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BULK DENSITY - OVERVIEW OF ASTM AND ISO METHODS WITH EXAMPLES OF BETWEEN LABORATORY COMPARISONS

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Abstract

The bulk density of petroleum coke is an important property when evaluating a coke for use in anodes in primary aluminum metal electrolysis. It is also an important property in petroleum coke trade. There are international standards for testing coke bulk density; ASTM has two vibrated bulk density (VBD) methods, D4292 and D7454, and ISO has a tapped bulk density (TBD) method, ISO 10236. There is a concern in anode production that it is difficult to obtain sufficiently good between-laboratory comparisons with any of these methods, both for use in comparisons, and when used for distinguishing coke qualities from different producers. The paper will present the methods, give results from several interlaboratory studies and discuss the between-laboratory comparison results.

Introduction

This paper is part of the 2011 TMS special session on petroleum coke bulk density. It is meant to give an overview of methods and some quantification of the precision of the methods as regards comparison between laboratories.

Due to variation in practice, both Tyler mesh and metric indication of sieve ranges are included.[1]

Bulk Density

A good discussion of the relationship between bulk density and anode quality is found in [1], starting on page 93.

Coke bulk density expresses a combination of grain size, grain packing and porosity. It is an indication of the potential a coke has to contribute to good anode density and is much in use as a petroleum coke specification by coke calciners and anode manufacturers.

The principle of measurement is an ordered, systematic filling of a volumetric cylinder with a test portion of a coke sample with a defined grain size range. For a specified time, vibration or tapping is applied to achieve packing. The mass to volume ratio is determined and the bulk density is reported in g/cm³.

It has been recognized for some time that the between-laboratory reproducibility, which determines the quality of comparisons between the coke producer and anode manufacturer, is less good than what is needed for monitoring coke quality at laboratories. The precision for within-laboratory comparison is acceptable, and makes it possible for the producer to monitor own production and fulfill specifications. But the poor between-laboratory comparisons are troublesome, especially as more and different cokes have to be considered and evaluated as anode raw materials. It is difficult for the anode manufacturer to

- Monitor the producers' coke
- Compare and evaluate different producers' cokes

Grain Fraction Size and Bulk Density Value

The reported VBD or TBD value is dependent on the selected grain fraction. By measuring over a wide range of sieves the variation with grain size can be shown. Taking VBD as an example, a 2008 Hydro test with 13 sieves and a bottom fraction of -0.180 mm is shown in two charts in Figure 1. Different anode raw materials were analyzed including three sponge cokes/blends, a soft sponge coke and a good quality butts.

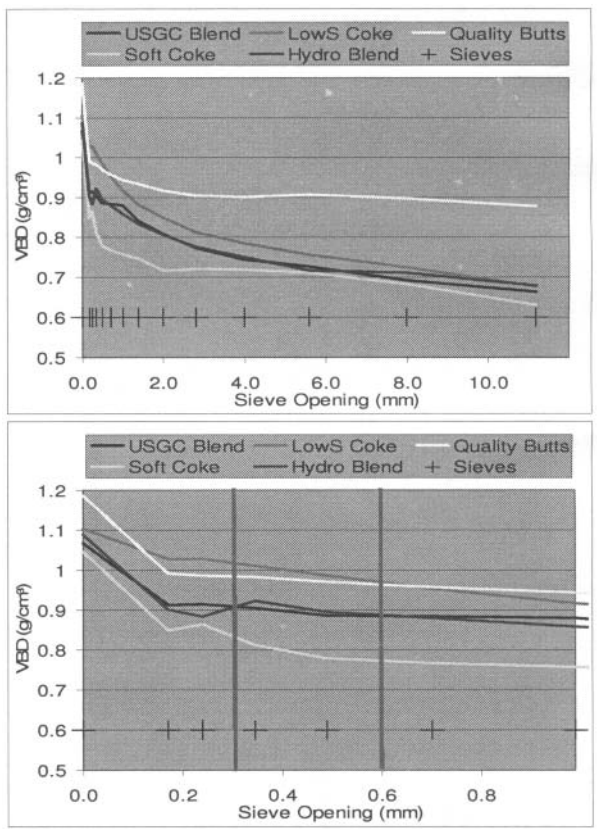

Figure 1: VBD for sieve fractions down to 0.180 mm. Both charts are linear, with details -1.0 mm in the lower chart. Vertical lines are the Tyler mesh 28x48 range (0.3-0.6 mm).

[1] Tyler mesh 28x48 is 0.30 to 0.60 mm particle size.

- The VBD increases as porosity is crushed out of grains.
- For the three regular sponge cokes/blends, the difference in level was stable across fractions so several grain fractions could equally be used for monitoring or comparisons.
- The soft coke differed from the sponge blends, and got low reported VBD especially if measured on medium fine grains.
- For the high quality butts, VBD was high and less dependent on the grain size across fractions than the cokes.
- In the detailed plot the size range 0.71 to 0.25 mm might look near horizontal, but the average VBD difference from the 0.710-1.0 mm fraction to the 0.250-0.355 mm fraction for the three cokes is as high as 0.036 g/cm³.

Different reported values when describing the same property

An example of how confusing the situation can be when comparing different laboratories' reported VBD was taken from a CII Carbon round robin, RR #17, run in 2004. It is a very large RR with 45 participants, 18 of which reported VBD.

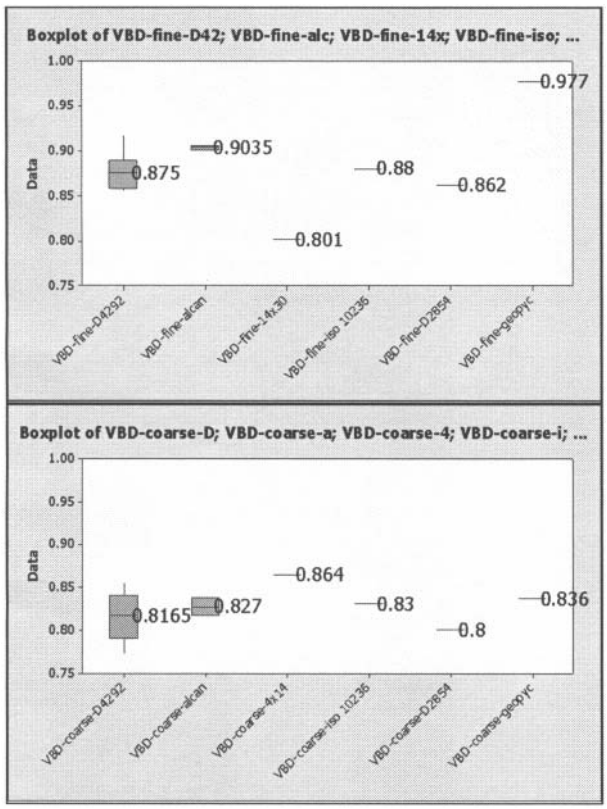

Figure 2: VBD (g/cm³) classed by method or grain size range. The upper chart is results for finer grains, lower for coarser grains. The value is the average. [2]

A calcined coke RR sample was distributed prepared to -4 Tyler mesh.[3] For VBD, each lab was to return results for analysis by ASTM D4292 for the two common grain ranges

- The finer ASTM VBD Tyler mesh 28x48 (0.30-0.59 mm)
- The coarser Kaiser VBD Tyler mesh 8x14 (1.17-2.36 mm)

A majority of 12 laboratories reported as requested, while six reported results with alternative grain ranges or analysis methods. Assuming this represents the standard practice of these laboratories, Figure 2 well illustrates the current situation with spread in practices and analyzed grain size ranges yielding a scatter of results for the same property.

Factors that cause variation in the bulk density results

The bulk density testing has historic roots and traditions, with companies having long-standing and different standard practices. This has led to a several coke grain fractions being in use; especially ASTM D4292, but to some degree also ISO 10236, were written to allow variation in grain size analyzed. This has over time been a disadvantage to comparison of cokes.

Other factors causing variation:

- Bulk density is a complex material property, with contribution from grain porosity, shape and packing.
- The sample preparation can be quite complex.
- The requirements of sample preparation are not adhered to.
- The spread in petroleum coke properties is widening; the wider range of sponge cokes, shot cokes and other anode raw materials is a challenge to traditional bulk density methods.
- Method development has been slow; anode quality has developed significantly to adjust to increased cell amperage and current density requirements, and the need for accurate analysis methods is now felt more keenly.

Precision

ASTM and ISO method precision is expressed by the within-laboratory repeatability limit, r, and the between laboratory reproducibility limit, R. Together they are called the r&R statement, and are obtained through an interlaboratory study (ILS) or a round robin (RR) where several laboratories participate and analyze materials that are as identical as possible. It should be noted that the precision values obtained tend to be best case as the voluntary participation attracts a good class of laboratories.

Vibrated Bulk Density, ASTM D4292[4]

ASTM D4292-92 (2007) – Standard Test Method for Determination of Vibrated Bulk Density of Calcined Petroleum Coke

Development of ASTM D4292, VBD

ASTM D4292 is the most widely used method for determining petroleum coke bulk density. It has gone through two revisions: original publication in 1983, and revisions in 1992 and 2010. The original round robin data for ASTM D4292-83 used a 20x48 Tyler mesh fraction (0.30-0.85 mm). The 1992 revision made a couple of minor changes, which include the addition of air drying the lab sample (section 8.1.1) and adding note 6 (precision of other sample size ranges not determined). The recent 2010 revision is an attempt to better specify equipment and procedures to reduce the variation in results between laboratories. In the industry, several particle size fractions are in use and it is critical to identify the appropriate particle size with the corresponding results.

[2] ASTM D2854 is "Standard Test Method for Apparent Density of Activated Carbon".

[3] -4 Tyler mesh is -4.75 mm.

[4] ASTM D4292 is under the jurisdiction of ASTM Committee D02 on "Petroleum Products and Lubricants" and is the direct responsibility of Subcommittee D02.05 on "Properties of Fuels, Petroleum Coke and Carbon Material".

The 2010 revision precision statement is still under development in an ongoing ILS and all examples of comparisons presented in this paper have used the 1992 revision (reapproved 2007).

Overview procedure pre-2010 D4292 VBD

- Grains within 3-65 Tyler mesh (0.21 to 6.68 mm)
- A sieved, crushed test portion from jaw- and roll-crusher retained between screens differing less than $2\sqrt{2}$
- Test portion 100.0±0.1 g
- Transfer time 70 to 100 sec prior to vibration
- Graduated cylinder foot loose inside retaining ring
- Vibration for 5 min at amplitude 0.20-0.22 mm
- The coke height measured at eight positions around cylinder to 0.5 mm, then averaged
- VBD is the average weight/volume ratio from two determinations, reported to 0.001 g/cm³

Users of the old D4292 had freedom of choice of grain range. The most common grain size ranges reported are

- The finer ASTM VBD Tyler mesh 28x48 (0.30-0.59 mm)
- The coarser Kaiser VBD Tyler mesh 8x14 (1.17-2.36 mm).

Precision D4292-92 VBD

The precision statement is based on determinations on the Tyler mesh 20x48 fraction (0.30-0.85 mm, USA mesh 20x50). Precision at 95% confidence level is

$$r = 0.014 \text{ g/cm}^3$$
$$R = 0.046 \text{ g/cm}^3$$

Comparison between laboratories, using the R limit: Given a determination on two test portions of the same material at two different laboratories, the difference in equivalent temperature should be within 0.046 g/cm³ for 95 out of 100 such comparisons.

The old between-lab precision of 0.046 g/cm³ is poor compared to commercial requirements. It is also not good when considering coke qualities from different producers, if these have been analyzed at different laboratories.

Precision 2010 D4292 VBD

The precision of the D4292-10 revision will be determined through an ILS to be run concurrent with the ILS for the D7454 method and a test of the Micromeritics' GeoPyc.

Vibrated Bulk Density, ASTM D7454[5]

ASTM D7454-08 – Standard Test Method for Determination of Vibrated Bulk Density of the 1.17 - 4.7 mm Calcined Petroleum Coke Fraction Crushed to 0.42-0.83 mm, using a Semi-Automated Apparatus

Overview procedure D7454 VBD

- Grains non-crushed (natural) within 1.17 to 4.7 mm (4x14 Tyler mesh) are crushed in multiple passes by a roll-crusher to within 0.425 to 0.85 mm (20x35 Tyler mesh)
- Volume based, test portion is 50 ml
- Feeding rate target is 150±15 s for the test portion
- Feeding is cut by an automated optical method when the cylinder is filled to 50 ml
- Test portion is weighed to nearest 0.01 g
- The VBD is the average weight to volume ratio from minimum three determinations, reported to 0.001 g/cm³

Figure 3: STAS' semi-automated VBD apparatus. Photo courtesy of Rain CII Carbon, LLC.

Precision ASTM D7454 VBD

A repeatability standard deviation was given of 0.0036 g/cm³; this is single laboratory determination of a single coke eight times and does not fulfill the ASTM requirements. The ASTM Committee has accepted this method provisionally without the precision statement and an interlaboratory study is being run concurrent with the ILS for the new D4292-10 revision and a test of the Micromeritics' GeoPyc.

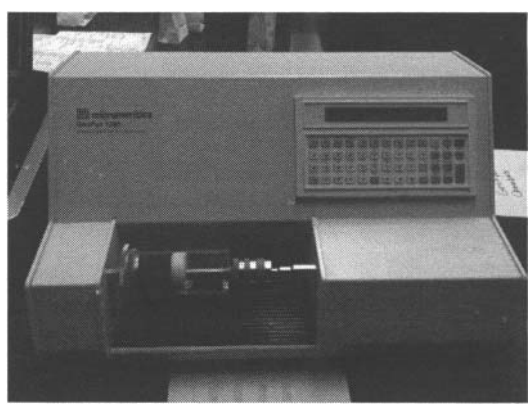

Figure 4: GeoPyc apparatus (Micromeritics model 1360). Photo courtesy of Rain CII Carbon, LLC.

[5] ASTM D7454 is under the jurisdiction of ASTM Committee D02 on "Petroleum Products and Lubricants" and is the direct responsibility of Subcommittee D02.05 on "Properties of Fuels, Petroleum Coke and Carbon Material".

GeoPyc

The GeoPyc measures bulk volume using a controlled vibration and rotation movement to agitate the test portion.

Precision GeoPyc VBD

A precision study for the GeoPyc is being run concurrent with the ILS for D4292-10 and D7454-08. It is uncertain if sufficient participants with GeoPyc will take part to qualify a precision statement.

Tapped Bulk Density, ISO 10236 Method[6]

ISO 10236 (1995) — Carbonaceous materials used in the production of aluminium — Green coke and calcined coke for electrodes — Determination of bulk density (tapped)

Overview procedure ISO 10236 TBD

- A sieved, non-crushed (natural) fraction, 4.0-8.0 mm, 2.0-4.0 mm, 1.0-2.0 mm, 0.5-1.0 mm or 0.25-0.5 mm
- With 1.0-2.0 mm most in use for instance by Esso, BP Veba, BP Lingen, ØMV, Statoil, Copetro Oxbow.
- Test portion 100±5 g weighed to 0.1 g
- Transfer time 45 ± 15 sec, tapping runs during feeding
- Gravity driven taps using a cam shaft with a step
- 1500 taps, each drop 3±0.1 mm
- The coke surface is flattened, and the volume recorded to 1 ml
- The TBD is the average weight to volume ratio from two determinations, reported to 0.01 g/cm³

The equipment description gives details of dimensions, requiring a 250 ml measuring cylinder of 190±15 g with ±1 ml gradation, a plunger with mass 450±5 g, a tapping device frequency of 250±15 Hz and the 3±0.1 mm gravity drop for the taps.

Precision ISO 10236 TBD

The test procedure requires two parallel determinations. The r&R statement gives acceptance criteria. The precision statement is based on determinations on the 1-2 mm fraction. Precision at 95% confidence level was determined according to ISO 5725.

$$r = 0.01 \text{ g/cm}^3$$
$$R = 0.02 \text{ g/cm}^3$$

Issues with TBD

Overall the TBD method seems simpler than the VBD method, especially the direct screening. But it has some issues.

- The r&R values are quite strict limits. R&D Carbon Ltd. was involved with the development of this ISO method and has commented that a critical step in the analysis is sample filling time. The given r&R limits were obtained with strict adherence to the standard requirement of a filling time of 45±15 seconds, as close to 45 seconds as possible. [2]
- Filling issues are coke bridging in hopper, delaying transfer, also TBD increases slightly with filling time.
- Regarding read-out, the adjustment of the coke level with the spatula to an even level before read-out is operator dependent and can shift the result. For a 100 g test portion with TBD 0.83 g/cm³ a 1 ml decrease in read-out volume will increase the TBD 0.007 g/cm.

[6] The TBD method ISO 10236 is the responsibility of ISO Technical Committee 226, "Materials for the production of primary aluminium".

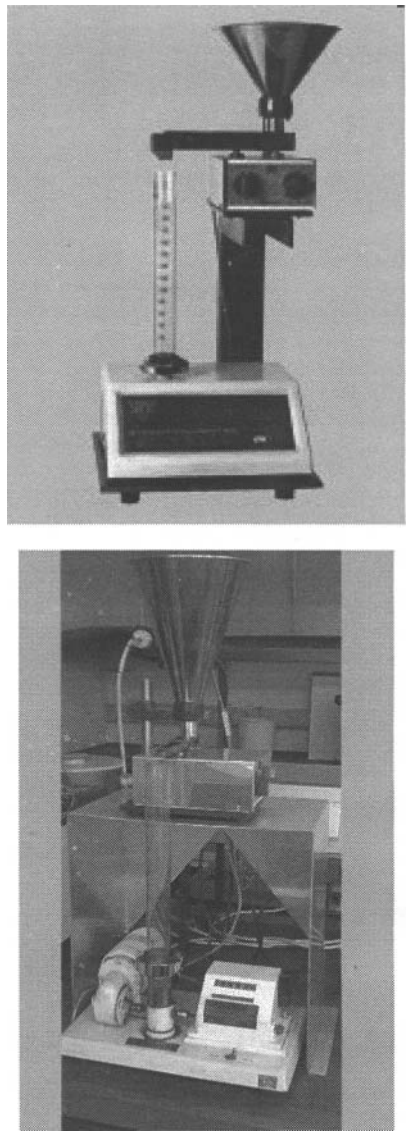

Figure 5: Example of TBD apparatus.

VBD –Comparative Studies

In these comparisons, the reported values have been input to ASTM E691 to determine the between-lab reproducibility at 95% confidence.

VBD, Comparative Study 1999

Keith Neyrey presented results from four CII Carbon RRs at the 1999 ASTM D02.05D committee meeting.[3] There was one material in each RR, see Table 1. Eight to sixteen laboratories reported results. The observed R values were above the R reproducibility limit of 0.046 g/cm³.

Table 1: VBD (g/cm³) average and between-lab R at 95 % confidence level from four CII Carbon RRs. [7]

RR	Average	R
R#09	0.89	0.11
R#11	0.84	0.07
R#12	0.85	0.09
R#13	0.86	0.06

VBD, 2008 R&D Carbon Interlaboratory Study

R&D Carbon ran a large interlaboratory study in 2008.[4] For VBD, two materials were distributed, a denser coke A and a more porous coke C. Eleven laboratories reported results.

For Tyler mesh 28x48, the VBD between-lab reproducibility came out as shown in Table 2. The observed R values were above the R reproducibility limit of 0.046 g/cm³.

Table 2: VBD (g/cm³) average and between-lab R at 95 % confidence level in the 2008 RDC RR.

	Size range	Average	R
Material A	Tyler 28x48	0.91	0.09
Material C	Tyler 28x48	0.86	0.12

In the R&D Carbon ILS, VBD was measured on several coke fraction sizes, see Table 3.

Table 3: VBD (g/cm³) average and between-lab R at 95 % confidence level in the 2008 RDC RR.

	Size range	VBD	R
Material A	2-4 mm	0.79	0.07
Material A	1-2 mm	0.86	0.04
Material A	0.5-1 mm	0.90	0.05
Material A	0.25-0.5 mm	0.91	0.04
Material C	2-4 mm	0.74	0.10
Material C	1-2 mm	0.81	0.10
Material C	0.5-1 mm	0.81	0.06
Material C	0.25-0.5 mm	0.84	0.09

- The increase in VBD with decreasing grain size is clear.
- The between-lab precision showed only a slight improvement with smaller grain size, so the level of porosity was not an important variation factor, and, somewhat surprisingly, neither was the number of grains in the test portion.

VBD, 2004 CII Carbon RR #17 [5]

This RR was mentioned above with Figure 2. A calcined coke RR sample was distributed prepared to -4 Tyler mesh. For VBD, each lab was to return results for analysis by ASTM D4292 for the two common grain ranges

- The finer ASTM VBD Tyler mesh 28x48 (0.30-0.59 mm)
- The coarser Kaiser VBD Tyler mesh 8x14 (1.17-2.36 mm)

Using ASTM E691, the average VBD and the between-lab reproducibility R came out as shown in Table 4. The observed R values were comparable to the reproducibility limit of 0.046 g/cm³ for the fine material, and above for the coarse.

[7] Data in lb/ft³ was converted to g/cm³ by dividing by 16.0.

Table 4. VBD (g/cm³) average and between-lab R at 95 % confidence level from four CII Carbon RRs.

	Average	R
R#17 Fine – 28x48	0.88	0.04
R#17 Coarse – 8x14	0.82	0.08

TBD –Comparative Study

TBD in the 2008 R&D Carbon Interlaboratory Study[4]

Some results from this RR were shown in Table 3. For TBD, sixteen laboratories reported results. TBD was measured on several coke fraction sizes. For the 1-2 mm fraction, the expected TBD range of sponge petroleum coke is 0.78 to 0.86 g/cm³ so the two cokes A and C were at each end of the TBD-range. Using ASTM E691, the TBD between-lab reproducibility R came out as shown in Table 5. The observed R values were above the ISO 10236 reproducibility limit of 0.02 g/cm³.

- The increase in TBD with decreasing grain size is clear.
- The between-lab precision showed no trend with grain size, so the level of porosity was not a significant variation factor, and, somewhat surprisingly, neither was the number of grains in the test portion.

Table 5: TBD (g/cm³) average and between-lab R at 95 % confidence level in the 2008 RDC RR.

	Size range	TBD	R
Material A	4-8 mm	0.73	0.04
Material A	2-4 mm	0.79	0.03
Material A	1-2 mm	0.86	0.04
Material A	0.5-1 mm	0.89	0.04
Material A	0.25-0.5 mm	0.89	0.04
Material C	4-8 mm	0.69	0.04
Material C	2-4 mm	0.74	0.04
Material C	1-2 mm	0.79	0.05
Material C	0.5-1 mm	0.82	0.05
Material C	0.25-0.5 mm	0.83	0.03

Method Development in ASTM – VBD

Method development has been slow partly due to uncertainty how to improve. However, in ASTM two major steps have been achieved in the last years.

ASTM D7454-08 VBD

A new method for vibrated bulk density has been published, ASTM D7454-2008. In this, the ASTM Committee and Rio Tinto Alcan has addressed what grain size is allowed, and also given a more strict procedural description for the test portion preparation. A new, semi-automated analysis instrument has been introduced. The measurement is mass of a fixed volume rather than the read-out of the level of a volumetric cylinder as in D4292 VBD and the TBD methods.

ASTM D4292-10 VBD

A new, 2010 version of this method has been published. It was developed by the ASTM Committee, mostly through the efforts of Bill Spencer.

Effect of Differences in Laboratory Practice

Examples of non-uniform practice are

- Feeding with or without starting vibration
- Fixing the measuring cylinder to the vibration table or not
- Speed of sample introduction into the measuring cylinder
- Different types of crushers for sample preparation
- Length of time for vibrating the test portion

Results of a bulk density test are dependent on the average particle size and particle size distribution. Because of this dependency, sample preparation of the material directly impacts the results. One aspect of measuring bulk density is to examine only "as-calcined" particles or particles that are of a "natural" fraction. The as-calcined or natural particles are particles of calcined petroleum coke that have not been subject to a crushing step. It is appropriate to perform a sieving step to separate the as-calcined or natural particles. If measuring bulk density of as-calcined particles, identify the results with the particle size and the label of as-calcined. Example: VBD result = g/cm³ (20x48 Tyler mesh range (0.30 x 0.85 mm), As-Calcined).

Prepared bulk density samples are from particles of calcined petroleum coke that have been crushed in the laboratory. It is critical for good repeatability and reproducibility results to have appropriate sample crushing equipment and procedures. The recent year 2010 revisions to ASTM D4292 (D4292-10) contains additional specifications on equipment and crushing operations. The roll crusher specification in D4292-10 specifies that both rolls must rotate to crush the material. Disc mills, disc type grinders or disc pulverizers are not appropriate since these contain only one stationary roll. D4292-10 also specifies in the crushing operations through the jaw crusher and roll crusher that the entire gross sample should pass through the crushers.

Method Development in ISO –VBD

The ISO VBD method study was based on screening a natural fraction and mixing it with the crushed and screened oversize fraction. The measurement procedure was similar to D4292 with 100 g coke in a 250 ml volumetric cylinder with even filling over 115 seconds with vibration, followed by vibration for 60 seconds. For read-out, the surface of the vibrated coke was flattened with a spatula and the volume read to the nearest 1 ml.

A comparison was run versus the TBD method ISO 10236 using two single source and two blended cokes, and using TBD fractions.[6] The ISO Committee concluded that the precision with the new VBD method was not better than for the TBD method, and the work was discontinued. The laboratory testers observed that the main contribution to the standard deviation was

- Leveling the test portion with the spatula
- The coarse volumetric cylinder gradation of 1 ml.

Discussion

The bulk density has fairly good within-laboratory repeatability, and has a useful role as a coke property if it is based on the reported values from one laboratory. But examples of between-laboratory comparisons have shown that the bulk density has severe limitations when comparing results from different laboratories. This is a severe drawback for a commercial standard. Furthermore, from the studies shown it is reasonable to say that the reproducibility limits given in the standards, although they are high, still are optimistic compared to practical experience. This might be an effect of quality laboratories participating in the precision statement development, but also an effect of differences in the actual practice of the standards.

For an anode producer, the one way to address and solve this dilemma is to establish the most relevant bulk density method available in their own laboratory, and do all required analyses.

In the comparative studies shown the TBD method yielded better between laboratory precision than the old D4292-92 VBD method. The results from the currently running ASTM interlab study for the new D7454-08 and the D4292-10 revision will add useful information to such a comparison. It will also shed light on the precision of the GeoPyc apparatus.

In the short term, other methods are unlikely to appear. For any anode manufacturer using bulk density to evaluate coke potential, developing a better bulk density apparatus for internal use might be an option. A larger test portion could address aggregate packing issues such as

- The wall effect and shape of grains
- Small 120 cm³ test portion volume versus read-out accuracy
- Large test portion surface to volume of the cylinder

Finally, there is the possibility of a reference material. The authors should like to suggest users of these methods to consider if a reference material could be established, e.g. through NIST, as an aid in tuning the bulk density analysis equipment.

Authors' Background in Standard Development

Dr.ing. Lorentz Petter Lossius is a voting member of ASTM Committee D02.05 and a Technical Expert in ISO/TC 226 Work Group 2 on Solid Carbon Materials.

Dr. Bill Spencer is Chair of ASTM Committee D02.05.

Dr. Tech. Harald A. Øye is Chair of ISO/TC 226 and Convenor of Work Group 2 on Solid Carbon Materials.

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[3] Keith Neyrey, CII Carbon, "Minutes of Meeting from the 1999 ASTM Committee D02.05D". Results reproduced courtesy of Rain CII Carbon, LLC.

[4] 2008 R&D Carbon Interlaboratory Study RDC 8843, results reproduced courtesy of R&D Carbon Ltd.

[5] Trey Neal, CII Carbon, Result Memo on RR # 17, 2004.

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