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VIBRATED BULK DENSITY (VBD) OF CALCINED PETROLEUM COKE AND IMPLICATIONS OF CHANGES IN THE ASTM METHOD D4292

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Abstract

Vibrated bulk density (VBD) is a quantitative measurement used in the aluminum industry to evaluate the density of calcined petroleum coke. In the calcining industry, the reproducibility of the current ASTM International (ASTM) method D4292 generates a wide range of VBD data. Therefore, Oxbow Calcining investigated the VBD procedure – D4292. Issues with D4292 include the use of the appropriate crushing equipment, crushing of the gross sample, sieving of the prepared sample, determination of the sample volume using appropriate graduated cylinder vibration time and apparatus setup. This investigation led to a revision in the ASTM D4292 method.

Introduction

Oxbow Calcining produces calcined petroleum coke (CPC) which is used to make anodes in aluminum smelters. Raw material from petroleum coker units is devolatilized and densified in kilns to meet customer specifications [1] such as sulfur content, trace metals, air reactivity and density. The smelter blends the CPC with pitch to form the carbon anode [2]. VBD is the most commonly-used procedure to determine bulk density and provides the smelter with the best overall estimate of coke suitability for anode manufacture. With lower bulk density, coke porosity increases, effective pitch level increases and the overall electrical resistance of the electrode increases [3].

As originally written, ASTM D4292-83 VBD test method [4] contained several ambiguities in the procedure leading to a repeatability and reproducibility of 0.014 and 0.046 g/cm^3, respectively. The ASTM research report [5], which discusses the method development, gives a few details about the original round robin used to develop the precision and bias statements for D4292. This original round robin consisted of 6 labs with 8 test samples. Samples were sized 20x48 mesh. Results on the 8 test samples were between 0.76 and 0.92 g/cm^3. There was no documentation in the research report that gives the actual method in use during the round robin. The round robin calculations were dated January 11, 1982. The original D4292 method has approval and publication dates of October 28, 1983 and January 1984, respectively. The time difference of 21 months between the round robin calculations and the ASTM approval of D4292 causes concern regarding to the actual procedure in use during the original D4292 round robin.

The reapproved method [6] made several revisions to improve testing results. Those included:

- Deleted section 1.3 of procedure not specifying how the 2-kg sample is obtained and the method of subsequent breaking up of particles with diameters greater than 20 mm, and riffling.
- Added reference to D2013 Method for Preparing Coal Samples for Analysis.
- Added note that VBD is based on packing of sized particles and the method of sample preparation can affect results.
- Added section on air drying lab sample
- Corrected note 3 (1983 version) about reduction of vibration time from 5 minutes to 1 minute only lower results 0.022 g/cm^3. The 1983 version states 0.002 g/cm^3. The opinion of the authors is this 0.002 g/cm^3 value is a typographical error since the repeatability of D4292 is 0.014 g/cm^3.
- Added note 6 – precision for VBD on other sample size ranges has not been determined.

In 2009, Oxbow Calcining investigated several sources of potential variability in the test method in an attempt to improve the method. The analytical testing to improve the method focused on sample preparation and on sample introduction to the test equipment.

The testing evaluated:

- Separation of the natural fraction and crushing the oversized vs. crushing the entire sample
- Roll crusher gap sizes
- Use of a Plate Mill instead of a Roll Crusher
- Rate of Sample Introduction into the VBD Apparatus
- Effect of vibration during filling of the cylinder

Sample Preparation

Separation of the Natural Fraction

One proposed idea for improvement in the results is to separate the natural fraction prior to jaw crushing (Figure 1). The premise was that the crushing may introduce variation in the pore distribution. By separating the natural fraction and crushing just the oversized fraction, this variation is minimized in the tested sample. An inter-laboratory study was conducted to evaluate this theory using seven different cokes.

Comparing the results of Table I to Table II reveals the difference in VBD reproducibility between crushing the entire sample vs. crushing just the oversized fraction. Only one sample of entirely crushed material (Sample B) produced a significantly higher reproducibility between the laboratories. The remaining six samples produced similar or lower reproducibility than the crushing-just-the-oversized-fraction results. This suggests that crushing the entire sample would improve reproducibility of the sample when compared to separating the natural fraction and crushing the oversized particles. For this reason, section 8.2 of the new procedure now requires that the entire sample is passed through the jaw crusher.

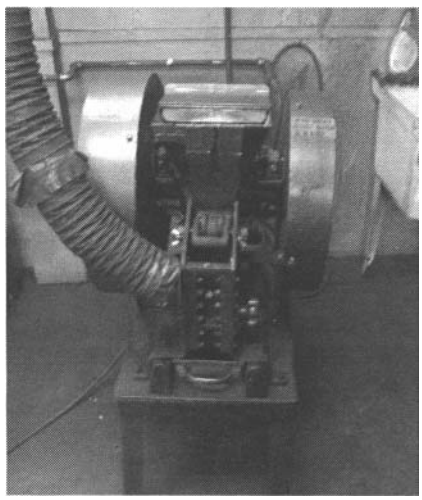

Figure 1. Chipmunk Jaw Crusher used at Port Arthur

Table I.
D4292 Crushing All Material with Jaw Crusher (g/cm^3)

Material	Lab 1	Lab 2	Lab 3	Lab 4	Reproducibility
Sample A	0.857	0.874	0.837	0.864	0.037
Sample B	0.881	0.901	0.870	0.887	0.031
Sample C	0.850	0.834	0.827	0.849	0.023
Sample D	0.865	0.855	0.857	0.867	0.010
Sample E	0.794	0.811	0.802	0.834	0.017
Sample F	0.850	0.851	0.839	0.857	0.018
Sample G	0.857	n/a	0.848	0.860	0.012

Table II.
D4292 Crushing Only +4 Mesh with Jaw Crusher (g/cm^3)

Material	Lab 1	Lab 2	Lab 3	Lab 4	Reproducibility
Sample A	0.850	0.832	0.837	0.871	0.034
Sample B	0.873	0.879	0.866	0.889	0.023
Sample C	0.850	0.835	0.828	0.848	0.022
Sample D	0.865	0.862	0.855	0.865	0.010
Sample E	0.814	0.799	0.800	0.839	0.040
Sample F	0.857	0.838	0.837	0.856	0.020
Sample G	0.842	n/a	0.842	0.869	0.027

Roll Crusher Gap Distance

The next series of tests evaluated the effect of gap distance between the rollers of a roll crusher (Figure 2) on the D4292-92 results.

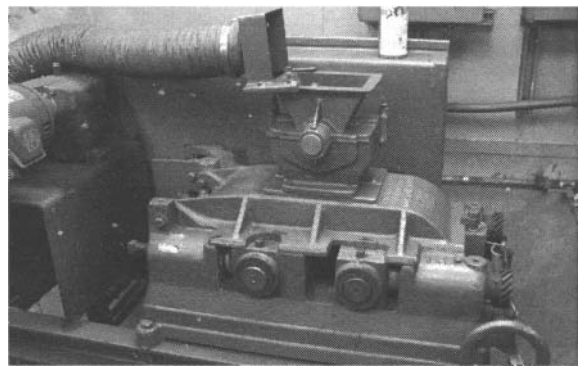

Figure 2. Roll Crusher

Table III.
Evaluation of a Roll Crusher in VBD Sample Preparation

Runs 1 and 2 are 300 grams each; Spring adjusted prior to test				
		Roller Opening		
		mm	mm	mm
	1 pass	2.5	1.5	
	1 pass	1.0	1.0	1.0
	4 passes	0.3	0.3	0.3
Run 1	% on + 28	n/a	7.4%	6.0%
	% 28x48	59.0%	55.3%	57.3%
Run 2	% on + 28	n/a	4.5%	2.3%
	% 28x48	58.3%	56.6%	59.7%
Run 1-A	VBD, g/cm^3	0.840	0.833	0.844
Run 1-B	VBD, g/cm^3	0.833	0.826	0.830
Run 2-A	VBD, g/cm^3	0.833	0.837	0.840
Run 2-B	VBD, g/cm^3	0.833	0.833	0.830
	Average VBD	0.835	0.832	0.836

Three tests were performed in duplicate. The first test used a 2.5 mm gap for the first pass followed by a run through a 1.0 mm gap between the rollers. The run ended with four passes through a 0.3 mm gap. The second test used a 1.5 mm gap for the first pass followed by a run through a 1.0 mm gap between the rollers. The test ended with four passes through a 0.3 mm gap. The third test

made one pass through a 1.0 mm gap between the rollers followed by four passes through a 0.3 mm gap.

Table III presents the results of varying the roll crusher opening. Three different parameters were tested. The 2.5 mm gap test yielded no oversized material. However, no real difference was seen between the average results of each test and thus the D4292 was not modified.

Evaluation of Plate Mill/Pulverizer

One concern with a roll crusher is that the rollers compress the sample, which may alter the pore shape and volume. Therefore, a plate mill/pulverizer was evaluated. A plate mill/pulverizer consists of serrated parallel plates with one stationary plate and one moving plate (Figure 3).

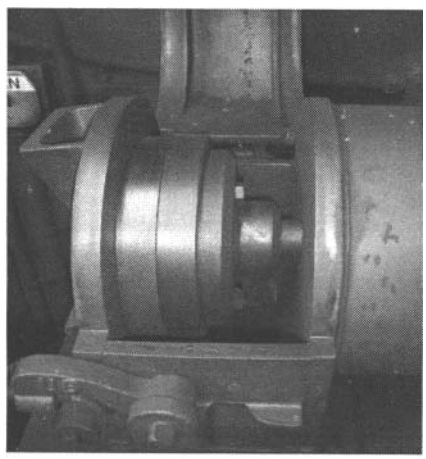

Figure 3. Plate mill/pulverizer

Table IV presents the results of experiments that were conducted to compare the difference in the VBD values of samples crushed by a plate mill/pulverizer and a roll crusher (two rotating cylinders). Four different grades of calcined petroleum coke were used. For each grade, a 28x48 Tyler mesh sample was prepared using both types of crushers and a two step grinding process. For all four grades, the samples prepared using the plate mill had higher VBD results than the samples prepared with a roll crusher. The average difference between the methods was 0.052 g/cm^3. For example, a sample prepared with the roll crusher would have a 0.854 g/cm^3 VBD versus 0.906 g/cm^3 VBD when prepared with a plate mill.

A second test, comparing different plate mill gap sizes, was performed on Material 1. One sample was crushed using a 1.5 mm initial gap followed by a 0.5 mm gap. An initial 2.0 mm gap size followed by a 0.8 mm gap was used on the second sample. The ratio of oversize (+28 Tyler) to undersize (-48 Tyler) was 0.59 for the 1.5/0.5 mm gapped sample and 2.63 for the 2.0 mm/0.8 mm gapped sample. The VBD result of the 1.5 mm/0.5 mm gap sample was on average 0.033 g/cm^3 higher than that of the 2.0 mm/0.8 mm gapped sample.

Ratios of oversize to undersize were calculated for all the samples. Section 8.3.7 of D4292-92 states that the crushing level is satisfactory when the ratio of the coarser to finer particles is between 0.8 and 2.0 with a sample yield of at least 30%. Gaps were set the same, but the ratio varied based on the grade of coke. The values ranged from 1.65 to 2.52. Compared to the roll crusher, the plate mill/pulverizer produced lower test material yield.

Based on the lower yield and much higher VBD results, the change to plate mill/pulverizer was not recommended. However, these results, as well as the gap size results, led to a change in section 6.2 in the new VBD procedure to provide clear specifications on the grinding. The new procedure specifies that only a roll crusher must be used for crushing.

Table IV.
Comparison of Plate Mill to Roll Crusher

Material	1			2		3		4	
Unit	Roll Crusher	Plate Mill		Roll Crusher	Plate Mill	Roll Crusher	Plate Mill	Roll Crusher	Plate Mill
Initial/final gap size, mm	1.5/0.5	1.5/0.5	2.0/0.8	1.5/0.5	2.0/0.8	1.5/0.5	2.0/0.8	1.5/0.5	2.0/0.8
Sieve Content, g									
+28 Mesh	269.1	64.7	551.3	200.3	510.1	166.8	482.0	176.4	539.0
28 x48 Mesh	155.9	101.4	176.6	164.0	177.2	147.6	125.0	171.3	149.2
-48 Mesh	106.7	109.9	210.0	96.6	189.2	92.6	269.6	107.2	257.2
Ratio +28/-48	2.5	0.6	2.6	2.1	2.7	1.8	1.8	1.6	2.1
Sample Yield (28x48), wt.%	29	37	19	36	20	36	14	38	16
VBD, g/cm^3	0.817	0.889	0.857	0.824	0.869	0.850	0.928	0.861	0.932

Sample Addition

The D4292 VBD apparatus is shown in Figure 4. Filling the graduated cylinder at a different rate can affect the particle distribution in the graduated cylinder, yielding a different VBD result. Tests were performed to determine the best fill rate.

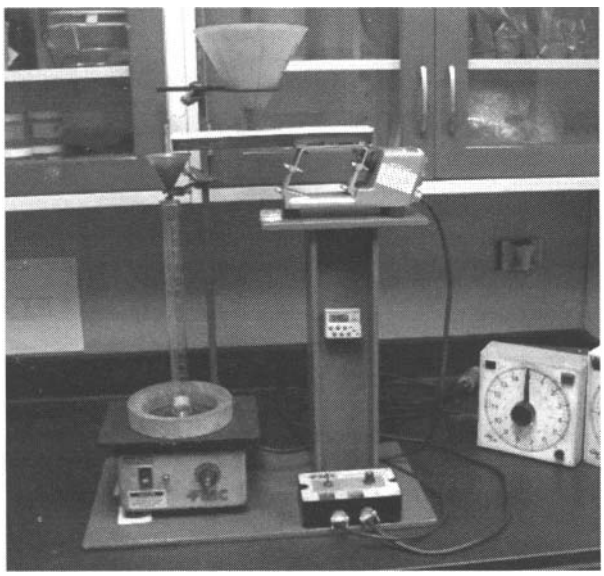

Figure 4. D4292 VBD Apparatus

An experiment was run comparing two different cylinder filling methods. For one method, a graduated cylinder was filled while the cylinder vibrated. Material flowed from a vibratory feeder into the funnel on top of the vibrating cylinder. The amount of time it took for 100 g of material to fill the cylinder was greater than 90 seconds. After the sample was in the cylinder, the vibration was stopped and the material height was recorded. For the second method, 100 g of material was added through a funnel into a stationary cylinder. Once all the material was in the cylinder, the cylinder was vibrated for 5 minutes; then the height was recorded. Samples from two different grades of coke were run 5 times with each method. The method of vibrating the cylinder during filling gave an average 0.04 g/cm^3 higher than the other method. Section 11.3 in the new ASTM procedure now specifies that the cylinder should not be vibrated during filling since this action will change the results.

Several different grades of coke were tested at various feed rates of filling the graduated cylinder. Data, presented in Table V, shows that the speed at which the material is added to the graduated cylinder can affect the final VBD results. As the time increases, the effect of the filling time decreases to a point where the VBD value is not affected. For this experiment, that point occurred around 90 seconds. Because of these results, Section 11.1 in the new procedure clarifies that the sample must be poured slowly and consistently into the graduated cylinder at a rate of 10 – 14 grams per 10 seconds. Since this is hard to accomplish by hand, using a vibratory feeder for sample introduction into the graduated cylinder is recommended.

Table V.
Average VBD (g/cm^3) vs. Cylinder Filling Time

	Filling Time, sec			
SAMPLE I.D.	30	60	90	120
1	0.798	0.815	0.833	0.833
2	0.843	0.872	0.882	0.893
3	0.862	0.872	0.882	0.882
4	0.824	0.862	0.872	0.862
5	0.824	0.852	0.862	0.872

Additional Changes

Since it was found that vibrations can affect the VBD results, Section 9.2 in the new procedure specifies that the graduated cylinder should not be attached to the vibrating table, but should be free-standing on the table.

The D4292 methods approved in 1983 [4] and 1992 [6] have a note which states that vibrating the graduated cylinder for only one minute instead of the required five minutes results in only 0.022 g/cm^3 difference and states that for routine use, the shorter time may be preferred. The implications of this time difference directly impacts the results. For greater consistency, the vibration time should not vary. Therefore, the note was removed in the most recent procedure.

Due to the highly dependent nature of VBD on sample preparation, several other changes were made to the VBD procedure to improve consistency between various facilities. Section 8.1 clarifies that dedust oil should not be removed from the sample, since the process of removing dedust can change the sample. Section 8.3.6 specifies that no sieving of samples should occur between crushing steps (with a roll crusher), and personnel must use a Ro-Tap sieve shaker for 15 minutes. Both of these steps are designed to reduce variability between facilities.

Conclusions

VBD values are dependent on the type of crusher used and the gap settings used. Different cokes will behave differently at the same gap setting. VBD results have been shown to be dependent on sample preparation as well as filling and vibrating techniques. In order to ensure that the test method is consistent, clearer instructions were required for the ASTM D4292 method. Changes mentioned in this paper were included to reduce variability in VBD testing. Special care should be taken when performing this method to adhere to the steps as closely as possible.

ASTM has incorporated these changes in the latest test revision, D4292-10 [7]:

a. Section 6.2: Roll crusher specifications, requirement that both rolls must rotate, requirement to check spring tension per manufacturer specifications.
b. Section 8.1: Comment added to not remove dedust oil from the sample.

c. Section 8.2: Requirement for entire sample to pass through a jaw crusher
d. Section 8.3.6: No sieving of sample between crushing steps (roll crusher). Also, the Ro-Tap sieve shaker must run for 15 minutes.
e. Section 9.2: Do not attach the graduated cylinder to the vibrating table. Allow graduated cylinder to vibrate freely.
f. Section 11.1: Pour sample slowly and consistently into graduated cylinder at rate of 10 – 14 grams per 10 seconds. Suggested using vibratory feeder for sample introduction into graduated cylinder.
g. Section 11.3: Do not vibrate graduated cylinder while adding coke fraction
h. Note 5: Deleted note 5 that suggested a lab could vibrate the graduated cylinder for only one minute instead of the required five minutes since the difference in results is only 0.022 g/cm^3.

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