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Pore analyses of highly porous diatomite and clay based materials for fluidized bed reactors

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ABSTRACT

Microstructure of diatomite-clay based granulates for fluidized bed reactors, heat treated at 800 and 1300 °C, were investigated by mercury porosimetry, nitrogen sorption using Barrett–Joyner–Halenda (BJH) model and scanning electron microscopy. Special considerations were made on characterisation of ink-bottle pores by performing a multi-cycle porosimetry. The comparison between extruded granulates and pure diatomite powders revealed that diatom structure is still intact after high shear process and that pore size distribution of the extrudates is mainly dominated by diatom structures. A mercury retention factor of 0.62 and 0.92 at 800 °C and of 0.99 and 0.98 at 1300 °C were obtained for Filter Cel and Super Cel powders, respectively. While, a retention factor of 0.28 and 0.91 has been found out for extrudates heat treated at 800 and 1300 °C. These data permits to determine the pore network heterogeneity. Coalescence of diatom frustules at 1300 °C leads to a decrease of pore volume in the meso- and macro-range when compared to at 800 °C, whereas the ink-bottle pore size did not change significantly. Apparition of large macropores occurred at 1300 °C caused by a higher shrinkage of diatoms compared to clay.

1. Introduction

Diatomaceous earth, also called diatomite, is a sedimentary rock resulting from the siliceous fossilized skeleton of diatoms (amorphous $SiO_2 \cdot nH_2O$ and crystallised silica). It is composed of rigid cell walls called frustules. Depending on their species, frustules dimensions from less than 1 to more than 100 μm can be found with features like protuberances and pores in the mesoscale range. Diatoms are very promising for high performance technologies (e.g. microelectronics, chemo- and bio-sensoring, transducers, etc.) [1] or as fillers, filters or membranes, catalysts, adsorbents, mild abrasives [2,3] due to their numerous properties, such as luminescence semiconducting properties of chemically altered frustules by TiO_2, GeO_2, ZrO_2 or SnO_2, high mechanical strength whilst having high porosity, high availability and low costs. Diatomite filter aid (DFA) is the crystallised form of the diatom and is often heat treated between 800 and 1000 °C in order to remove the small organic structure of the fossil.

In this work, DFA structures are of interest as support for gasification applications in fluidized bed reactors, due to their highly open porous structure in combination with their high mechanical properties. Such properties were previously reported [4] by analysing the influence of clay content and sintering temperature on the microstructure, material structure and attrition resistance. A bimodal porosity is usually preferable because smaller pores (micro- and mesopores) enhance specific surface area, while macropores increase transport and gas diffusion. The porous structure, porosity and pore size distribution, of granulates can be investigated by imagery techniques such as optical, scanning electron microscopy or tomography [5–7], by calorimetric methods such as thermoporometry [5,8] or SAXS and SANS [9]. Mercury porosimetry (MP) can be used to characterize open pore size distribution in the meso- and macro-range and to determine the volume of interconnected porosity. Its main difficulty is the determination of the so-called ink-bottles, which consist of large pores connected by narrow ones or necks. In this particular case, the total volume of large pores will be attributed to the narrows due to network effect (e.g. higher pressure will be necessary to infiltrate first the narrow pores or necks situated close to the surface before infiltrating the

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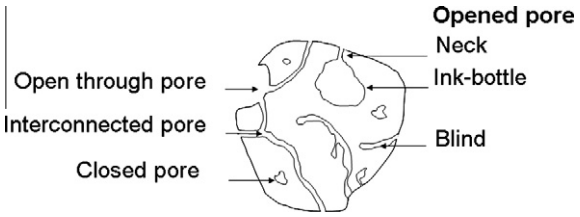

Fig. 1. Pore terminology for this paper.

largest) [10]. Such porosity can be called heterogeneous porosity and can be described by the bottle neck pore size. Pore size distributions are derived from the Washburn equation [11]. Mercury porosimetry can be coupled with nitrogen sorption analysis at −195.7 °C with Barrett–Joyner–Halenda (BJH) model [12,13] for a better understanding of pore size distribution in the meso-range. N_2 sorption is based on the combination of Kelvin equation and the use of the adsorption or desorption branch of the isotherm according to the porous structure.

In this paper, IUPAC terminology [5] is used for the investigation of porous diatomite filter aids based materials. A porous structure is usually composed of random pore sizes from the free (interparticle voids) or internal (intraparticle voids) pore volume. The pore size is grouped into three categories; the first one, called micropore corresponds to pores with a radius smaller than 1 nm. The second one, mesopore, has a size between 1 and 25 nm. Finally, the third one, macropore, is composed of pores larger than 25 nm in radius. Complementary terminology [4] is shown in Fig. 1.

The aim of this study is the investigation of highly porous diatomite filter aids – clay granulate bed materials by mercury porosimetry and nitrogen sorption to be able to understand the formation of pore network during the sintering process and to determine the ink-bottle structure for later gas flow simulations in fluidized bed reactors.

2. Porosity characterization

2.1. Mercury porosimetry

This technique permits the evaluation of meso- and macro-open porosities. At low pressure, larger pores will be filled and by increasing the pressure hydraulically up to 200 MPa, smaller pores will be infiltrated down to approximately 3.7 nm in radius.

Kaufmann et al. [14] performed a multi-cycle porosimetry to separate the network effect involved during the first porosimetry measurement. This method is based on the assumption that ink-bottles are still filled with mercury Hg after the first extrusion step of a cycle. Ink-bottle pores accessible by necks can be evaluated by calculating the difference of pore distribution between first and second intrusion. Using this method, heterogeneous pore network can be described in a better way. Liu and Winslow [15] assimilated the first intrusion curve as the "total intrusion distribution", the second one as the "reversible" portion and the difference between the second and the first intrusions as the "irreversible sub-distributions". This terminology was used because the difference between both curves corresponds to the pore structure which is irreversibly filled by mercury (e.g. ink-bottle pores and heterogeneous pore network).

Fig. 2(b) schematically presents the filling of open pore types, e.g. small and large blind, open interconnected through, and ink-bottle pores according to the applied pressure during a multi-cycle test (Fig. 2a). During first intrusion, larger pores are filled at low pressure, whereas smaller ones are filled with the non-wetting liquid at higher pressure. In the extrusion step, decreasing pressure leads to the retreat of mercury first in the small pores followed by the largest (ink-bottle pores). It is assumed in this model that in open-through ink-bottle pores, mercury retreat from the necks, but cannot from smaller pores behind the ink in the case of blind pores. However, if pores are open-through or connected to neck pores, it is also possible that mercury remains trapped in the solid network due to breaking-off of mercury into droplets ("snap-off effect"). The so-called "energy barrier" or "snap-off factor" corresponds to the additional energy necessary to extrude mercury out of the pores. It is affected, for example, by the opening angle of conical cylindrical pores, the contact angle between mercury and the material and the network of the surrounding pores [16]. For example, a filled throat surrounded by three empty ones will empty at an earlier stage of the extrusion than one connected to two or three filled ones. Influence of the variation of Hg contact angle during extrusion step was not characterized in the present work. However, several papers already refer to mercury entrapment [17–20], the fact that it can still continue to extrude some hours after a porosimetry cycle [21] and determination of the network by modelling [22,23]. It is known that extrusion kinetics depend on the tortuosity of pore network and surface chemistry of the material. Indeed, Smithwick and Fuller [24] stipulated that equilibrium during intrusion steps can take 2–3 min, but 20–30 min during extrusion in a macroporous material. Androutsopoulos and Salmas [22] proposed a pore structure model (CPSM) that permits the determination of the trapped mercury as a function of the pore size. As mentioned earlier, mercury remaining in the sample at lower

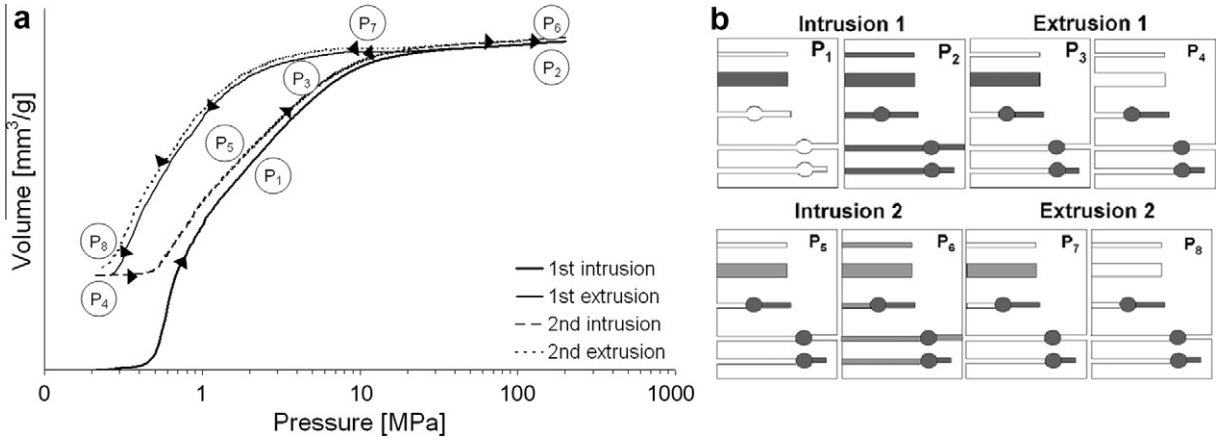

Fig. 2. Scheme of two intrusions (pressurization)/extrusions (depressurization) curves (a) and the filling of open and blind pores at applied pressures (b). Dark grey corresponds to the first filling and light grey to the second one.