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EFFECTS OF PHYSICAL PROPERTIES OF ANODE RAW MATERIALS ON THE PASTE COMPACTION BEHAVIOR

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Abstract

The current study investigates the effects of coke particle characteristics and paste formulation on the flowability and the compression behavior of anode pastes. Shape factor and texture of different fractions of cokes were characterized using an image analysis system where the characteristics of each coke were correlated to its vibrated bulk density (VBD). A compression test was designed to study the effects of particle characteristics and paste recipe on the compactability of pastes. The test was applied on four anode pastes, prepared from different coke types, particle size distributions and pitch contents. It was observed that the compression test is significantly sensitive to any changes in raw materials characteristics and formulations. Consequently, the compression test may be used as a tool for evaluating anode quality in relation with material variations.

Introduction

Consistent high quality anodes are a basic requirement of anode plants. Anode properties are influenced by several factors including raw materials properties, anode formulation and anode making parameters. Variations in raw materials properties are considered as one of the most significant challenges in anode manufacturing industry which affect anode quality and consistency. The influences of coke properties, particle size and distribution in the anode formulation have been reported by several authors [1-4]. Such an enormous number of variables involved in anode manufacturing process makes difficult the control and optimization of the final anode quality. Thus intermediate quality indices are required to control each step of the process and to take the corrective actions within the subsequent steps in order to keep the anode quality consistent.

Green and baked anode properties are conventionally used as indicators of anode quality. Green anode density and permeability are measured as quality indices. However, these indices are still influenced by a number of variables including raw materials properties and mixing and compaction parameters. By defining specific paste quality as an intermediate process quality index, it would be possible to limit the number of variables to be controlled in the subsequent manufacturing steps. These indices would be used to correlate materials properties, paste formulation and mixing factors with anode properties. These paste indices could also be used as indicators for paste compaction behavior for the purpose of modelling the anode forming, fabricated either by hydraulic pressing or by vibro-compaction.

In the current research study, a compression test was used to study the paste compression behavior. Sensitivity of this test to variations in materials and formulations was evaluated. When using this specific test, it is possible to investigate the effects of coke type, particle size distribution and formulation on the formability of paste. In addition, shape factor and texture of coke particles were measured using an image analysis system to investigate the influence of coke particles characteristics on their flowability and compaction behavior.

Experimental procedures

Two commercially available calcined petroleum cokes and a coal tar pitch were used as raw materials for anode manufacturing. The cokes used were Conoco coke (A) and ZCGG coke (B) with a real density of 2.075 g/cm^3 and 2.063 g/cm^3, respectively, and with a chemical composition, as shown in Table I. The softening point of pitch was 109°C and its quinoline insoluble content was 15.5%. The cokes were crushed using jaw and roll crushers and sieved to seven size fractions. Four formulations were prepared with different particle size distributions, as listed in Table II, to reveal the effect of size distribution. Particle size distributions consisted of a reference distribution, which is used in the industry, and two other distributions; one with 5% more large aggregates and the other with 5% more fine particles than reference. In addition, one formulation of coke B with reference granulometry was used to reveal the effect of particle properties in different coke types. The coke types and coke/pitch ratios are listed in Table III. Pitch contents were chosen based on the fine fraction in the formulation. Large amount of fine particles increases the specific surface area of coke particles and consequently for wetting these fine particles, a higher content of pitch is required.

Table I. Chemical composition of Conoco (A) and ZCGG (B) cokes

Coke	Na ppm	Si ppm	%S	Ca ppm	V ppm	Fe ppm	Ni ppm
Conoco	<50	10	1.1	130	120	70	90
ZCGG	<50	20	3.2	<10	260	60	150

Vibrated bulk density (VBD) was measured for four fractions of cokes A and B, and the blended coke fractions, to study the effects of coke particle characteristics on their packing behavior. ASTM D-4292 standard test method [5] with vibration time of 2 minutes was used for VBD tests.

Table II. Particle size distribution of pastes

Particle size (mesh)	Reference size	5% More fine	5% More large
+6	13.6%	12.8%	14.4%
-6+14	15.6%	14.8%	16.4%
-14+30	16.3%	15.4%	16.9%
-30+50	10.4%	9.8%	11%
-50+100	8.1%	7.5%	8.6%
-100+200	10.5%	9.7%	10.7%
-200	25.5%	30%	22%

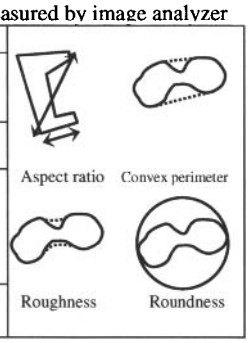
Table III. Coke type and pitch content of pastes

	Reference size	5% More fine	5% More large
Coke	A and B	A	A
Pitch, wt%	13.8	15.8	13

*Coke A: Conoco and coke B: ZCGG

Single coke fractions were impregnated by a polishing resin under mechanical vacuum and polished for microscopic analysis. In the current study, a Nikon Ephiphot optical microscope equipped with an image analysis system (Clemex, vision) was used to analyse the particles characteristics which include aspect ratio, compactness, roughness, sphericity, roundness and porosity. These parameters describe various aspects of a particle which may be correlated to packing and flow behavior of the particle. Based on the definitions of these parameters, given in Table IV, a more circular particle has lower aspect ratio and higher values for compactness and roundness. Higher values of roughness show smoother surface of the particle.

Table IV. Particle characteristics measured by image analyzer

Factor	Definition	
Aspect ratio	Ratio of longest dimension to shortest dimension	
Compactness	Ratio of area over convex perimeter	
Roughness	Quantifies the jaggedness of object's edges and is the ratio of convex perimeter to perimeter.	
Roundness	Roundness of object's edges	

A rigid steel cylindrical mold with the internal diameter of 89 mm was used to study the compression behavior of anode pastes. Coke fractions and pitch were preheated at 185°C for 120 and 30 minutes, respectively, and then were mixed at 185°C for 10 minutes using a domestic Hobart N50 mixer. The paste was then cooled to 125-130°C to allow the fumes to be escaped before pressing. Compression test was carried out at 130°C, using an MTS Servohydraulic press working at a constant displacement rate of 10 mm/min and a maximum force of 220 kN. The MTS machine provides displacement-force data at a rate of 10 readings per second. The apparent density of pressed samples was measured based on the final volume and mass. Having the final height of the sample and displacement rate of the punch during the test, the apparent density was calculated for each displacement value as a function of the applied force. The evolution of the paste density was then plotted as a function of applied pressure and presented in the form of pressure-density curves.

A Micromeritics helium pycnometer (AccuPyc II 1340) was used to measure the volume of green anode samples where a core sample, with a diameter of 2.5 cm, was drilled in each green sample for this purpose. The percentage of porosity in green samples could be determined using the green apparent density and pycnometry results.

Results and discussion

The current section presents the results related to the effects of granulometry and particle properties on the flowability of the particles based on the results of vibrated bulk density tests. Compression behavior of anode paste then will be used to study the effects of size distribution and coke type on the compactability of the pastes and the utility of this test will be emphasized. The green apparent density and the vibrated bulk density results will be correlated to the measured porosity of the green samples.

The vibrated bulk densities of blended coke fractions used to prepare the samples are shown in Figure 1. Bulk density of coke A has increased with reducing the large fractions (>300 μm) and increasing the fine portion (<74 μm) in the formulation. These results had been expected since the smaller particles fill the inter-particle voids without increasing the volume [6, 7]. It has also been reported by other authors [8] that higher amounts of fine particles, results in higher VBD of dust fraction and multi-fraction mixtures, up to a maximum value. In addition, the bulk density of particles increases with decreasing the particle size, because large pores are destroyed with size reduction [6].

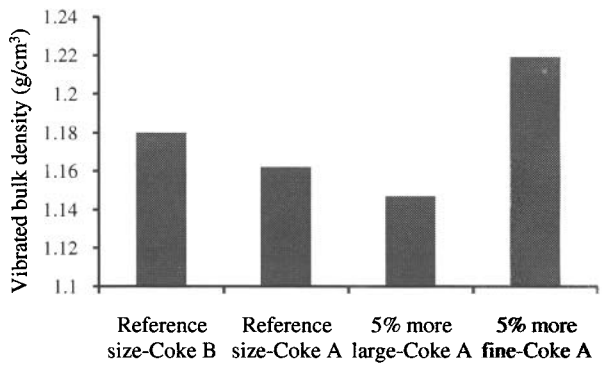


Figure 1. Vibrated bulk density (VBD) of blended coke fractions

With regard to blends of cokes A and B with reference particle size, it may be observed that they exhibit different bulk densities, as shown in Figure 1. This difference is an indication of the influence of physical properties of coke particles on the flowability and rearrangement during vibration. This different behavior may be related to irregularities on the particle surface which result in inter-particle friction and bridging of the particles. These effects will be elaborated in the following paragraph.

Coke particles were characterized using an image analysis system to study the correlations which may exist between particle characteristics and their flowability. Table V shows the image analysis results and VBD for each coke fraction. Regarding coke A compared to coke B, for the same size range, it may be observed that vibrated bulk density of the particles increases with

lower values of aspect ratio; with lower level of porosity; and with higher values of compactness, roughness, sphericity and roundness. More spherical particles are expected to display better packing behavior and higher bulk density values than platelike or needlelike particles [6, 9-11]. Although coke B displays lower real density than coke A, it provides higher VBD values for all fractions except for -200 mesh particles. Coke B particles revealed lower aspect ratio and higher compactness and roundness values than did coke A. Since these factors affect particle flowability, coke B has better packing behaviour which most likely compensates the effect of coke density and results in higher VBD values. For -200 mesh particles, on the other hand, coke A with better flowability factors and lower porosity resulted in higher VBD.

Table V. Shape factors, texture and VBD of coke particles

Particle properties	Coke type and size (mesh)			
	-6+14		-14+30	
	A	B	A	B
Aspect ratio	1.86	1.69	1.87	1.74
Compactness	0.607	0.657	0.719	0.761
Roughness	0.802	0.766	0.915	0.957
Sphericity	0.406	0.4	0.678	0.794
Roundness	0.41	0.474	0.527	0.569
%Porosity	28.73	25.98	23.41	19.51
VBD	0.841	0.953	0.927	1.02
Particle properties	Coke type and size (mesh)			
	-30+50		-200	
	A	B	A	B
Aspect ratio	1.99	1.75	2.02	2
Compactness	0.707	0.766	0.663	0.638
Roughness	0.95	0.963	0.93	0.885
Sphericity	0.707	0.804	0.583	0.507
Roundness	0.5	0.567	0.437	0.427
%Porosity	21.34	20.74	3.3	4.64
VBD	0.919	1	0.969	0.945

Compression tests were carried out for four formulations to study the influences of size distribution on the compaction behavior of paste. The formulations were prepared using two coke types with different particle size distributions and three coke/pitch ratios, as shown in Tables II and III. Figure 2 shows the average curves obtained from three compression tests for each paste formulation. It may be observed that there is a meaningful difference among these curves and the test is capable of illustrating the effects of materials variations on the paste compression behavior. When using coke A, the final achieved density decreased by increasing the content of large fractions; while the formulation with higher percentage of fine particles revealed higher apparent density compared to the reference granulometry. These observations agree with other studies where it was reported that green apparent density increases when using higher amounts of fine fraction and using suitable amount of pitch [7]. Small and fine particles display better filling ability to the inter-particle voids which lead to improved density. In addition, by increasing the fine content, more binder matrix is available to fill the coke pores. However, fine content beyond a specific upper limit may not have any significant effect on the green density [8] or may reduce it due to more inter-particle friction and particle bridging [9]. For the three pastes made with coke A, the trend of VBD of the coke blends is the same as that of green apparent density. Both VBD and green apparent density are observed to increase with increasing the fine fraction.

The pastes with the same particle size and pitch content, but different sources of coke, showed quite separated curves. This may be related to particle characteristics, as observed in the case

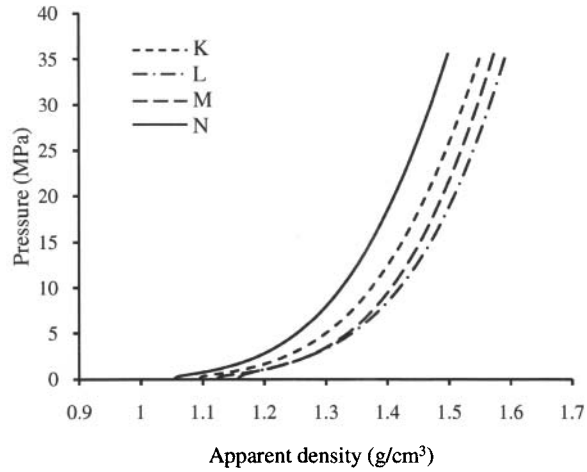


Figure 2. Compression curves with variations in paste formulations and coke source (K: Coke A, 5% large more than reference; L: Coke A, 5% fine more than reference; M: Coke A, reference granulometry; N: Coke B, reference granulometry).

of VBD results. In the present study, the interesting result is that coke A with more elongated and rough particles and lower bulk density provided samples with higher green apparent density, as shown in Tables V and VI. These results agree with other studies where it was reported that although aggregate bulk density is an indication of porosity, packing and size distribution in a powder bed, there is no consistent correlation between aggregate bulk density and green apparent density [7]. On the other hand, other studies reported that irregular shape and rough surface of particles up to 12 mm prevent the movement in a viscous medium and affect the final anode properties [12]. This misleading may be related to the fact that the flow behavior of particles is different in the presence of binder matrix. The inconsistency between particle porosity and bulk density is another reason for this contradiction [11]. In addition, some open pores of coke A may be filled with binder matrix which increases the green apparent density. The results show that VBD cannot be used alone to show the compression behavior. In other words, cokes with higher vibrated bulk density will not necessarily result in denser anodes.

Table VI. Density and porosity of green samples

Sample	Helium pycnometry	GAD g/cm^3	VBD of blend	%Porosity
Reference size-Coke B	1.875	1.498	1.18	20.11
Reference size-Coke A	1.88	1.572	1.162	16.38
5% more large-Coke A	1.893	1.551	1.147	18.07
5% more fine-Coke A	1.847	1.592	1.219	13.81

Generally, the compression tests used in this study could be used to investigate the influences of materials properties and paste formulation on the compression behavior of paste during forming process. The data and curves obtained from this particular test provide a better knowledge of the paste behavior when it is formed by hydraulic pressing and may be used for modelling the compaction behavior.

The percentage of porosity in green samples was determined using the green apparent density and pycnometry results. Table VI shows the density of green core samples measured by helium pycnometry compared with the green apparent density. This comparison could reveal the volume fraction of open pores within a porous material. Porosity of green samples can therefore be calculated using equation (1):

$$\%Porosity = \frac{(He\ Pycnometry) - GAD}{He\ Pycnometry} \times 100 \quad (1)$$

where He pycnometry and GAD are density measured by pycnometer, and green apparent density, respectively. The results of helium pycnometry confirmed the green apparent density measured for pressed samples. It was observed that, increasing the porosity level in the pressed samples results in reducing their green density, as shown in Table VI. However, sample with 5% more fine particles has higher GAD but lower helium density than sample with 5% more large particles. This may be related to the fact that some pores may be blocked by the binder matrix to create closed pores which increases the volume of the material measured by pycnometer and reduces the helium density.

Conclusions

Paste characterization may be used as an indicator to estimate anode quality. Paste compression test is sensitive to variations of raw materials properties. Compression behavior, as a paste property, may be used to correlate paste formulation and physical properties of coke to its compactability. Shape factor and texture of the particles influence the bulk density of coke and may be used to describe the compactability of the particle bed. Vibrated bulk density, however, is not the only factor which controls the density after compaction.

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