A. Tomsett and J. Johnson (Eds.), *Essential Readings in Light Metals*

EVALUATING CALCINED COKE FOR ALUMINUM SMELTING BY BULK DENSITY

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Improved tests were developed for rating calcined cokes for aluminum smelting according to bulk density. The maximum density possible in blending particle size fractions of a coke and the sizing which produced the maximum density were reliably predicted from simple bulk density measurements of selected fractions. Green apparent densities and baked apparent densities of small scale anodes were correlated with coke bulk densities.

Introduction

Calcined cokes having high bulk densities produce aluminum smelting anodes with good properties. As examples, Pippin (1) has related that anode performance deteriorates and carbon usage increases as coke bulk density falls below 0.72 g cm^{-3} (45 lb. $ft.^{-3}$; -8+14 mesh, vibrated) and that if bulk density falls below 0.64 g cm^{-3} (40 lb. $ft.^{-3}$), cell operation can be seriously disrupted by poor anode performance. Rhedey (2) found a 0.45 percent decrease in anode consumption per 0.01 g cm^{-3} increase in coke bulk density (-20+35 mesh, vibrated) for both prebaked and Soderberg test anodes.

The present work was carried out to develop an accurate indicator of coke bulk density. The maximum bulk density possible from blending of fractions was determined for twelve cokes and correlated with more rapidly performed bulk density determinations. In addition, relationships among coke bulk density, green anode apparent density, and baked anode apparent density were determined for small test anodes.

Determination of Maximum Coke Bulk Density

Coke Selection and Preparation

Eight of the cokes used in this investigation were petroleum cokes used commercially in anodes for smelting aluminum. Coked gilsonite, a gilsonite coke-petroleum coke product, and two coal tar pitch cokes (from Japan) were tested for comparison. All were calcined in commercial rotary kilns. The cokes were crushed in a roll crusher and the finest sizes produced with a Sturtevant No. 2 sample grinder. Cokes were separated into seven Tyler fractions ranging from -4+8 mesh to -200 mesh.

Experimental Procedure

While, of course, an absolute maximum bulk density determination would involve optimization of many closely sized fractions, this would not only be extremely tedious but impractical from a production standpoint. Therefore, the procedure adopted in this work was to test only blends which could be derived using the typical plant coarse, intermediate, and fine fractions shown in Table I.

Table I. Sizings Used in Maximum Bulk Density Determinations

	Percent Tyler Fraction		
Tyler Fraction	Coarse	Intermediate	Fine
-4+8	15	0	0
-8+14	43	1	0
-14+28	31	12	1
-28+48	7	29	3
-48+100	2	25	15
-100+200	1	17	28
-200	1	16	53

Four hundred gram blends of coke fractions were placed in a 1000-ml graduated cylinder clamped to the head of a vibrator (Syntron Jogger Model J-1A) and the coke vibrated to maximum compaction. Bulk densities were calculated and plotted on triangular coordinate paper (as percent coarse, intermediate, and fine fractions) and iso-density lines drawn. Potentially higher density compositions suggested by the iso-density lines were tested and maximum bulk density reached in 20 or more trials.

Results

Maximum bulk densities as well as some of the other coke properties are given in Table II.

Maximum bulk density sizing was not constant for the twelve cokes but varied according to density. While there was considerable overlap among the individual cokes, arranging them into groups of four (low, medium, and high bulk density) exemplifies the trend (Figure 1). All were "hole-in-the-middle" type formulations (less intermediate material than coarse and fine material); but as maximum bulk density increased, the aggregate became coarser. (The reason for this will be discussed below.)

From the trend shown in Figure 1, it is obvious that maximum bulk density sizing for a given coke can be estimated if the maximum bulk density can be predicted on the basis of some more rapidly performed bulk density determination.

Table II. Maximum Bulk Densities and Other Coke Properties

Arbitrary Coke Designation	Type of Coker Feedstock	Maximum Bulk Density, $g\ cm^{-3}$	Ash Content*, %	Sulfur Content, %	Real Density**, $g\ cm^{-3}$
A	gilsonite	1.342	0.86	0.30	1.96
B	petroleum resid	1.333	0.51	0.84	2.03
C	gilsonite-petroleum resid	1.319	0.79	0.30	1.97
D	petroleum resid	1.311	0.23	0.97	2.07
E	coal tar pitch	1.306	0.13	0.12	2.02
F	" " "	1.300	0.14	0.12	2.07
G	petroleum resid	1.286	0.25	1.18	2.05
H	" "	1.247	0.30	1.00	2.07
I	" "	1.226	0.20	1.74	2.06
J	" "	1.222	0.65	1.22	2.06
K	" "	1.194	0.28	1.01	2.04
L	" "	1.189	0.46	0.99	2.10

*Determined at 750°C.
**Density of -200 mesh fraction in kerosene.

Correlation of Bulk Densities of Closely Sized Fractions with Maximum Bulk Densities

Determination of Bulk Densities of Closely Sized Fractions

Bulk densities (vibrated) of fractions ranging from -4+8 mesh to -200 mesh were determined for each coke (Figure 2).* As coke particle size decreases, bulk density generally increases since large pores are annihilated in the grinding process. Some of the cokes have a fairly continuous pore size distribution, as indicated by a more or less uniform increase in bulk density with decreasing particle size, but most of the curves have plateaus, indicating a discontinuous pore size distribution. The coal tar pitch cokes are characterized by more uniform bulk densities (except for the -200 mesh material), indicating a uniform fine pore structure. These deductions on pore size distributions were qualitatively verified by photomicrographs of polished sections of coke particles and could probably be demonstrated more precisely with a porosimeter.

The reason for the increase in the amount of fines in the maximum bulk density formulation as coke bulk density decreases can also be deduced from the data in Figure 2. The spread in bulk densities is greater in the coarse fractions than in the fine fractions (especially the -200 mesh fraction). For a material consisting of particles of different porosity as well as size, the maximum bulk density is a compromise between minimization of interparticle voids (best packing) and minimization of pores within particles (use of high density particles). For the low bulk density cokes, use of a large amount of high density fine particles increases bulk density even though packing may not be as efficient as with a coarser blend.

Results

The best correlation between maximum bulk density and the bulk density of a closely sized fraction was determined by fitting the data (by computer) to second order equations. Figure 3 shows that the -28+48 mesh fraction was the best single fraction indicator of overall bulk density. Average of the bulk densities of the -14+28 and the -28+48 mesh fractions and average of the bulk densities of the -28+48 and the -48+100 mesh fractions were slightly better. Average of the -14+28, -28+48, and -48+100 mesh fractions was the best indicator, and correlation with maximum bulk density is shown in Figure 4. Neither any other average of fractions (including the average of up to all seven fractions) nor a blend of equal amounts of all fractions was a better indicator. Based on these data, of the two bulk density tests reported in use, the density of the -20+35 mesh fraction (which should be close to the average of the -14+28 and -28+48 mesh fractions) appears to be a much better indicator of overall bulk density than the density of the -8+14 mesh fraction.

Estimation of Maximum Bulk Density Sizing

Prediction of maximum bulk density of a coke makes possible an estimation of maximum bulk density sizing. From the data in Figure 1 and using the average of the bulk densities of the -14+28, -28+48, and -48+100 mesh fractions, Figure 5, which indicates the approximate amount of each fraction in the maximum bulk density formulation, was constructed and successfully used to predict the maximum bulk density sizing of several cokes not included in the original investigation.

Relationships Among Coke Bulk Density, Green Anode Apparent Density, and Baked Anode Apparent Density

Preparation of Anode Samples

Two thousand gram mixtures of coke (sizing for maximum bulk density) and various amounts of coal tar pitch (110°C softening point) were blended for 30 min. at 140°C in a 3.8 liter (1 gal.) sigma-blade mixer and pressed into 10.1 cm (2 in.) diameter, approximately 13 cm (5 in.) long samples by the application of 27.6 Mn m^{-2} (4000 psi) pressure in a mold preheated to 140°C. Green apparent density was calculated after weighing in air and water.

Green anodes were packed in calcined coke and baked under a nitrogen purge in an electrically heated furnace at an upheat rate of 10°C $hr.^{-1}$ to 550°C and 30°C $hr.^{-1}$ to 1100°C and held at 1100°C for 10 hr. Baked apparent density was calculated after weighing in air and water. Volume contraction (or expansion) during baking was also calculated.

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*The bulk density of the -200 mesh fraction is to a large extent dependent upon the minimum particle size and particle size distribution in this fraction, which probably varied from coke to coke, so this value is not as reliable as the others.

Effect of Coke Bulk Density on Green Anode Apparent Density

Green anode apparent density increased linearly with increasing maximum bulk density of the coke. Figure 6 shows this for anodes containing 18 percent pitch; results were similar with 16 and 20 percent pitch. However, green apparent densities were higher than predicted on the basis of merely forcing pitch into voids and pores; i.e., assuming no change in aggregate volume during anode forming. These predicted values are indicated by the dashed line, which doesn't take into account separation of particles by a coating of pitch (which would make the predicted green apparent densities even lower). Possibly, fracturing of protrusions on particles, enabling them to fit together more closely, takes place during pressing. In general, anodes containing low density cokes deviated more from the predicted green apparent densities, probably because these cokes can be more readily fractured. Of anodes containing high density coke, those containing coal tar pitch cokes deviated most, possibly indicating that these cokes can be fractured more easily than the other cokes of equivalent bulk density.

Relationship Between Green Anode Apparent Density and Baked Anode Apparent Density

At the lowest pitch level, 16 percent, baked anode apparent density increased linearly with green anode apparent density (Figure 7). Net contraction took place during baking (formation of pitch into binder coke). At relatively low temperatures (before coking begins), expansion of pitch is much greater than that of the coke particles. At a low pitch level, there are ample interparticle voids and pitch accessible coke pores to accept the expanding pitch without overly disturbing the tightly packed coke structure. As coking takes place, the binder shrinks as it loses close to 50 percent of its weight (in these small scale anodes) and there is a net decrease in volume.

At the 18 percent pitch level, baked anode apparent density increased linearly with green anode apparent density for most cokes, with the ratio of baked apparent density to green apparent density a little lower than with 16 percent pitch because there was less free void space and pore volume to accept the expanding pitch during initial heating. However, anodes containing cokes which have the highest bulk densities (least porosity) in the finest fractions (cf Figure 1), which contribute most heavily to available coke surface area, had much lower ratios of baked apparent density to green apparent density. In these anodes, there was not ample pore volume to accept all the expanding pitch during initial heating and excess expansion took place. Even the shrinkage of binder during further heating (coking of pitch) could not return the aggregate to its original tightly packed condition and net expansion and low baked apparent densities resulted. Thus, bulk densities of particles of a given size, as well as overall bulk density, determine baked anode apparent density.

At the 20 percent pitch level, only anodes containing cokes with the most porous fine fractions attained relatively high baked apparent densities, though generally not as high as at the 18 percent pitch level. Because of their characteristic of high overall bulk density but only moderately high density in the fine fractions, the coal tar pitch cokes produced anodes having the highest baked apparent densities at all pitch levels.

Conclusions

The densities of calcined petroleum coke particles increase with decreasing particle size by irregular amounts which depend upon pore size distribution; bulk densities of the coal tar pitch cokes tested do not vary much with particle size, indicating a more uniform fine pore structure. Because of the irregular change in coke particle density with decreasing particle size, a bulk density test on a closely sized fraction is not necessarily a good indicator of relative coke density. However, for the twelve cokes tested, bulk density of the -28+48 mesh fraction did correlate quite well with the maximum bulk density produced by blending fractions, and correlation was improved by averaging the bulk densities of the -14+28, -28+48, and -48+100 mesh fractions. A systematic trend toward more fines in the maximum bulk density formulation as coke bulk density decreases permits a prediction of maximum bulk density sizing of a coke from the single fraction (or average of single fractions) test.

Green apparent densities of pressed anodes having a given pitch level increase linearly with coke bulk density but are higher than predicted on the assumption of no change in aggregate volume during forming. This is probably due to fracturing of particles during pressing and the effect is greatest for the low density cokes. At a relatively low pitch level, baked anode apparent density increases linearly with green apparent density. At higher pitch levels, anode containing cokes having high density fine fractions have lower baked apparent densities than anodes containing cokes having similar overall bulk densities but lower density fine fractions, such as coal tar pitch coke.

References

1. Pippin, B. H., "The Production of Petroleum Coke for Aluminum Cell Anodes," presented at 100th Annual Meeting, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, N.Y., March 1-4, 1971.

2. Rhedey, P., "A Review of Factors Affecting Carbon Anode Consumption in the Electrolytic Production of Aluminum," presented at 100th Annual Meeting, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, N.Y., March 1-4, 1971.

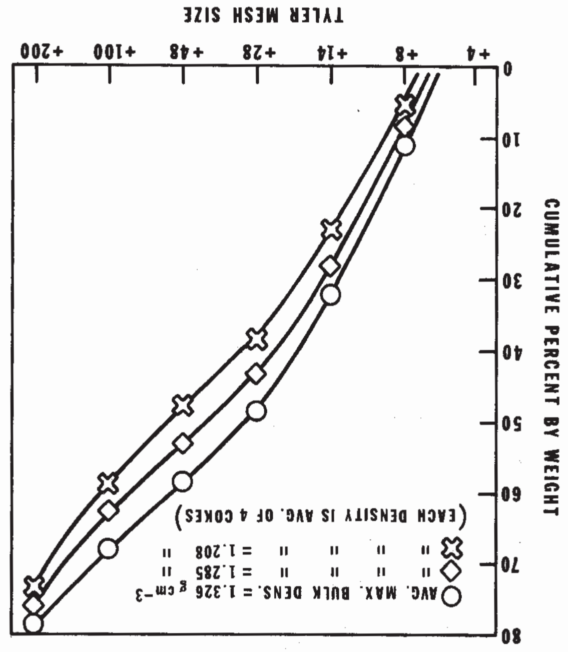

FIGURE 1. SCREEN ANALYSIS DATA FOR COKE MAXIMUM BULK DENSITIES

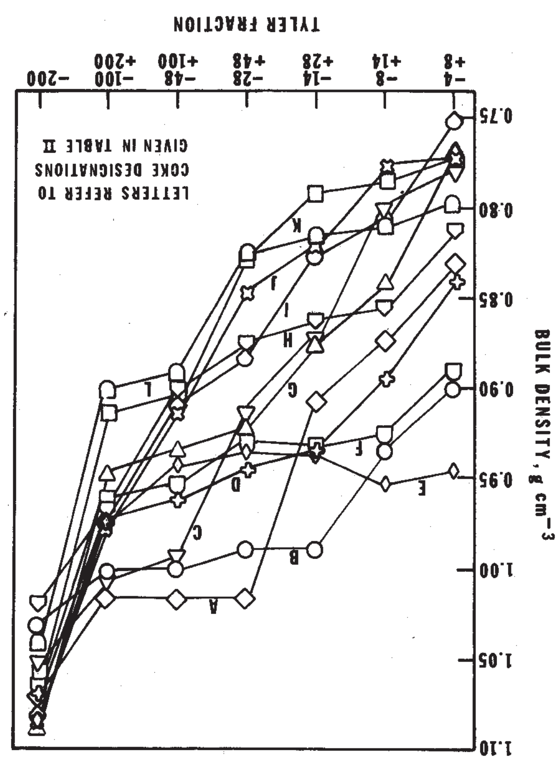

FIGURE 2. VARIATION OF CALCINED COKE BULK DENSITY WITH PARTICLE SIZE

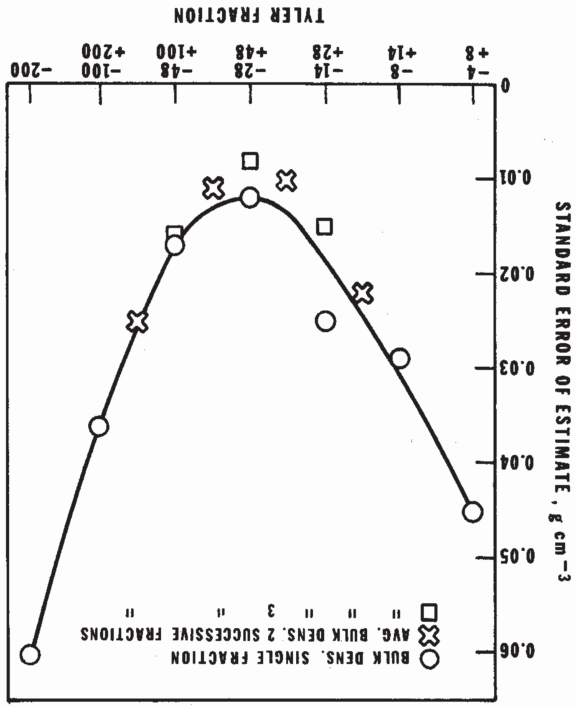

FIGURE 3. STANDARD ERROR OF ESTIMATES FROM CORRELATING SINGLE COKE FRACTION BULK DENSITIES WITH MAXIMUM BULK DENSITIES BY SECOND ORDER EQUATIONS

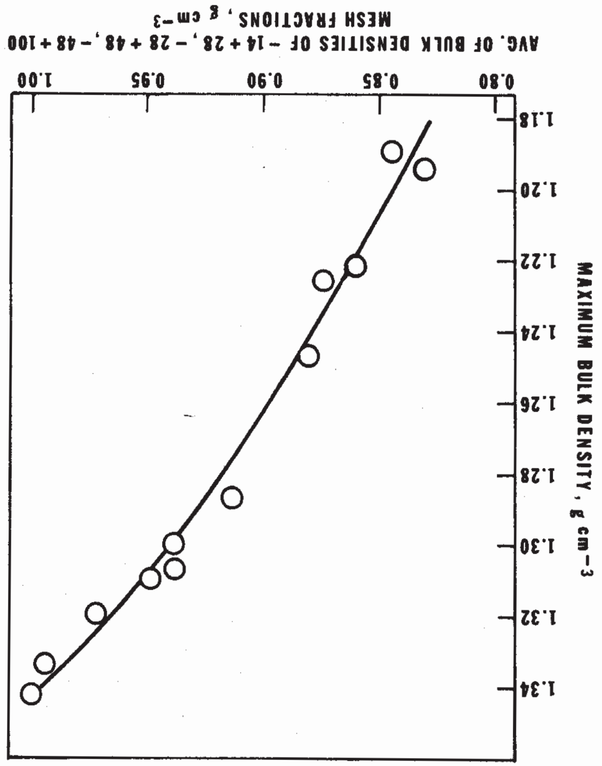

FIGURE 4. RELATIONSHIP BETWEEN THE AVERAGE OF THE BULK DENSITIES OF THE -14+28, -28+48, AND -48+100 MESH FRACTIONS AND MAXIMUM COKE BULK DENSITY

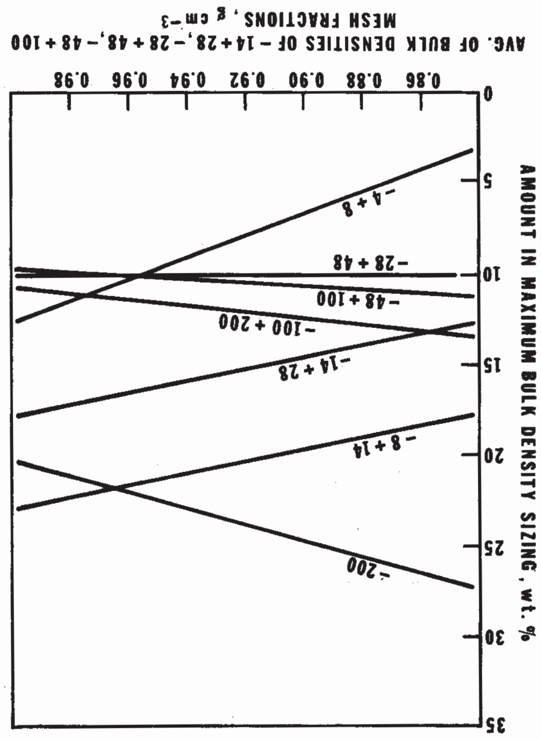

FIGURE 5. PREDICTION OF MAXIMUM BULK DENSITY COKE SIZING FROM THE AVERAGE OF THE BULK DENSITIES OF THE -14+28, -28+48, AND -48+100 MESH FRACTIONS

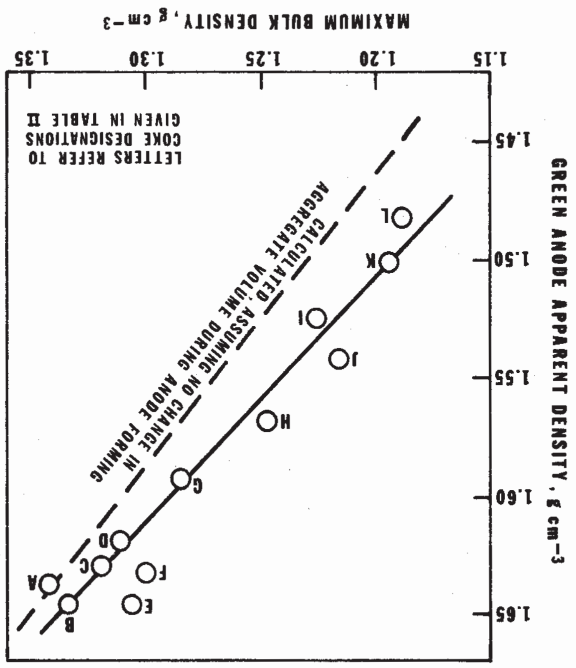

FIGURE 6. RELATIONSHIP BETWEEN BULK DENSITY OF COKE AND GREEN ANODE APPARENT DENSITY (18 WT. % PITCH; MAXIMUM BULK DENSITY AGGREGATE)

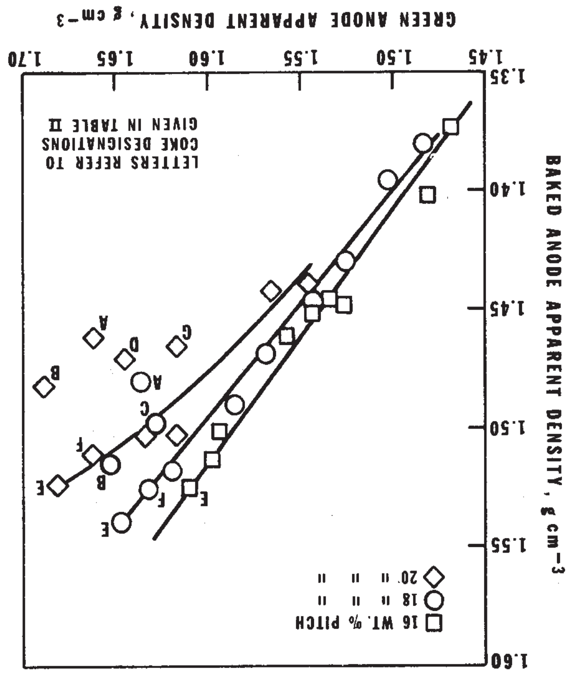

FIGURE 7. RELATIONSHIP BETWEEN GREEN ANODE APPARENT DENSITY AND BAKED ANODE APPARENT DENSITY (MAXIMUM BULK DENSITY AGGREGATE)