and J measured by EPMA do not match the bulk particle concentrations measured by XRF exactly (Table 3) but they are quite close given the very different methods used. The data shows very clearly that S, V and Ni are uniformly distributed throughout the carbon matrix and are not present as discrete particle inclusions.

Coke E is a ~2% S coke produced in the US which normally has relatively low levels of trace elements. The sample was selected for analysis because of the unusually high silica level (Table 3) which was known to be caused by a catalyst fines problem. The refinery was blending a stream of fluid catalytic cracker (FCC) decant oil with the coker feed. They were experiencing a problem with the hydrocyclones which normally remove catalyst fines. The coke was therefore known to be produced with coker feed containing discrete particles of alumino-silica catalyst fines.

The EPMA results for all cokes show that the concentration of silicon in the carbon matrix is low (<60ppm). When the coarse particles are crushed and analyzed however, the silicon concentrations are significantly higher: ~110, 330 and 260ppm for cokes A, E and J respectively. This is consistent with the primary

source of silicon being inclusions of silica containing particles. In the case of coke E and J, aluminum concentrations were high as well pointing to alumino-silicate catalyst fines (zeolite catalysts) as being the major source of particulate Si contamination.

The situation with calcium is quite different. In coke A, the level of Ca in the carbon matrix is high at 427ppm. This suggests a significant portion of the Ca is present as an organo-calcium complex in the coker feed. This will be discussed in more detail in the next section. Ca is also present as fine, discrete particles of calcite and species like fluoroapatite as shown in Figures 3 and 5.

Coke E and J on the other hand contain very little Ca in the carbon matrix. Coke E also contains a relatively small amount of Ca in the form of inclusions or discrete particles but coke J contains a much higher level of Ca containing particles in the fines fraction.

Review of Impurity Sources in Green Coke

Several papers have been published recently highlighting the wide range of GPC qualities and impurity levels used in anode coke blends and the most recent is referenced [2]. Despite this, relatively little has been published on the origin and form of the impurities in GPC beyond general comments.

It is commonly known that V, Ni and S levels are driven by the crude oils processed by the refinery. On the other hand, very little data exists to explain the origin of contaminants like Fe, Si, Ca and Na beyond general comments about refinery desalter operation, corrosion in pipelines, chemical additives used in the refinery, water quality etc. The following section provides more detail on the above.

Vanadium and Nickel

Crude oils contain a large suite of trace metals but vanadium and nickel are the most abundant. They are present predominantly as metalloporpyhrins with the typical structure shown in Figure 6. They are derived primarily from chorophylls deposited in sedimentary environments. The paper by Filby [3] provides an excellent reference on the formation of these porphyrin complexes and the reasons V and Ni levels are higher than other trace metals.
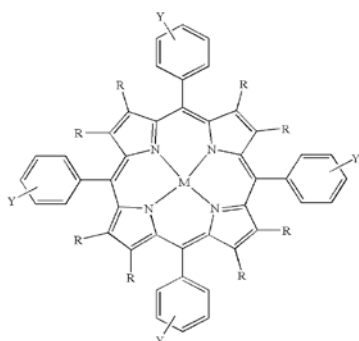

Figure 6: Typical metalloporphyrin structures. M = VO^{2+} or Ni^{2+}

The organometallic structure of these porphyins explains why V and Ni are distributed uniformly throughout GPC and are essentially part of the carbon matrix as supported by the EPMA results in Table 4. The results in Table 3 show that all the cokes have a more or less uniform concentration of V and Ni through all particle size ranges. A recent paper by Gagnon et al [4] which used SEM and EDS analysis methods reported similar results.

Sulfur

The sulfur in coke is derived from sulfur containing compounds in crude oil and its distribution is also very uniform as indicated by the uniformity between different particle sizes and the EMPA results. Most of the sulfur in green coke is believed to occur in thiophene ring structures [5]. There is some speculation that a small amount of sulfur occurs as elemental sulfur trapped with the pores of green coke and as sulfates and sulfides within the coke. The current study supports the existence of very small amounts of sulfur in the form of extraneous contaminants like FeS.

Iron

Iron in petroleum coke can come from several different sources. Like V and Ni, Fe can form porphyrin complexes with Fe^{2+} [3] and the Fe is likely to remain in this form as it is processed through the refinery. Fe can also occur in the form of Fe-napthenates in high TAN (total acid number crudes) as mentioned in the next section. This accounts for some of the variation in Fe levels in different GPC but Fe is also common in many extraneous contaminants that can be introduced through a variety of sources. Crudes often contain sediments with suspended solids, and Fe is a common contaminant in sediment. Fe can also be introduced through corrosion in the refinery and transport through pipelines.

Calcium Levels and Desalter Operation

Crude oil typically contains water and a range of water soluble inorganic salts and trace metals and suspended solids and sediments. Basic sediment and water (BS&W) is the overall technical specification for these contaminants and a typical specification is <0.2l volume %.

The concentration of specific contaminants in crude is expressed by the ratio: pounds of contaminant (lbs) per 1000 barrels (bbl) of oil, typically written as ptb. A typical range is 3-200ptb. Water soluble salts or brines include, primarily, NaCl (~75wt%) with lesser amounts of $MgCl_2$ (~15wt%) and $CaCl_2$ (~10wt%). The desalter plays a critical role in reducing overall BS&W, and specifically, the concentration of salts and sediment. This helps mitigate downstream refinery operability issues such as corrosion, fouling, catalyst deactivation and product contamination.

During desalting, a water-in-oil emulsion is intentionally formed through the addition of around 5 volume % water. The water is mixed intimately with the crude to transfer impurities from the crude to the water phase. Coalescence of the water droplets is promoted by operating the desalter at an elevated temperature and employing a high voltage electric field. Through gravity separation, coalesced water settles out of the crude oil and is removed from the bottom of the desalter. Contaminate free crude oil rises to the top of the desalter. Demulsification agents are typically added to improve the separation.

A well operated desalter is very effective for reducing levels of Na and Ca introduced through water soluble salts. It can also be very effective in removing Si, Ca and Fe impurities entering with the crude in the form of suspended solids. All three of these contaminants are commonly found in sediments and clays in a wide range of mineral forms including some of the minerals identified earlier in this paper.

Cokes A and B in Table 3 standout with their high Ca levels in both coarse and fine particles. Both these cokes are from China and it is not uncommon to see GPC with high levels of Ca from

this region [6,7]. The source of the high Ca levels has received little attention in previous publications. In a book that deals specifically with Chinese raw materials [8], the cause is attributed to the absence of desalters or poor operation of desalters.

The high Ca in coke A is caused primarily by the type of crude processed by the refinery. The refinery imports ~40% of its crude from West Africa. West African crudes such as the Doba crude from Chad are high TAN crudes containing napthenic acids which are complex mixtures of cyclo-aliphatic carboxylic acids. Under certain pH and temperature conditions, Ca ions in the water react with the various napthenic acids to form Ca-napthenates [9] which are often referred to as organo-calcium compounds.

These stable, organic based Ca compounds in the crude are very problematic for the refinery since they are neither oil nor water soluble and their relative density means they accumulate at the oil-water interface in desalters and other separation devices. They act as emulsifiers which interfere with the normal operation of a desalter and can cause all sorts of fouling and processing problems in the refinery. The Shengli and Bohai Bay crudes from China are other examples of such crudes.

The technology for removing Ca napthenates is still evolving and not universally employed [10]. Acetic acid and other carboxy acids are commonly used for napthenate control but must be used in combination with careful pH control upstream of the desalter.

The presence of high Ca levels in the carbon matrix of coke A and the appearance of fine particle size Ca precipitates along fracture surfaces and grain boundaries within coarse coke particles is consistent with a refinery processing high Ca crudes. Whilst it may have been possible for the refinery to reduce Ca levels by using a more sophisticated chemical treatment, higher than typical levels of Ca would still be expected. The paper by Zurlo [11] provides a good example of a refinery that reduced Ca levels in coke through improved chemical treatment in the desalter.

To investigate the above further, visits were made to the refineries in China producing cokes A and B. Both have relatively modern, two-stage desalters which are operated with efficiencies in the range of 85 to 97%. An efficiency of 85% is relatively low and could contribute to higher contaminant levels. It was not possible to determine if refinery A was using a sophisticated Ca-napthenate treatment technology but it was thought unlikely. Both refineries feed only vacuum bottoms to the coker and do not blend in other waste streams (eg sludge injection) which could contain mineral contaminants. The water used to cut coke from the drum is recovered from a water treatment system employing solids settling, but the refinery engineers did not believe this water was the source of contamination in the coke.

Sodium and Silicon Levels
The two other common impurities in coke are Na and Si. Na levels are controlled largely through desalter operation and control of water chemistry in both the refinery and calciner (coke drum cutting and cooler quench water). None of the cokes shown in Table 3 shows a particular problem with high Na levels.

Si entering the refinery in the form of silica based sediments in the crude should be removed with an efficiently operated desalter but the presence of Ca-napthenates in the crude can reduce this efficiency. Si can also be introduced through catalyst carryover in

the refinery as described earlier for coke E. The catalyst particles were readily observed inside coarse coke particles as shown in Figure 7. They were uniformly distributed through all the size fractions suggesting intimate mixing and distribution in the coker feed. For reference purposes, the normal Si level of coke E when the hydro-cyclones are functioning correctly is <60ppm. Figure 8 shows a trend graph of the coke Si level before, during and after the hydrocyclone problem.
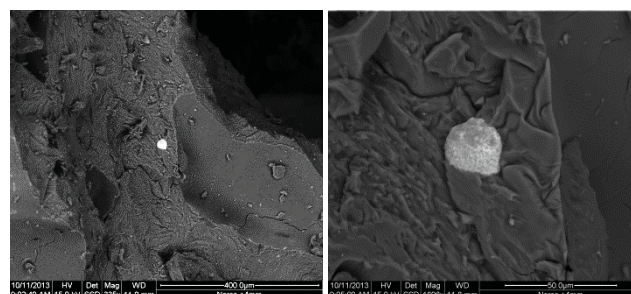

Figure 7: Zeolite (Al_2O_3-SiO_2) catalyst particle inside coarse coke particle. Low mag. left (335x) and high mag. right (2000x).
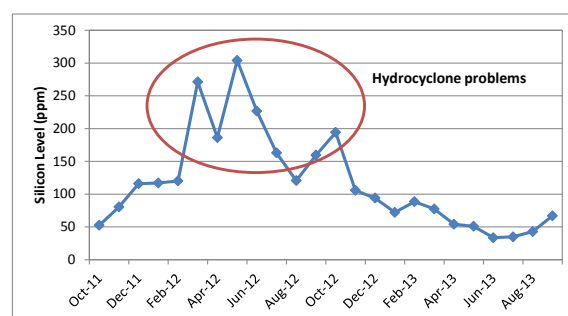

Figure 8: Si level increase in GPC from refinery process problem

Discussion

The results presented in this paper provide more detail on the nature and source of impurities in coke A and other GPC's relative to typical bulk analysis methods. It is clear that the elevated levels of Fe, Si and Ca in the fines fraction of coke A are due to the presence of common mineral contaminants with sizes in the range of 5-50µm. These same contaminants can be found inside larger coke particles but the concentrations are lower and average particle sizes are smaller. This means that at least some, if not all, of the contaminants were present in the coker feed.

If all the contaminants were present in the coker feed, a more uniform distribution would have been expected in the coke as was the case for the catalyst fines contamination in coke E. It is possible that the larger contaminant particles in the coker feed settled out in the coke drum or were pushed towards the edges of the grain boundaries during solid coke formation. Some support for this was found in two earlier papers [12,13]. In this case, higher ash levels were consistently found in coke from the bottom of the drum. When the coke is cut from the drum, a higher percentage of these contaminants could end up in the fines fraction if they concentrate at grain boundaries which the coke fractures along during cutting.

The presence of mineral contaminants in the coke drum cutting water could also explain a higher concentration of contaminants in

the coke fines. The refinery did not believe water quality was an issue however, but this could not be verified. It is also possible that contamination of the coke occurred post production through mixing with dust, dirt etc. An inspection of the refineries storage practices and port storage practices did not support this, and both areas were clean and well maintained. Contamination like this would also be expected to be very inconsistent but the entire 30,000 ton shipment of this coke showed a similar level of contamination in the fines fraction.

In addition to the fines contamination problem, coke A also contained a high concentration of Ca in the carbon matrix. The presence of Ca-napthenates in the crude will almost certainly increase the level of Ca in the coke and as a consequence, the CO_2 reactivity. Ca napthenates are also likely to result in a higher level of mineral contaminants containing Si, Fe and Ca through the negative impact on desalter operations. Whilst chemical and process technology continues to improve for dealing with Ca napthenates, it complicates the operation and adds cost and is not universally employed.

A simple solution to the problem reported in this paper is to avoid the use of cokes like coke A in anode blends. The combination of low S and high Ca makes cokes highly reactive to CO_2 and this phenomenon has been reported frequently in relation to Chinese cokes. Whilst this sounds easy in principle, it is not so easy in practice due to the limited availability of low S GPC. This is a global problem and the significant price premium that low S GPC commands in the market reflects the relatively short supply.

The best approach for dealing with the above is to work closely with refineries to minimize these sorts of problems and to recognize and deal with them when they occur. The quality of coke A improved significantly in 2013 after the refinery visit in Oct 2012 where details of the Ca problem were shared. A sample analyzed in Aug 2013 showed a bulk Ca level of ~220ppm and a fines Ca level only slightly higher at 260ppm. It is not clear if crude changes or process changes were responsible for this improvement but the refinery visit may well have helped.

Conclusions

The following conclusions can be drawn from the results presented in this paper:

- Care needs to be taken when sourcing new supplies of GPC and CPC to properly understand the distribution of impurities throughout the particle size range.
- Higher concentrations of Ca in the fines fraction of CPC can give a disproportionate increase in anode CO_2 reactivities which may not be obvious when looking at a bulk analysis of the sample including analysis of coke CO_2 reactivities on 12x16 mesh (1.0-1.4mm) particles.
- For most cokes, impurities are distributed uniformly throughout all size fractions and V, Ni and S are always distributed uniformly throughout the carbon matrix.
- Crudes containing high levels of calcium in the form of Ca-napthenates will typically show elevated Ca levels in the coke matrix as a result of the difficulty of removing these compounds in the desalter.
- Most cokes contain at least some Si, Fe and Ca contamination in the form of discrete mineral/particle contaminants. The level can be dependent on many factors including the type of crudes processed (eg high

TAN crudes), the efficiency of desalter operations, corrosion, addition of waste streams to the coker, cutting water quality, chemical additives including catalyst fines, calciner water quality etc.
- Collaboration with refineries on the sorts of problems described in this paper can be helpful and is highly recommended to explore improvement opportunities.

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