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Wetting dynamics and contact angles of powders studied through capillary rise experiments

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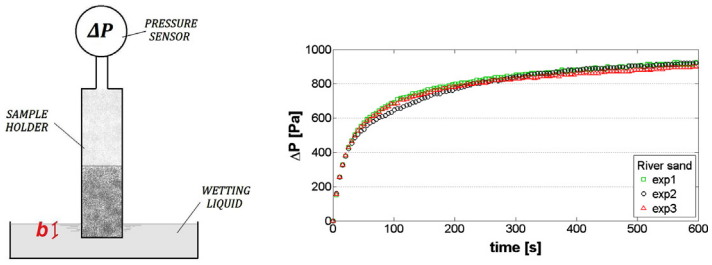
HIGHLIGHTS

- A method to measure advancing and equilibrium contact angles in powders is proposed.
- A new equivalent capillary radius for packed bed is used.
- We improve the measure of powder effective porosity accounting for their flowability.

GRAPHICAL ABSTRACT



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ABSTRACT

Wettability is an important property involved in the industrial use of granular solids and powders. It is commonly described with the contact angle and an experimental method for its determination in dynamic conditions is proposed in this work. The method is based on the capillary rise of the wetting liquid into a packed bed of the material under analysis. Differently from the classical Washburn method, the packed bed is closed to the atmosphere and the air pressure increase is measured allowing to evaluate the powder contact angle through a dynamic balance of the pressure forces. In the expression of such forces a new equivalent capillary radius for the powder bed is used based on an alternative definition of the particle equivalent diameter. This diameter is closely related to the length of the three phase line which divide the wet portion of the bed from the dry one and mirrors the physics of wetting process better than the classical Sauter diameter. A way to determine it with optical microscopy is given. Also the measure of the packed bed porosity (entering in the equivalent capillary radius definition) has been improved by using the effective porosity concept [Hapgood et al., J. Coll. Interface Sci. 253 (2002) 353–366] and by modifying the way of estimating it. The proposed experimental technique, coupled to the theoretical model for the packed bed, can describe accurately the packed bed geometry and the wetting dynamics by following the changes of the contact angle from its initial maximum value up to the final equilibrium one.

1. Introduction

The wettability is a physicochemical property which has an important role in the industrial use of powdered and granular solids. Granulation, flotation and dissolution are just some examples of the several operations where powder wettability is important. In the wet granulation process the size of primary particles is increased by binding them into agglomerates using capillary forces [1,2] and the affinity between the liquid binder and the solid impact on the final size of the granules [3]. In the mineral processing, flotation is widely used to quickly and efficiently separate valuable minerals from the gangue minerals. The separation is controlled to a large extent by the relative wettability of mineral particles in a pulp [4,5]. In the dissolution process of commercial powders (for instance instant drink powders) a larger affinity between the liquid and the solid phase leads to a faster wetting and sinking of the particles and therefore increases the dissolution rate [6]. In all these operations the contact angle plays a major

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Nomenclature

b	immersion depth of the sample holder in the liquid [m]
d_{OM}	diameter obtained from optical microscopy [m]
d_{pa}	mean equivalent diameter related to the ratio (projected area)/(wet perimeter) [m]
$d(x)$	diameter of the exposed circumference in a spherical particle cross sectioned at height x [m]
d_{sv}	Sauter mean diameter [m]
g	gravitational acceleration [m/s^2]
h	height reached by the liquid [m]
H_{sh}	height of the sample holder assumed cylindrical with constant section [m]
K	proportionality factor between height and pressure [m/Pa]
l	length covered by the liquid in the bed [m]
P_0	atmospheric pressure [Pa]
P_f	final pressure after the compression [Pa]
R	radius of the cylindrical capillary tube [m]
R_{eq}	equivalent capillary radius [μm]
R_h	hydraulic radius [m]
t	time [s]
x	(for a particle) height covered by the liquid [m]
γ_{LV}	liquid–vapor surface tension [J/m^2]
γ_{SL}	solid–liquid surface tension [J/m^2]
γ_{SV}	solid–vapor surface tension [J/m^2]
ΔP	relative pressure (referred to the atmospheric one) [Pa]
ΔP_{cap}	capillary pressure [Pa]
ε	generic porosity of the powder bed [–]
ε_{eff}	effective porosity [–]
ε_{tap}	tap porosity [–]
ε_{min}	porosity value related to the maximum packing of the powder bed [–]
η	viscosity of the wetting liquid [Pa s]
θ	generic value of the contact angle [°]
θ_A	advancing contact angle [°]
θ_E	equilibrium contact angle [°]
θ_R	receding contact angle [°]
ρ_b	bulk density of the powder bed [kg/m^3]
ρ_L	density of the wetting liquid [kg/m^3]
ρ_M	density value related to the maximum packing of the powder bed [kg/m^3]
ρ_s	solid intrinsic density [kg/m^3]
τ	tortuosity factor [–]

role in the wetting process. The contact angle is an indicator of the liquid–solid affinity and originates from the equilibrium balance between adhesive and cohesive forces [7]. The Young equation:

$$\cos\theta_E = \frac{\gamma_{SE} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

links the contact angle to the three surface tensions involved in the formation of a sessile drop of liquid on a flat horizontal solid surface in presence of a third phase (a gas or an immiscible liquid), as represented in Fig. 1a.

The three surface tensions are the solid–liquid γ_{SL}, the solid–vapor γ_{SV} and the liquid–vapor γ_{LV} tension. The condition of zero contact angle is referred to as perfect wetting while the cases with angles lower or greater than 90° are referred to as wetting and non-wetting, respectively. In the above definitions the drop is in static equilibrium and therefore the angle is called *equilibrium contact angle* θ_E. In several industrial application however the liquid is in motion with respect to the solid so that also an *advancing* θ_A and a *receding* θ_R *contact angle* can be defined (Fig. 1b) [8].

The evaluation of the contact angle through Eq. (1) is not a trivial task because the solid–vapour and the solid–liquid tensions are difficult to evaluate [7] so that the direct measurement is the preferred method in practice. Considering powders however, even the direct measurement is not trivial at all. Because of the discrete nature of the particles, the surface of powder sample is irregular and porous. The droplet of liquid can spread and sink into the porosities with a kinetics that can be also very fast, depending on the solid–liquid affinity, on the particle size, on the consolidation state of the powder and obviously on the viscosity of the liquid.

As an alternative to the sessile drop method the contact angle of powders can be evaluated with the rising liquid method [7]. It relates the contact angle to the rising rate of the liquid into a packed bed of the powder under test. The packed bed is assumed to be equivalent to a bundle of capillary tubes with circular section and equivalent (or effective) radius, R_{eq}. The driving force is assumed to result only from the capillary pressure (the hydrostatic head contribution related to the height h reached by the liquid is neglected). A proportionality between the square of the height h reached by the liquid in the bed and the time t can be found. This relationship is expressed in the Washburn's equation (2) as:

$$h^2 = \frac{R_{eq}\gamma_{LV}\cos\theta_A}{2\eta}t \quad (2)$$

where η is the viscosity of the wetting liquid. As alternatives to the direct measurement of the height h, also the weight [9] or the overpressure (generated by the rising liquid when the sample holder is closed to the atmosphere) can be measured [10,11].

Unfortunately in Eq. (2) besides θ_A also R_{eq} is unknown and needs to be evaluated. R_{eq} can be determined by using a reference liquid assumed to "perfectly" wet the powder under test. For a perfectly wetting liquid the $\cos\theta_A \sim 1$ so that R_{eq} can be found from the experimental evaluation of the $h^2(t)$ slope. Provided that R_{eq} is independent of the wetting liquid and does not change during the packing procedure, it can be used then in Eq. (2) to calculate $\cos\theta_A$ by measuring the slope of $h^2(t)$ for the liquid under test.

The evaluation of R_{eq} is in any case a critical step in the determination of the contact angle. The use of a perfectly wetting liquid can present some drawbacks. First of all it is necessary to find a liquid that perfectly wets the powder under study [7,12]. This can be problematic when several materials have to be analyzed so that a different perfectly wetting liquid could be necessary for each of them [12]. It is common to assume as perfectly wetting liquid, the most wetting one among those available to whom is doing the experiments [6] but this produces results that depend on the choice of the reference liquid. Moreover the method requires that the geometry of the powder bed (i.e. R_{eq}) is the same in the tests with the reference liquid and with the liquid under study. This is possible only applying a systematic procedure that guarantees a reproducible packing of the powder among different experiments [13].

A different approach is that of modeling, under simplifying assumptions, the structure of the solid bed and the solid–liquid physical interaction during wetting [13,14] so that to find an analytical expression for R_{eq}. This approach has been followed in the present work. In particular, with respect to published literature, an alternative particle equivalent diameter and an improved way of estimating the effective porosity of the packed bed have been proposed for the calculation of R_{eq}. The overpressure generated by the liquid rise has been measured in order to estimate the contact angles as in [10,11], but differently from Iveson et al. [10] the perfectly wetting liquid was not necessary (because of the analytical estimation of R_{eq}) and differently from Wei et al. [11] an