Effects of Bulk Density and Inter-particle Contacts on Electrical Resistivity of Calcined Coke Mixes

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Abstract

Packing density of particles is an important factor for a variety of applications of granular materials. In the present work, a three dimensional imaging technique is coupled with the Discrete Element Method (DEM) to model anode grade calcined coke particles. Coke aggregate recipe of industrial pre-baked anodes is modeled with DEM and then the pore size distribution in this packing is numerically measured. Results of the measurements are used to propose a new aggregate recipe. The proposed recipe is examined by its electrical resistivity and packing density. Results show that the proposed recipe holds a better packing density and lower electrical resistivity. It is shown that the inter-particle contact density is lower in the new recipe which results in lower electrical resistivity.

Keywords: Calcined coke, Discrete Element Method, Packing density, Electrical resistivity

1. Introduction

Particle packing is an old problem [1] which exists in different applications and industries such as construction, pharmaceuticals, food processing and agriculture [2]. Determination of conditions leading to maximum packing density is still a challenging work when the particles have irregular shapes and a wide size distribution.

Electrical current transfer in granular media has also considerable importance in a variety of applications such as electronics, metallurgical processes, railway transportation and geology [3]. Packing density and electrical resistivity of particles both are of interest for aluminum production. Pre-baked carbon anodes for the aluminum smelting process are made with granulated calcined coke mixed with binder pitch. Coke particles make up around 65 wt. % of an anode and thus the physical, chemical and mechanical properties of the coke have a considerable impact of anode quality. Effects of coke particles' bulk density on the air permeability of the baked anodes [4] and shape of coke particles on the compaction behavior of green anode paste [5] have been already investigated. Homogeneity, high density, low air permeability and low electrical resistivity are important quality factors which anodes are expected to hold.

Industrial dry mix recipe of anode paste is given in Table 1. Coke particles make up the skeleton for the anode and pitch binds the particles together providing the integrity of the mixture. A part of the pitch is vaporized during the baking process causing pores and shrinkage cracks. Binder matrix (pitch + fine coke particles) is also the most reactive part of the anode block to air and CO_2 attacks [6,7]. Underpitched anodes, on the other hand, have low apparent density and poor mechanical properties [8]. Therefore, if the coke aggregate recipe can be modified to have higher amount of coarse particles without compromising the density, pitch demand for this recipe could be reduced, resulting in positive effects on final properties of anode.

The Discrete Element Method (DEM) has a proven capability [9-13] in investigating the packing behavior of irregular-shape particles. For example in [9] the authors have reported the performance of DEM simulations in predicting the vibrated bulk density of coke aggregates.
In 2015, the authors have used DEM with a technique called void tracking [13], to study and modify the industrial recipe for aggregates in anode paste.

In the present work, void tracking is engaged to study the dry aggregate recipe used in aluminum industry to make anodes and the modified recipe is investigated for its density and electrical resistivity. Then, DEM is used to understand the variations in electrical resistivity for different samples.

Table 1. Typical coke particle recipe, used as reference

Size range (US sieve No.)	Size range (mm)	Content (wt. %)
-4+8	2.36 - 4.75	33.6
-8+14	1.4 - 2.36	15.3
-14+30	0.600 - 1.4	17.7
-30+50	0.300 – 0.600	19.4
-50+100	0.150 – 0.300	13.9

2. The Numerical Model

In DEM complex behavior of material is simulated by assigning an appropriate force-displacement law to the contacts between the elements of the model. Newton's law of motion is then applied to all the elements to determine the acceleration and thus the new position of the elements at the next time-step. This concept is shown in Figure 1.

Simple elastic contact is a common model in DEM simulations to define force-displacement behavior of elastic materials. This model is equivalent to mechanical springs in normal and shear directions. The stiffness of the springs is a consequence of the material's properties and is related to the elastic modulus. Details of this model can be found in [14].

Coke particles have irregular shapes but the basic elements of DEM are spheres in 3D. Thus, rigid clusters of overlapping spheres are used to model the real shape of coke aggregates. Sliding motion between the clusters is characterized by an inter-particle friction coefficient which was determined using the angle of repose of a pile of powder with a given particle size. Details of this method have been described in [9].

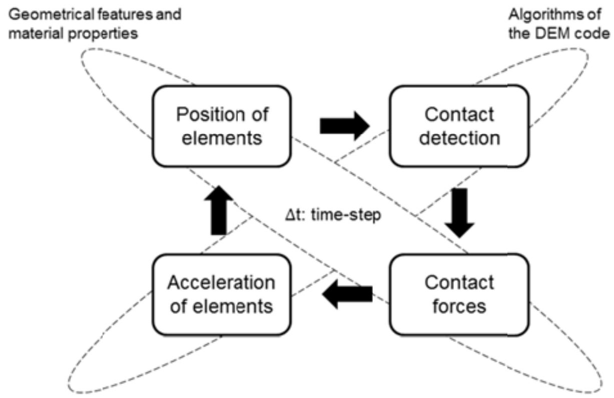

Figure 1. Calculation cycle in discrete element simulations

3. Experimental Procedure

The method proposed in [14] was adapted to measure the apparent density of coke particles in the size fractions present in the industrial dry mix recipe (Table 1). Table 2 shows the apparent density for each size fraction, obtained experimentally.

Then, shape parameters such as sphericity and the size distribution for each size range were obtained by means of an optical microscope integrated with Clemex software. The size distribution of coke particles in the range of -4+8 US sieve No. which is shown in Figure 2 indicates that there is distribution of size within each size fraction as well. The average sphericity was also obtained by similar image analysis. All of these variables were considered in creating the numerical models.

Coke particles of different size ranges were scanned (at Cogency Co, in South Africa) to generate three-dimensional digitized and meshed shapes. 3D DEM models of coke particles were created by Automatic Sphere-clump Generator (ASG) software, developed by Cogency Co. Using ASG, any closed 3D shape can be modeled with overlapping spheres. An example of coke particle modeling is shown in Figure 3. The various individual particle models obtained in this way were then mixed and in some cases resized to have numerical particles of each size range of Table 2, thus matching the size distribution (such as the one shown in Figure 2) of the real particles. Average sphericity was also monitored and matched the experimental value.

Table 2. Apparent density of different size ranges of coke [15]

Size Range (US sieve No.)	Apparent density (g/cm^3)
-4+8	1.377
-8+14	1.532
-14+30	1.524
-30+50	1.586
-50+100	1.586

A Vibrated Bulk Density (VBD) test was used to study the packing density of coke samples. In the VBD test, 100 g of the powder is allowed to fall from a vibrating conveyor into a 250 ml graduated cylinder. The cylinder is placed on a table which vertically vibrates with 60Hz of frequency and amplitude of 0.2mm for 2 minutes. The vibrated bulk density of the sample is then calculated by measuring the occupied volume inside the container.

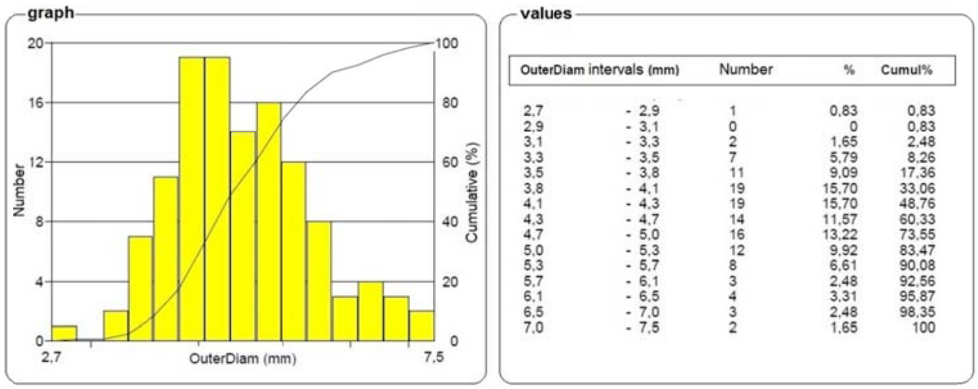

Figure 2. Size distribution of coke particle in the range of -4+8 (US sieve No.). A similar distribution was generated by the numerical clumps.

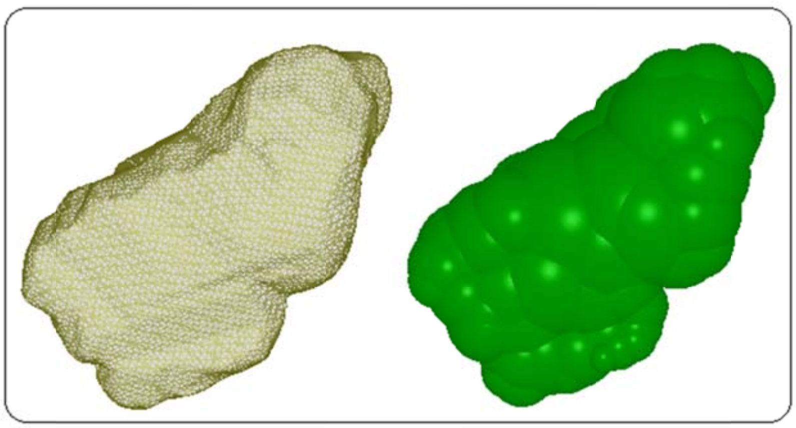

Figure 3. Coke particles modeling by overlapping spheres for DEM simulations (gray: 3D shape of a particle obtained by 3D scanning, green: equivalent clump generated by using spherical elements)

4. Results and Discussion

4.1. Vibrated Bulk Density

A coke sample consisting of only the largest fraction particles (2.38 - 4.76 mm) was numerically created in Particle Flow Code (PFC) software. The sample was subjected to vibration, according to the VBD test protocol, to reach a dense packed state, henceforth called skeleton. The mass of the sample, however, was reduced to 10 g to save the computation time. Three dimensional DEM model of such a sample after vibration is shown in Figure 3. The bulk density of this sample was 0.786 g/cm^3, thus with 42.9% inter-particle porosity.

Void tracking was performed on this numerical sample in PFC3D to obtain its void size distribution. The code takes spheres with a radius as big as 1.19 mm and puts them in the pores between the coke particles. It continues filling all the available pores until there is no more room for that size of sphere. Then, it reduces the size of the filling sphere and continues filling the remaining pores until all pores are filled out. The size of the filling spheres was reduced incrementally down to 0.0745 mm, which corresponds to the lower bound of 0.149 – 0.297 mm range in the reference recipe (Table 2). Results of void tracking are presented in Figure 4. It can be seen that in the skeleton sample, there are voids for only 0.078 g of spheres belonging to 1.41 - 2.38 mm range, representing less than 1 percent of the whole recipe. However, as given in table 1, the reference sample has 9.9% of particles in this size range. This value is more than ten times the available space for this size range.

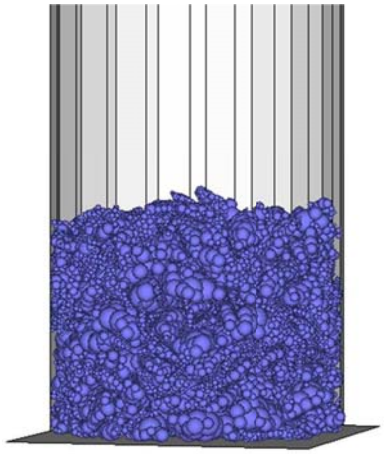

Figure 3. 3D DEM model of Vibrated Bulk Density test of the skeleton sample

Based on the void tracking results, new recipes of coke aggregates were defined as shown in Table 3. These recipes were defined with the aim of increasing the large fraction of particles, at the expense of the smaller ones, without the packing density being compromised. Vibrated Bulk Density tests were conducted on the samples.

As can be seen in figure 5, the large particle skeleton sample (S5) has an expected low VBD of 0.786 g/cm^3. The standard sample, however, has a quite high density of 0.955 g/cm^3. S1 was designed to contain more large particles (60% instead of 33% in standard sample) while all other fractions are less than those used in the standard recipe. In spite of this drastic change in the recipe, the VBD of this sample is the same as that of the standard one. This result confirms that removing the -8+14 fraction allows increasing the large fraction at the expense of the fine particles without compromising the packing density. Comparing the samples S3 and standard reveals also an important fact that the VBD can even be further increased by slightly increasing the -50+100 fraction (from 13.9 to 15%), while keeping the large fraction at 60%.

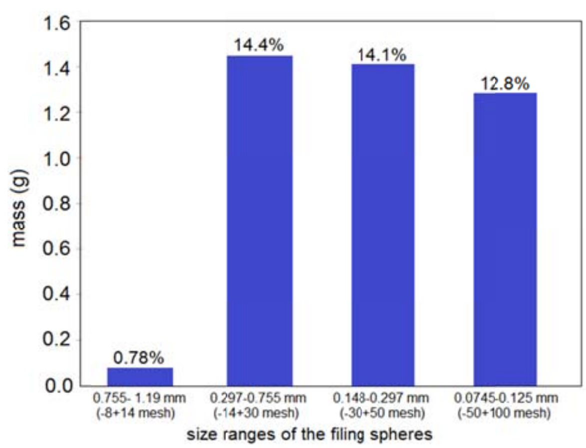

Figure 4. Results of voids tracking test: Distribution of mass of the filling spheres within various size-ranges. The values on each column give the weight percentage of filling spheres compared to the weight of skeleton sample.

Table 3. Coke aggregates size distribution of new samples based on results of voids tracking method. The values show the weight percentage of each size range in the sample.

Size range (US sieve No.)	Size Range (mm)	Sample					
		S1	S2	S3	S4	S5	Standard
-4+8	2.36-4.75	60	60	60	65	100	33.6
-8+14	1.4-2.36	0	0	0	0	0	15.3
14+30	0.600-1.4	15	20	15	15	0	17.7
-30+50	0.300-0.600	15	10	10	15	0	19.4
-50+100	0.150-0.300	10	10	15	5	0	13.9

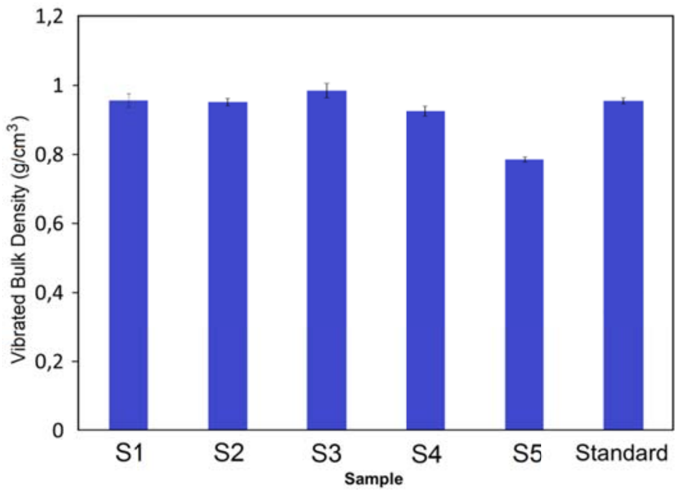

Figure 5. Experimental results of VBD test for samples given in table 3

4.2. Electrical Resistivity

Electrical resistivity of the coke aggregate mixes was investigated in the second step of the work. Electrical resistivity of the particle bed was measured using a four-point probe set up, as schematized in Figure 6, in which electrical current is provided by a Laboratory DC Power Supply GW GPR-1810HD. Current was injected through the aluminum plungers and voltage was measured using two gold-plated electrodes, insulated from the plungers. An external load is applied to the top of the sample creating a stress of 3MPa.

Standard industrial aggregate mix has the electrical resistivity of 350μΩ.m. As is presented in Figure 7, all other samples have electrical resistivities less than the standard sample. The sample with the lowest electrical resistivity is S3 with 301.8μΩ.m. This represents 13.8% reduction in electrical resistivity. P.A. Eidem et al. [16] have already shown that in mono-size mixes, as the size of particles increases the bulk electrical resistivity decreases. It is believed that the electrical resistance of a bed of particles is the sum of the resistance of the material and the resistance of contacts. Thus, when the particles are coarse the number of contacts is much less compared to a bed of fine particles and so the resistance of contacts is smaller. However, the case of particle assemblies with irregular shapes and multi size fractions is complicated. DEM is thus used in this work as a tool to evaluate the contact information in different samples and to reveal its effects on the electrical resistivity of the particle bed.

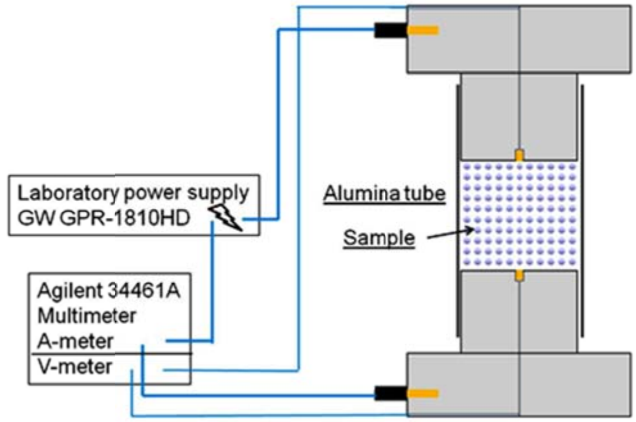

Figure 6. Experimental set-up to measure the electrical resistivity in four-probe configuration

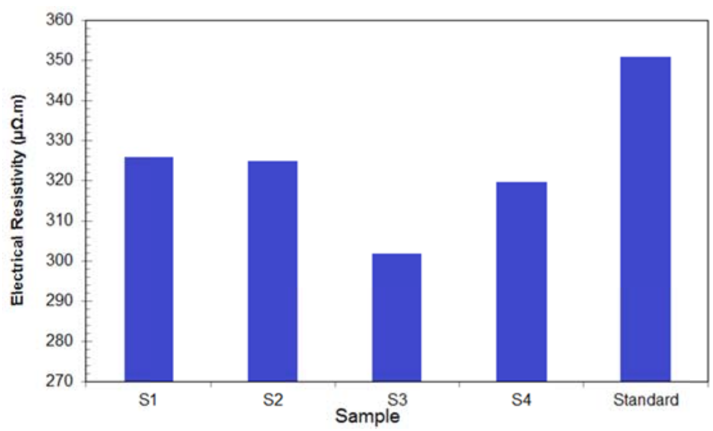

Figure 7. Electrical resistivity of different samples measured by four-probe method

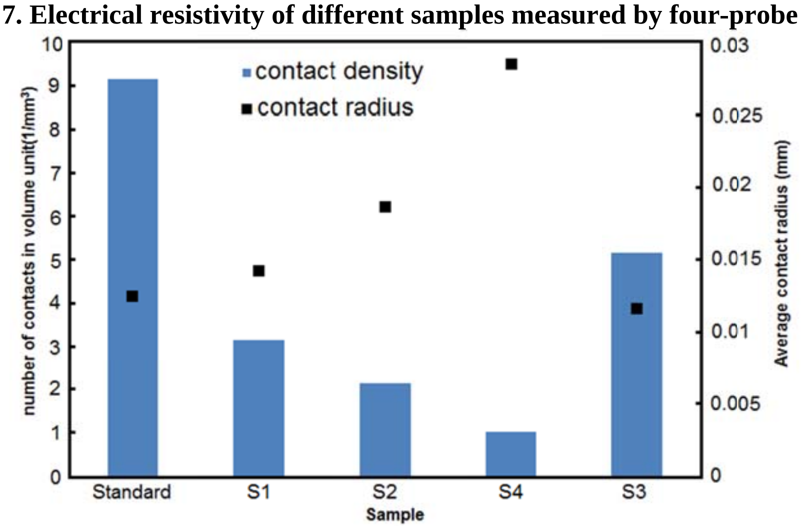

Figure 8. Contacts data for different samples obtained from DEM models.

In Figure 8 average contact radius and also number of contacts in volume unit (mm^3) of aggregate mixes are compared. As the content of coarse particles (-4+8 range) in standard sample is 33.6% and in all other samples is 60% or more, there is a remarkable distinction between the standard sample and the modified ones. The standard sample has a very high contact density of 9.16 mm^{-3}.

If only samples S1, S2, S4 and standard are considered, there is a clear relation between electrical resistivity, contact density and average contact radius. High density of contacts is associated with small contact radius and a high electrical resistivity. Comparing these four samples can lead us to the conclusion that, using the void tracking technique, a better compaction of coke aggregates can be obtained in which the percentage of coarse particles is almost twice the standard recipe. The recipe modification also alters the inter-particle contacts and with almost the same sample bulk density, a packing with far fewer particle interfaces is realized. Reducing the particle interfaces without a compromise in bulk density has a positive effect in electrical conductivity (by reducing the resistivity as shown in figure 7).

The observed difference between the electrical resistivity of S3 and S4, however, does not follow the same logic of other samples. Content of fine (-50+100 range) particles in S3 is three times bigger than S4. This results in, as expected, a higher contact density as can be seen in Figure 8. Similar to the other samples, this means a smaller average contact radius. These all are supposed to contribute in increasing the electrical resistivity. However, S3 has the lowest electrical resistivity among the samples. It is clear that increasing the amount of fines makes the contact density higher which is believed to increase the resistivity. However, as schematically shown in figure 9, fines in S3 mostly fill the voids between the coarse particles which increases the bulk density. Figure 5 confirms the increased bulk density of S3 compared to S4. The number of contacts per cubic millimeter between coarse (-4+8 range) particles of both S3 and S4 were measured in the DEM models. This value for S3 is 0.0717 and for S4 is 0.0768. Considering the fact that S3 has five percent less coarse particles, this confirms that fines in S3 are filling the voids between the coarse particles without pushing them away. Thus, it can be concluded that although particle-particle contacts in a granular assembly must be minimized to have a better electrical conductivity, there is an optimum for this. Increasing the amount of coarse particles should not affect the bulk density. Reduced bulk density results in a poor electrical conductivity.

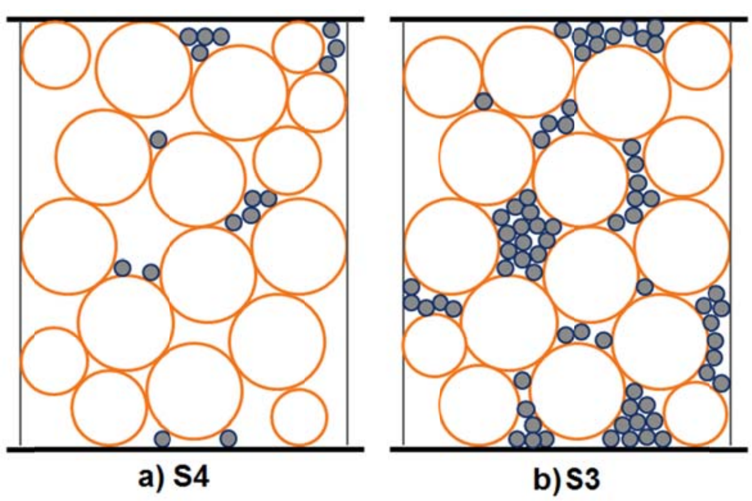

Figure 9. Schematic illustration of contact in S3 and S4: Fines in S3 decrease the average contact radius but fill the voids as well.

5. Conclusions

Three dimensional imaging was used to capture the shape and size distribution of coke aggregates. Modeled coke aggregates were used to investigate the packing density and electrical resistivity of coke particle mixes by means of discrete element method. Determining the pore size distribution in the sample with only coarse particles was performed through void tracking on the numerical model of S5. An industrial aggregate recipe of coke aggregates for making anode paste was then modified according to the results of void tracking. The modified recipes have higher content of coarse particles and fewer fines but their vibrated bulk density is comparable to standard sample. Electrical resistivities of the samples were also measured. Results showed that modified recipes not only provide a comparable or better bulk density but they have a smaller electrical resistivity as well. DEM investigations on inter-particle contacts show that reducing the amount of fine particles decreases the contact density and increases the average contact radius within the sample. These two effects, if the bulk density is not compromised, result in a lower electrical resistivity.

6. References

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