Abstract

When dispersing powder agglomerates in polymeric media, liquid infiltration driven by capillary pressure occurs affecting both agglomerate strength and hydrodynamic forces transmitted to the solid. It is of paramount importance to be able to predict the extent of polymer infiltration in powder agglomerates. In this chapter we present experimental data and a model describing the influence of powder morphology and packing properties on the permeability of fine particle agglomerates. Capillary rise experiments were performed to study infiltration behavior of polymers into powder compacts with different densities. The infiltration curves showed two different regimes which can be attributed to changes in the agglomerate permeability upon compaction. We explain these regimes in terms of a hierarchical structure for the agglomerates and different packing behavior at the level of aggregates and primary particles. Inter-aggregate pores have larger size and allow faster infiltration whereas pores within the aggregates are smaller and show a retarded infiltration. Using $\varepsilon_a$ as the void fraction between “solid” (full) aggregates and $\varepsilon_p$ as the void fraction inside the aggregates, the overall porosity, $\varepsilon$, is calculated from $\varepsilon = \varepsilon_a + \varepsilon_p(1 - \varepsilon_a)$.

Reworking the Carman-Kozeny equation, we identify two main contributions to the overall permeability, namely one due to inter-aggregate porosity and one due to intra-aggregate porosity. This last term in turn, can be identified as contrived of two terms: one referring to the pores inside

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the aggregates, the second reflecting the collapse of large pores upon compaction. At low density
the first term is predominant and leads to fast infiltration. Upon compaction beyond a critical
density, the intra-aggregate porosity takes the leading role changing drastically the infiltration rate.

Introduction

The uptake of liquids by particle agglomerates due to capillary action has a variety of practical
implications. For example the dispersion of fine particle agglomerates into liquids is influenced by
fluid infiltration into the clusters. It is therefore important to gauge and analyze the extent of fluid
infiltration during a processing operation.

Infiltration experiments may be used to probe powder morphology and macroscopic properties
related to their structure. Therefore understanding the relationship between cluster permeability and
the powder properties is important.

Infiltration of liquids into porous media has been studied by several researchers who tried to
formulate macroscopic laws relating the flow field with important powder characteristics such as
porosity and particle size. These studies mainly rely on Darcy's law:

$$ q = -\frac{k}{\eta} \nabla P $$

(1.1)

correlating the linear flow rate $q$, with fluid pressure gradient $\nabla P$ (with $P$ the capillary pressure
due to fluid surface tension), fluid viscosity $\eta$, and the porous media permeability, $k$.

One very well known equation which relates the permeability $k$ to porous media properties, was
derived by Kozeny [Scheidegger, 1957]. Kozeny viewed the porous bed as an assemblage of
channels of various cross sections and expressed the permeability as:

$$ k = c \frac{\varepsilon^3}{S^2T} $$

(1.2)

where $\varepsilon$ is the porosity of the porous media, $S$ the specific surface of the channel, $T$ the
tortuosity factor and $c$ a proportionality parameter which depends on the shape of the channels. The
tortuosity factor takes into account the complexity of the channels in the porous media.

The Kozeny equation has been largely applied and also modified by other researchers. Carman
introduced the specific surface exposed to the fluid $S_0$ ($S_0=S(1-\varepsilon)$) and set the constant $c$ to 1/5
which gave the best fit to his experimental results [Scheidegger, 1957]. The result is known as the Kozeny-Carman equation:

\[ k = c \frac{\varepsilon^3}{5S_0^2(1 - \varepsilon)^2} \]  

(1.3)

A more recent modification of the Kozeny-Carman equation is due to Blake [Bird, 1960], who related permeability to the void fraction \( \varepsilon \) and primary particle size \( D_p \) and introduced a correction factor derived from experimental results. In this case the permeability \( k \) is written as:

\[ k = c \frac{D_p^2 \varepsilon^3}{150(1 - \varepsilon)^2} \]  

(1.4)

This equation is considered to be valid for media consisting of individual particles.

Dullien and MacDonald addressed the problem of multisized particles present in a porous media. Dullien [Dullien, 1976] modified the Kozeny-Carman equation assuming pores with periodic step changes in their diameter. The result is an apparent capillary diameter which is a function of all capillary sizes present in the porous media. MacDonald [MacDonald, 1991] generalized the Blake-Kozeny equation for multisized spherical particles showing that \( D_p \), in the Blake-Kozeny equation, has to be replaced by \( M_2/M_1 \), where \( M_2 \) and \( M_1 \) are the second and first moment of the size distribution function for the spherical particles. These models find good agreement with experimental data.

Bohin [Bohin, 1994] studied infiltration into spherical agglomerates driven by capillary pressure. Starting from the Blake-Kozeny equation, he developed a quantitative model able to accurately describe the process.

We try to explain the different regimes in an infiltration process brought about by the compaction of a powder bed which is used to represent powder agglomerates. Experimental results obtained at high density are well described by the Blake-Kozeny equation. However, the powder bed permeability at tap density appears to be well above that predicted by the theory.

In this paper we attempt to explain these results in terms of a hierarchical structure of the powder bed, presenting a permeability model which makes distinction between the porosity at the level of primary particles and aggregates.
Experimental

Materials

Several powders were tested, namely precipitated silica, titanium dioxide, calcium carbonate and carbon black. These powders provide a variety of morphologies and are fillers commonly used in polymer processing [Ottino, 2000]. The fluids used to study infiltration were polydimethylsiloxane (PDMS) liquid polymers. These are very important silicone oils and samples, spanning in a range of viscosity, are available.

Selected properties of the materials are summarized in Table 1.

Procedures

Infiltration of liquids into the powder at tap density was performed in capillary rise experiments (Washburn experiment). The apparatus consists of a beaker containing a reservoir of liquid (allowing the assumption of an infinite reservoir [Washburn, 1921] and a glass tube supported by a clamp. The schematic of the apparatus is presented in Fig. 1.

Glass wool placed at the bottom of the tube, allows fluid to pass while supporting the powder. The tube, that has volume markers (e.g. a pipette), is filled with a known amount of powder and shaken until no further changes are observed in the volume occupied by the powder. At this condition the density is considered to be the tap density. Higher density powder beds are obtained by compressing the powder inside the tube from both ends.

The cylinder is lowered in the beaker up to the point that the fluid level reaches the top of the glass wool. Time zero is chosen when the liquid first meets the powder. The length of infiltration and time are recorded using a CCD video camera connected with an image analysis system.

Theory

The model assumes a porous bed composed of randomly packed monosized spherical particles. Capillary forces drive the infiltration process. The porous bed structure leads to capillaries whose dimensions are related to particle size and bed porosity. The total permeability, $k$ can be expressed in terms of the porosity $\epsilon$ and particle size $D_p$ through the Blake-Kozeny equation (Eq. 1.4). Using Darcy's law the fluid velocity is given by:
\[ \frac{dl}{dt} = \frac{k \Delta P}{\eta l} \] (2.1)

where \( l \) is the linear extent of fluid in the porous bed, \( \eta \) is the fluid viscosity and \( \Delta P \) is the capillary pressure difference. The porous structure of a packed bed of monosized spherical particles of size \( D_p \) can be assimilated to an assemble of cylindrical channels with effective radius determined by the hydraulic radius theory. For cylindrical tubes, the capillary pressure depends on the liquid surface tension \( \gamma_{l,v} \), the powder-fluid contact angle \( \theta \) and the pore radius \( r_p \):

\[ \Delta P = \frac{2\gamma_{l,v} \cos \theta}{r_p} \] (2.2)

For a packed bed, the effective pore size can be taken as the hydraulic radius \( R_h \), written as

\[ R_h = \frac{\varepsilon D_p}{6(1 - \varepsilon)} \] (2.3)

Substituting Eqs. 1.4, 2.2 and 2.3 into Eq. 2.1 and integrating we obtain:

\[ l^2 = \frac{12}{150} \frac{D_p}{\eta \gamma_{l,v} \cos \theta} \frac{\varepsilon^2}{(1 - \varepsilon)} t \] (2.4)

Note that the hydraulic radius of a cylinder was considered to be one-half of the pore radius. Equation 2.4 is the well known Washburn equation. Combining all material parameters into an infiltration rate, \( W \) (Washburn coefficient), Eq. 2.4 can be simplified to:

\[ l^2 = Wt \] (2.5)

where

\[ W = \frac{12}{150} \frac{D_p}{\eta \gamma_{l,v} \cos \theta} \frac{\varepsilon^2}{(1 - \varepsilon)} \] (2.6)

The Washburn coefficient depends on powder and fluid characteristics and fluid-powder interfacial properties. In deriving the expression for the Washburn coefficient, we made the assumption of randomly packed spherical units of diameter \( D_p \). In some instances, \( D_p \) does not necessarily reflect the size of primary particles randomly packed into a porous bed. One can envision larger units (i.e. small clusters of primary particles) randomly packed into a porous structure. Whether the primary particles or larger units govern the bed permeability will depend on the packing characteristics.
Moreover, one also has to consider a particle size distribution. Following the lead of Dullien and MacDonald [Dullien 1976, MacDonald, 1991] we will consider an average pore size related to an apparent diameter, $D_{\text{app}}$, for the primary units.

**Results and Discussion**

Infiltration experiments were performed following two different schemes:

- capillary rise experiments with powder beds at tap densities and fluids of various viscosities
- capillary rise experiments with powder beds at various density, using the same fluid.

Figure 2 shows a typical plot of data of one infiltration experiment. The linear relationship between the square of infiltrated length, $l^2$, and time $t$, predicted by Eq. 2.4, can be observed.

The infiltration experiments performed on silica at tap density with different fluid viscosities showed good agreement with the theory. In Figure 3 the infiltration rates are plotted versus the reciprocal viscosity of the fluids. The linear relationship is evident and from the slope (least square fit method) we can determine the apparent diameter $D_{\text{app}}$, considering a surface tension value $\gamma_{l,v}=0.020 \text{ J/m}^2$ ([Krevelen, 1990] and good wetting of the powder by the polymer ($\cos\theta \sim 1$). The data in Figure 3 indicate a value of $D_{\text{app}} \sim 700 \text{ nm}$. The value is well above the primary particle size calculated from BET surface data (28 nm). This indicates very large primary units which may be representative of large aggregates. The scatter observed in these experiments derive from errors in determining the exact porosity of the sample and the velocity of the infiltration phenomena. It is clear that for faster infiltration phenomena, one expects a larger scatter.

Looking at the experiments performed at different densities however, one can realize that these large aggregates characterize the infiltration process only at tap density. Experiments at lower porosity were performed using PDMS of 10 cS viscosity. Results for silica powder are presented in Fig. 4.

A plot of Washburn coefficients versus $\varepsilon^2/(1-\varepsilon)$ (which we will call porosity factor in this chapter) shows a linear dependence for high density compacts with a sharp transition at porosity values corresponding to the tap density (Figure 4). The apparent size of the primary units extrapolated from the high density region is 200 nm which is different than the value for $D_{\text{app}}$ at tap density. At tap density the size of the pores appears to be much larger than at higher compact density, although there is only a small difference in the value of the overall porosity (e.g., the porosity at tap density is 0.88 while high density compacts have porosity equal or lower than
The value of $D_{\text{app}}$ extrapolated from the high density data suggests that the porosity and, in turn, the pore sizes are determined by voids between smaller clusters of primary particles, while at tap density these seem to be determined by voids between larger clusters of primary particles.

For comparison purposes, we undertook the same experiments with the other powders.

Results of the infiltration experiments performed with the same fluid (PDMS, 10 cS) and powder beds at different densities are presented in Figures 5, 6 and 7 for CaCO$_3$, TiO$_2$, and carbon black respectively.

The apparent size of structural units determined for the three powders at high density are reported in Table 2. Calcium carbonate and titanium dioxide have an apparent particle size which is close to the primary particle size.

This suggests that primary particles in this case well represents the primary units which govern infiltration in this density range. Carbon black shows a size larger than primary particles indicating, as in the case of silica, that infiltration may be affected by small clusters of primary particles. However, both calcium carbonate and titanium dioxide still show the same transition for porosity close to the tap density, but carbon black did not show the same type of transition. The large difference in the apparent diameter of primary units in powder beds at tap density ($D_{\text{app}}^{\text{TAP}}$) and the values obtained with compacted structure ($D_{\text{app}}^{\text{HIGH}}$) suggests that important structure rearrangements happen upon powder compaction.

**Powder Compaction Model**

To explain the strong dependence of the permeability upon compaction density, we assume a hierarchical structure and consider two levels: primary and secondary units. In most cases these can be identified with primary particles and aggregates. It is logical to assume that the inter-aggregate pores have larger size than the intra-aggregate pores. However the process of compaction may change the role that inter-aggregate and intra-aggregate porosity play in the infiltration process. Adams [Adams, 1994] describes the process of compaction dividing it into two separate stages. During the first stage powder is compressed starting from its tap density. In this stage large conformational rearrangements occur and high pressure is not needed to compress the powder. In the second stage failure of agglomerates and interpenetration of aggregates occurs and the pressure needed for compaction increases exponentially with the strain of the compact. A very similar
explanation is offered also by Song and Evans [Song, 1994]. It is during the first stage and the beginning of the second that we believe the largest changes in pore size occur.

To the hierarchical structure of the agglomerates, we can associate a hierarchical structure of the pores. Generally speaking, voids between aggregates are larger than voids within aggregates (although it depends on the packing stage). At tap density the concentration of large pores may be enough to create a complete path of large pores for the fluid (percolation threshold). Flow through larger channels will be faster than in the smaller pores. In the experiments we would be able to detect only the fastest flow flux in the porous media. Infiltration within aggregates will occur with slower kinetics and we would not be able to observe it directly. When the powder bed is compacted and rearrangements occur, the permeability changes. As the concentration of large pores decreases the large path for fluid becomes blocked and fluid can travel only through the small paths. An additional increase in the density causes interpenetration of the aggregates reducing their inner porosity. At this level, the powder bed can be pictured as a collection of monodispersed channels.

This phenomenological picture can be formulated in a mathematical fashion and explain the experimental results.

The Blake Kozeny equation and its modifications due to Dullien and MacDonald take into account a collection of particles of single or different size, but they do not consider a hierarchical structure for the powder bed.

A porous bed has a total volume $V_T$, which is the summation of the aggregate volume, $V_a$, and the void volume among them, $V_v$. Therefore we can write:

$$V_T = V_a + V_v$$  \hfill (4.1)

The volume of the aggregates can be in turn decomposed in primary units volume $V_p$ and void volume $V_v'$:

$$V_a = V_p + V_v'$$  \hfill (4.2)

We define inter-aggregate porosity the ratio of the void volume between aggregates, $V_v$, and the total volume $V_T$:

$$\epsilon_a = \frac{V_v}{V_T}$$  \hfill (4.3)

from which follows that
Similarly we define the intra-aggregate porosity, $\varepsilon_p$, as the ratio of the void volume among primary units and the total volume of the aggregate

$$
\varepsilon_p = \frac{V'_{v}}{V_a}
$$

(4.5)

The volume occupied by the primary units can be conversely written in this fashion:

$$
V_p = (1 - \varepsilon_p)Va = (1 - \varepsilon_a)(1 - \varepsilon_p)V_T
$$

(4.6)

Here $\varepsilon_a$ is the porosity of the powder bed considering solid aggregates, while $\varepsilon_p$ is the porosity of a single aggregate. The total void volume of the powder bed can be obtained summing the void volume between and within aggregates. Combining Eq. 4.3-4.6 we obtain the expression for the total porosity $\varepsilon = (V_{v} + V'_{v})/V_T$:

$$
\varepsilon = \varepsilon_a + \varepsilon_p (1 - \varepsilon_a)
$$

(4.7)

Eq. 4.7 expresses the contribution of the inter-aggregate and intra-aggregate porosity to the overall porosity. In the case of very loose agglomerates ($\varepsilon_a = O(1)$), the inter-aggregate porosity is the dominant term, while in case of close packed aggregates ($\varepsilon_a \sim 0$) the porosity is determined by the intra-aggregate porosity.

In the case of randomly packed spherical primary units, where no hierarchical structure can be identified ($\varepsilon_a = 0$), Eq. 4.7 reduces to an identity.

We can calculate the hydraulic radius for intra-aggregate pores and for inter-aggregate pores as follows:

$$
R_{hp} = \frac{\text{cross section available for flow}}{\text{wetted perimeter}} = \frac{\text{intra-aggregate volume available for flow}}{\text{total wetted primary units surface}}
$$

$$
= \frac{V'_{v}}{\rho_p S_{pu}(1 - \varepsilon_p)V_a} = \frac{\varepsilon_p D_p}{6(1 - \varepsilon_p)}
$$

(4.8)

with $S_{pu}$ the specific surface of the primary units, $\rho_p$ their density and $D_p$ their size. The two quantities are related through the following equation:
Similarly we can derive the hydraulic radius for the inter-aggregate porosity, considering solid aggregates and noting that in this case the wetted surface is only the external surface of aggregates:

\[
R_{ha} = \frac{\text{cross section available for flow}}{\text{wetted perimeter}} = \frac{\text{inter-aggregate volume available for flow}}{\text{total wetted aggregate surface}} = \frac{V_v}{\rho_a S_a (1 - \varepsilon_a) V_T} = \frac{\varepsilon_a D_a}{6(1 - \varepsilon_a)}
\]

where \(S_a\) is the specific surface of the aggregates, \(\rho_a\) their density and \(D_a\) their size.

The velocity of a laminar flow in a circular tube of radius \(R\) for a fluid with viscosity \(\eta\) is [Bird, 1960]:

\[
v_z = \frac{R^2}{4\eta} \left( -\frac{dP}{dz} \right) \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
\]

The superficial velocity is defined as \(v_0 = \varepsilon \langle v \rangle\) where \(\langle v \rangle\) is:

\[
\langle v \rangle = \frac{1}{\pi R^2} \int_0^{2\pi} \int_0^R v_z r dr d\theta = \frac{\Delta P R_h^2}{8\eta l}
\]

where we have replaced the radius \(R\) with the hydraulic radius \(R_h\) and \(\Delta P\) can be expressed as in Eq. 2.2.

In the presence of a hierarchical structure of pores with two main sizes, the media will be infiltrated by two flows with different flow rates. The superficial flow velocity \(v_{0a}\) between aggregates of mean size \(D_a\) can be written in this fashion:

\[
v_{0a} = \frac{\gamma_{ls} \cos \theta D_a \varepsilon_a^2}{48\eta l_a \left( 1 - \varepsilon_a \right)}
\]

Similarly one can derive the velocity within one aggregate \(v_{0p}\):

\[
v_{0p} = \frac{\gamma_{ls} \cos \theta D_p \varepsilon_p^2}{48\eta l_p \left( 1 - \varepsilon_p \right)}
\]
where \( l_a \) and \( l_p \) is the level of fluid in the porous media between and inside aggregates respectively.

The flow velocities calculated for the two separate channels depend on a characteristic size, aggregate and primary particle size respectively. A first comparison may indicate that the superficial velocity between aggregates may be larger due to the larger characteristic size (\( D_a >> D_p \)) than the velocity inside the aggregates. Without being able to measure the degree of saturation of the infiltration process (as in the Washburn experiment) one would detect the fastest flow and therefore the different regimes of infiltration upon compaction. However a full comparison of the velocities has to take into account the relative contributions of inter and intra-aggregate porosity as function of total packing density.

In the physical picture given above we separated the compaction process into two steps: a first rearrangement of aggregates without interpenetration followed by an interpenetration of the aggregates which leads to changes also in the intra-aggregate porosity. We consider as initial stage the tap density which will correspond to an initial total porosity \( \varepsilon_i \). We call \( \varepsilon_{pi} \) and \( \varepsilon_{ai} \) the initial intra-aggregate porosity and inter-aggregate porosity. At tap density we assume that aggregates are not interpenetrated and \( \varepsilon_{pi} \) can be identified with the porosity of the native aggregates. Therefore we can derive the initial inter-aggregate porosity from the initial overall porosity \( \varepsilon_i \) through Eq. 4.7:

\[
\varepsilon_{ai} = \frac{\varepsilon_i - \varepsilon_{pi}}{1 - \varepsilon_{pi}} \quad (4.15)
\]

The first stage of rearrangement of the aggregates is quantified by a reduction in the inter-aggregate porosity (\( \varepsilon_a \)) with an unchanged intra-aggregate porosity (\( \varepsilon_p = \varepsilon_{pi} \)) and it lasts until aggregates have reached a maximum packing configuration (or minimum porosity \( \varepsilon^* a \)) and cannot be rearranged and packed any further without interpenetration. Increasing the density causes aggregates to interpenetrate and reduce the intra-aggregate porosity \( \varepsilon_p \). As interpenetration occurs, pores between aggregates are soon filled and the powder compact can be seen as a collection of primary particles (\( \varepsilon_a = 0 \)).

We assume a value of porosity (critical porosity \( \varepsilon^*_a \)) which represents the stage where spheres cannot rearrange further without interpenetration. The critical porosity therefore represents the
transition between the two stages explained above: a first rearrangement of aggregates \((\varepsilon_a > \varepsilon^*_a)\) followed by a rearrangement and interpenetration of aggregates \((\varepsilon_a < \varepsilon^*_a)\).

Figure 8 presents a phenomenological picture of the stages of the compaction process described above. As a consequence of the compaction process one can start to picture the relative contributions of porosity between and inside aggregates, represented in Fig. 8 as white and black pattern channels respectively. Channels between aggregates (white) are present at low density and their contribution is drastically reduced as rearrangement occurs.

**Model Predictions**

The actual relative contributions of inter and intra-aggregate porosity depend on morphological properties of the powder, such as the density of the native aggregates \((\varepsilon_{pi})\) and the ability of aggregates to rearrange and pack \((\varepsilon^*_a)\). We assume, as a first approximation, to have monodispersed spherical aggregates able to pack in random fashion. Therefore we fix \(\varepsilon^*_a\) to 0.36 (porosity of a collection of randomly packed monodispersed spheres [Zallen, 1983] and analyze the two contributions \(\varepsilon_a\) and \(\varepsilon_p\) as a function of the powder bed packing density and the density of the native aggregates. The appendix section presents in more detail the assumptions used to calculate the relative contributions of \(\varepsilon_a\) and \(\varepsilon_p\) as a function of packing density.

Taking into account Eq. 4.7, we can calculate the intra-aggregate and inter-aggregate porosities as a function of the powder bed solid volume fraction for two cases, one considering very loose aggregates \((\varepsilon_{pi} = 90\%)\) and one considering dense aggregates \((\varepsilon_{pi} = 70\%)\). Results are shown in Figures 9 and 10 respectively, where we plotted the values of inter-aggregate porosity \(\varepsilon_a\) and intra-aggregate porosity \(\varepsilon_p\) as functions of packing density.

For very loose aggregates \((\varepsilon_{pi} = 90\%)\) one can observe that the contribution from inter-aggregate porosity is always lower than the intra-aggregate porosity. For a dense aggregate instead, a change in the trend is expected. At high density the intra-aggregate porosity is leading, while at lower density the inter-aggregate porosity gives the higher contribution. At lower density, combining the greater extent of inter-aggregate pores with their larger size, the flow among aggregates can be dominant. However, upon compaction when interpenetration occurs \((\varepsilon_a = \varepsilon^*_a)\) the contribution of the inter-aggregate pores decreases. At this point, the fastest flow will be within the aggregates,
suggesting that a change in the regime of the infiltration process may occur. Therefore two main regimes could govern infiltration: one characterized by large intra-aggregate pores \((D_a)\) and the second through inter-aggregate pores of smaller size \((D_p)\). The transition shown in the experiments can reflect the change in the infiltration regime upon compaction.

So far, the two porosities \(\varepsilon_a\) and \(\varepsilon_p\) have been compared and their contribution to permeability assessed in terms of their relative magnitude. However in the case of inter-aggregate porosity, one has to take into account that the inter-aggregate pores have larger volume, leading to a larger contribution to the overall permeability even when the percentage is low.

To have a better comparison of the two contributions one has to know \(D_a\) and the reduction in size of the inter-aggregate pores when interpenetration occurs. This is however extremely difficult to predict. A simplification is to consider the aggregates as collections of spherical primary particles and to derive a single hydraulic radius. This entails that while fluid is traveling through smaller or larger pores (intra-aggregate and inter-aggregate pores), it is always wetting the entire open surface. Thus we calculate \(R_h\) as the ratio between the total pore volume available for fluid infiltration and the total wetted surface:

\[
R_h = \frac{\text{cross section available for flow}}{\text{wetted perimeter}} = \frac{\text{volume available for flow}}{\text{total wetted surface}} = \frac{V_v + V_v^p}{\rho_p S_{pa} (1 - \varepsilon) V_T} = \frac{\varepsilon_a V_T + \varepsilon_p (1 - \varepsilon_a) V_T}{\rho_p S_{pa} (1 - \varepsilon)V_T} = \frac{\varepsilon_a D_p}{6(1 - \varepsilon_a)(1 - \varepsilon_p)} + \frac{\varepsilon_p D_p}{6(1 - \varepsilon_p)}
\] (5.1)

\(R_h\) still shows two main contributions belonging to the different porosities. Following the same line used to derive Eq. 4.13 and 4.14, we can write the superficial velocity in this fashion:

\[
v_0 = \frac{\gamma_{lv} \cos \theta}{8 \eta l} \left[ \frac{D_p \varepsilon_a^2}{(1 - \varepsilon_p)(1 - \varepsilon_a)} + D_p (1 - \varepsilon_a) \frac{\varepsilon_p^2}{(1 - \varepsilon_p)} + \frac{2 D_p \varepsilon_p \varepsilon_a}{6(1 - \varepsilon_p)} \right]
\] (5.2)

The Washburn coefficient will therefore be:

\[
W = \frac{12 \gamma_{lv} \cos \theta}{150 \eta} \left[ \frac{D_p \varepsilon_a^2}{(1 - \varepsilon_p)(1 - \varepsilon_a)} + D_p (1 - \varepsilon_a) \frac{\varepsilon_p^2}{(1 - \varepsilon_p)} + \frac{2 D_p \varepsilon_p \varepsilon_a}{6(1 - \varepsilon_p)} \right]
\] (5.3)
The same result can be obtained by replacing $\varepsilon$ in Eq. 2.6 with its expression from Eq. 4.7. Looking closer to Eq. 5.3 we can recognize mainly three terms which contribute to the infiltration rate. The first term ($\frac{D_p}{1-\varepsilon_p} \frac{\varepsilon_a^2}{1-\varepsilon_a}$) represents the inter-aggregate porosity and it has a size ($\frac{D_p}{1-\varepsilon_p}$) larger than the primary particle size. However the size will change as soon as $\varepsilon_p$ starts to change, which happens when interpenetration occurs. The second term ($D_p(1-\varepsilon_a)\frac{\varepsilon_p^2}{1-\varepsilon_p}$) represents the effective porosity within the aggregates while the third term ($D_p \frac{2\varepsilon_p\varepsilon_a}{1-\varepsilon_p}$) takes into account the collapse of larger pores into smaller ones when the overall porosity is reduced.

The second and third term may be grouped together and Eq. 5.3 rewritten in a different fashion:

$$W = \frac{12}{150} \frac{D_p^2 \varepsilon_a^2}{\eta D_p} \frac{6 4 4 4 4 4 \varepsilon_p^4 4 4 4 4 4 \varepsilon_p^4 4 4 4 4 4 \varepsilon_p^4 4 4 4 4 4 \varepsilon_p^4}{(1-\varepsilon_p)(1-\varepsilon_a)} + D_p^2 \frac{1-\varepsilon_a}{1-\varepsilon_p} \left( \varepsilon_p + \frac{2\varepsilon_a}{1-\varepsilon_a} \right)$$

(5.4)

In this way the physical picture is more clear. The first term in Eq. 5.4, $k_a$, represents an inter-aggregate aggregate permeability while the second term, $k_p$, represents the intra-aggregate permeability. For this latter term there are two main contributions: the inner porosity of the aggregates and the collapsed pores between aggregates. Eq. 5.4, derived by assuming that the fluid is wetting the entire open surface (see Eq. \ref{hydrradius}), is appropriate for the high density region. At low density, the $k_a$ term predicts a change in the infiltration regimes, but it may not be able to fully represent the fast infiltration rate observed at TAP density, where it is more reasonable to believe that the fluid will wet only the aggregate surface.

We can now compare the contributions which each term gives to permeability as a function of total porosity.

Following the same line of the previous comparison we calculated the two contributions $k_a$ and $k_p$ of Eq. 5.3 normalized on the $D_p^2$ term and plotted them versus the porosity factor $\varepsilon^2/(1-\varepsilon)$. Results are presented in Figures 11 and 12. In the case of loose aggregates ($\varepsilon_p = 90\%$) $k_p$ dominates Eq. 5.3 similarly to the previous comparison, while in the case of dense aggregates ($\varepsilon_p = 70\%$) there is a change in the dominant term. The inter-aggregate porosity dominates at low density while the
intra-aggregate porosity dominates at high density. The transition however happens at a lower value of total porosity than illustrated in Fig. 10. This is the effect of the larger size of the inter-aggregate pores.

It is important to note that the transition between the two regimes occurs before $\varepsilon_a$ reaches the critical value $\varepsilon^*_a$ (0.36).

It is indeed the strong reduction of larger pores upon aggregate reorganization that drastically decreases the contribution of the larger pores. However the larger size of the inter-aggregate pores make the inter-aggregate flow still dominant even if the relative contribution $\varepsilon_a$ is lower than the intra-aggregate contribution $\varepsilon_p$.

The critical porosity $\varepsilon^*_a$=0.36 was based on the assumption of monodisperse sphere randomly packed. However, aggregates may have different sizes and shapes, which can lead to interpenetration at higher values of inter-aggregate porosity. Although this could change the relative contributions of $\varepsilon_a$ and $\varepsilon_p$ as a function of packing density, the general results still hold true.

A direct comparison of the model with experimental results requires morphological information of the powder, in particular the value of porosity for the native aggregates.

Unfortunately among the powders tested, this value is known only for carbon black. In this case $\varepsilon_{pi}$ can be calculated from the dibutyl phthalate (DBP) absorption values (in units of cm$^3$/100g) through the following equation [Yamada, 1997]:

$$
\varepsilon_a = \varepsilon - (1-\varepsilon) \left(1 + 0.02139 \frac{\text{DBP}}{1.46} \right) - 1
$$

$\varepsilon_p = \frac{\varepsilon - \varepsilon_a}{1 - \varepsilon_a}$ (5.5)

The initial porosity (tap porosity) can be measured experimentally and through Eq. 5.5 we can calculate the initial intra-aggregate porosity $\varepsilon_{pi}$. For the carbon black tested (Monarch 880) the tap porosity is 0.93 and initial intra-aggregate porosity is 0.57. This indicates a morphology of very dense aggregates.

In Figure 13, $\varepsilon_a$, $\varepsilon_p$ and $\varepsilon$ are plotted versus the porosity factor $\varepsilon^2/(1-\varepsilon)$ for the initial value of $\varepsilon_p$ calculated. The intra-aggregate porosity $\varepsilon_p$ appears to be always smaller than $\varepsilon_{as}$, explaining the single regime in the infiltration process as exhibited by carbon black. This is concurrent also with the size $D_{app}$ determined from the experimental results, which is more representative of aggregate
size rather than primary particles. In the range of densities tested, the morphology of this powder can be easily represented as a collection of very dense aggregates.

For the other powders tested in this work, the intra-aggregate initial porosity is not known. However, one may speculate that a transition between the two infiltration regimes occurs when the contributions from the inter-aggregate and intra-aggregate porosities on the overall permeability become comparable. This assumption \((k_a \sim k_p)\) translates into:

\[
e_{at} = \frac{\epsilon_p ^2}{1 + 2 \epsilon_p - \epsilon_p ^2},
\]

which upon replacing \(\epsilon_a\) in terms of the overall porosity \(\epsilon\) and \(\epsilon_p\) (from Eq. 4.7) gives

\[
e_t = \sqrt{2} \epsilon_p \frac{1 + \sqrt{2} - \epsilon_{pi} ^2}{1 + 2 \epsilon_{pi} - \epsilon_{pi} ^2},
\]

In Eq. 5.7 we have considered \(\epsilon_t\) the total porosity at the transition regime where \(\epsilon_p\) (the intra-aggregate porosity) has not been affected by the compaction process and therefore can be replaced by the native aggregate porosity \(\epsilon_{pi}\). Experimental results showed a change in the infiltration regime for values of \(\epsilon^2/(1-\epsilon)\) between 5 and 7 (Figures 4-6) and they were use to estimate the native intra-aggregate porosity \(\epsilon_{pi}\) for silica, CaCO3 and TiO2. The values, summarized in Table 3, show highly porous structures for the aggregates of these powders.

A closer look at Eq. 5.3 reveals another interpretation of the infiltration results. At small overall porosity, powder bed permeability will be governed by the term representing the intra-aggregate porosity, \(k_p\), while at larger porosities it is the flow between the aggregates which dominates. In other words, at value of \(\epsilon\) below \(\epsilon_t\), powder bed permeability is well approximated by the intra-aggregate porosity contribution \(k_p\). At values of \(\epsilon\) above \(\epsilon_t\), the dominant contribution is related to inter-aggregate porosity, i.e. \(k_a\).

Indeed one can calculate the contributions to the overall system permeability where the transition point \(\epsilon_t\) is related to the native aggregate density \(\epsilon_{pi}\) and plot the dominant contributions against the experimental results. Figures 14-16 show these plots for the various systems investigated together with the experimental results. In fitting the experimental data with the model we have extrapolated \(D_{app}\) from the slope of the Washburn coefficient versus the intra-aggregate permeability contribution \(k_p\). It is evident in the case of silica and CaCO3 that the fittings show a
positive intercept with the y axis. This is most likely due to the fact that the Blake-Kozeny formulation is not able to describe permeability of powder at very low porosity and that closed porosity is probably present in the powder bed. By fitting the data at low porosity where the linear behavior is observed, one can actually explain the change in the infiltration regime by the increasing contribution of the inter-aggregate porosity to permeability.

The infiltration rates observed in the high porosity region are even larger than the ones predicted by the model. When we separated the two contributions to the hydraulic radius theory for inter-aggregate and intra-aggregate porosity, we made the assumption that the fluid between aggregates would wet the entire surface of the primary particles. From a phenomenological point of view, one can envision that the wetted surface by the fluid would be smaller and smaller as the porosity increases, reaching eventually the stage where only the external surface of aggregates is wetted. This would translate in a faster flow between aggregates which can easily explain the experimental results.

Conclusions

The Blake-Kozeny equation was modified taking into account a hierarchical structure of the powder bed, considering a different packing behavior at the level of aggregates and primary particles. We distinguished between inter-aggregate porosity and intra-aggregate porosity and modified the Blake-Kozeny equation highlighting the contributions that both porosities give. At high porosity the inter-aggregate pores dominate in the infiltration process, while, at higher density, the intra-aggregate terms become the most important.

This can explain a sudden change observed in the experiments of infiltration kinetics that occurs upon compaction of the powder bed above its tap density.

Acknowledgment

The financial support from Pirelli Pneumatici S. p. A. is gratefully acknowledged.
Appendix

Assuming spherical aggregates, one can calculate the extent at which interpenetration will fill the inter-aggregate pores. Although the specific values depend of course on the configuration of the aggregates, however the differences among different configurations are probably irrelevant for the purpose of this study. We considered, as an example, an assemblage of spherical aggregates in an octahedral configuration. This is represented as planes of sphere, with each sphere on one plane at the center of four adjacent spheres in the plane below and above. The schematics is presented in Fig. 17.

Assuming a uniaxial compression, the pores between the spheres will be filled when the center of the spheres of the upper plane will be tangent to the top surface of the spheres of the lower plane. This allows us to calculate the changes in void fraction inside the spheres in order to relate the changes in $\varepsilon_p$ with $\varepsilon_a$. Each upper sphere increases its density due to the intersection with the spherical caps of four spheres below. The intersection volume can be calculated indirectly considering a cube of side $r$ with each vertex in the center of one sphere. The intersection volume between the cube and sphere is one eighth of the volume of the sphere which leads to a void volume:

$$V_{\text{void}} = r^3 \left(1 - \frac{\pi}{6}\right)$$  \hspace{1cm} (A.1)

When the void is filled, the intersection volume between the two spheres is the volume of the cube minus twice the void volume. The total intersection volume of the sphere with the lower plane is therefore:

$$\delta V_{\text{int}} = 4r^3 \left(\frac{\pi}{3} - 1\right)$$  \hspace{1cm} (A.2)

The solid volume fraction of sphere A will therefore change from its value $\phi$ to a value $\phi'$:

$$\phi' = \frac{\phi V_{\text{sph}} + \phi V_{\text{int}}}{V_{\text{sph}}} = \phi + \delta \phi$$  \hspace{1cm} (A.3)

where $V_{\text{sph}}$ is the volume of the sphere and $\delta \phi$ represents the added solid volume fraction $\phi \delta V_{\text{int}}/V_{\text{sph}}$. 
The changes in porosities can be easily calculated and lead to the following expression:

\[
\varepsilon'_p = 1 - \phi' = \varepsilon_{pi} - \delta\phi = \varepsilon_{pi} \left(1 + \frac{\delta V_{int}}{V_{sph}}\right) - \frac{\delta V_{int}}{V_{sph}} \tag{A.4}
\]

where \(\varepsilon_{pi}\) is the void fraction of an unmodified sphere. Thus there is a linear relationship between the changes in void fraction inside and between the spheres.

The value of \(\delta V_{int}\) is 0.045 which leads to the conclusion that a small changes in the void fraction of the spheres is enough to fill completely the pores between them. The numerical value is related to the octahedral configuration we have analyzed. However one can generalize and extend the calculation to different configurations.

These assumptions can be translated in a mathematical formulation:

\[
\varepsilon_a = \min(\varepsilon_{ai}, \varepsilon^*) \cdot \frac{\varepsilon_p - \varepsilon_{pi}}{\varepsilon_{po} - \varepsilon_p} \cdot \varepsilon'_p \leq \varepsilon_p \leq \varepsilon_{po} \tag{A.5}
\]

The first stage is present only if the initial inter-aggregate porosity is larger than the critical porosity \(\varepsilon^*\). If \(\varepsilon_{ai} < \varepsilon^*\) it is not meaningful to consider a hierarchical structure. A low inter-aggregate initial porosity means that we do not recognize aggregates as a separate structure governing infiltration. The porosity \(\varepsilon_{ai}\), in this case, would represent larger pores due to loose arrangement of large clusters of primary particles. The second term in Eq. A.5 describes the collapsing of large pores into small ones. The process is fast compared to the reduction of the overall porosity. This should be representative of the fact that interpenetration causes almost immediate filling of the large pores between aggregates. The last stage represents a reduction in porosity when no aggregates are any longer present.

References

[Alchemy Program]{alchemy} Alchemy software package by Scivision


## TABLES

<table>
<thead>
<tr>
<th>Powder</th>
<th>$\rho_{pp}$ (g/cm$^3$)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>DBPA (cm$^3$/100g)</th>
<th>$D_{prim}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>2.2</td>
<td>98</td>
<td>NA</td>
<td>28</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>2.7</td>
<td>10</td>
<td>NA</td>
<td>250</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4.1</td>
<td>9.4</td>
<td>NA</td>
<td>167</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>1.86</td>
<td>205</td>
<td>112</td>
<td>16</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Viscosity @ 25 °C (cS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>10, 50, 100, 500, 1000</td>
</tr>
</tbody>
</table>

Table 1: Main characteristics of powders and polymers used in the experiments. $\rho_{pp}$ indicates the density of primary particles, $S_{BET}$ indicated the BET surface, $D_{prim}$ indicates the primary particle diameter calculated from the BET surface [Bird, 1960]. DBPA is the dibutyl phthalate absorption number.
Table 2: Structural characteristics for selected powders extrapolated from infiltration experiments.

$\varepsilon_{TAP}$ indicates the total porosity of the powder bed at tap density

<table>
<thead>
<tr>
<th>Powder</th>
<th>$D_{prim}$ (nm)</th>
<th>$\varepsilon_{TAP}$</th>
<th>$D_{app}$ (nm) (tap density)</th>
<th>$D_{app}$ (nm) (high density)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>28</td>
<td>0.879</td>
<td>737</td>
<td>200</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>250</td>
<td>0.871</td>
<td>700</td>
<td>250</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>167</td>
<td>0.883</td>
<td>800</td>
<td>70</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>16</td>
<td>0.93</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>
Table 3: Values of intra-aggregate porosity for different powder extrapolated from the experimental results.

<table>
<thead>
<tr>
<th>Powder</th>
<th>$\epsilon_t$</th>
<th>$\epsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>0.860</td>
<td>0.670</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>0.854</td>
<td>0.630</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.850</td>
<td>0.690</td>
</tr>
</tbody>
</table>
Figure 1: Schematic representation of the experimental apparatus for measurement of infiltration. A cylindrical glass is filled with powder and lowered into a beaker full of liquid of known viscosity. The length of infiltrated powder is recorded as a function of time.
Figure 2: Raw data for Washburn experiment. The linear relation between $l^2$ and time $t$ is evident.
Figure 3: Plot of Washburn coefficients for fluids of different viscosities $\eta$ infiltrating silica powder at tap density.
Figure 4: Plot of Washburn coefficients at different porosities for infiltration of PDMS into silica powder.
Figure 5: Plot of Washburn coefficients versus porosity for $CaCO_3$. 
Figure 6: Plot of Washburn coefficients versus porosity for TiO$_2$. 

Dapp = 70 nm
Figure 7: Plot of Washburn coefficients versus porosity for carbon black powder.
Figure 8: Schematic representation of the compaction process.
Figure 9: Plots of $\epsilon_a$ and $\epsilon_p$ versus powder bed solid volume fraction for a very loose aggregate ($\epsilon_{pi} = 0.9$).
Figure 10: Plots of $\varepsilon_a$ and $\varepsilon_p$ versus powder bed solid volume fraction for dense aggregates ($\varepsilon_{pi} = 0.7$).
Comparison of $k_a$ and $k_p$; ($\varepsilon_{\text{pi}} = 90\%$)

Figure 11: Plot of the two main contributions $k_a$ and $k_p$ to the permeability for initial intra-aggregate porosity of 90\%
Figure 12: Plot of the two main contributions $k_a$ and $k_p$ to the permeability for initial intra-aggregate porosity of 70%
Figure 13: Plot of $\varepsilon_a$, $\varepsilon_p$ and $\varepsilon$ versus $\varepsilon^2/(1-\varepsilon)$ for a powder with initial intra-aggregate porosity 0.57, as calculated for Carbon Black.
Figure 14: Plot of the Washburn coefficient for Carbon Black. $\varepsilon_{pi} = 0.57$ (from DBPA) which corresponds to $\varepsilon_t = 0.82$. Also shown are the experimental results.
Figure 15: Plot of the Washburn coefficient for CaCO$_3$. $\varepsilon_t = 0.85$ which corresponds to $\varepsilon_{pi} = 0.64$

Also shown are infiltration experiments results.
Figure 16: Fit of the inter-aggregate and intra-aggregate contributions to the infiltration rate for silica powder.
Figure 17: a) Representation of octahedral configuration; side view and b) top view. c) Configuration corresponding to $\varepsilon_a = 0$. 

Side View: Filled pores