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CALCINED PETROLEUM COKE DENSITY SEPARATION PROCESS: SOLUTION TO MAINTAIN ANODE QUALITY WITH DEGRADING COKE DENSITY

Marie-Josée Dion [1], Cyril Gaudreault [1], and Yvon Ménard [2]
[1] Rio Tinto Alcan, Arvida Research & Development Centre, 1955 Boulevard Mellon, Jonquière, QC, Canada
[2] Rio Tinto Alcan, Grande-Baie Plant, 5000 Route du Petit-Parc, La Baie, QC, Canada

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Abstract

In the context of degrading coke quality, Rio Tinto Alcan has implemented different measures to maintain and even improve anode quality. Over the last twenty years, coke vibrated bulk density (VBD) has decreased and its variability has increased. In order to cope with this challenge, a separation process based on coke density was developed. High density particles are used in medium and coarse fractions, whereas low density particles are crushed and used as fines. Use of a coke separator has resulted in an increase of baked anode density (BAD) by ~0.015 g/cm³. Furthermore, the BAD variation upon use of different cokes was reduced. Different phases of the technology development (from laboratory experiments to industrial implementation) and results from six years of operation are presented.

Introduction

Changes in the refinery industry result in changing calcined coke properties. Cokers are often the bottleneck of a refinery. Options to increase coker throughput include reducing the coker cycle time [1] and reducing the coker temperature [2]. These practices result in increased green coke volatiles and a corresponding decrease of the calcined coke VBD [2].

In addition to the decreasing VBD, the VBD of cokes used by Rio Tinto Alcan became more variable. Increased VBD variations are highly undesirable. Consequences include BAD variations, which may result in varying carbon under stud. If the carbon under stud becomes too low, iron contamination increases and pot stability decreases.

There are several options to mitigate the impact of VBD variations, including:

- Adjustment of the amount of butts in the anode recipe
- Increase the carbon under stud by increasing the anode height
- More frequent adjustment of pitch in the anode recipe
- Increase of the paste mixing energy

Which options are appropriate differs between the plants. In the present document, the situation at the Grande-Baie plant is discussed in more detail.

Rio Tinto Alcan's Grande-Baie Carbon plant sources calcined coke from different suppliers including Rio Tinto Alcan's calciners in Strathcona (AB, Canada) and Arvida (QC, Canada) as well from external calciners. This results in a significant variability of the coke supply. Furthermore, the Grande-Baie plant has just two coke silos with a combined storage capacity of 2,000 tonnes, corresponding to about half a week's consumption. Working with two to four regular coke sources and just two silos means that it is not possible to perfectly control the recipe of the coke blend. Knowing that pitch dosing is strongly related to coke properties (including the VBD) [3], the variability of the coke sources represents a daily challenge.

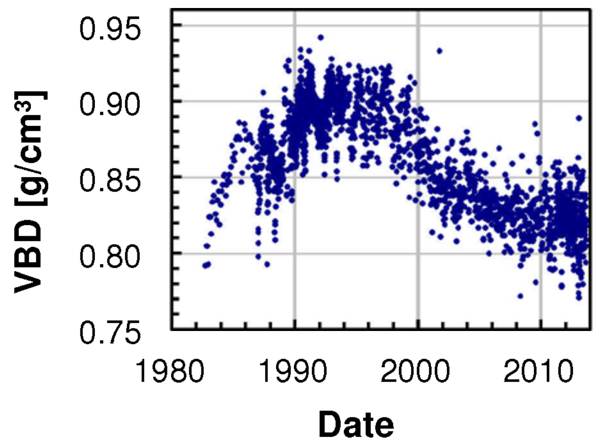

Figure 1. Vibrated Bulk Density (ASTM D7454) of Coke Received at the Grande-Baie Plant

From the end of 1990s until today, the quality of the calcined coke supplied to the Grande-Baie plant has degraded significantly. This is evidenced by a decrease of the average VBD from ~0.90 to ~0.82 g/cm³ (Figure 1). Furthermore, the VBD varied considerably. For example, in the first half of 2014 the standard deviation (σ) of the VBD was 0.022 g/cm³ and VBD values as low as 0.77 g/cm³ were observed.

Considerable effort was deployed by the Grande-Baie plant to mitigate the impact of degrading coke quality and increasing variability. This includes improvements to the Baker-Perkins paste mixer and improvement of the pitch dosing practices. These measures resulted in increased and less variable BAD. However, in order to continue increasing amperage at Grande-Baie and Laterière (receiving anodes from Grande-Baie) [4], a further increase of the anode mass was required. One important enabler was the coke separator described in the following sections.

Process Development

Concept

The BAD can be increased by separating coke particles according to their bulk density. The low-density particles are crushed in a ball mill (thereby destroying their porosity) to produce the fines fraction. The high-density coke particles are used in the coarse and intermediate fractions of anode recipe to enhance the BAD [5].

In 2005, a project was initiated at the Arvida R&D Centre with the objective to assess the gains of using a density separation system. Anticipated gains included increased BAD, reduced binder demand, and reduced impact of coke variability on anode properties.

Based on several criteria (separation quality, costs, capacity, equipment size, and reliability), a destoner was selected for the feasibility tests. A destoner is a density separation system that can separate granular materials according to particle density. Destoners are largely used in agriculture, minerals, and recycling. The basic principle of this equipment is that air flows through the coke bed moving on an inclined canvas (Figure 2). The air flow causes the lights to float on an air cushion downwards to the lower end of the canvas. Due to vibration of the canvas, heavy particles move upwards to its higher end.

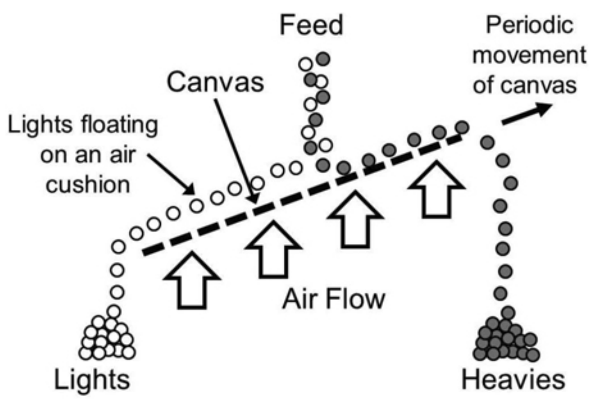

Figure 2. Sketch of the destoner used to separate calcined coke into a light (low-density) and a heavy (high-density) fraction

Proof of concept

Destoners usually treat mixtures that contain fewer heavies (*e.g.* stones) than lights (*e.g.* grains). The situation is different for calcined coke, which typically contains 10–20 % of very light particles (popcorn structure, Figure 3) with a low VBD (< 0.70 g/cm³). For the feasibility study, a destoner located at a laboratory of the equipment supplier, was adapted for coke use.

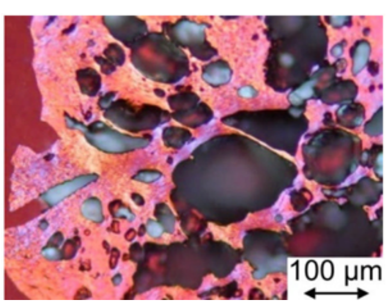

Figure 3. Micrograph of popcorn structure in calcined coke

Table I. Coke Samples Used in the Feasibility Test

Coke	VBD [g/cm³]
A (single source, high VBD)	0.882
B (single source, low VBD)	0.777
C (80:20 mixture of coke A & B)	-

Separation of three different cokes was studied (Table I). Assuming that separation is more effective for particles of similar dimensions, each coke was pre-sieved into two different fractions: (-0.371" + 4M) and (-4M + 14M) prior to testing. During the tests, the equipment parameters were adjusted so that the lights represented ~15-20% of the initial sample.

The properties (VBD and impurities) of the initial coke, of the light, and of the heavy fraction, respectively were determined. Furthermore, laboratory anodes were manufactured from the light and heavy coke fractions obtained by separation. The light particles were ground and used in fines fraction (-200M), whereas heavy particles were used in coarse and intermediate fractions. As reference for comparison, anodes were also prepared from the initial coke samples.

Results. The results of the proof of concept study can be summarised as follows:

- The VBD of the heavy fractions was 0.03 to 0.11 g/cm³ higher as compared to the initial coke
- In general, the concentration of popcorn structures in the lights was significantly higher as compared to the initial coke, whereas less popcorn structures were found in the heavies
- The amount of lights removed influenced the VBD of the heavies
  - The lower the VBD of the initial coke was and the more popcorn structure it contained, the more lights had to be removed in order to obtain high-VBD heavies
- The Hardgrove Grindability Index (HGI) of the light particles was higher as compared to the initial coke and the heavies
  - Fines production from lights by milling was expected to be easier as compared to initial coke
- For the three cokes tested, the lights contained less impurities (sulphur, vanadium, and nickel) as compared to the initial coke
- The separation depended on the coke particle size
  - Fine coke yielded more lights
- Anodes made from light and heavy fractions had better or similar properties as compared to anodes made with the initial coke
  - The BAD was 0.02 – 0.04 g/cm³ higher (Figures 4-6)
  - The binder demand was ~0.5% lower (Figures 4-6)
  - The electrical resistivity was lower (not shown)
  - The compression resistance was higher (not shown)

Conclusions. Based on these preliminary tests, it was concluded that:

- The gain from the separation process for -4 + 14M and -14M fractions was higher as compared to a very coarse fraction (-0.371" + 4M) and to cokes with a large particle size distribution
  - Due to its very low content of popcorn coke content, there is no gain in treating very coarse fractions of high-VBD cokes

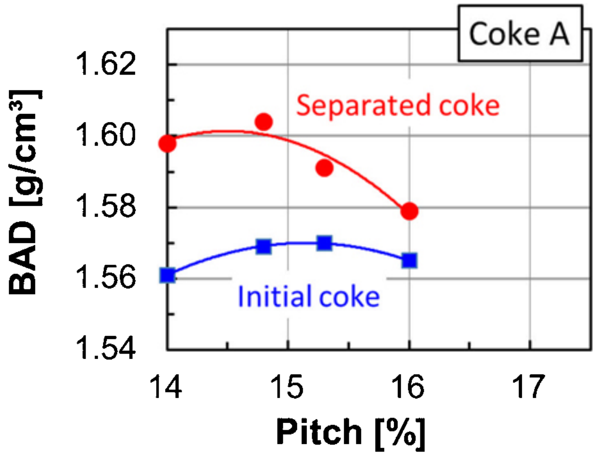

Figure 4. Baked density of laboratory anodes made with coke A (initial, and after separation, respectively)

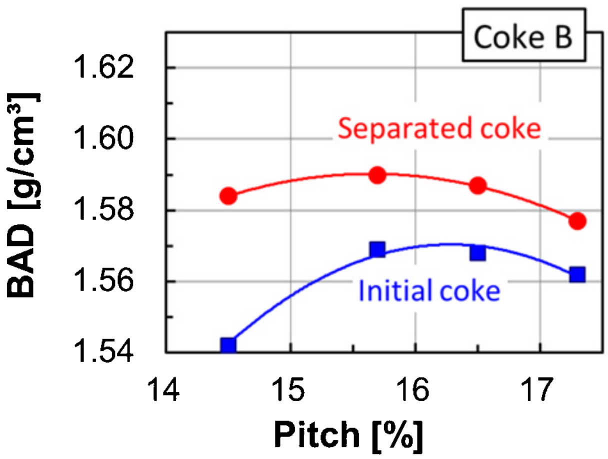

Figure 5. Baked density of laboratory anodes made with coke B (initial, and after separation, respectively)

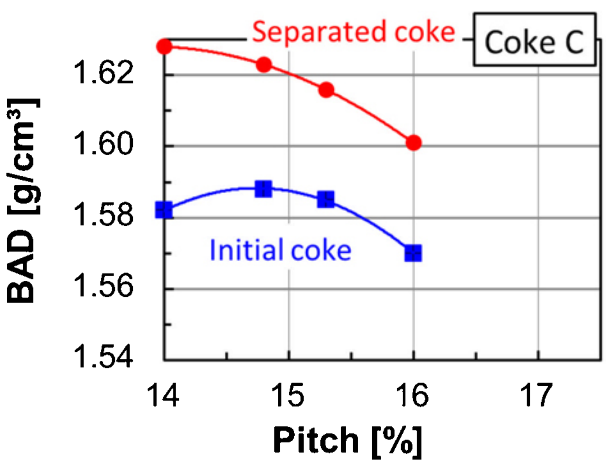

Figure 6. Baked density of laboratory anodes made with coke C (initial, and after separation, respectively)

  - The optimum separation parameters depend on the coke VBD and on the concentration of popcorn structures
- A laboratory study should be conducted

Laboratory Study

Following the successful proof of concept, a pilot destoner was installed at the Arvida R&D Centre with additional instrumentation to better characterise its operation.

Experimental Details. The laboratory destoner was about 20 times smaller than the equipment later installed at the Grande-Baie plant. The laboratory study included two series of tests based on a design of experiment (DOE) to assess the impact of the equipment parameters. The tests were realised using one fraction (-4M + 14M) of single source cokes. The following parameters were varied:

- Air flow passing through the coke bed
- Elevation (angle of the canvas, Figure 2)
- Amplitude (vibration of the canvas)
- Height of dam at the lower end of the canvas (lights outlet)
  - Constant in one DOE

The yield of lights was fixed at 20 % in one DOE and allowed to vary in the other. In additional tests, other coke sources and feed rates were studied.

Results. The results of the laboratory study can be summarised as follows:

- The air flow is the most important parameter with respect to the yield of lights and the bulk density of the heavies. Both increase with increasing air flow
- The canvas elevation and amplitude also strongly influence the separation. At high levels of elevation and amplitude, the separation can be better controlled by the air flow
- The height of the outlet dam influences the height of the coke bed on the canvas. It must be adjusted as function of the granulometry of the coke to be separated

It is desirable to increase the bulk density of the heavies as much as possible while still recovering the required amount of coarse and medium fractions for the anode recipe (*i.e.* without removal of too many lights). This means that a compromise has to be found between the VBD of the heavies and yield of lights. Usually, it is advantageous to increase the yield of lights as long as the VBD of the heavies still strongly increases. Above a certain yield of lights, the yield of desired heavies decreases without increasing their VBD (schematically shown in Figure 7).

The position of the optimum depended on the coke used. For the coke used at Grande-Baie, it corresponded to ~40 % for the intermediate fraction and to ~10-20 % for the coarse fraction.

At given separation equipment parameters (air flow, elevation, and amplitude), the yield of lights depended on the VBD of the coke feed. Low-VBD cokes yielded more lights. However, the VBD of the heavies remained more or less constant. This is illustrated in Figure 8 for a laboratory test where the coke feed was shifted every 10 minutes between a high and a low-density coke. The possibility to attenuate the impact of fluctuations of the coke feed properties is very important at a plant like Grande-Baie where the blending of the different coke sources cannot be perfectly controlled.

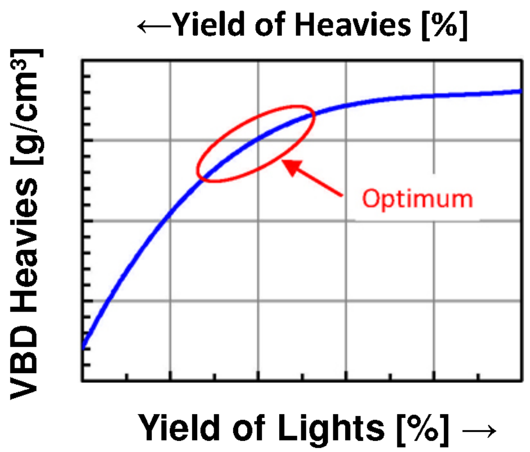

Figure 7. Schematic representation of the correlation between the yield of lights and bulk density of the heavies

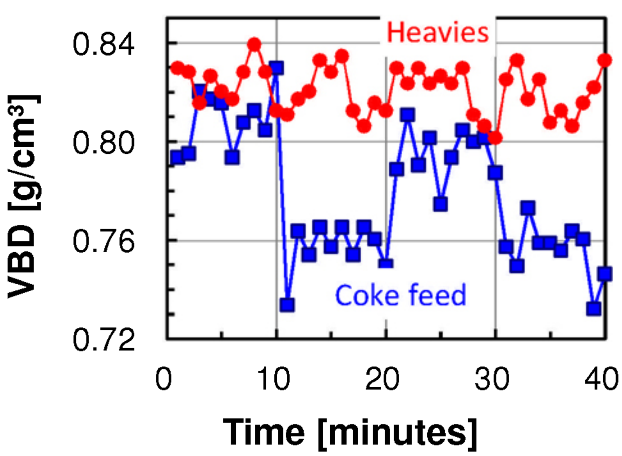

Figure 8. Vibrated bulk densities of cokes fed to the separator and of heavies after separation

If the particle size range of the coke feed was too large (largest/smallest diameter > 4), the VBD difference between the feed and heavies became small. In this case, separation was governed by weight and density as opposed to by density alone. It is therefore advantageous to process coarse and intermediate fractions separately.

Conclusions. Based on the test results, it was recommended to:

- Proceed to industrial demonstration
- Protect the intellectual property [5]

Industrial demonstration

In September 2005, the Grande-Baie plant was identified as the best choice to host the prototype, considering coke VBD variations and the amperage creeping challenges at this site.

Based on the lessons learned from the laboratory study, the flow sheet included two separators for the coarse and intermediate fractions, respectively.

Construction was performed by Rio Tinto Alcan and was completed in June 2007.

Experimental Details. The optimisation tests were performed separately on each separator. A bypass system allowed operation to continue without separators. A DOE including the following factors was designed:

- Elevation (angle of the canvas)
- Amplitude (vibration of the canvas)
- Height of dam at the lower end of the canvas

The starting values were based on experience from the laboratory tests. The coke feed rate to the paste plant was fixed at 30 t/h. For each test, the air flow was varied (corresponding to yield of lights from 5-10% to 40-50%). Once the optimum parameters were established, the impact of the coke feed rate and of the coke granulometry were studied.

The following parameters were measured:

- Coke bulk density
- Coke granulometry
- Yield of lights
- Pressure loss trough the coke bed on the canvas

Results. The results of the optimisation of the coarse separator can be summarised as follows:

- The ease of control of the yield of lights depended on the dam height
- At high elevation (angle of the canvas) control of the yield of lights was affected by sliding of the coke bed
- Maximum amplitude (vibration of the canvas) resulted in better control of the yield of lights due to better evacuation of the heavies

Optimisation of the intermediate separator yielded similar results as for the coarse separator. However, as opposed to the coarse separator, evacuation of the heavies was not affected by the amplitude (vibration of the canvas). This can be explained by easy transport of the small particles of the intermediate fraction. Furthermore, the VBD gains were somewhat higher for intermediate amplitudes as compared to the maximum amplitude.

Conclusion. The plant optimisation tests permitted the detection of phenomena not observed in the laboratory study (*e.g.* sliding coke bed) and guided the choice of operating parameters for the official start-up.

It was decided to industrialise the prototype and to use it in routine operation. To do so, several performance tests were scheduled in order to validate the technology.

Performance test

These tests were repeated three times during the validation phase from July to December 2007. The binder level was continuously optimised, including periods with and without separator operation. In addition to the binder level, the BAD also depends on the coke VBD and the butt level. Both varied during the test period. In order to facilitate comparison between different anodes, the BAD was normalised to a standard VBD of the coke feed (*i.e.* 0.82 g/cm³) and butt level (*i.e.* 19%). This was done by applying empirical correlations between these properties and the BAD.

Results. Findings of the validation phase can be summarised as follows:

- Use of the separators increased the coke VBD by 0.02-0.04 g/cm³ (heavies – initial coke)
- The corresponding BAD increase was ~0.015 g/cm³
- The carbon under studs increased by ~3 mm
- In general, the use of the separators had no significant impact on other anode properties (electrical resistivity, air permeability, and CO_2 reactivity)

According to the Student t-test between two means, these differences are statistically significant (P-values < 0.001). The corresponding data are shown in Figure 9 for average BADs of anodes successively produced with and without separators.

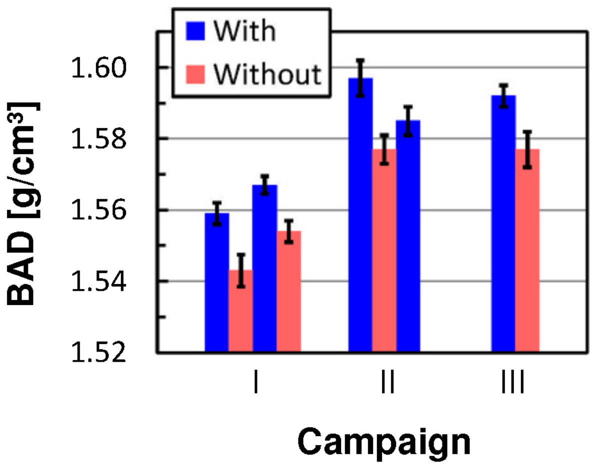

Figure 9. Average baked densities and corresponding standard deviations of anodes produced at the Grande-Baie plant with and without separators (only data for pressed anodes shown for clarity)

Routine Operation

Since 2008 the separators have operated without any special R&D effort. Only occasionally, the quantity of a fraction becomes too low and one separator has to be bypassed in order to produce the desired amount of the fraction. Furthermore, from a maintenance point of view, the separators have been modified to increase their reliability.

Upon start-up of the separators in 2007, the BAD increased by ~0.02 g/cm³. Afterwards, in spite of a decreasing coke VBD (Figure 1, first page), the plant was able to increase the BAD further (Figure 10). The BAD depends, among other factors, on the coke VBD and on the separators. In order to separate the impact of these two parameters, the VBD-BAD relation was examined. This is shown in Figure 11 for the periods before and after start-up of the separators. For the same VBD (*i.e.* 0.83 cm³), the BAD was ~0.025 g/cm³ higher after start-up. Of this difference, a portion (~0.01 g/cm³) can be attributed to process improvements in the paste plant other than the separators. Thus, the BAD increase due to the separators is ~0.015 g/cm³ (*i.e.* the same as observed during the performance test).

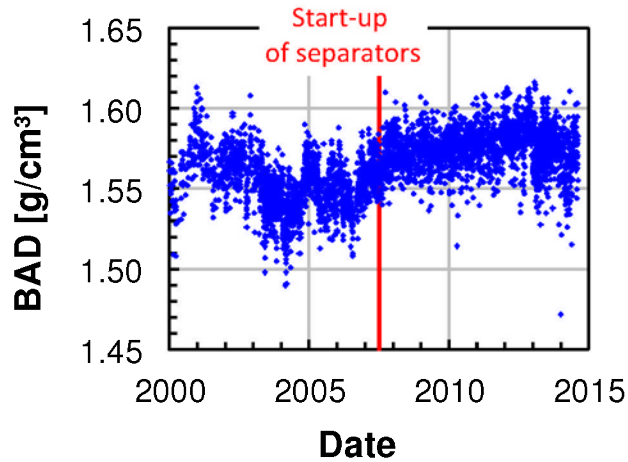

Figure 10. Baked density of anodes produced at the Grande-Baie plant (only data for line 1 and oven 1 shown for clarity)

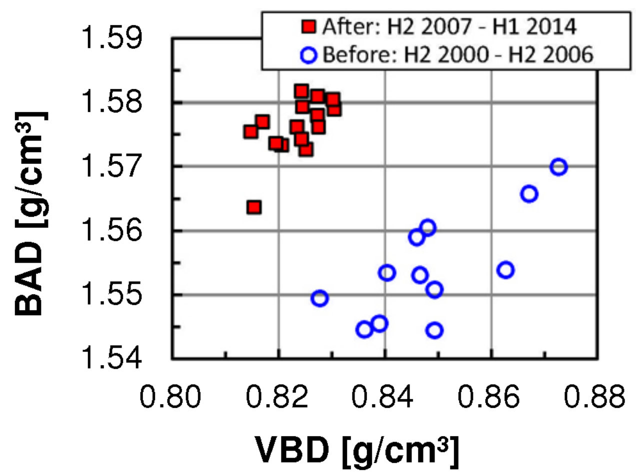

Figure 11. Coke VBD and the BAD of the corresponding anodes before and after start-up of the separators (six month averages for VBD and BAD)

The laboratory study showed that a coke separator attenuates fluctuations of the coke feed VBD (Figure 8, previous page). It was therefore pertinent to verify if the separators reduced the BAD variability during routine operation. Factors influencing the variability of the BAD include variations of the:

- VBD
- Green anode manufacture process (including the separator)
- Baking process

The following approach was used to remove the impact of VBD variations. The standard deviation of the BAD (σ BAD) was plotted as a function of the standard deviation of the VBD (σ VBD). At a given σ VBD, σ BAD mainly depends on variations of the anode manufacture process. The corresponding plot is presented in Figure 12. After start-up of the separators, σ BAD was smaller than before start-up (at a given σ VBD). This strongly suggests that the separators indeed reduced the BAD variability.

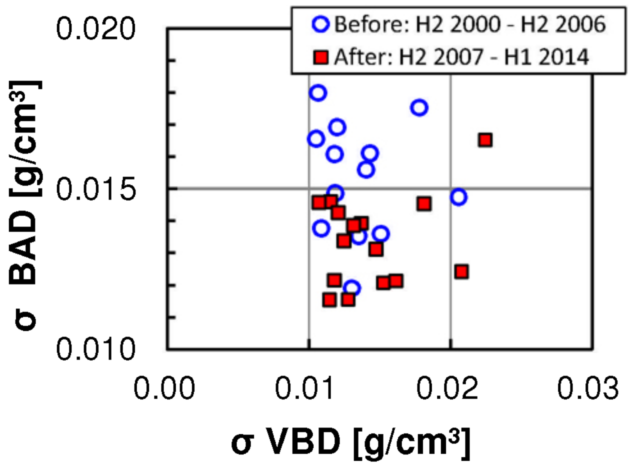

Figure 12. Standard variations of coke VBD and the anode BAD, before and after start-up of the separators (six month averages for VBD and BAD)

Conclusions

Calcined coke supplied to paste plants is a heterogeneous material containing low and high-bulk density particles. Separation of these particles and the use of the high-density particles in the medium and coarse fractions of the anode recipe results in an increase in anode density. In the context of degrading coke bulk density this contributes to an improvement in anode quality.

The coke separators were successfully integrated into the Grande-Baie paste plant and implementation is possible in most existing paste plant flow sheets.

Close cooperation between the R&D Centre and the Grande-Baie plant permitted the successful development of a new process in three years from concept to start-up in the plant. Modifications of the separation equipment have improved its reliability and improved the design for future installations.

Acknowledgment

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