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IMPROVING THE REPEATABILITY OF COKE BULK DENSITY TESTING

[1]Les Edwards, [2]Marvin Lubin, [2]Jim Marino
[1]Rain CII Carbon, 2627 Chestnut Ridge Rd, Kingwood, Texas, 77339, USA
[2]Rain CII Carbon, Lake Charles Lab, 1920 Pak Tank Rd, Sulphur, Louisiana, 70665, USA

Carbon, Petroleum Coke, Bulk Density

Abstract

The "Pechiney" mercury apparent density test was used by the aluminium industry for many years to measure the density of calcined petroleum coke. Over the last five years, the industry has moved away from this test for occupational health and safety reasons. The current alternative tests are based on vibrated or tapped bulk density. The value of measuring bulk density is reduced by poor reproducibility due to differences in equipment and sample preparation. This paper reviews different bulk density test methods and presents repeatability data on a new method for measuring bulk density. The method is based on automated equipment which uses transverse axial pressure to measure bulk volume. The new equipment shows improved repeatability compared to existing equipment and can also be used to measure envelope density which eliminates intra-particle porosity problems associated with bulk density tests.

Introduction

The mercury apparent density (Hg AD) test was the test preferred by many anode producers for predicting the pitch demand and anode density potential of different calcined cokes. The procedure was developed by Aluminium Pechiney and uses relatively large volumes of mercury. This makes it hazardous from an occupational health and safety standpoint and the test has now been largely abandoned by the industry.

Although the Hg AD test has been widely used, many other tests are also commonly used for measuring coke density/porosity. These tests are based on vibrated bulk density (VBD) or tapped bulk density (TBD). Most have been around for a long time and many papers have been published on the value of these tests. At least one aluminum producer [1] routinely uses a VBD test for determining pitch demand during anode production

Rain CII has the capability to run four different bulk density tests: three VBD tests and one TBD test. The repeatability and reproducibility of these tests varies widely. This paper will present a brief review of the different test methods and will then focus on work done to quantify and improve the repeatability of the measurement portion of the tests. Results with an automated bulk density analyzer will be presented.

This paper will not make recommendations about the merits of using any particular VBD or TBD test to monitor coke quality or predict pitch demand and anode density. It will however, look at correlations between the results of the various VBD tests, the TBD test and the Hg AD test across a range of different cokes.

Hg AD Test versus VBD/TBD Tests

There are different opinions about whether the Hg AD test is a reliable indicator of pitch demand and anode density but the reality is that the Hg AD test will not be around much longer. The one advantage of the test relative to VBD/TBD tests is its ability to measure coke density/porosity independent of particle shape.

The test uses the Archimedes principal where particle volume is measured by mercury displacement. The 1.70 to 0.85mm (10x20 Tyler mesh) particles used for the test are placed in a pycnometer and mercury is added at atmospheric pressure. The mercury is non-wetting to carbon and is not affected by pore capillary forces. The Hg surrounds the particles uniformly and enters open pores. Based on the pressure exerted by the weight of mercury, it is estimated that pores down to a diameter of ~13µm [2] are penetrated by mercury. This is approximately the pore size pitch penetrates when making anodes so the Hg AD test provides a useful analog.

VBD and TBD tests are capable of giving the same type of information but particle shape is a complicating factor. All VBD and TBD tests rely on measuring the bulk volume of a packed bed of coke particles. The bulk density of the coke bed is therefore always a function of the density of individual coke particles and the packing density of the particles.

Vitchus et al [3] presented a good summary of the importance of particle packing and the impact of parameters such as particle size, shape and roughness on packing density and bulk density. Porosity or void space between particles is referred to as intra-particle porosity. For cokes crushed to a particle size of 0.6 to 0.3mm (28 x 48 Tyler mesh), intra-particle porosities of 42-50% are reported for two different cokes crushed in different ways. To complete the picture, 41-46% of the volume space is occupied by solid coke and 8-13% by porosity within the coke particles.

The above highlights one of the challenges of using VBD or TBD as a reliable indicator of coke porosity and anode pitch demand and density. Sample preparation and anything that has the potential to affect particle shape and packing density will always have a significant impact on the final bulk density result.

VBD/TBD Procedure Review

There are three well known VBD and TBD procedures in common use: ASTM D4292 (VBD), ASTM D7454 (VBD) and ISO 10236 (TBD). Without the Hg AD test, most anode producers use one of these tests when setting coke bulk density specifications with suppliers and/or when trying to correlate coke properties with pitch demand and anode density.

Rain CII conducts all these tests and one additional test known as the "Kaiser" VBD test. It was developed many years ago by Kaiser Aluminum and is used to monitor daily calcined coke quality. The test is a little quicker and easier to run than the ASTM VBD tests but it is not a certified standard test procedure.

The following provides a brief summary of the sample preparation steps required for each of these tests. A more detailed description is provided in a parallel paper in these proceedings [4]. The published standards for each test also contain much more detail and should be read before any of the tests are undertaken.

ASTM D4292 (0.6 - 0.3mm or 28x48 Tyler mesh)
The sample is jaw-crushed first and then fed through a roll crusher three times at successively smaller gap settings to produce material in the 28x48 mesh size range. 100 grams of the 28x48 sample is used for the VBD measurement. The test can also be used for different size ranges such as 1.18-2.36mm or 3.3-6.7mm.

ASTM D7454 (0.85 - 0.425mm or 20x35 Tyler mesh)
The sample is hand screened to remove coke in the 4.75 - 1.18 mm (4x14 mesh) size range. The 4x14 fraction is then fed to a roll crusher three times at successively smaller gap settings to produce coke in the size range of 20x35 mesh. The 20x35 mesh sample is run in duplicate on semi-automated equipment to measure VBD.

Kaiser VBD (2.36 - 1.18 mm or 8x14 Tyler mesh)
The sample is hand-screened at 8x14 mesh. The +8 mesh fraction is jaw crushed once and then roll-crushed repeatedly until it is all less than 8 mesh. All the 8x14 mesh fractions are re-combined for the VBD analysis which is run on a 100 gram sample.

ISO 10236 TBD
The ISO TBD test is the simplest and easiest of all the procedures since it involves no crushing. The sample is screened at the following screen sizes: 8.0 - 4.0mm, 4.0 - 2.0 mm, 2.0 - 1.0 mm (9x16 Tyler mesh), 1.0 - 0.5 mm and 0.5 - 0.25 mm. 100 grams of any one or all of these fractions is then measured for TBD.

The purpose of the above is to illustrate that all of the preparation methods are different. The particle size ranges used for tests are different and this has a large impact on the bulk density result. For a given coke sample, the ASTM D4292 test at 28x48 mesh always gives a higher bulk density than the ASTM D7454 test at 20x35 mesh or the Kaiser VBD test at 8x14 mesh. Porosity is removed by crushing and the finer particles pack to a higher bulk density.

An interesting comparison between the tests is the yield in the size fraction measured. Typical yield data from Rain CII's lab are shown in Table I. For some tests, a relatively small portion of coke ends up being measured for VBD or TBD. For the TBD test, some labs measure TBD on all size fractions whereas others measure only one fraction, typically the 1-2 mm fraction. The downside of a lower yield, is that it may not reflect the average coke density or porosity as well. This is the primary reason Rain CII uses the Kaiser VBD test – it gives a relatively high yield.

Test Method	Typical Yield (%)
ASTM D4292 (28x48 mesh)	30
ASTM D7454 (20x35 mesh)	15
Kaiser VBD (8x14 mesh)	55
TBD Overall (0.25-8mm)	75
TBD (0.25-0.5mm)	12
TBD (0.5-1.0mm)	12
TBD (1.0-2.0mm)	15
TBD (2.0-4.0mm)	15
TBD (4.0-8.0mm)	20
Mercury AD (10x20 mesh)	45

Table I: Yield of coke in measuring size range after preparation

The rest of this paper will focus on the measurement portion of each test. Differences in sample preparation will always have a significant effect on the final VBD result and changes in the measurement method will not overcome this problem. Unless the sample preparation steps are followed exactly as stated in the published standards, different results can be expected between labs analyzing the same samples. This goes back to the problem of particle shape, surface roughness, etc.

In contrast to the VBD and Hg AD tests, the TBD test involves no sample preparation other than screening. This eliminates a source of error that occurs in the all the other preparation methods.

VBD/TBD Measurement Procedures
The three VBD tests all use the same principal where sample is added to a graduated cylinder and vibrated for a specified time. The TBD measurement is similar but instead of being vibrated, the graduated cylinder is tapped. Photographs of equipment used for the D4292 VBD and ISO TBD test are shown in Figure 1.

For the ASTM VBD, Kaiser VBD and TBD tests, a fixed weight of sample is added to the graduated cylinder and the height of the coke bed is read (by eye) at the end of the test to estimate the volume. The VBD or TBD is calculated simply as mass/volume.

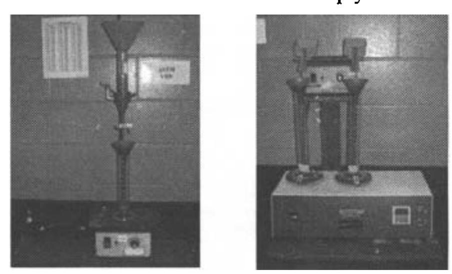


Figure 1: ASTM D4292 and ISO TBD tests

ASTM D7454 is the most recently published VBD procedure (Oct 2008) and it requires the use of semi-automated equipment, Figure 2. The coke is added to the graduated cylinder with a specially designed vibrating bowl and feeder system. A photoelectric sensor detects the coke bed height when it reaches the pre-set, 50 ml level. The feeder shuts off and the coke in the graduated cylinder is then weighed and the bulk density calculated.

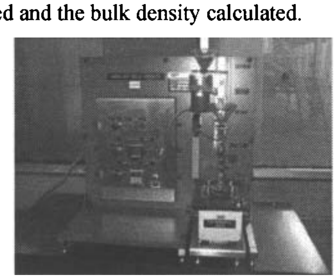


Figure 2: ASTM 7454 semi-automated VBD equipment

Not surprisingly, the precision of the measurement in ASTM D7454 is better than the other two VBD methods and the TBD method (3-sigma is about half). Weighing the sample instead of estimating the volume by eye is more precise. The coke feeding and table vibration are also controlled very precisely

Another difference with the ASTM D7454 test is the requirement to use calibration standards. The test was developed by Alcan and the standards are now available through Rio Tinto Alcan (RTA). The equipment must be calibrated before first use and then checked routinely thereafter (typically once/week). There are several adjustments that can be made for recalibration and these are all well documented in the procedure.

Micromertics GeoPyc Equipment

The Micromeritics GeoPyc 1360 Envelope Density Analyzer has been available since 1995. It is used to measure particle and solids bulk densities. Rain CII first tested the equipment in 1996 as a potential replacement for the Hg AD test. Initially, the instrument was available only as an envelope density analyzer. For this test, a special dry flow media (DryFlo) is used which comprises small, spherical particles that are non-wetting and free-flowing. The DryFlo media behaves like a fluid and when mixed with solid particles, it surrounds the particles eliminating intra-particle voids. This negates particle shape problems and their impact on packing density. A photograph of the equipment is shown in Figure 3.

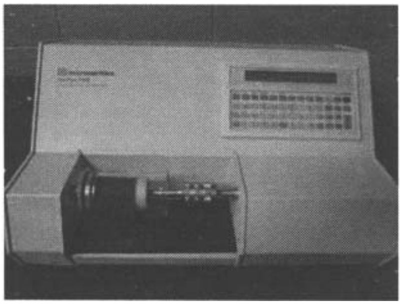


Figure 3: GeoPyc 1360 Density analyzer

Rain CII did not find a good correlation between envelope density and Hg AD for samples prepared by the Pechiney method in 1996. The test repeatability was not particularly good so no further testing was done. Micromeritics later developed a bulk density option for the equipment referred to as the T.A.P option (Trans Axial Pressure). It measures the bulk density in a horizontal cylinder as shown in Figure 3. This option was not available when the equipment was tested by Rain CII in 1996.

With the abandonment of the Hg AD test, Rain CII decided to re-evaluate the GeoPyc equipment, particularly the T.A.P option. In principal, it provides a very accurate way of measuring the bulk density by controlling the force and measuring the displacement of a Teflon plunger used to compact the bed of coke.

The plunger applies the compaction force in stages and the sample is agitated by rotating the cylinder during measurement. After each compaction cycle (referred to as a consolidation cycle), the plunger retracts a short distance and then moves forward again until the desired force is reached. Multiple consolidation cycles allow the particles in the coke bed to re-arrange to ensure maximum packing density without particle breakage. When the cycles are complete, the instrument uses stored data to calculate plunger displacement and hence bulk volume. The sample weight is input via the keypad and bulk density is calculated.

The rest of this paper reports on the results of bulk density testing with the various different types of VBD/TBD equipment. In the first part, the repeatabilities of the various tests are evaluated and compared to the GeoPyc using quality control (QC) standards from Rain CII's lab. In the second part, a wide range of different calcined coke samples are evaluated by the various VBD/TBD methods and compared to Hg AD results. In the final part, the GeoPyc envelope density test is evaluated.

Repeatability of Test Methods

The repeatability data generated in the following section was produced by running QC samples 25 times (once/day) on each piece of equipment. Each test has its own QC sample due to differences in particle size. The QC tests were run on the standard equipment and then on the GeoPyc. The GeoPyc is fully programmable and several test parameters can be varied including cylinder diameter and volume, force and number of consolidation cycles. A standard set of conditions was used for all tests.

An example of the frequency histograms for repeatability of the ASTM D4292 test is shown in Figure 4. This shows the range of bulk densities measured with the QC standard on the standard equipment and the GeoPyc equipment.

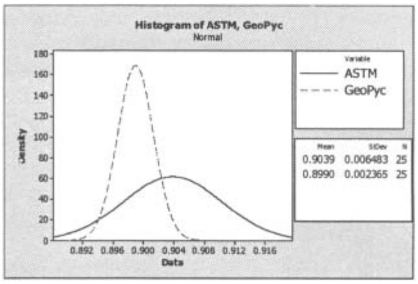


Figure 4: Frequency histograms for ASTM D4292 test

Results for all tests are summarized in Table II. The first point to note is that, for the three VBD tests, the GeoPyc bulk densities were very similar to those measured on the standard equipment. This was a little surprising given the obvious differences in the mode of analysis (different vibration table amplitude settings, methods of clamping, feeding of samples, etc.).

Test		Standard Equipment	GeoPyc Equipment	Difference in Means
ASTM D4292 (28x48 mesh)	Mean	0.904	0.899	0.005
	3-Sigma	0.019	0.007	
ASTM D7454 (20x35 mesh)	Mean	0.870	0.875	0.005
	3-Sigma	0.010	0.009	
Kaiser VBD (8x14 mesh)	Mean	0.819	0.825	0.006
	3-Sigma	0.022	0.006	
ISO 10236 (9x16 mesh)	Mean	0.874	0.882	0.012
	3-Sigma	0.023	0.016	

Table II: Bulk density results with QC standards (g/cc)

The other point to note is that the repeatability of the bulk density measurement with the GeoPyc equipment is significantly better (lower 3-sigma) than the standard equipment for the ASTM D4292 and Kaiser VBD tests. This was not unexpected because both tests rely on manual reading of the coke bed height in a cylinder. For the ASTM D7454 test, the repeatability of the GeoPyc was about the same as the semi-automated equipment.

For the TBD test, the repeatability was better for the GeoPyc but the 3-sigma was higher than all the VBD tests.

For the ASTM D7454 test, one of RTA's certified reference standards was used (0.870 g/cc standard). One of the benefits with the GeoPyc is that no standard is required and no form of calibration is required. The instrument does its own zero calibration with the Teflon plunger when the glass cylinder is empty. Another benefit of the GeoPyc is that the sample can simply be poured into the glass cylinder. For all the other bulk density tests, it is critical to feed the coke into the graduated cylinder at a constant, well-controlled rate.

For the TBD test, repeatability testing was done only with a 9x16 QC standard. Rain CII does not have any customer specifications based on this test but the 9x16 fraction is used by some in the industry. The TBD test results differed from those of the GeoPyc by the greatest amount. The repeatability of the standard equipment was about the same as the other two VBD tests, which makes sense given that all rely on manual reading of a graduated cylinder. The reason for the poorer repeatability of this test with the GeoPyc relative to the other tests has not been fully established but is likely due to the lack of any form of sample preparation (crushing). Naturally occurring particles may be more irregular in shape and/or more susceptible to breakage during the measurement itself. Crushing removes some of this variation.

Comparison of Results Across a Wide Range of Samples

A wide range of samples with different bulk densities were analyzed using the standard equipment (Std.) and the GeoPyc (Geo.) equipment. The results are summarized in Table III. The TBD test was not included in this evaluation. Most of the samples were production or shipment samples containing multiple cokes.

Test	ASTM D4292		ASTM D7454		Kaiser VBD	
	Std.	Geo.	Std.	Geo.	Std.	Geo.
# Samples	62		33		80	
Mean	0.868	0.864	0.839	0.846	0.772	0.763
Difference in Means	0.004		-0.007		0.008	
Max	0.909	0.895	0.867	0.870	0.840	0.837
Min	0.806	0.812	0.810	0.820	0.685	0.699
Range	0.103	0.083	0.057	0.050	0.155	0.138

Table III: Bulk density results across wide range of samples (g/cc)

There are more Kaiser VBD results in Table III because Rain CII runs this test on all daily production samples. The differences in the means are all statistically significant but are well below the stated repeatability and reproducibility limits for the various tests. For example, the published repeatability and reproducibility limits for the ASTM D4292 test are 0.014 g/cc and 0.046g/cc respectively. For all tests, the range between maximum and minimum values was lower for the GeoPyc equipment which is consistent with lower variability in the measurement method.

Next, a wide range of samples with different bulk densities and other properties were selected. All initial testing was done on straight-run cokes generated during full-scale, calcination trials. Testing is still underway on coke blends and has not been completed yet. Rain CII typically blends cokes to meet specifications.

Sulfur, vanadium, real density and Hg AD results for the straight run cokes are shown in Table IV. The Hg AD tests were run by an external laboratory since Rain CII no longer runs this test in the USA. Coke I is a highly isotropic coke and coke J is a shot coke.

Coke	Sulfur %	Vanadium ppm	Real Density (g/cc)	Hg AD 1 (g/cc)
Coke A	4.00	740	2.088	1.73
Coke B	1.52	95	2.079	1.71
Coke C	2.72	320	2.055	1.75
Coke D	1.45	110	2.071	1.74
Coke E	1.48	115	2.078	1.75
Coke F	3.72	490	2.044	1.79
Coke G	2.22	290	2.060	1.75
Coke H	0.78	270	2.076	1.74
Coke I	4.66	620	1.988	1.76
Coke J	4.54	1750	2.009	1.79
Coke K	2.85	190	2.041	1.82
Coke L	2.49	170	2.083	1.83

Table IV: Straight run coke samples

The bulk densities of all the cokes above were measured by the four tests already described. Standard preparation procedures were followed and bulk densities were measured using both the standard equipment and the GeoPyc equipment. This generated a large amount of data, some of which is shown in Table V. All the VBD and TBD measurements were performed with both standard equipment and GeoPyc equipment, but only GeoPyc results are shown. Standard equipment results are shown in Table VI.

Coke	ASTM D4292	ASTM D7454	Kaiser	TBD 5x9	TBD 9x16	TBD 16x32
A	0.920	0.914	0.841	0.806	0.879	0.893
B	0.848	0.797	0.726	0.661	0.724	0.791
C	0.882	0.862	0.784	0.759	0.823	0.887
D	0.858	0.821	0.754	0.707	0.766	0.803
E	0.889	0.821	0.756	0.708	0.769	0.831
F	0.839	0.832	0.754	0.706	0.727	0.749
G	0.923	0.911	0.836	0.843	0.927	0.960
H	0.875	0.847	0.776	0.722	0.784	0.837
I	1.014	0.960	0.913	0.919	0.973	1.025
J	0.983	1.019	1.066	0.996	1.128	0.999
K	0.943	0.838	0.888	0.808	0.900	0.986
L	0.972	0.889	0.859	0.814	0.892	0.973

Table V: VBD and TBD results with GeoPyc equipment (g/cc)

The data were analyzed by Minitab to check correlations. All correlations between the Hg AD results from Table IV (Hg AD 1) and the various VBD/TBD preparations were poor with R^2 values <0.3. The correlations between most of the VBD/TBD preparations were much better. The best correlation ($R^2 = 0.95$) was between the Kaiser GeoPyc bulk density and the GeoPyc bulk density on 9x16 particles prepared via the TBD test.

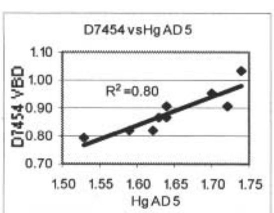
The lack of correlation between any of the above bulk density measures and the Hg AD results was a concern, so a slightly smaller subset of the cokes (A-J) were sent out to several different laboratories for Hg AD analysis. A combination of Pechiney Hg AD equipment and mercury intrusion porosimeters (MIP) were used for this round of testing. MIP is a well established method that allows accurate characterization of pore size distributions with Hg up to pressures as high as ~400 MPa.

Most of the correlations improved, suggesting that the Hg AD 1 results reported in Table IV were unreliable. This highlights one of the problems with the Hg AD test - it has relatively poor reproducibility. In past industry round robins, Rain CII has reported reproducibilities of ~0.030 g/cc. The new Hg AD results along with the standard equipment results for all the other tests (non-GeoPyc) are shown in Table VI.

Coke	D4292	D7454	Kaiser	TBD 9x16	Hg AD 2	Hg AD 3	Hg AD 4	Hg AD 5
A	0.909	0.908	0.844	0.859	1.73	1.73	1.75	1.64
B	0.847	0.792	0.687	0.704	1.70	1.71	1.71	1.53
C	0.901	0.868	0.781	0.800	1.73	1.75	1.77	1.64
E	0.887	0.819	0.771	0.741	1.70	1.70	1.76	1.62
F	0.847	0.823	0.761	0.714	1.67	1.66	1.73	1.59
G	0.926	0.907	0.826	0.944	1.77	1.78	1.82	1.72
H	0.885	0.869	0.769	0.788	1.75	1.74	1.74	1.63
I	1.031	0.954	0.926	0.962	1.76	1.76	1.77	1.70
J	0.990	1.032	1.048	1.106	1.79	1.79	1.79	1.74

Table VI: VBD/TBD and Hg AD results (g/cc)

The best correlations were observed with the Hg AD 5 results. These were Hg AD's run at a lower pressure with a MIP. At the pressure used, it was estimated that pores down to a size of ~100µm were penetrated instead of the 13 µm pores in the regular Pechiney Hg AD procedure. Figure 5 shows correlations for the D7454 and 9x16 TBD tests with the Hg AD 5 results.



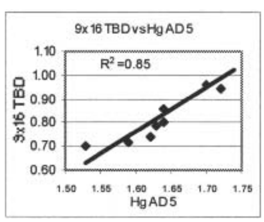


Figure 5: Correlations for ASTM D7454 and TBD vs Hg AD 5

These results make intuitive sense. Bulk density tests include all forms of open and closed porosity in the coke as well as intra-particle porosity. The Hg AD test, on the other hand, excludes open porosity >13 µm and all intra-particle porosity. An MIP test run at lower pressure where Hg penetrates pores down to 100 µm should show a better correlation to bulk density test results.

Envelope Density Testing

In the final phase of this work, the GeoPyc equipment was tested in the envelope density mode. The recommended particle size of the sample when measuring envelope density is >2mm. This is due to the relatively large particle size of the DryFlo media (100-150 µm). A scanning electron microscope (SEM) image of the DryFlo media is shown in Figure 6 along with a photograph of the coke and DryFlo mixture in the GeoPyc. For this work, it was decided to compare results across all the various preparation methods and sizes from 28x48 mesh in the ASTM D4292 test to 5x9 mesh sizes (4.0 – 2.0 mm) in the ISO TBD test.

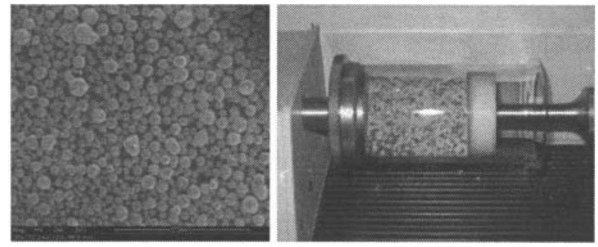


Figure 6: SEM image of DryFlo media and mixture of DryFlo and calcined coke in GeoPyc instrument

When using the DryFlo media, ~25% of the sample (by volume) must be mixed with ~75% of the DryFlo media. The DryFlo surrounds or "envelopes" each particle. When the test is complete, a screen is used to separate the DryFlo media from the sample and the separation is very clean due to the non-wetting nature of the DryFlo. It can be reused multiple times.

Results for envelope densities are shown in Table VII and they were significantly better than expected. Correlations with all tests were generally good. A correlation matrix for all the GeoPyc bulk density tests and the Hg AD results is shown in Table VIII.

Coke	Envelope Density (g/cc)	Real Density (g/cc)	Porosity %
A	1.418	2.088	32.1
B	1.256	2.079	39.6
C	1.386	2.055	32.6
D	1.332	2.071	35.7
E	1.344	2.078	35.3
F	1.279	2.044	37.4
G	1.461	2.060	29.1
H	1.423	2.076	31.4
I	1.530	1.988	23.1
J	1.610	2.009	19.9
K	1.437	2.041	29.6
L	1.462	2.083	29.8

Table VII: Envelope densities and calculated porosities

	Kaiser GEO	ASTM GEO	ALCAN GEO	9X16 Geo	Hg AD 1	Hg AD 2	Hg AD 3	Hg AD 4	Hg AD 5	Envel Den.
ASTM GEO	0.72									
D7454 GEO	0.81	0.65								
ISO 9X16 GEO	0.95	0.76	0.88							
Hg AD 1	0.25	0.24	0.06	0.16						
Hg AD 2	0.53	0.50	0.55	0.65	0.02					
Hg AD 3	0.46	0.45	0.48	0.61	0.00	0.91				
Hg AD 4	0.34	0.38	0.44	0.51	0.14	0.54	0.58			
Hg AD 5	0.69	0.69	0.79	0.81	0.26	0.75	0.64	0.81		
Envelope Density	**0.85**	**0.80**	**0.83**	**0.91**	**0.16**	**0.74**	**0.64**	**0.51**	**0.87**	
Envelope Porosity	**0.88**	**0.79**	**0.84**	**0.92**	**0.18**	**0.68**	**0.58**	**0.48**	**0.85**	**0.96**

Table VIII: R^2 correlations between different density measurements for cokes A – L

Among the Hg AD tests results, the envelope densities correlated very well with those of the Hg AD 5 test with an R^2 of 0.87. The correlation with the Hg AD 2 and the Hg AD 3 results were 0.74 and 0.64 respectively. The correlation with the Hg AD 4 results was not so good at 0.5, and there was no correlation with the Hg AD 1 results (0.16), confirming the poor quality of this data.

Among the VBD and TBD tests, R^2 values with the envelope densities were generally excellent except the TBD test with 32x60 mesh particles. This is not unexpected given the fine particle size of this fraction. For the Kaiser VBD and coarser particle size TBD results, the correlations were all >85% which makes sense given the coarser sizing relative to the DryFlo sizing.

Real density data can be entered into the GeoPyc and it calculates particle porosity as shown in Table VII. This includes open porosity not penetrated by the DryFlo media which is likely to be most of the open porosity in coke. MIP data for 3 of the cokes (B, G and J) are shown below. The cokes represent high, medium and low porosity cokes, and Figure 7 shows pore size distribution curves at a pressure of ~400Mpa of pressure. The data show that most of the differences in density and porosity are due to differences in the macropores >1 μm in size.

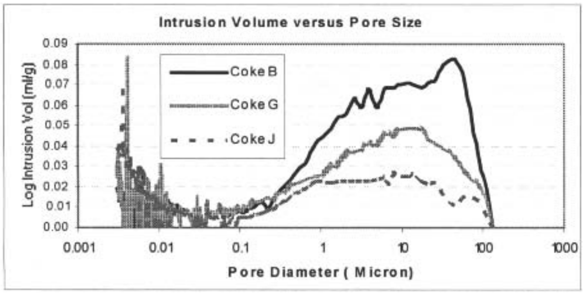


Figure 7: Hg porosimetry plots of cokes B, G and J

Discussion and Conclusions

The Micromertics GeoPyc 1360 appears to be a versatile piece of equipment for measuring coke bulk densities when used with the T.A.P option. It does not require calibration standards and has a higher level of precision than the graduated cylinder and vibrating/tapping equipment used in the ASTM D4292, Kaiser VBD and ISO TBD tests. The precision is comparable to the semi-automated equipment used in the ASTM D7454 test.

The results presented in the paper show that the mercury apparent density test does not correlate well with some of the common VBD tests. The Hg AD test itself is subject to sample preparation and measurement errors just like the other tests. The Pechiney procedure quotes a repeatability of 0.011 g/cc for samples run in the same lab. Reproducibilities between labs of 0.03 g/cc were more typical of Rain CII's experience with the test. At least one set of data analyzed by a lab in this study was unreliable (Hg AD 1). The other Hg AD results (AD 2 - AD 5) showed better correlations with a number of the VBD and TBD test results.

It is important to note that the correlations between Hg AD and bulk density reported in the paper were limited to straight run cokes. Some work has been completed with coke blends but further work is in progress. Correlations between several of the VBD and TBD tests appear to deteriorate significantly when blended cokes are used, and this is probably not surprising given the different densities and hardness of cokes used in blends.

The GeoPyc envelope density analysis shows great promise. When the equipment is used in this mode, it eliminates the effects of particle shape and roughness that contribute to packing differences in traditional VBD and TBD tests. Preliminary repeatability testing on 8x14 mesh samples shows a 3-sigma of ~0.030 g/cc. Controlling the volume ratio of coke to DryFlo media within a narrow range (25-30%) appears to be important for achieving good repeatability.

The envelope density test is simple and avoids the occupational health problems of mercury. It may not give results fully comparable to the Hg AD test, but it could offer an improvement over traditional bulk density tests as a predictor of pitch demand and anode density. It will not give the sort of detailed pore size distribution data available with an MIP, but MIP equipment is expensive and costly to operate and is more of a research tool than a routine analysis tool. It still uses mercury, of course.

No attempt was made in this paper to quantify the effects of sample preparation differences on bulk density results. All samples were prepared as consistently as possible in one lab. The same samples prepared in other labs could give different bulk density results due to different preparation methods. The GeoPyc envelope density analysis has the potential to significantly mitigate sample preparation issues that contribute so much to differences in packing density. This is arguably the most compelling reason to investigate this analysis in more detail.

The ISO TBD test avoids sample preparation differences between laboratories, but correlations between TBD and Hg AD results appear to decrease significantly for blended cokes. This is still being investigated but is likely due to the lack of crushing in the TBD method. All other methods, including the Hg AD test, require crushing during sample preparation. Anode plants also crush coke before use.

No recommendations are made on the merits of the various bulk and apparent density tests as predictors of pitch demand and anode density. The Micromeritics GeoPyc 1360 instrument can be used for either envelope or T.A.P density analysis and it offers some significant advantages over other types of equipment being used today. Rain CII will continue to evaluate the equipment and will look at comparisons between Hg AD, MIP and envelope densities for coke blends rather than straight-run cokes.

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