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# Measurement of the porosity of a pseudo-spherical nanostructured particle deposit formed by filtration

Jonathan Nuvoli<sup>1,2</sup>, Soleiman Bourrous<sup>1</sup>, François-Xavier Ouf<sup>1</sup> and Dominique Thomas<sup>2</sup>

<sup>1</sup>Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SCA, Gif-sur-Yvette, 91192, France

<sup>2</sup>Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

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Contact: soleiman.bourrous@irsn.fr

## Abstract

In many applications involving nanoparticles, the question of controlling the properties of the films formed (particularly in terms of porosity) remains incomplete. These applications cover an extensive array of fields ranging from the manufacture of nanofilms to the prediction of the pressure drop of nanoparticle films formed on the surface of air purification filters. A review of the literature shows that the porosity of nanometric particle deposits has mainly been studied by numerical simulation. The few experimental studies conducted have focused on micron-sized particles or nanoparticle aggregates under limited operating conditions. The objective of this study is to confirm the porosity results of nanometric particle deposits obtained by the previous simulations and to correlate the porosity with relevant dimensionless numbers. The changes in porosity according to the various operating conditions confirm those obtained during the numerical simulations. All the experimental porosity values could be correlated to the Stokes number alone.

## 1. Introduction

Nanoparticles, due to their reactive properties (due to their high surface area to mass ratio), are currently generating a lot of interest owing to their wide variety of applications in fields such as the manufacture of batteries (Poizot *et al.*, 2000), catalysis, separation and purification techniques, ultra-light structural materials (Naderi *et al.*, 2019), electrical insulation, gas transport (Khaleel & Hashim, 2019), and, more generally, application requiring the use of physical properties of nanomaterials. There is a real need to control the deposition structure, whether for the performance of sensors (Maheshwari & Saraf, 2006, Castillo *et al.*, 2014) cells and, for our interest, filter clogging.

Fibrous media are currently the most efficient devices in the field of gas-particle separation. However, they have the disadvantage of an increased pressure drop when clogging occurs, which strongly depends on porosity. Specific facilities require containment solutions adapted to their applications (nuclear, bacteriological laboratory, nanomaterials manufacturing, etc.), and relevant way of estimation of the service life of the filters used in given conditions or of optimization of the filter media structure, it is essential to develop physical models able to predict the evolution of the pressure drop of these filters when clogging occurs (Novick *et al.*, 1992, Endo *et al.*, 2002, Kim *et al.*, 2009, Thomas *et al.*, 2014). However, an estimation of the pressure drop requires that the porosity of the deposit formed be known (Schmidt & Löffler, 1991, Yu *et al.*, 2003, Rodriguez-Pérez *et al.*, 2007, Kasper *et al.*, 2010, Elmoe *et al.*, 2011). In most cases, such predictions still remain on empirical considerations and Table 1 proposes a short review of correlations reported in the literature.

*Table 1: Various porosity correlations reported in the literature*

Most of these correlations only take into account the size of the particles, although not the operating conditions which can nevertheless influence the value of the porosity (filtration velocity, pressure, density, etc.). It should also be noted that these correlations are limited to particles larger than 0.2  $\mu\text{m}$  and cannot be easily extended to the nanometer range without further experimental developments.

A few authors have focused on the formation of a monodisperse particles (Tassopoulos *et al.*, 1989, Kulkarni & Biswas, 2004, Lindquist *et al.*, 2014) or aggregates (Mädler *et al.*, 2006) on flat surface and most of them have considered a simulation approach. The deposits resulting from the simulations could be characterized in terms of porosity. For agglomerated or isolated nanometric particles ( $10 < d_p < 30 \text{ nm}$ ), Tassopoulos *et al.* (1989) and Kulkarni *et al.* (2004), Mädler *et al.* (2006) show an evolution of the porosity as a function of the Peclet number following an inverted S-shaped curve. The simulations by different authors shows an increase in the porosity value with the size of particles when Pe tends toward 0 (diffusion limit) and a substantially identical value ( $\varepsilon =$

0.84), regardless of the particle size ( $5 < d_p < 100$  nm), when Pe tends toward infinity (ballistic limit). It should be noted that Lindquist *et al.* (2014) also find a value that is relatively close ( $\varepsilon = 0.846$ ).

This evolution in the form of an inverted S-shaped curve, obtained numerically for non-agglomerated nanoparticles, was also experimentally observed by Thomas *et al.* (2014) for deposits formed by filtration and consisting of agglomerates/aggregates of soot and carbon nanoparticles.

Such a representation, based exclusively on the Peclet number does not, take into consideration the possible inertial effects generally associated with the Stokes number. However, Lindquist *et al.* (2014) point out that both Peclet and Stokes numbers depend on the advection velocity and the pressure of the gas. These authors thus recommend expressing porosity as a function of two dimensionless numbers depending only on the pressure of the gas and the advection velocity respectively, the diffusive Knudsen number  $Kn_D$  (eq 5) and  $\chi_F$ , the ratio between translational kinetic energy and thermal energy (eq 6).

$$Kn_D = \frac{\sqrt{kT m_p}}{f d_p/2} \quad (\text{eq 5})$$

with  $kT$  the thermal energy,  $m_p$  the particle mass,  $f$  the particle friction factor and  $d_p$  the particle diameter.

$$\chi_F = \frac{m_p U_f^2}{kT} = (Pe Kn_D)^2 = \left(\frac{Stk}{Kn_D}\right)^2 \quad (\text{eq 6})$$

where  $U_f$  is the filtration velocity and  $Stk$  is the Stokes number.

Apart from the case of nanoparticle agglomerates/aggregates, there is a latent lack of experimental data about the porosity of a deposit of isolated nanoparticles. Such experimental data is thus required in order to validate the numerical developments available in the literature (Kulkarni & Biswas, 2004, Mädler *et al.*, 2006, Wang *et al.*, 2008, Neesse *et al.*, 2009, Lindquist *et al.*, 2014).

The purpose of this work is to experimentally and systematically study the porosity of a deposit of spherical particles through analytical experiments with controlled particle production and over a wide range of Peclet and Stokes numbers varying from  $10^{-2}$  to  $10^2$  and from  $10^{-3}$  to 10, respectively. To isolate the contribution of phenomenological properties of gas particle transport, the aggregate/agglomerate morphology of nanoparticles will not be taken into account but will be considered in a future publication. Then, in the present study, isolated spherical or nearly spherical particles will be considered. A wide range of the Peclet number makes it possible to isolate the contribution of the diffusion and inertia of the particles. The influence of the following parameters is studied individually for each: density ( $2,000 < \rho_p < 4,000 \text{ kg.m}^{-3}$  according to Zhenhua *et al.* (2003), Lide (2004), Stabile *et al.* (2013) and Zhai *et al.* (2017))), particle diameter ( $60 < d_p < 110 \text{ nm}$ ), filtration velocity ( $0.04 < U_f < 70 \text{ cm.s}^{-1}$ ), and mean free path of the aerosol (66 and 135 nm).

## 2. Equipment and methods

### 2.1. Test bench

The main objective of each experiment is to determine the porosity of non-agglomerated nanoparticle deposits formed by filtration. The experimental set-up used is shown in Figure 1. It aims to simultaneously measure the pressure difference between the upstream and downstream side of the filter as well as the growth rate (ratio of the variation in thickness to the variation in the mass of the deposit) of the particle deposit. These deposits are produced by filtration of various aerosols consisting of non-agglomerated, polydispersed nanometric particles generated by pneumatic dispersion (TSI 3076 atomizer, 1 bar), salt solution (KCl or CsCl). The setup is short enough to neglect any agglomeration. Indeed, dealing with potential agglomeration of particles in the aerosol phase, the particle concentrations are too low ( $10^6 \text{ \#/cm}^3$ ) and the residence time of the particles in the bench is too short to induce a coagulation of the aerosol in the bench (according to Park *et al.* (1999)). The aerosol produced is then dried (Diffusion Dryer 3060-NC TSI) and its particle size distribution is characterized using an SMPS (Grimm 5.403). The mass concentration was monitored using a TEOM 50 microbalance and compared with the successive weighings of the virgin filter and the filter after deposition using a precision balance (Sartorius MSA125P-000-

DA). In order to study the porosity of the deposit formed on the surface of the media (the filtration efficiency is assumed to be constant), PTFE membranes (Merck FSLW, pore size 3  $\mu\text{m}$ ) were used as the filtration media as the penetration of particles into the media is limited and facilitates the study of the surface deposit. These filters have a filtration diameter of 17 mm and 36 mm.

Figure 1: Diagram of the test bench (black line: standard condition, dashed green line: low-pressure condition; black and red line: variable filtration velocity)

Various experimental conditions, representative of ideal nanoparticle filtration and deposition configurations, were considered (Peclet number ranges from 0.01 to 23). To do this, the test bench was set according to the purpose of each experiment:

- *Standard condition* (ambient temperature and ambient pressure) to observe the influence of the filtration velocity, particle diameter and density.
- *Low-pressure condition* to highlight the influence of the mean free path. Since the characterization instruments were not adapted to these experimental conditions (SMPS and TEOM), they were isolated from the rest of the experimental set-up. In the "low pressure" configuration, the experimental points were conducted under the same conditions as in the "standard" configuration in order to preserve the characteristics of the particles measured. A spring valve reduces the pressure upstream the filter to a value of 500 mbar. This pressure, controlled throughout the test, is proportional to the mean free path, which has increased from 66 nm, at ambient pressure, to 135 nm.
- *Dynamic particle filtration* to measure the evolution of porosity as a function of the filtration velocity. When a significant influx of particles occurs, the flow rate through the filter may decrease. Two types of experiments were performed. The first included a calibrated leak (constant pressure drop of the deposit) and for which the leakage rate was measured throughout the experiment. The second involved manually modifying the flow rate during

the experiment by starting at a high filtration velocity (11.1 cm/s equivalent to a Peclet number near 10). After stabilization of the particle deposition growth rate, another lower flow rate was set.

## **2.2. Measurement of the porosity of a particle deposit**

To measure the growth rate of particle deposition, a device, based on a laser trigonometric method developed by Bourrous *et al.* (2016), was improved to minimize measurement uncertainties. The filter membrane remains on a perfectly flat porous support. During filtration, the particles collected on the surface of the membrane form a deposit, the thickness of which increases over time. By monitoring the drift of a laser spot projected at a known angle on the surface of the deposit, its thickness can be determined at any given moment, and its growth rate  $R_x$  can be deduced. This measurement technique (Bourrous *et al.*, 2016, Loulergue *et al.*, 2011, Qiao *et al.*, 2012) has the advantage of being able to determine the evolution of the thickness of the deposit over time with a resolution of 3  $\mu\text{m}/\text{pixel}$  and an experimental uncertainty of 5  $\mu\text{m}$ .

Assuming incompressible particle deposit, a hypothesis that has been validated in light of the cohesive forces of the nanometric particles and the linear evolution of the pressure drop over time, equation 7 makes it possible to determine the porosity of the deposit.

$$\varepsilon = 1 - \left( \frac{m}{\rho_p e S_f} \right) = 1 - \left( \frac{1}{\rho_p R_x S_f} \right) \quad (\text{eq 7})$$

Where  $\varepsilon$  is the porosity,  $m$  is the mass of the deposit measured by weighing the filter before and after the deposit, and also monitored during the experiment by a TEOM microbalance,  $S_f$  is the filtration surface area,  $\rho_p$  is the density of the particles,  $e$  is the thickness of the deposit and  $R_x$  is the growth rate of the deposit ( $\frac{\partial e}{\partial m}$  to minimize the error on the porosity).

The ULTRAPAN device used to form and measure the thickness of deposits is presented Figure 2. It is equipped with 4 lasers and 4 cameras that can be adjusted using micrometric screws. These screws allow the angle and the target of the laser pointer on the membrane to be modified. The

lasers are positioned opposite “two” different diameters of the filtration surface, as shown on the right of Figure 2, and ensure the homogeneity of the deposit by comparing the growth rate of the four targets. An algorithm is used to process each image in order to minimize measurement error. During the clogging, a video was recorded of the drift of the laser spot projected onto the surface of the deposit. This video is broken down into images, and these are converted into grayscale, and the sum of the pixels' intensity calculated along the x/y axes in the direction in which the beam drifts. In addition, a Gaussian function is adjusted on the projection of the spot on the surface of the medium in order to compensate for the variation in absorbance of the deposit formed.

Figure 2: ULTRAPAN device consisting of 4 cameras and 4 lasers for measuring the growth rate at various places on the filter

In order to avoid laser flicker due to the absorption of this beam by the particles and speckle of the laser, the measurement is integrated into several images. This has no effect on the quality of the measurement given the large number of images available (30 per second). The measurement is therefore obtained by summing the acquisition over a considerable time step (greater than 1,000 images). Figure 3 represents the thickness deduced from each laser/camera pair of the ULTRAPAN device. Regardless of the position of the laser beam's interaction with the deposit, the measured thickness is identical, highlighting at the same time its homogeneity as shown by the value of the determination coefficient near one.

Figure 3: Thickness measurement by the 4 lasers of the ULTRAPAN device

Typical examples of experimental curves of the evolution in the pressure drop and the thickness of the deposit as a function of the mass deposited per unit area are shown in Figure 4. The confirmation of this hypothesis, associated with the conclusions from the analysis of Figure 3, allows us to determine an average porosity from the local measurements recorded at the four measuring points of the deposit.



Figure 4: Respective evolutions, as a function of the deposited mass per unit area, the pressure drop (left) and the deposit thickness (right) of a deposit of spherical KCl particles having a diameter of 62 nm

### ***2.3. Characteristics of the particles generated and operating conditions***

Two types of particles were used in this study: pseudo-spherical particles of potassium chloride (KCl), cesium chloride (CsCl). The particle size distribution of the monomodal test aerosols follows a log-normal size distribution (Figure 5), characterized by geometric electrical mobility diameter ( $d_m$ ) and a geometric standard deviation ( $\sigma_g$ ). The characteristics of the aerosols and the operating conditions are listed in Table 2.

Table 2: Experimental conditions and characteristics of the aerosols generated

The choice of aerosols and operating conditions will make it possible to isolate the contributions likely to condition the deposit's porosity: the mass, the particle diameter, the filtration velocity and the diffusion coefficient through a change in pressure.

Figure 5: Particle size distribution of the various aerosols generated

## **3. Results and discussions**

In agreement with previous works in the literature (Kim *et al.*, 2009, Liu *et al.*, 2013, Thomas *et al.*, 2014), we will represent the experimental porosity of a deposit of spherical particles as a function of the Peclet number (computed according to the count geometrical electrical mobility diameter reported in tables 2 and 3). By varying the characteristics of the aerosol generated and the flow conditions, a wide range of Peclet numbers could be scanned (from  $10^{-2}$  to  $10^2$ ). All the tests performed are summarized in Table 3.

### Table 3: Experimental results

Figure 6 groups together all the porosities measured for deposits of different types and under different conditions. For each of the tests, the evolution of the porosity as a function of the Peclet number follows an inverted sigmoid form. This evolution can be divided into 3 zones:

- The diffusion zone ( $0.01 < Pe < 0.1$ ), where the motion induced by diffusion is predominant, is characterized by constant porosity. In view of the experimental limits (filtration velocity  $< 10^{-5} \text{ cm.s}^{-1}$ ), it should be noted that, in this area, no porosity measurements could be made below a Peclet number significantly lower than 0.01 and therefore, we limit our conclusions to this range of Peclet numbers for which the porosity is between 96% and 98%.
- The transition zone ( $0.1 < Pe < 10$ ), where the diffusion phenomenon is no longer dominant and which is characterized by a significant decrease in porosity with the Peclet number. In this zone, the porosity varies significantly between 84% and 97.5%. Moreover, a significant dispersion of porosity values can be noted in this zone, thus highlighting that porosity is not a simple function of the Peclet number.
- The ballistic zone ( $Pe > 10$ ), where particle inertia dominates, is characterized by constant porosity. In this range, all the points are concentrated around a porosity value of 84%, in accordance with the simulations by Madler *et al.* (2006) and Lindquist *et al.* (2014).

Figure 6: Evolution, as a function of the Peclet number, of the porosity of nearly spherical particle deposits formed under different conditions

#### ***3.1. Influence of physicochemical properties of nanoparticles on porosity***

Figure 7 presents the evolution, as a function of the Peclet number, of the porosity of a deposit of KCl nanoparticles for geometric electrical mobility diameters of the aerosol of 62, 87 and

108 nm. It should be noted that for each of the geometric diameters considered, the Peclet number was modified by modifying only the filtration velocity.

Figure 7: Influence of the particle diameter on the porosity of KCl nanoparticles

Table 4: Limit porosity values in the diffusive and ballistic zones

By taking an inverted sigmoid curve adjusted to the experimental points and extracting the limit porosity values in the diffusive ( $\varepsilon_{lim_{dif}}$ ) and ballistic level ( $\varepsilon_{lim_{bal}}$ ) for each diameter studied, it is possible, through Table 4 to quantify the influence of the diameter on porosity.

Thus, in the diffusive zone, an increase in particle diameter leads to a non-significant increase in porosity. Nevertheless, this increase in porosity, although in line with the simulations by Mädler *et al.* (2006), is visible only with the adjustment of the curve on our experimental points. As a result, a porosity limit value of 98% can be assumed.

In the ballistic zone, the measured porosity appears to be constant at around a value of 84%. The porosity does not seem to depend on the diameter of the particles. Excluding compression effects due particularly to particle adhesion, particle diameter has no influence on the porosity of a deposit of spherical particles for a Peclet number greater than 10. Once again, these experimental results validate the conclusions of the simulations by Mädler *et al.* (2006) and Lindquist *et al.* (2014) and are in line with the porosity values of Ou (2013), deduced from the empirical correlation of porosity proposed by Yu *et al.* (2003).

In the transition zone, according to the results of Mädler *et al.* (2006), for the same Peclet number, porosity increases with the diameter of the particles. For a Peclet number of 1, the porosity measured is 0.896, 0.919 and 0.954 for a particle diameter of 62, 87 and 108 nm, respectively.

Figure 8 presents the evolution of porosity values as a function of the Peclet number on a deposit of CsCl and KCl particles of the same geometric diameter but with significantly different densities (here a density ratio near 2).

Figure 8: Influence of the density on the deposition porosity of nanoparticles of the same geometric diameter

The porosity values of a CsCl and KCl deposit are identical in the ballistic and diffusive domains. However, in the transition zone, a higher density leads to a decrease in porosity. This difference may also be due to the shape of the particles. As shown in the TEM (JEOL 2100F) images in Figure 9, the CsCl particles are nearly spherical, whereas the KCl particles are cubic.

Figure 9: TEM image of CsCl particles (left) and KCl particles (right)

### ***3.3. Influence of filtration conditions on porosity***

The objective is to evaluate the influence of a variation in the filtration velocity on the deposition structure over time. This situation is encountered on the majority of filtration installations where the filtration flow rate decreases with an increasing pressure drop of the filter media. Such variations are also highly probable when deposits form on surfaces to produce sensors and in the case of imposed external force fields (thermophoresis, electrophoresis) to control the structure of the deposits (Rodriguez-Pérez *et al.*, 2007). In such situations, the gradual formation of a deposit causes a change in these external force fields, resulting in a change in the deposition rates and deposition regime. Under such conditions, it is necessary to question the relevance of the values and predictive models of deposition porosity obtained under static deposition rate conditions. In an attempt to emulate this operating mode, an air inlet was added between the regulator and the filter of the sampling pump on the test bench. Indeed, in real conditions, the flow rate decrease is a function of the fan capacity and the ventilation configuration.

Two operating protocols were implemented on CsCl particles (Figure 10).

- *Continuous decrease*: A variation in the filtration velocity of 11.1 to 0.15 cm/s by changing the set point on the flow control valve over a given period of time. The porosity is determined at each step.
- *Step-by-step decrease*: A variation in the filtration velocity using the air inlet upstream from the sampling pump. In this situation, the flow rate is measured but not regulated.

The porosity is then determined periodically over short periods of time for which the variation of the filtration velocity can be assumed to be constant.

Figure 10: Evolution of the filtration velocity according to the three approaches

The porosities measured in these two approaches (Figure 11) were compared to experiments conducted at a constant flow rate throughout the entire test. Figure 11 does not show significant differences between these three approaches.

Figure 11: Influence of a variable velocity on the porosity of the deposit

The explanation suggested is that the decrease in flow rate is slow enough to form a homogeneous deposit layer-by-layer. The decrease in the filtration velocity can, therefore, be considered as a succession of steady states.

Experiments at low pressure were conducted in order to observe the influence of particle diffusion on the construction of the deposit. As the air pressure decreases, the mean free path increases and thus, the diffusion coefficient increases. For the same aerosol and by setting the Peclet number as precisely as possible, the influence of the pressure can be observed. Figure 12 summarizes the experimental values obtained with the CsCl aerosol for two pressure values, 1013 and 500 mbar.

Figure 12: Influence of pressure on the porosity of the deposit

At a pressure of 50 kPa, the mean free path is 135 nm as opposed to 66 nm at atmospheric pressure. A drop in pressure results in a decrease in porosity. In the diffusive zone, a decrease in the threshold can be observed, and a substantial decrease in porosity is visible in the transition zone. These results are in line with the simulation performed by Tassopoulos *et al.* (1989).

### 3.4. Empirical correlation

Lindquist *et al.* (2014) established three correlations to evaluate the porosity of a nanometric particle deposit incorporating the two dimensionless numbers  $Kn_D$  (from  $10^{-3}$  to  $10^1$ ) and  $\chi_F$  (from  $10^{-4}$  to  $10^3$ ). Figure 13 presents the porosities determined by Lindquist's correlations as according to experimental porosities. In this study, the comparison was performed on 34 measurements for which the values of  $Kn_D$  and  $\chi_F$  were within the validity range of the various correlations proposed by Lindquist *et al.* (2014).

Figure 13: Parity diagram: porosity according to Lindquist as a function of the experimental porosity

The experimental porosities and the porosities from correlations proposed by Lindquist *et al.* (2014) do not agree, underlining the limitations of these correlations but also the importance of having experimental data. As it stands, the developments proposed by Lindquist *et al.* (2014) results in a significant overestimation of the porosity of deposits.

In order to overcome these limitations, we propose a correlation which is also based on the dimensionless numbers proposed by Lindquist *et al.* (2014) but allowing the continuous evolution of the porosity observed experimentally to be described as a function of the physicochemical characteristics of the deposits studied (eq 8):

$$\varepsilon = \varepsilon_{limit_{dif}} + \frac{(\varepsilon_{limit_{bal,min}} - \varepsilon_{limit_{dif,max}})Kn_D^2 Pe}{a + Kn_D^2 Pe} = 0.9876 + \frac{(0.82979 - 0.9876)Stk}{0.06498 + Stk} \quad (eq\ 8)$$

Figure 14 compares all the experimental and calculated porosities (eq 8) as a function of the Stokes number alone (with the characteristic length of the deposition apparatus to be half the particle diameter), which is defined as follows:

$$Stk = \frac{\rho d_p C_u U_f}{9\eta}$$

where  $C_u$  is the Cunningham coefficient and  $\eta$  is the gas dynamic viscosity.

Figure 14: Experimental and calculated porosities (eq 4) as a function of the Stokes number

The porosity related to the Stokes number (Figure 14) the dispersion of the values to be minimized in the transition zone contrary to the metric associated with the Peclet number (Figure 6). When the Stokes number tends towards large values, the calculated porosity tends towards 0.830; a value near 0.846, which was noted in the simulations by Lindquist *et al.* (2014) and the experimental value 0.84. In the diffusion zone, the porosity tends towards 0.988.

In order to account for all the test aerosols produced in this study, the porosities deduced from the model, and those measured have been documented and are presented in parity chart in Figure 15. By taking into account a relative uncertainty ( $\Delta\epsilon/\epsilon$ ) of 1 and 3% respectively, we find 72 and 95% of the experimental porosity values in these two envelopes. This highlights the possibility, using equation 8, to accurately estimate the porosity of a spherical nanoparticle deposit.

In view of the different aerosols used during this study, we can conclude that this semi-empirical model is reliable for the determination of the porosity of a spherical nanoparticle deposit.

Figure 15: Parity chart between porosity from the new model and porosity from experiments

#### 4. Conclusion

A test bench has been specially developed in order to measure the porosity of a deposit of pseudo-spherical nanometric particles obtained by filtration and to validate the simulation results from the literature. The porosity of a filtration deposit is determined by measuring the evolution of its thickness coupled to the mass deposited over time.

The contributions of particle mass and diameter, filtration velocity and diffusion coefficient to the porosity of the deposit were studied over a wide range of Pe ( $10^{-2} < Pe < 10^2$ ) allowing the contribution of diffusion and particle inertia to be isolated. More specifically, the different parameters studied, associated with their ranges of variation are i) density ( $1,000 < \rho_p < 4,000 \text{ kg/m}^3$ ), ii) particle diameter ( $60 < d_p < 110 \text{ nm}$ ), iii) filtration velocity ( $0.04 < U_f < 70 \text{ cm/s}$ ) and iv) mean free path of the aerosol (66 and 135 nm).

The various experiments made it possible to validate the trends observed in the simulations conducted by Mädler *et al.* (2006) and Lindquist *et al.* (2014). The evolution of the porosity as a function of the Peclet number having an inverted sigmoid shape can thus be divided into 3 zones:

- The diffusion zone ( $Pe < 0.1$ ) characterized by a porosity near 97.5%. A slight decrease in porosity can be observed with a decrease in pressure or particle diameter.
- The transition zone ( $0.1 < Pe < 10$ ) characterized by a strong decrease in porosity with the Peclet number. In this zone, everything else being equal, an increase in the diameter, particle density or the pressure induces an increase in the porosity of the deposit.
- The ballistic zone ( $Pe > 10$ ) characterized by constant porosity equal to 84%.

The metric used (Porosity vs. Peclet number) shows a certain dispersion of the points essentially in the transition zone because the inertial effects of the particles are not taken into account through the Peclet number. The representation, according to the Stokes number, allows this dispersion to be reduced and seems to be a better indicator for estimating the porosity of a deposit of pseudo-spherical nanoparticles. A correlation based on the Stokes number could be established with all the experimental results. Ninety-five percent of the porosity values are within the envelope, taking into account an uncertainty of 3%.

For further work, a study devoted to the deposit formed by nanoparticles aggregates would be a logical and relevant continuation in order to validate the simulations and existings models .

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## **References**



- Bourrous, S., Bouilloux, L., Ouf, F., Lemaitre, P., Nerisson, P., Thomas, D., & Appert-Collin, J. C. (2016). *Measurement and modeling of pressure drop of HEPA filters clogged with ultrafine particles*. Powder Technology, 289, 109–117.
- Castillo, J. L., Martin, S., Rodriguez-Perez, D., Perea, A., & Garcia-Ybarra, P. L. (2014). Morphology and nanostructure of granular materials built from nanoparticles. KONA Powder and Particle Journal, 31(1), 214–233.
- Elmoe, T.D., Tricoli, A., Grunwaldt, J-D., Pratsinis, S.E., (2011) *Characterization of highly porous nanoparticle deposit by permeance measurements*. Powder Technology 207 (1-3), Pp. 279-289
- Endo, Y., Chen, D.R., Pui, D.Y.H. (2002). *Theoretical consideration of permeation resistance of fluid through a particle packed layer*. Powder Technology, 119-126
- Hoffmann, A. C., & Finkers, H. J. (1995). A relation for the void fraction of randomly packed particle beds. Powder Technology, 82(2), 197–203.
- Kasper, G., Schollmeier, S., Meyer, J. (2010). *Structure and density of deposits formed on filter fibers by inertial particle deposition and bounce*. Journal of Aerosol Science 41, 1167–1182.
- Khaleel, R. S., & Hashim, M. S. (2019). Fabrication of TiO<sub>2</sub> sensor using rapid breakdown anodization method to measure pressure, humidity and sense gases at room temperature. Iraqi Journal of Science, 60(8), 1694–1703.
- Kim, S.C., Wang, J., Shin, G.W., Scheckmann, J.H., Pui, D.Y.H., (2009) *Structural Properties and Filter Loading Characteristics of Soot Agglomerates*. Aerosol Science and Technology 43(4), Pp. 344-355
- Kulkarni, P., & Biswas, P. (2004). *A Brownian dynamics simulation to predict morphology of nanoparticle deposits in the presence of interparticle interactions*. Aerosol Science and Technology, 38(6), 541–554.
- Lide, D. R. (Ed.). (2004). CRC handbook of chemistry and physics (Vol. 85). CRC press.
- Lindquist, G. J., Pui, D. Y. H., & Hogan, C. J. (2014). *Porous particulate film deposition in the transition regime*. Journal of Aerosol Science, 74, 42-51.
- Liu, J., Swanson, J.J., Kittelson, D.B., Pui, D.Y.H., Wang, J., (2013) *Microstructural and loading characteristics of diesel aggregate cakes*. Powder Technology 241, Pp. 244–251.
- Loulergue, P., André, C., Laux, D., & Ferrandis, J. (2011). In-situ characterization of fouling layers : which tool for which measurement ?, Desalination and Water Treatment; 34, 156–162.
- Mädler, L., Lall, A. A., & Friedlander, S. K. (2006). *One-step aerosol synthesis of nanoparticle agglomerate films: simulation of film porosity and thickness*. Nanotechnology, 17, 4783–4795.
- Maheshwari, V., & Saraf, R. F. (2006). High-Resolution Thin-Film Device to Sense Texture by Touch, Science, 312(June), 1501–1504.

- Naderi, S., Heath, J. P., & Dean, J. S. (2019). Morphology characterisation of inclusions to predict the breakdown strength in electro-ceramic materials: Microstructure modelling. *Ceramics International*, 45(1), 361–368.
- Neesse, Th., Dueck, J., & Djatchenko, E. (2009). Simulation of filter cake porosity in solid/liquid separation. *Powder Technology*, 193(3), 332–336.
- Novick, V., Monson, P. et Ellison, P. (1992). The effect of solid particle mass loading on the pressure drop of HEPA filters. *J. Aerosol Sci.*, 23(6):657–665.
- Ou, Q. (2013), *Aerosol Filtration – Agglomerate particle filtration and particle deposition uniformity*; Doctoral thesis defended publicly in May 2013, Washington University
- Park, S. H., Lee, K. W., Otto, E., & Fissan, H. (1999). The log-normal size distribution theory of Brownian aerosol coagulation for the entire particle size range: Part I - Analytical solution using the harmonic mean coagulation kernel. *Journal of Aerosol Science*, 30(1), 3–16.
- Poizot, P., Laruelle, S., Grugeon, S., Dupont, L., & Tarascon, J. (2000). Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature*, 407 (September).
- Qiao, Z., Wang, Z., Zhang, C., Yuan, S., Zhu, Y., & Wang, J. (2012). PVAm–PIP/PS composite membrane with high performance for CO<sub>2</sub>/N<sub>2</sub> separation. *AIChE Journal*, 59(4), 215–228
- Rodriguez-Pérez, D., Castillo, J.L., Antoranz, J.C. (2007), Density scaling laws for the structure of granular deposits, *Physical Review*, 76(1), 1-5.
- Schmidt, E., Löffler, F. (1991). *The analysis of dust cake structures*. *Particle & Particle Systems Characterization*, 8, 105-109.
- Stabile, L., Trassiera, C. V., Dell’Aglì, G., & Buonanno, G. (2013). Ultrafine particle generation through atomization technique: the influence of the solution. *Aerosol and Air Quality Research*, 13(6), 1667-1677.
- Tassopoulos, M., O'Brien, J.A. and Rosner, D.E. (1989). *Simulation of microstructure mechanism relationships in particle deposition*. *AiChE J.*, 35, 967-80.
- Thomas, D., Ouf, F. X., Gensdarmes, F., Bourrous, S., & Bouilloux, L. (2014). *Pressure drop model for nanostructured deposits*. *Separation and Purification Technology*, 138, 144–152.
- Thomas, D., Penicot, P., Contal, P., Leclerc, D. and Vendel, J. (2001). Clogging of fibrous filters by solid aerosol particles. Experimental and modelling study. *Chem. Eng. Sci.*, 56(11):3549–3561.
- Wang, X., Kim, K., Lee, C., & Kim, J. (2008). Prediction of air filter efficiency and pressure drop in air filtration media using a stochastic simulation. *Fibers and Polymers*, 9(1), 34–38.
- Yu, A.B., Feng, C.L., Zou, R.P., Yang, R.Y., 2003. *On the relationship between porosity and interparticle forces*. *Powder Technology* 130, 70–76.

Zhai, J., Lu, X., Li, L., Zhang, Q., Zhang, C., Chen, H., ... & Chen, J. (2017). Size-resolved chemical composition, effective density, and optical properties of biomass burning particles. *Atmospheric Chemistry and Physics*, 17(12), 7481.

Zhenhua, C., Gang, C., Hongge, Y., & Ding, C. (2003). Solid atomization technology and process of molten metal and alloy. *Materials research bulletin*, 38(9-10), 1487-1492.

## Appendix: Measurement uncertainties

### On the Peclet number:

The Peclet number is defined by:

$$Pe = \frac{d_p U_f}{D}$$

With  $d_p$  being the particle diameter, here the geometric electrical mobility diameter determined from the SMPS,  $U_f$  being the filtration velocity and  $D$  being the diffusion coefficient. We thus study the error on each of the parameters:

- $\sigma_{dp}$ :

From the SMPS data, we obtain a standard deviation associated with several measurements of the electrical mobility diameter. The table 5 summarizes this uncertainty.

Table 5: Properties of particles generated

- $\sigma_{Uf}$ :

The filtration velocity is determined experimentally by setting a flow rate. The flow rate uncertainty is reported by the instrument and is 2% of the full range, equivalent to 0.2 L/min.

$$\sigma_{Uf} = \sqrt{\left(\frac{\partial \Delta U_f}{\partial Q_f}\right)^2 \sigma_{Q_f}^2}$$

- $\sigma_{Cu}$ :

$$\sigma_{Cu} = \sqrt{\left(\frac{\partial \Delta Cu}{\partial d_p}\right)^2 \sigma_{d_p}^2}$$

- $\sigma_D$ :

$$\sigma_D = \sqrt{\left(\frac{\partial \Delta D}{\partial d_p}\right)^2 \sigma_{d_p}^2 + \left(\frac{\partial \Delta D}{\partial C_u}\right)^2 \sigma_{C_u}^2}$$

- $\sigma_{Pe}$ :

Thus to arrive at the uncertainty on the Peclet number, the following equation is solved for each experiment.

$$\begin{aligned} \sigma_{Pe} &= \sqrt{\left(\frac{\partial \Delta Pe}{\partial d_p}\right)^2 \sigma_{d_p}^2 + \left(\frac{\partial \Delta Pe}{\partial U_f}\right)^2 \sigma_{U_f}^2 + \left(\frac{\partial \Delta Pe}{\partial D}\right)^2 \sigma_D^2} \\ &= \sqrt{\left(\frac{U_f}{D}\right)^2 \sigma_{d_p}^2 + \left(\frac{d_p}{D}\right)^2 \sigma_{U_f}^2 + \left(\frac{-d_p U_f}{D^2}\right)^2 \sigma_D^2} \end{aligned}$$

The total uncertainty ranges from  $1.2 \cdot 10^{-3}$ , for low Peclet numbers ( $< 10^{-3}$ ), to 6.5 for higher Peclet numbers ( $> 10^2$ ).

### On the Stokes number:

The Stokes number is defined by:

$$Stk = \frac{\rho d_p C_u U_f}{9\eta}$$

With  $d_p$  being the particle diameter, here the geometric electrical mobility diameter determined from the SMPS,  $U_f$  being the filtration velocity,  $\rho$  being the density of particle,  $\eta$  being the gas dynamic viscosity and  $C$  being the Cunningham coefficient. We thus study the error on each of the parameters:

- $\sigma_{dp}$ : From the SMPS data, like for the Peclet number.
- $\sigma_{Uf}$ :

$$\sigma_{U_f} = \sqrt{\left(\frac{\partial \Delta U_f}{\partial Q_f}\right)^2 \sigma_{Q_f}^2}$$

- $\sigma_{Cu}$ :

$$\sigma_{Cu} = \sqrt{\left(\frac{\partial \Delta C u}{\partial d_p}\right)^2 \sigma_{d_p}^2}$$

- $\sigma_\rho$  and  $\sigma_\eta$ : From the instructions manual
- $\sigma_{Stk}$ :

Thus to arrive at the uncertainty on the Stk number, the following equation is solved for each experiment.

$$\begin{aligned} \sigma_{Stk} &= \sqrt{\left(\frac{\partial \Delta Stk}{\partial \rho}\right)^2 \sigma_\rho^2 + \left(\frac{\partial \Delta Stk}{\partial d_p}\right)^2 \sigma_{d_p}^2 + \left(\frac{\partial \Delta Stk}{\partial C u}\right)^2 \sigma_{C u}^2 + \left(\frac{\partial \Delta Stk}{\partial U_f}\right)^2 \sigma_{U_f}^2 + \left(\frac{\partial \Delta Stk}{\partial \eta}\right)^2 \sigma_\eta^2} \\ &= \sqrt{\left(\frac{d_p C u U_f}{9 \eta}\right)^2 \sigma_\rho^2 + \left(\frac{\rho C u U_f}{9 \eta}\right)^2 \sigma_{d_p}^2 + \left(\frac{\rho d_p U_f}{9 \eta}\right)^2 \sigma_{C u}^2 + \left(\frac{\rho d_p C u}{9 \eta}\right)^2 \sigma_{U_f}^2 + \left(\frac{-\rho d_p C u U_f}{9 \eta^2}\right)^2 \sigma_\eta^2} \end{aligned}$$

The total uncertainty ranges from  $1.10^{-3}$ , for low Stokes numbers ( $< 10^{-2}$ ), to 0.1 for higher Stokes numbers ( $> 1$ ).

### On the porosity of the particle deposit:

The porosity of particle deposits formed on the surface of planar filters is determined based on the measurement of the growth rate of the deposit from the following relation:

$$\varepsilon = 1 - \left(\frac{1}{\rho_p R x S_f}\right)$$

The total uncertainty  $\sigma_\varepsilon$  related to the measurement of the porosity of a particle deposit depends on the following uncertainties:

- $\sigma_{\rho_p}$ : From the literature

$\sigma_{Rx}$  : - By linear progression. a straight line has been identified on the gross thickness measurement. This line constitutes the "theoretical deposit growth".

Figure 16: Deviation from the theory of thickness values measured by MEGAPAN

The difference between this theoretical line and the experimental data were expressed by a normal law in 0 and standard deviation  $\sigma_p$ .

Figure 17: Distribution of the deviation from the theory of thickness values measured by MEGAPAN

- Measurement of the deposited mass depending primarily on the error of the instrument used to determine the mass concentration (in this case, the TEOM).

$\sigma_{Sf}$ : - Determination of the filtration surface area, estimated at 5%

Thus to arrive at the uncertainty on the porosity of the particle deposit, the following equation is solved for each experiment.

$$\begin{aligned} \sigma_{\varepsilon} &= \sqrt{\left(\frac{\partial \Delta \varepsilon}{\partial \rho}\right)^2 \sigma_{\rho}^2 + \left(\frac{\partial \Delta \varepsilon}{\partial Rx}\right)^2 \sigma_{Rx}^2 + \left(\frac{\partial \Delta \varepsilon}{\partial S_f}\right)^2 \sigma_{S_f}^2} \\ &= \sqrt{\left(\frac{-1}{\rho^2 Rx S_f}\right)^2 \sigma_{\rho}^2 + \left(\frac{-1}{Rx^2 \rho S_f}\right)^2 \sigma_{Rx}^2 + \left(\frac{-1}{S_f^2 \rho Rx}\right)^2 \sigma_{S_f}^2} \end{aligned}$$

The total uncertainty on the porosity obtained is therefore very low:  $\Delta \varepsilon = 0.003$