

Prediction of Calcined Coke Bulk Density

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Abstract

The vibrated bulk density (VBD) is one of the most important calcined coke properties. In the context of changing green coke quality, a reliable forecast of the calcined coke VBD from small samples of green coke is required. To a certain extent, the VBD can be predicted from green coke properties, such as the Hardgrove Grindability Index (HGI) and the volatiles content. However, the precision of this forecast is not sufficient for procurement decisions which can reach millions of dollars. Thus, Rio Tinto Alcan (RTA) studied several laboratory calcination techniques, including the use of two different laboratory rotary kilns at BP Coke and COREM (*Consortium de recherche minérale*). There was good agreement between the VBD and the degree of calcination (L_c) of calcined cokes produced in the kiln at COREM and in RTA's Arvida calciner. Adequate agreement for the VBD was reached with the BP kiln. Furthermore, it was possible to replicate phenomena in the BP kiln that cause problems on industrial scale, such as the formation of coke rings. The methods will therefore be used in the future to support RTA's calcining operations.

Introduction

RTA operates three rotary kiln calciners in Canada that supply the majority of the calcined coke consumed by RTA's North American smelters. The land-locked Strathcona calciner mainly procures its green coke from local refineries, whereas the Arvida and Kitimat calciners, with near-by sea ports, have different and sometimes new suppliers. In the context of changing green coke quality, a reliable forecast of the calcined coke quality is required, ideally based on characterization of green coke samples of some kilograms. Calcined coke impurities and coke structure can be reasonably well predicted from green coke properties. However, this is not straightforward for one of the most important calcined coke properties, the VBD. The VBD is used to predict the optimum binder content [1] and it correlates with the baked anode density (BAD) [2,3]. In the context of deteriorating coke quality (such as lower VBD) there is strong pressure to increase BAD in order to support amperage increases. Consequently, selection of the best available green cokes is a priority for RTA.

To a certain degree, the VBD can be predicted from the green coke properties, such as the HGI and the volatiles content. The quality of such a prediction is illustrated in Fig. 1 for different cokes produced at the Strathcona calciner. There is a fair correlation between the green coke HGI and the VBD of the corresponding calcined cokes. The quality of the correlation is only slightly increased when other green coke properties are considered as well. For example, inclusion of the green volatile content in the correlation increases the r^2 value only insignificantly (0.6059 vs. 0.6050). It can be concluded that although a rough prediction of calcined coke VBD from green coke properties is possible, it is somewhat risky to base

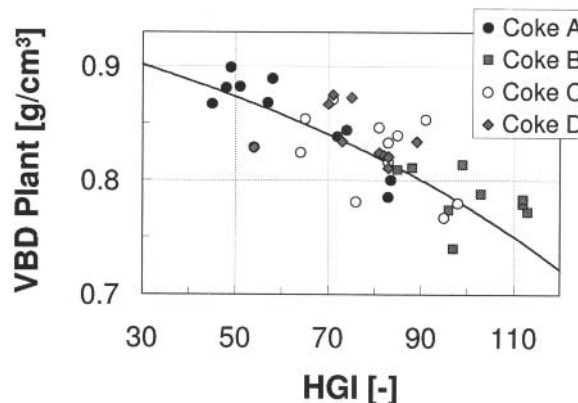


Fig. 1. VBD of calcined cokes as function of the HGI of corresponding green cokes calcined at Strathcona

procurement decisions on such correlations alone. The three RTA calciners routinely perform single source calcination tests to assess the quality of new sources and verify the properties of regular supplies. Typically, these tests correspond to about 6 h of production. This corresponds to some 100 t of green coke feed. Thus, these tests cannot be used for exploring potential new coke supplies on a routine basis. For this, techniques based green coke samples of some kg are needed.

For VBD prediction from small samples, the former Alcan developed a lab "flash" calcination method [4]. Historically, the VBD of lab-calcined and of plant-calcined cokes correlated well. However, in the recent years, the lab method considerably overestimated the VBD of some plant-calcined cokes, which is most probably due to the changing anode grade coke quality [5,6]. It was therefore decided to evaluate alternative methods. An important difference between the Alcan lab "flash" calcination and plant calcination is that in a plant rotary kiln the coke bed is strongly agitated, whereas during the "flash" calcination the coke bed is static. As it was believed that this has significant impact on the VBD, only lab calcination methods with agitated coke beds were considered.

Experimental Details

Coke calcination tests were performed in two labs: COREM (Quebec City, QC, Canada) and BP coke (Huntington Beach, CA, USA). Single source calcination tests of the same cokes were also performed at RTA's Arvida plant calciner (Jonquiere, QC, Canada).

COREM Lab Kiln

The COREM lab kiln is usually used for the induration of iron pellets simulating the grate-kiln process. It is heated with propane,

which is mixed with primary air and, if so desired, with secondary air and oxygen (Fig. 2).

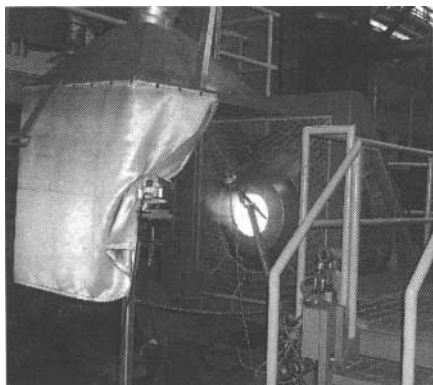


Fig. 2. COREM lab rotary kiln

For the coke calcination tests, the following procedure was used. The kiln was preheated to a temperature of 350-400°C. Once this temperature was reached, 13 kg of green coke were quickly introduced and the kiln was heated with a rate of 50 °C/min up to a final temperature of 1400 °C. Starting at 1100 °C, typically every 50 °C, 500 g coke samples were removed from the kiln with a ladle. Removal of larger amounts would disturb the thermal equilibrium of kiln. Once the final temperature was reached, the kiln was tilted to remove the remaining coke. Throughout the test, the kiln rotation was maintained at 3 RPM.

BP Lab Kilns

The BP lab kilns are exclusively used for studies on anode grade cokes such as:

- Impact of refinery operations on commercially calcined cokes
- Verification if the structure of “opportunity” green cokes produced in the BP refining system is appropriate for the use in anodes
- Under-calcined coke

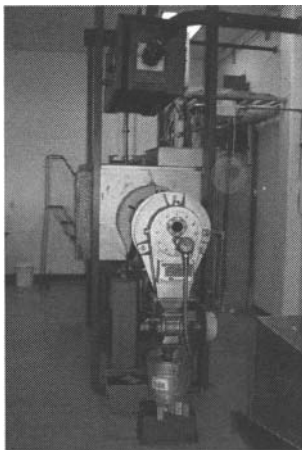


Fig. 3. BP lab rotary kiln used for calcination

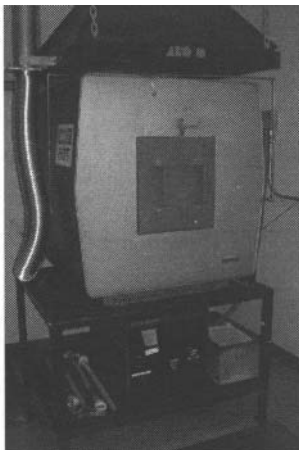


Fig. 4. BP static kiln used for the adjustment of the calcination level

Typically, coke is sequentially treated in two kilns. Calcination is performed in an electrically heated rotary kiln with an inconel shell (length ~ 3 m, external diameter ~ 15 cm, Fig. 3). The kiln is equipped with a coke feeding system and a water-cooled coke outlet system. At the discharge end, the kiln is purged with nitrogen. However, air enters the kiln via leaks. The air inlet is controlled by the draft which is regulated by a valve close to the exhaust.

As the maximum temperature of the rotary kiln is limited to 950 °C, a second static kiln (Fig. 4) is used to increase the calcination level of the coke to the desired level. For the calcination tests, the rotary kiln was heated to 950 °C. Once this temperature was reached, some 4 kg green coke (particles smaller than 1.25 cm and at least 50 % of the particles larger than 0.63 cm) were fed over a period of 45 min to the kiln. The coke residence time in the kiln was also approximately 45 min, which is comparable to the residence time in a plant kiln.

After calcination in the rotary kiln, the samples were re-heated in the static oven at a temperature of 1225 °C for 30 minutes to obtain the desired L_c value.

Arvida Plant Calciner

Cokes calcined in the lab kilns were also calcined at the Arvida plant calciner. This plant is equipped with two kilns. The kiln gases of each kiln pass through a boiler for heat recovery and a bag house before they reach a common stack. During the single source tests, the kilns were run as during normal production. As the calciner moves towards under-calcination [7], the targeted coke calcination level presently corresponds to an L_c value of 24 Å. Routine operation is without external fuel using burning coke volatiles as heat source instead. The calcination level is mainly controlled by the amount of tertiary air admitted [8].

Analytical Methods

The VBD was determined according to the ASTM method D7454 (Alcan VBD), whereas determination of the calcination level L_c is described in ref. [9].

Results and Discussion

COREM Lab Kiln

Properties of Lab-Calcined Cokes and Repeatability. As coke samples are collected over a range of calcination temperatures from the kiln, the dependence of calcined coke properties (such as the VBD and L_c) on the calcination temperature is obtained. The corresponding graphs show the known relationships for a lab setting (Fig. 5). The coke calcination level (L_c) steadily increases with the calcination temperature, whereas the VBD approaches a maximum which is associated with the start of coke desulfurization [10].

The repeatability of the method was tested by calcining the same green coke three times. The corresponding VBDs are presented in Fig. 6. Up to a calcination temperature of 1200 °C, the VBDs were very similar (standard deviation ≤ 0.006 g/cm³). However, for higher calcination temperatures small differences between the VBD values were observed. The standard deviation reached 0.013 g/cm³ after calcination at 1400 °C. Given that such high

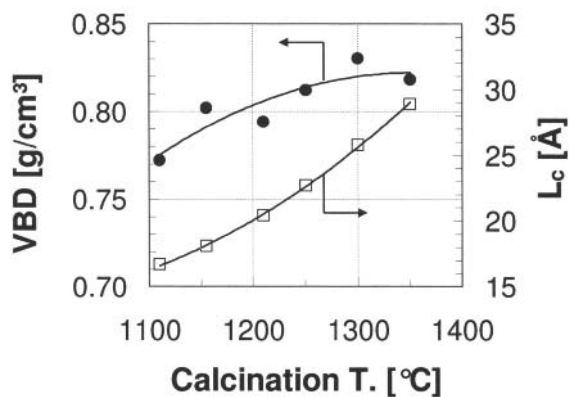


Fig. 5. VBD and L_c values of coke "A" calcined in the COREM kiln as function of the calcination temperature

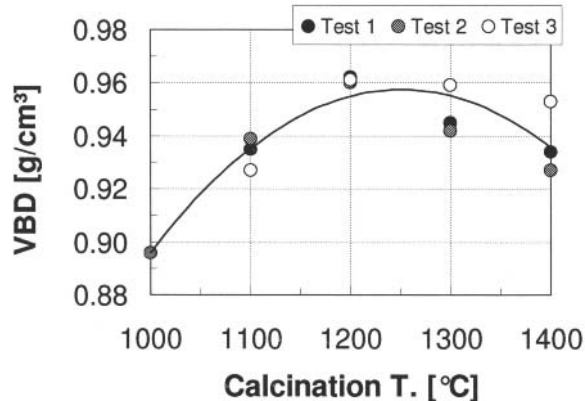


Fig. 6. Repeatability of the COREM method. VBD of cokes obtained from the green coke "B" in three calcination tests

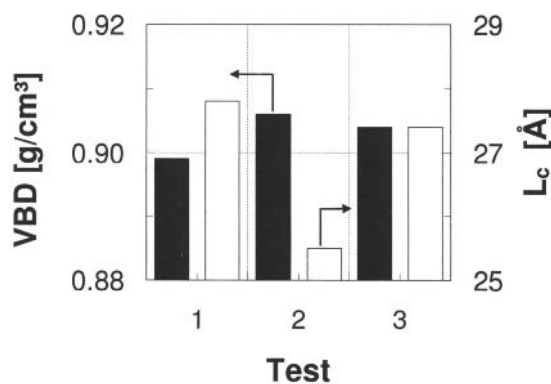


Fig. 7. Repeatability of the COREM method. Properties of cokes obtained from green coke "C" heated to 1325 °C

temperatures are rarely reached during plant calcination, the VBD differences at high lab calcination temperatures were judged acceptable. It is also believed that these differences could be reduced by minimizing the number and the size of the coke samples collected during the calcination, which may have a significant impact on the thermal balance inside the kiln.

In another series of tests, three calcinations were performed up to a temperature of 1325 °C which corresponds to the temperature reached during plant calcination of the coke used. Once this temperature was reached, the kiln was emptied. In spite of the relative high calcination temperature, there were little differences between the VBD and L_c values of the corresponding calcined cokes (Fig. 7). The standard deviations were 0.004 g/cm³ for the VBD and 1.2 Å for the L_c value. However, in this specific case, it has to be mentioned that no coke samples were collected during the tests, which may have contributed to a better thermal stability and hence, more consistent calcined properties.

Properties of Lab vs. Plant-Calcined Cokes. Comparison of the properties of the cokes calcined in the Arvida plant and in the COREM kiln at the same temperature showed good agreement for the VBD of four of the five cokes studied (Fig. 8). For coke Y, however, the plant VBD was considerably overestimated by the lab test. This coke had an extremely fine granulometry and a high volatile content. It is assumed that this changed the flow of the coke particles in the coke bed upon calcination, which is known to impact coke properties [11,12]. Furthermore, it is also well known that cokes with more volatiles have a tendency to release them faster, creating more porosity [10]. Given the very different dimensions of the plant and lab kilns, the lab method was most probably not capable to reproduce the plant heating rate for this "unusual" coke.

Not considering coke Y, the r^2 value of the correlation was 0.96. For high VBDs, however, the lab method slightly overestimates the plant VBD. Nevertheless, the prediction is much better as compared to the method based on green coke properties (Fig. 1, $r^2 = 0.61$)

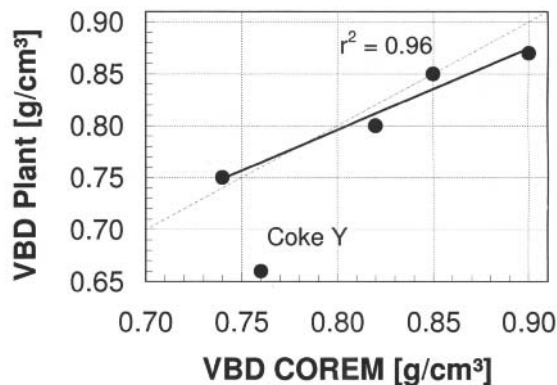


Fig. 8. Correlation between the VBD of cokes calcined in the COREM lab kiln and at the Arvida plant calciner

The agreement between the calcination levels (L_c) of the cokes calcined in the two kilns was, with one exception, good as indicated by a r^2 value of 0.84 (Fig. 9). Furthermore, the L_c value of coke Y calcined in the plant was reasonably well predicted by the lab test. Apparently, for a given calcination temperature, the coke granulometry and volatile content had less impact on the coke calcination level than on the VBD.

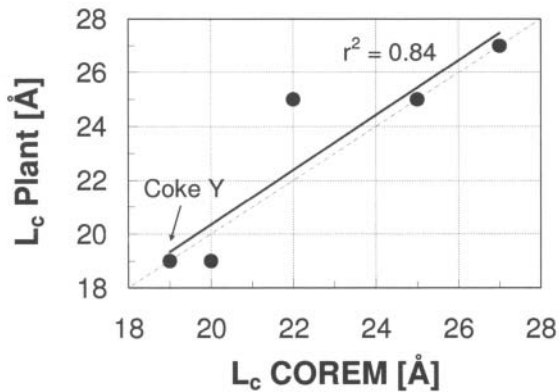


Fig. 9. Correlation between the calcination level (L_c) of cokes calcined in the COREM lab kiln and at the Arvida plant calciner

Prediction of Properties of Plant-Calcined Cokes from Lab Tests.

After it was confirmed that for green cokes (without extremely fine granulometry and high volatiles content) the VBD of cokes calcined in the COREM lab kiln and in the Arvida plant kiln correlates well, a method for the prediction of the plant-calcined coke VBD from lab data was developed.

The present control strategy of the Arvida kiln is based on a target coke calcination level, as opposed to a fixed calcination temperature. Under these conditions, the calcination temperature strongly depends on the green coke volatile content. The higher the volatile content the lower is calcination temperature (Fig. 10). Based on this correlation and the volatiles content of the green coke to be evaluated, the calcination temperature in the plant kiln is estimated. For example, upon calcination of a green coke with 10 % volatiles in the Arvida kiln a calcination temperature of about 1275 °C is expected. The properties of the corresponding calcined coke produced at this temperature are obtained from the lab tests. As shown in Fig. 5, calcination at 1275 °C is expected to yield a coke with a VBD of 0.82 g/cm³ and a L_c value of 24 Å. This method allows therefore prediction of properties of plant-calcined cokes from reasonable small samples (~ 13 kg) of green coke.

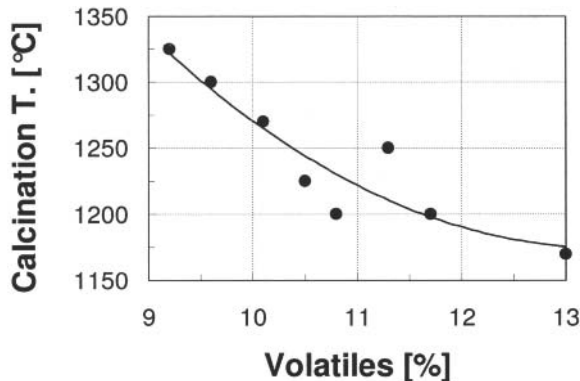


Fig. 10. Temperatures reached in the calcination zone of the Arvida plant calciner upon calcination of green cokes with different volatile contents

It should be mentioned that the correlation between the green coke properties and the calcination temperature is unique for every kiln and even for a given operation philosophy. However, once this relationship is known (as shown in Fig. 10 for the Arvida plant), the lab data (as shown in Fig. 5 for one coke) can be used to predict the properties of a calcined coke produced in a given plant.

Furthermore, usually the plant calciners are fed with coke blends. These blends often contain green cokes with different volatiles levels. Thus, the calcination temperature reached and the properties of the corresponding calcined cokes differ between single source calcinations and calcination of coke blends. The data presented here allow predictions to be made even in these cases. Instead of predicting the plant calcination temperature from the green coke volatiles content of a single source, the volatiles content of the blend is used to estimate the plant calcination temperature (from graphs as shown in Fig. 10) and to estimate the properties of the corresponding calcined cokes (from graphs as shown in Fig. 5).

BP Lab Kiln

Properties of Lab vs. Plant-Calcined Cokes. The VBDs of cokes calcined in the BP lab in the kiln are compared in Fig. 11 with the corresponding plant-calcined cokes. For the samples without subsequent heat-treatment in the static oven, there was good agreement (except for one coke discussed below). However, the lab calcination slightly underestimated the VBD. This was attributed to the fact that the lab calcination temperature (950 °C) was lower than the plant calcination temperature (Fig. 10). As the VBD decreases with decreasing calcination temperature (before significant desulfurization occurs), this lead to lower VBDs for the lab-calcined cokes. This assumption is supported by the observation that upon subsequent heating in the static oven, the VBD of the lab samples increased (Fig. 11).

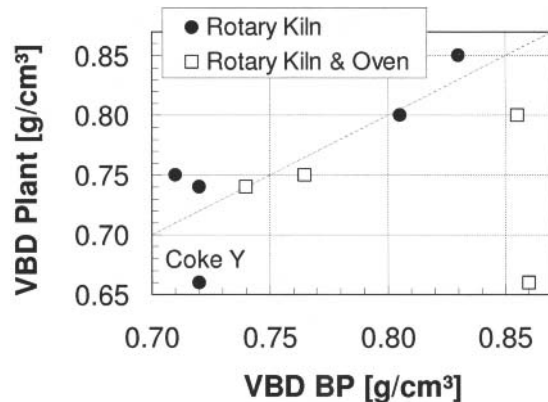


Fig. 11. Correlation between the VBD of cokes calcined in the BP lab kiln (with and without additional heating in the static oven) and at the Arvida plant calciner

After the additional heat-treatment, for some samples the lab results considerably overestimated the plant VBD. This was in spite the fact that the lab heat-treatment temperature (1225 °C) was close to the plant calcination temperatures (Fig. 10). The structural changes in both kilns were apparently different. This is also suggested by the important differences between the

calcination levels (L_c) of cokes from the lab and the plant kiln (Fig. 12).

As for the COREM kiln, the BP lab data considerably overestimated the VBD of plant-calcined coke Y. Apparently the lab methods did not replicate the behavior of this high-fines, high-volatiles coke during plant calcination. However, there were clear indications during the BP lab calcination experiments that coke Y has unusual calcination behavior. A glass window at the coke outlet end of the kiln allows the observation of the burning coke volatile flames. The desired flame has a corkscrew-like shape and follows the kiln wall, occupying only a portion of the kiln cross-section (Fig. 13). With all cokes studied, with the exception of coke Y, such a flame shape could be easily obtained by manipulating the draft. However, upon calcination of coke Y, most of the time a turbulent flame, occupying the entire kiln cross-section of the kiln was observed (Fig. 14). Even by regulating the draft, a flame shape as shown in Fig. 13 could not be obtained. The turbulent flame was most probably due to the fast release of large quantities of volatiles. This usually causes a low VBD as the coke structure is blown-up (popcorn effect). It can be concluded that although the VBDs of lab and plant-calcined coke Y differed, there were clear indications during the lab test that the VBD of plant-calcined coke Y will be low.

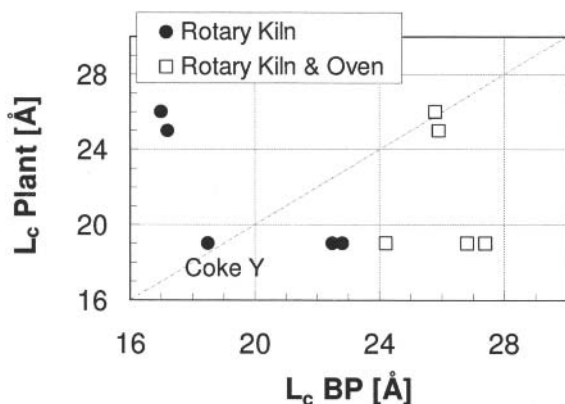


Fig. 12. Correlation between the calcination level (L_c) of cokes calcined in the BP lab kiln (with and without additional heating in the static oven) and at the Arvida plant calciner

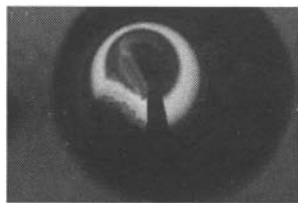


Fig. 13. Desired shape of flame upon calcination in BP lab kiln



Fig. 14. Undesired shape of flame obtained upon calcination of coke Y in BP lab kiln

Formation of Coke Ring. Upon calcination of coke Y, a so-called coke ring was formed in the coke pre-heating zone, close to the feed end of the BP lab kiln (Fig. 15). Such a ring consists of solid carbonaceous material (for example coke fines and condensed

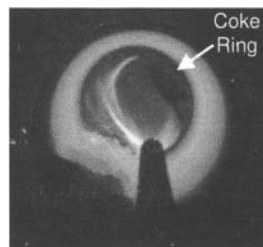


Fig. 15. Coke ring formed upon calcination of coke Y in BP lab rotary kiln

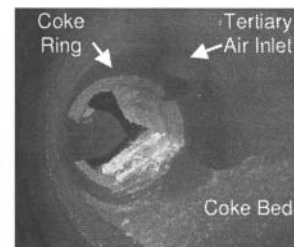


Fig. 16. Coke ring formed in RTA's Kitimat plant calciner

coke volatiles) adhering to the kiln shell. Coke ring formation is also observed in plant kilns, where it has a significant negative commercial impact. The coke ring hinders the downhill flow of the coke bed towards the discharge end. Furthermore, the decreased free kiln cross section increases the velocity of the kiln gases, which increases entrainment of coke fines. Once the coke ring reaches a certain size, coke spills at the feed end of the kiln occur and the coke recovery rate decreases. The coke ring has therefore to be mechanically removed, which requires temporary shut-down of the calciner.

It is known that the tendency for coke ring formation increases with the amount of coke volatiles and also depends on the nature of the volatiles [13]. Furthermore, it is especially observed in short kilns where the release of coke volatiles is concentrated in a relative small zone of the kiln. RTA adopted some operational changes which limit coke ring formation. However, until now, coke ring formation cannot totally be avoided at the Kitimat calciner (Fig. 16), which has the shortest kiln in the RTA system. More knowledge on coke ring formation is therefore required.

The BP lab kiln allows easy removal of coke ring samples. Characterization of these samples (Fig. 17) allows to gain more insight on early stages of coke ring formation. This is very difficult with samples removed from the plant kiln as they have been exposed for long times to very high temperatures and therefore underwent important structural changes (Fig. 18). Furthermore, the impact of kiln surface (such as its morphology and temperature) on coke ring formation can be studied.

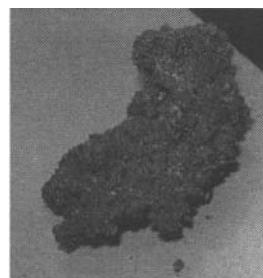


Fig. 17. Coke ring sample removed from the BP lab kiln

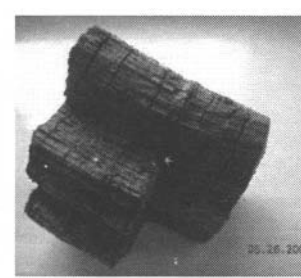


Fig. 18. Coke ring sample removed from the RTA Kitimat plant kiln

Conclusions

Based on green coke properties alone, reliable prediction of the VBD of plant-calcined coke is not possible. Due to the required

logistics single source plant calcination tests cannot be used on a routine basis for the prospection of potential new coke sources. Prior lab calcining methods due to their static nature also had limited success in predicting industrial calcination results. On the other hand, the lab calcination methods that have been described in this paper, have been determined to provide good prediction of large scale rotary kiln calcined coke properties with reasonable effort.

Lab calcination also allows the replication of phenomena such as coke ring formation that represent important problems on commercial scale. This makes it possible to test and develop strategies to improve the calcination process.

Such lab calcination methods will therefore be used in the future to support the RTA and BP calcining operations. This includes the prospection of potential new coke sources as well as the optimization of calcination of coke blends.

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