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Petroleum Coke VBD

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Historical and Future Challenges with the Vibrated Bulk Density Test Methods for Determining Porosity of Calcined Petroleum Coke

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Keywords: Calcined Petroleum Coke, Vibrated Bulk Density, Porosity

Abstract

Over several decades, calcined petroleum coke producers and the aluminum industry have been using various techniques such as Vibrated Bulk Density (VBD), Mercury Intrusion Porosimetry (MIP), and Mercury Apparent Density to predict the porosity of calcined petroleum coke. Better knowledge of the coke porosity allows a more accurate estimation of coke quality and pitch demand for fabricating anodes of optimum performance. Industry has had limited success in accurately predicting porosity using the existing VBD methods. Direct measurement of porosity by MIP is an alternative way to measure porosity accurately. Currently there is limited correlation between VBD and MIP. Any improvements to the VBD test method should demonstrate improved correlation to the results obtained from MIP.
This paper covers the historical and traditional approach to predict calcined coke porosity, correlation study of VBD test method and porosity by MIP, and input to the development of superior test methods to meet industry requirements.

Introduction

Relationship Between Porosity/VBD And Anode Properties

The methodologies for qualitative analysis of calcined petroleum coke and the effects of coke quality on the properties of anodes are well known and have been well researched over several decades. The porosity of calcined coke is one of the important properties to determine the quality of coke in terms of pitch demand, and optimum pitch quantity is very important for optimizing anode performance. Collier Carbon introduced an indirect measurement of porosity by measuring Bulk Density of coke. In 1961, Alcan adopted the method, and in 1976 modified it, with a slight change in granulometry to the present version. During the years from 1971 to 1978 several efforts were made to improve the method, to gain worldwide acceptance. In the mean time, industries adopted their own granulometry and bulk density methods. In 1978, ASTM was requested to form a study group and ASTM D4292 Standard Test Method for Determination of Vibrated Bulk Density of Calcined Petroleum Coke was introduced in 1983.

In the past, many attempts have been made to correlate different test methods to reveal the effectiveness of each test and to try and correlate them with anode pitching demand. During 1971-1980, several publications (1-6) indicated satisfactory correlation between important anode properties and VBD tests. In 1977, S.S. Jones (4) indicated that porosity of a certain pore diameter range (1-10 μm) is particularly significant to carbon anode consumption efficiency.

In 1980, Gehlbach (3) reported that an increase in anode baked apparent density correlated well with an increase in the -20+48 mesh coke vibrated bulk density, but not as well with other coke density measurements or with mercury porosimetry values. In 1988-89, Belitskus and Danka (5) reported that anode density correlated well with coke vibrated bulk density and coke porosity below 5 μm in diameter. From the previous studies, it clearly appears that, coke porosity is a key factor in optimizing pitch demand and anode density. The easiest and fastest way of measuring coke porosity is Vibrated Bulk Density. A literature search reveals that 1) the precision statement for ASTM D 4292 and other VBD methods are inadequate, and 2) correlation between macro and micro porosity and VBD has not been published.

Review Of Porosity And VBD Measurement Techniques

At present, VBD (28x48 Tyler Mesh (TM)) or VBD (30x50 US Mesh), VBD (8x14 TM), VBD (9x16 TM), VBD (28x48 TM) Natural, AD (10x20 TM) or Pechiney AD, Mercury Intrusion Porosity (16x20 TM) or (10x20 TM), test methods are used widely to determine coke quality for the purpose of estimating the pitch demand. Aluminum Industries are using one or more of the above methods, or their own proprietary methods, to estimate pitch demand. Calcined coke producers are also using one or more of the above tests methods as specified by their customers.

The actual optimum pitch demand observed by the aluminum industry is not universally well predicted by VBD. However, Mercury Intrusion Porosimetry (MIP), which measures porosity directly, works universally to quantify porosity, and therefore can be used to reliably estimate pitch demand. A. J. Edmond Company has performed multiple design experiments and has established relationships of MIP to optimally pitched anodes. Most of the data is governed by confidentiality agreement, and thus can not be published. For many years, VBD has adequately predicted pitch demand between a single buyer and seller. Each VBD method uses a different particle size, and a different preparation method, but they all predict porosity and packing density.

Current Challenges With VBD

The ASTM D4292 VBD method has been questioned several times in the past twenty years, and it is still in question. The current methods are not very specific and can be interpreted in several ways. A decade ago, there were few producers of calcined coke and the problem with the determination of VBD and correlating VBD with pitch demand was low. In the last 10 years, the number of calcined coke producers has doubled, which has increased the likelihood of misinterpretation of VBD test method(s) and the results. In the last several years the coke and pitch quality has deteriorated, and producers are not able to provide coke of consistent quality. Aluminum industries are blending different quality cokes together in the manufacturing of anodes, and with the drawbacks of the VBD test methods they are not getting enough insight into the porosity of the coke, to

optimize the anode properties. ASTM has been working to improve the precision of the methods, both inter-laboratory (repeatability) and intra-laboratory (reproducibility).

As an independent laboratory, A. J. Edmond Company receives coke from all over the world for quantitative and qualitative analysis. Out of all the ASTM and ISO test methods performed on calcined coke, the VBD method reproducibility is among the worst. The strength of the VBD method is that it is a rapid and easy way to estimate the coke porosity. With the current methodology, the coke may meet the specifications set by the marketing and technical groups when it is produced or sold, but it fails in universally predicting pitch demand. Every once in a while, the calcined coke producers and/or aluminum companies, audit the VBD test method D4292 with the hope of resolving this discrepancy. But there has been limited success, due to the poor precision of the test method and the variability of the results obtained. Also, with the increased use of near anode grade calcined coke (shot, under pyrolyzed, higher impurities) in making anodes, it is very important to improve the precision of the test method.

This paper examines correlations between MIP and VBD and provides information to the study group to improve existing and future methods.

Initial Investigation

One focus of our study was to find an alternate test method or a back up method to support VBD. From the historical data, we performed a correlation study of all VBD test method(s) with Mercury Apparent Density and Total Porosity by MIP as shown in Figures 1, 2 and 3. The data used in Figures 1, 2, and 3 were collected over 6-7 months by several technicians. Even though the methods have different particle size and sample preparation, the data showed some correlation, although poor, between the methods. We believe the poor correlations are due to the precision (repeatability) of the VBD test method, different particle size, and different preparation methods. This also reflects that analysis of different particle sizes does not always reveal the actual characteristics of the coke.

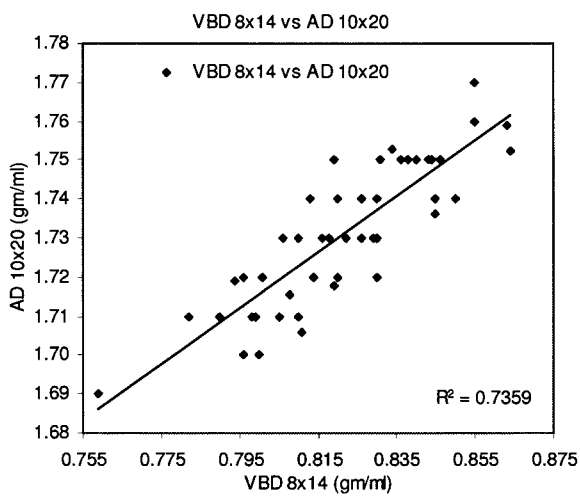

Figure 1. Correlation of VBD (8x14) and AD (10x20)

The correlations were not very promising, but it inspired us to initiate a project to determine Mercury Apparent Density and Porosity by Mercury Intrusion Porosimetry of a single size fraction produced by a single method. We chose a size fraction of 8x14 TM, and 28x48 TM prepared in accordance ASTM D4292 for the study.

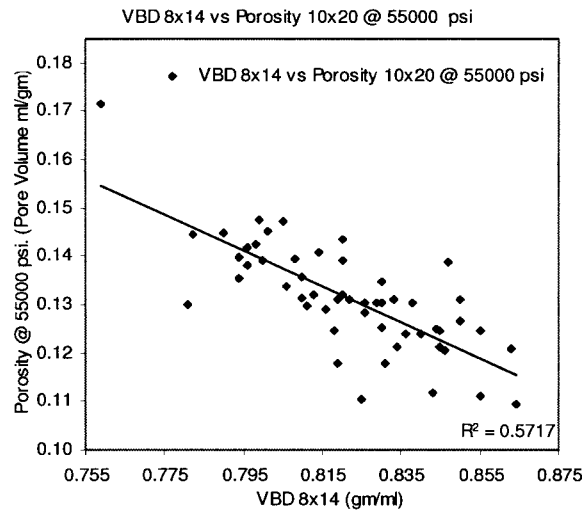

Figure 2. Correlation of VBD (8x14) and Porosity (10x20)

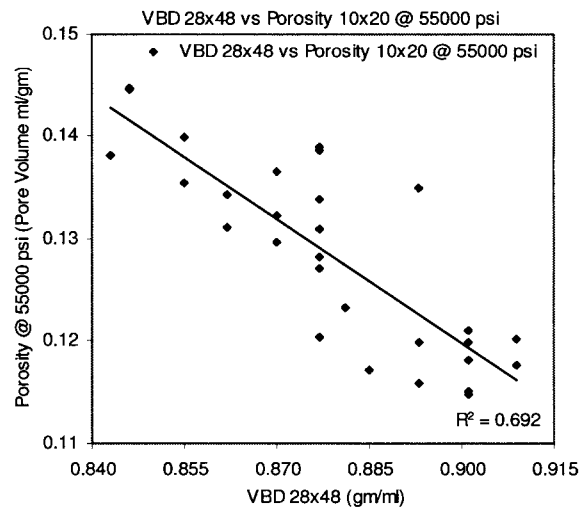

Figure 3. Correlation of VBD (28x48) and Porosity (10x20)

Experimental

Commercial calcined cokes produced by BP and Rain CII, and Laboratory Pilot Plant Rotary Kiln Calcined Coke produced at A. J. Edmond Company were used for the study. The samples for VBD (8x14 TM and 28x48 TM) were prepared in accordance with ASTM D4292-92 (2007) at A. J. Edmond Company, Long Beach. A split of the prepared material was analyzed for VBD as prescribed in the method and another split was analyzed for Porosity using a Micromeritics Autopore IV Mercury Intrusion Porosimeter.

The sample preparation for the MIP analysis was modified for this study, the common practice accepted by industry for porosity involves deoiling of the sample to remove any dedust oil. But here, the goal was to determine the effectiveness of VBD test method for porosity measurement, so the samples were not deoiled and the same particle size was used to determine porosity. All samples were run in duplicate to ensure the quality of analysis.

Initially, 12 samples produced by different commercial calciners using Rotary Kiln technology were studied. The data of VBD and Porosity were correlated against each other. The selected samples had VBD (8x14) values ranging from 0.766 to 0.847 g/cc and total porosity ranging from 19% to 25%.

The second experiment was carried out on a second set of 12 samples produced by different commercial calciners using Rotary Kiln technology. Some of the coke samples were blended with non anode grade coke. The selected samples had VBD (28x48) values ranging from 0.833 to 0.980 g/cc and total porosity ranging from 22% to 35%.

Results and Discussion

The results from the VBD (8x14) analysis were correlated against total porosity obtained by MIP. Figure 4 shows that the VBD data correlates well with the total porosity with a coefficient of determination (R^2) > 0.89. This shows that the VBD method is effective enough to estimate the total porosity. Figure 5 shows a plot of the coefficient of determination of VBD and Porosity at different pore diameters and pressures.

The data indicates that the correlation is better when porosity obtained at high pressure is included. At 20,000 psi 92% of total porosity is filled by Mercury and the coefficient of determination (R^2) is above 0.80. While at atmospheric pressure MIP fills on average 30% of total pores and the coefficient of determination (R^2) is below 0.60. MIP at atmospheric pressure produces identical results as Pechiney Apparent Density, but it does not reveal any details useful for optimizing total pitch demand, since it does not include meso-micro porosity. The comparison of MIP and Pechiney Apparent Density is not included in this study.

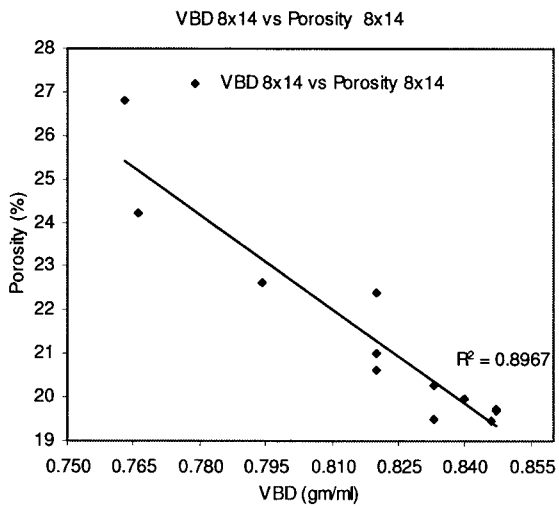

Figure 4. Correlation of VBD 8x14 vs Porosity 8x14

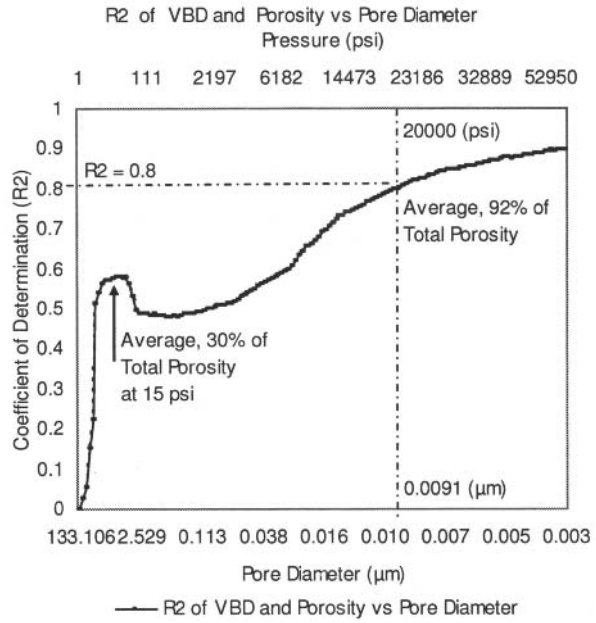

Figure 5. Coefficient of determination of VBD 8x14 and Total Porosity vs Pore Diameter

Figures 6 and 7 show the pore size distribution of samples with different VBD. The samples having high VBD are showing low porosity and vice versa. The samples with VBD 0.820, 0.833 and 0.846 showed a similar pore size distribution pattern with a moderate difference in porosity of macro pores up to 0.5 µm pore diameter. The porosity pattern for samples with VBD 0.766 and 0.794 was very different. The sample of VBD 0.794 showed high macro (>0.05 µm pore diameter) porosity compared to the sample of VBD 0.766, but the latter sample showed high Meso and Micro (<0.05 µm pore diameter) porosity. The total porosity of sample with VBD 0.766 was higher than sample with VBD 0.794.

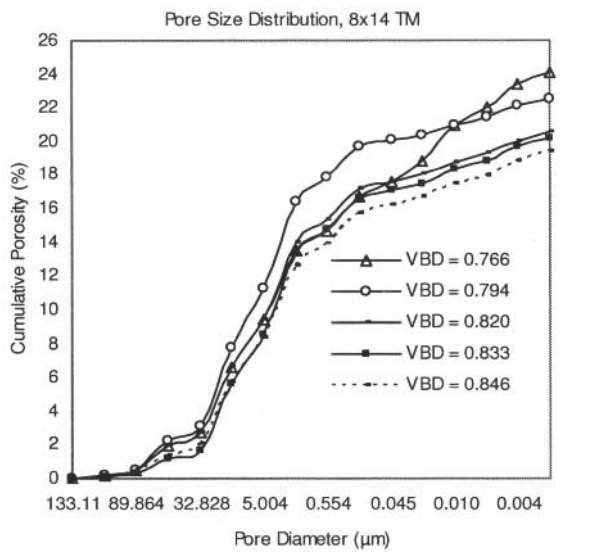

Figure 6. Pore size Distribution chart for samples of different VBD 8x14

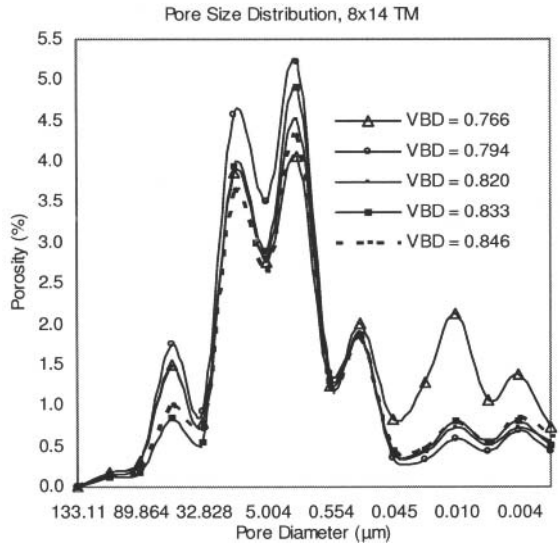

Figure 7. Pore size Distribution chart for samples of different VBD 8x14

Figure 8 shows a comparison of pore size distribution data for samples having 0.820 and 0.766 VBD 8x14. These four samples are from different calcined coke producers. The difference in porosity between both sets of samples is 1.7% and 2.6% respectively. Sample 1 and Sample 2 have identical VBD values of 0.820. The VBD results are same, but the pore size distribution is very different. Both samples showed a delta porosity (difference of cumulative porosity above 0.10 µm between two samples) of -2.77% up to 0.10 µm pore diameter, but below 0.10 µm, delta porosity (difference of cumulative porosity below 0.10 µm between two samples) is +1.08%. A similar trend was observed for sample 3 and sample 4.

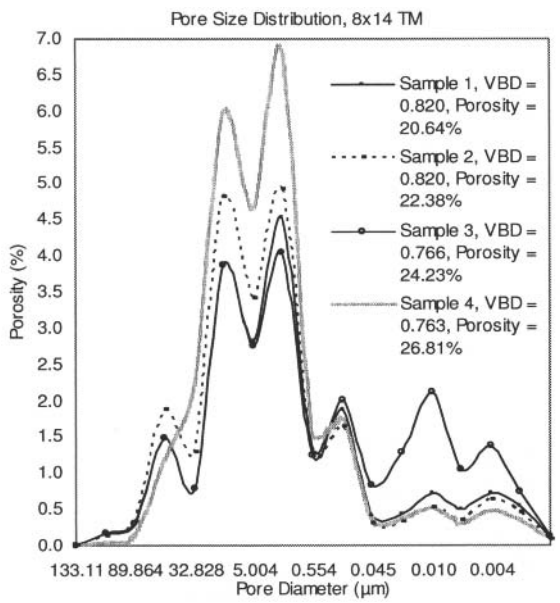

Figure 8. Pore Size Distribution chart for samples of same VBD 8x14

Sample 1, VBD 0.820 and Sample 3, VBD 0.766 showed a very similar pore size distribution up to 0.10 µm with a delta porosity (difference of cumulative porosity above 0.10 µm between two samples) of +0.5%, but below 0.10 µm the delta porosity (difference of cumulative porosity between two samples below 0.10 µm between two samples) is -4%. Due to this difference in porosity below 0.10 µm, sample 3 showed a lower VBD compared to sample 1. This shows that the micro porosity has a significant influence on VBD.

Table 1 shows the delta porosity at different pore diameter between sample 1&2, sample 1&3 and sample 3&4.

	Delta Porosity	Delta Porosity	Delta Porosity	Pore Diameter (µm)
Sample	1-2	1-3	3-4	
	0.01	0.00	0.00	133.106
	0.04	0.00	0.12	111.231
	-0.04	-0.02	0.17	89.864
	-0.38	-0.01	0.32	45.122
	-0.50	0.01	-1.45	32.828
	-0.95	0.00	-2.10	11.319
	-0.59	0.05	-1.90	5.004
Cumulative Delta above 0.1	-0.41	0.47	-2.80	1.051
	0.07	-0.01	-0.29	0.554
	-2.77	0.50	-7.91	
	0.25	-0.12	0.26	0.095
	0.10	-0.41	0.48	0.045
	0.10	-0.85	0.92	0.023
	0.21	-1.40	1.60	0.010
	0.17	-0.55	0.75	0.007
	0.11	-0.64	0.90	0.004
Cumulative Delta below 0.1	0.14	-0.08	0.39	0.003
	0.01	0.04	0.04	0.003
	1.08	-4.02	5.33	

Table 1. Cumulative Delta Porosity (%) for Samples 1, 2, 3 and 4.

The above observations showed that the VBD correlates well with overall porosity but it does not reveal the proportion of macro and meso-micro porosity.

A similar set of experiments and comparisons were carried out on calcined coke commercially produced from different sources and calcined in rotary kilns. Some of these coke samples were blended with non anode grade coke. In this set of experiments, VBD and Porosity was analyzed on 28x48 TM size fraction prepared according to ASTM D 4292 (2007). The VBD results were correlated against the total porosity obtained by MIP as shown in Figure 9. The VBD 28x48 data correlated well with the Porosity with coefficient of determination R^2 >0.84. Figure 10 shows a plot of coefficient of determination of VBD and Porosity at different pore diameter and pressure. At 800 psi 87% of total porosity is filled by Mercury and the coefficient of determination (R^2) is above 0.80. This data indicates that the VBD correlates well with the total porosity.

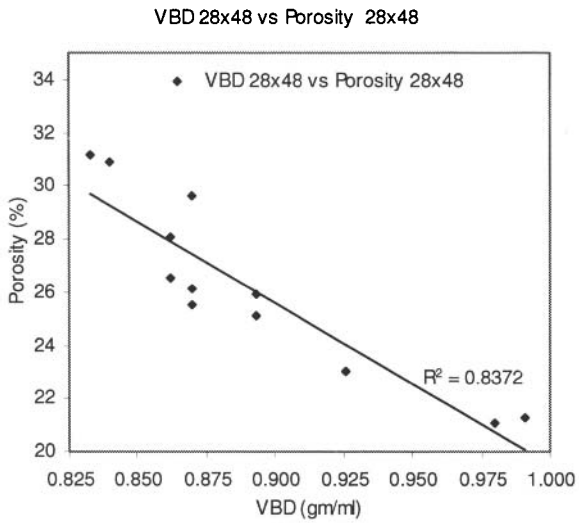

Figure 9. Correlation of VBD 28x48 vs Porosity 28x48 TM

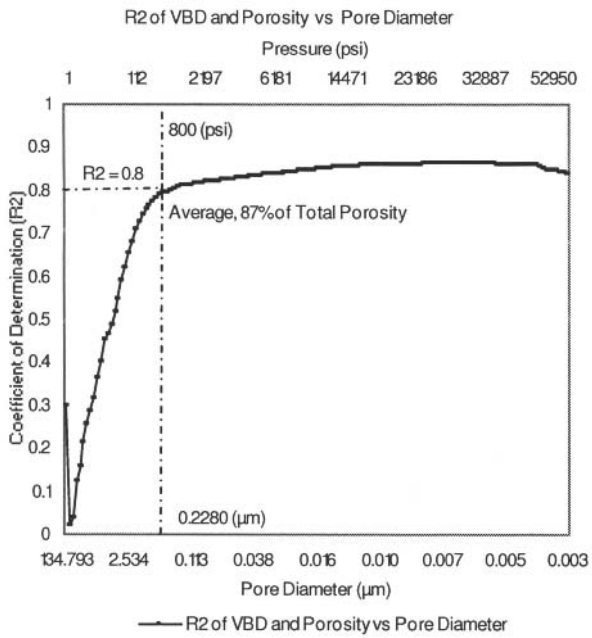

Figure 10. Coefficient of determination of VBD 28x48 and Total Porosity vs Pore Diameter

Figure 11, shows the pore size distribution pattern for samples with different VBD 28x48. The samples having high VBD are showing low porosity and vice versa. Figure 12 shows the comparison of three VBD 28x48 samples having similar VBD results. These samples have the same VBD results but different total porosity. All three samples; A, D and E showed significant difference in the porosity above 0.5 µm. and below 0.5 µm the difference in porosity was minor.

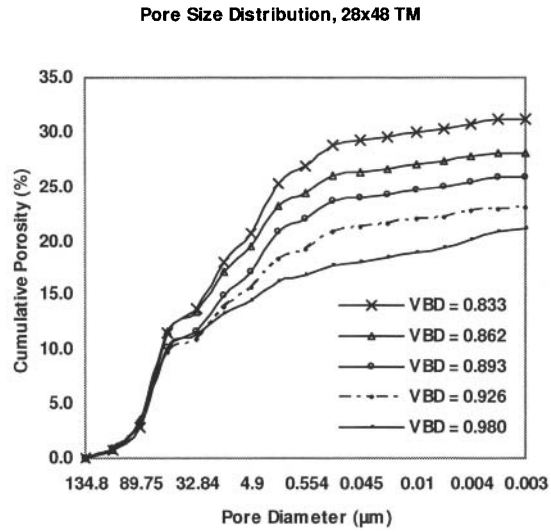

Figure 11. Pore size Distribution chart for samples of different VBD 28x48

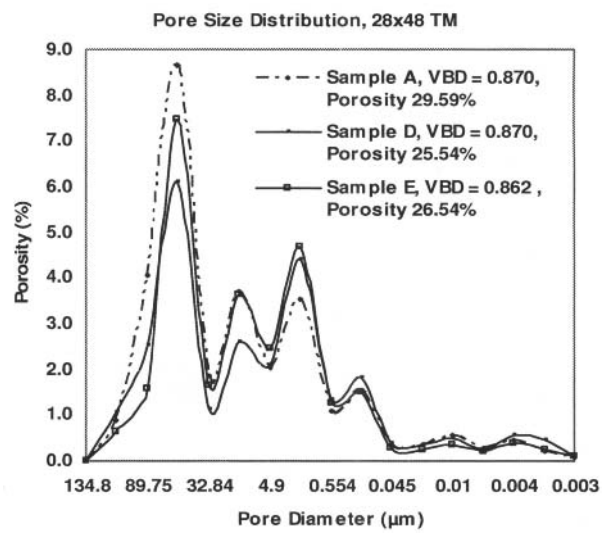

Figure 12. Pore size Distribution chart for samples of same VBD 28x48 TM

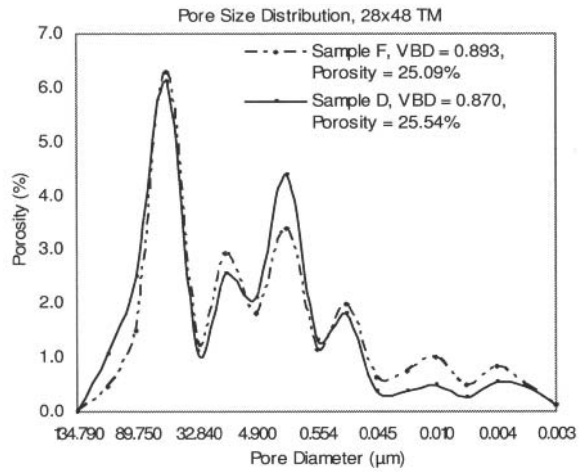

Figure 13. Pore Size Distribution of a Sample with different VBD 28x48

Figure 13 shows the pore size distribution of two VBD 28x48 samples. The total porosity of these samples is very similar but the VBD results are very different.

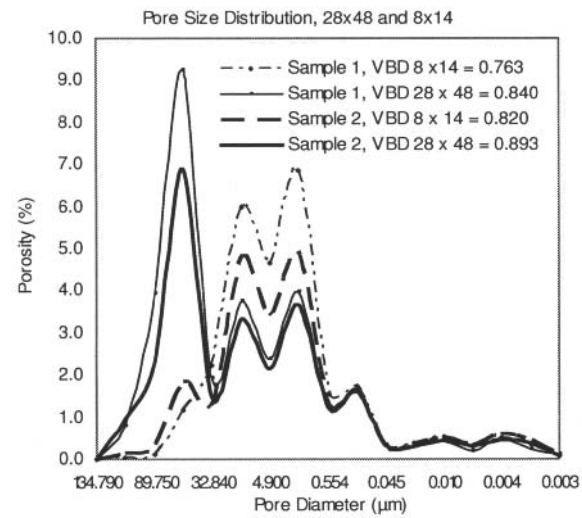

Figure 14. Pore Size Distribution of a Sample (Two Different Particle Size)

Figure 14 shows a comparison of pore size distribution of two size fractions, 8x14 and 28x48, prepared from two different coke samples. For both samples for different particle size, there is a different pattern for porosity, but the porosity below 0.55 µm pore diameter (above 400 psi) is very similar. This observation reveals the fact that the large pores are destroyed on reduction to smaller particle size (7). Also, the 28x48 material is showing high macro porosity especially up to 32 µm pore diameter (5.5 psi) compared to 8x14 material. This observation could be due to the fact that internal voids (large pores) are more easily accessible to mercury through cracks or paths in the smaller particles because they are closer to the surface of these smaller particles. This observation may also be a function of surface irregularities (jagged edges with pits larger than 32 µm) present on the surface of the smaller particles generated with greater crushing energy. Gehlbach (8) mentioned in his study that the coke isotropy, coke porosity, severity of crushing and scalping of oversize or undersize coke during sample preparation has great influence on particle size, shape, surface irregularities and VBD. The current study could not determine the influence of such surface irregularities on VBD, but it is observed that the low VBD coke has more porosity associated with surface irregularities.

Conclusions

- Vibrated Bulk Density does not universally correlate to total porosity.
- VBD correlates best with total porosity obtained by MIP, but it is not a good predictor of micro (less than 0.05 µm) or macro porosity (pore size distribution).
- Mercury Apparent Density at atmospheric pressure does not reveal sufficient data on pore volume distribution to be a reliable predictor of total porosity.
- Historical correlation between important anode properties and simple vibrated bulk density tests could be ineffective in the present calcined petroleum coke industry due to blending of different quality coke, degradation of coke quality, likelihood of misinterpretation of VBD test method(s) and other problems associated with correlating the test methodologies revealed in this study.
- Presently VBD results must be corroborated by MIP to provide all necessary information for predicting the pitch demand for a calcined coke and behavior of the sized aggregates for making higher quality anodes.

References

1. P. Rhedey, "A review of Factors Affecting Carbon Anode Consumption in the Electrolytic Production of Aluminum," Light Metals 1971, TMS-AIME, New York, NY (1971) pp. 385-408.
2. D. Belitskus, Optimization of Raw Materials and Formulations for Hall-Heroult Cell Electrodes," Third Yugoslav Symposium on Aluminum, (preprints) Edited by Prof. Andrej Paulin, University of Ljubjana (1978).
3. R. E. Gehlbach, E. E. Hardin, L. I. Grindstaff, and M.P. Whittaker ; " Coke Density Determination and Its Relationship to Anode Quality," Paper Presented at the 109th AIME Annual Meeting, Las Vegas, NV, Feb 24-28 (1980).
4. S. S. Jones, R. D. Hilberbrandt and M.C. Hedlund, "Variation of Anode Performance with Coke Quality," Paper No. A77-97, presented at the 106th AIME Annual Meeting, Atlanta, GA, 1977.
5. D. Belitskus, D. J. Danka, "A comprehensive determination of effects of coke properties on aluminum reduction cell anode properties, Light Metals, 1989, 429-439.
6. D. Belitskus, "Evaluating Calcined coke for Aluminum Smelting by Bulk Density," Light Metals 1974, TMS-AIME, New York, NY (1974) pp. 863-878.
7. D. Belitskus, "Standardization of a calcined coke bulk density test," Light Metals, 1982, TMS-AIME, Dallas, Texas, (1982) pp. 673-689.
8. R. E. Gehlbach and W. E. Walsh, "Influence of Sample Preparation on Petroleum Coke Properties", Light Metals 1995, pp. 539-543