Method for probing the microstructure of particle beds using infiltration behavior

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ABSTRACT

An approach for investigating the microstructural features that govern the capillary-pressure driven infiltration of liquid within beds of particles has been developed. Simultaneous measurement of the rate of liquid mass uptake and the volume occupied by that liquid within the particle bed provides information about the fraction of pore volume that participates in liquid infiltration as well as the effective size of the geometric unit that governs infiltration kinetics. Experiments involving the infiltration of squalane within different grades of silica and titanium dioxide illustrate the technique. The method is sensitive enough to enable interpretation of how variations in the morphology of the particles comprising the bed, or small changes in packing density within the particle bed, can lead to large changes in infiltration behavior.

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1. Introduction

A fundamental understanding of the wetting of particle beds or individual particle agglomerates is of significant technological interest in chemical and material manufacturing processes. For example, the dispersion of fine-particle clusters is strongly affected by liquid infiltration behavior, and often this determines the final product quality [1–6]. In general, the size, shape and microstructural characteristics of particles or agglomerates and the interfacial interactions between the solids and the wetting liquids govern liquid infiltration.

The Washburn method is a classical experimental approach to study the wetting behavior of powders as driven by capillary pressure [7–11]. In this method, the rate of liquid incorporation into a powder bed is measured, and this information can be used, for example, to determine relevant characteristics of the solids [9–22]. The basic Washburn analysis often does not apply accurately to beds of particles possessing complex microstructures [22], and empirical models are sometimes proposed to correct for any discrepancies that are observed [14]. One of the root causes for these inconsistencies is that the standard Washburn analysis is based on the assumption that all void space within the powder compact is accessible to liquid infiltration, and that pores are of a consistent size. However, this is not the case for beds of particles with complicated shapes or hierarchical microstructure which may contain closed pores or interstitial regions that are difficult to access by the infiltrating liquid.

In order to provide additional insight on fluid infiltration in beds comprised of complex particles, we developed an experimental approach in which the kinetics of liquid uptake is assessed simultaneously by two measurements. One involves the determination of the mass of liquid imbibed, which allows for the determination of the actual volume of liquid incorporated within the powder bed. Concurrently, we make visual observations of the volume of the powder bed occupied by infiltrating liquid. Comparing these two sets of observations provides information about filled and unfilled pores within the powder bed. Thus, this technique provides a tool to probe powder microstructure on the length scale that governs infiltration.

2. Experimental

2.1. Concept

For a powder bed of uniform cross-sectional area A_{bed}, the rate of fluid infiltration is described by the classical Washburn equation [2,7,23]:

$$l^2 = W_l \, t \tag{1}$$

where l is the distance to which the bed has been infiltrated at time t, and the physical properties of the system are grouped into the Washburn coefficient

$$W_l = \frac{12 D_{app} \varepsilon^2 \gamma_{lv} \cos\theta}{150(1-\varepsilon)\eta}. \tag{2}$$

Here, ε is the bed porosity, γ_{lv} is the liquid surface tension, θ is the liquid–solid contact angle, η is the fluid viscosity, and D_{app} is an apparent average diameter of the particles within the powder bed. The value of W_l can be determined from experimental observations of $l(t)$.
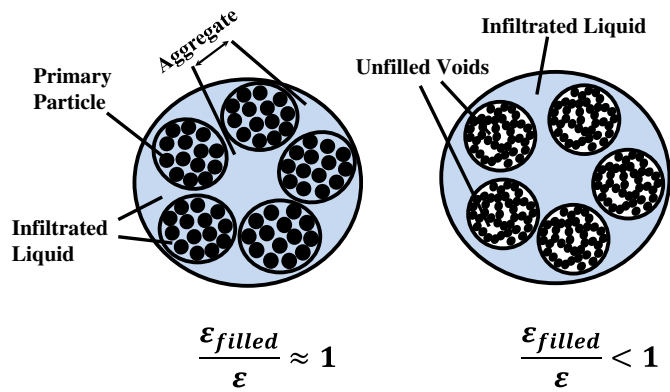
Fig. 1. Schematic illustration of agglomerates with different degrees of liquid infiltration.

Table 1
Selected properties of squalane.

Surface tension (mN/m)	Density[a] (kg/m³)	Viscosity [27] (Pa·s)
26.9 ± 1.7	810	0.035

[a] Value from supplier.

Since only a portion of the pores may be occupied by the infiltrating liquid, the mass of liquid taken up by the powder bed is given by

$$m = \varepsilon_{filled} \rho_l A_{bed} l \tag{3}$$

where ρ_l is the density of the infiltrating liquid and ε_{filled} is the volume fraction of the bed actually filled with liquid. Based on the expectation that $l^2 \propto t$, we have:

$$m^2 = Ct. \tag{4}$$

From measurements of $m(t)$, the parameter C can be computed. Comparison of the experimentally determined values of W_l and C data leads to

$$\varepsilon_{filled} = \frac{1}{\rho_l A_{bed}} \sqrt{\frac{C}{W_l}} \tag{5}$$

where we expect that $\varepsilon_{filled} \leq \varepsilon$. The ratio $\varepsilon_{filled}/\varepsilon$ gives the pore filling factor, which is expected to be related to the microstructure within the powder bed. Fig. 1 schematically illustrates the degrees of liquid infiltration in agglomerates with different pore filling factors (i.e. the powder bed is saturated for the pore filling factor close to unity).

2.2. Materials

Three types of amorphous, precipitated silica (denoted as A, B1, and B2; manufactured by the Rhodia, PPG, and Evonik, respectively) with different agglomerate morphology were tested. Silica A is in micropearl (highly spherical microparticles with a circularity shape factor of 0.83) form, with a BET nitrogen surface area of 160 m²/g, while silicas B1 and B2 are in granular form, with agglomerates of circularities of 0.69

and 0.65, and BET nitrogen surface areas of 135 m²/g and 175 m²/g, respectively. The values of the BET nitrogen surface area indicate that the primary particles for the various grades range from 13.5 to 17.5 nm. Fig. 2 shows micrographs of the various silica agglomerates to illustrate the differences in their morphologies. Silica A agglomerates have relatively smooth surfaces and are spherical in shape. Silicas B1 and B2 have irregular shapes and rough surfaces. In addition, two as-received titanium dioxide samples, TiO₂-I (DuPont) and TiO₂-II (Kronos Worldwide, Inc.), having agglomerates size<400 μm were also tested. These particles do not have a hierarchical structure, as does silica. Moreover, solid glass microspheres (Spheriglass A-Glass, Potter Industries, LLC), with an average diameter of 160 μm (sieved) and specific gravity of 2.5, were used as a control sample to single out the influence of primary particle and pore sizes.

Squalane (Sigma-Aldrich) was chosen as the infiltration liquid due to its expected non-specific interaction with the solids studied. Table 1 provides some relevant properties of squalane. The surface tension reported was measured using a tensiometer (K100, KRÜSS GmbH).

2.3. Experimental methods

The surface energy of the silica powders used in this study was assessed via a Zisman plot using data obtained from a series of Wilhelmy plate experiments. For these measurements, spray adhesive (3M™ Photo Mount Spray Adhesive) was applied to a glass plate (Corning Inc.), which was subsequently dusted with silica powder, previously ground using a mortar and pestle [24,25]. Fig. 3 shows sessile drops of water (9.00 μL) on these plates with and without silica present and confirm the integrity of the coverage by silica on the plate. For the Wilhelmy plate experiments, only advancing contact angles were used, and methanol–water mixtures (see Table 2) were employed as probe liquids [26]. The length of the liquid-plate contact line was measured using a caliper.

The contact angle of squalane on silica was also estimated by flotation tests. Silica powder was placed on the surface of squalane liquid, and the tendency of the silica to float at the interface was observed.

Fig. 4 shows a schematic of the apparatus used for the infiltration experiments. For infiltration experiments with the silica powders, sieves were used to obtain agglomerates in the range of 150–300 μm. The powder to be tested was poured into an open-ended, graduated glass tube (inner diameter=1.22 cm) containing glass wool at the bottom to
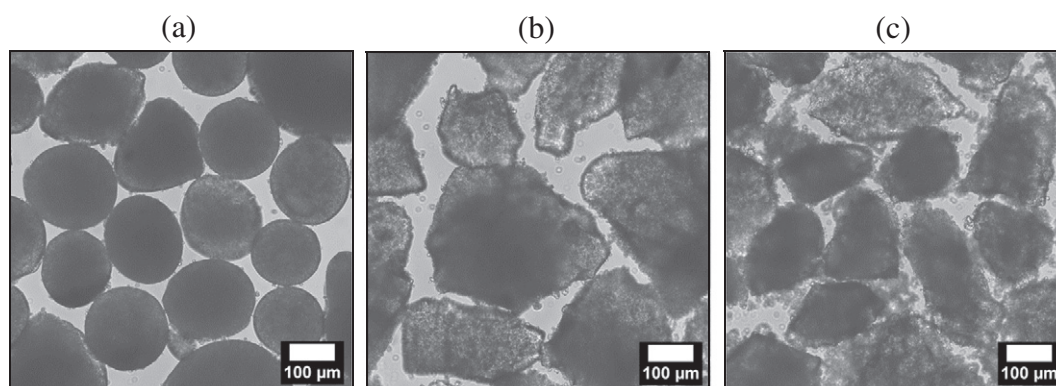

Fig. 2. Micrographs of the silica powders: (a) silica A; (b) silica B1; and (c) silica B2. The scale bar in each micrograph represents 100 μm.