

# THE EFFECT OF TEMPERATURE ON THE MINIMUM FLUIDIZATION CONDITIONS OF INDUSTRIAL COHESIVE PARTICLES

Roberto Chirone<sup>1</sup>, Massimo Poletto<sup>2</sup>, Diego Barletta<sup>2</sup> and Paola Lettieri<sup>1\*</sup>

1. Department of Chemical Engineering, University College London, London, WC1E 7JE, UK

2. Dipartimento di Ingegneria Industriale, Università degli Studi di Salerno Via Giovanni Paolo II, 132 – I-84084 Fisciano (SA) – Italy

\* Corresponding author: tel. +39 089 964 132; fax +39 089 968 781; email: p.lettieri@ucl.ac.uk

## 1 INTRODUCTION

Fluidization is one of the most used processes involving granular material. It is a common knowledge that fluid-particle processes are largely governed by the forces acting on individual particles<sup>1-10</sup>. The existence of solid-solid interparticle forces such as van der Waals forces, capillary forces and electrostatic forces may explain the non-ideal behavior of fine powders during fluidization. These forces generate links between the particles of the bed, making their free movement difficult and causing a poor fluidization state. It should be noted that solid-solid interaction forces are always present, but they play a different role depending on the relative importance between gravitational and hydrodynamic forces<sup>2,11-13</sup>. In most cases the operating conditions (temperature and pressure) of industrial fluidized bed reactors are far from ambient values<sup>1</sup>. Design criteria and performance predictions for fluidized bed units working at high temperature have been largely based on fluid-dynamic models and correlations established from tests developed at ambient temperature. Generally, the influence

of the working temperature on the dynamic features of the system has been considered by simply accounting for the changes of the gas properties, specifically its viscosity and density. However, extrapolating the results and relationships available at ambient conditions to elevated temperatures can lead to misleading predictions of the fluidized bed performance at high temperature. Drastic changes can occur in the fluidization behaviour between low and high temperatures, due to possible modifications induced by the temperature in the structure of the bed. In order to understand the factors responsible for such changes in fluidization behaviour, the role of the interparticles forces (IPFs) and hydrodynamic forces (HDFs) has been studied, but much controversy still remains to define their relative importance. Although several studies have been carried out on the influence of operating conditions on fluidization, the findings are still controversial and a satisfactory understanding of the phenomena which cause differences between ambient and high temperature conditions has not yet been achieved<sup>2,4,6,8,14-22</sup>. In addition, it must be considered that in the case of high temperature processes, the intensity of interparticle cohesive forces, such as capillary, electrostatic and van der Waals forces, can be different from ambient values. These changes are principally due to the variations of particles hardness, the formation of liquid bridge and the modification of the particle dielectric properties<sup>4,23</sup>. Crucial parameters for describing and designing a fluidized bed system are the minimum fluidization velocity and the bed voidage. Several authors studied the dependence on the process temperature of the parameters that characterize the fluidization quality of Geldart A, B and C particles<sup>4,6,11,14,21,24-32</sup>. A non-unique temperature dependency on these parameters was found leading to the conclusion that the temperature effect is the product of the combined variation of both gas properties and dense phase properties with temperature.

The main objective of this work is to provide a basis for the understanding the factors responsible for changes in the fluidization behaviour of industrial cohesive powders. On this

purpose, the results of an experimental campaign dealing with the influence of process temperature on the minimum fluidization condition and the bed expansion profiles are presented and where possible results are compared with previous finding on the effect of temperature on the powder flow properties <sup>33</sup>.

## **2 EXPERIMENTAL**

### **2.1 Apparatus**

The experimental apparatus used for the experimental campaign is shown in Figure 1. The fluidized bed reactor is 3 mm thick and it is made in Inconel. The vessel ID is 140 mm and its height is 1000 mm. The vessel is fitted with a very fine (i.e. pore size of 40  $\mu\text{m}$ ) Hastelloy X distributor plate to ensure high pressure drops for uniform fluidization. The windbox, below the distributor plate, is made in Inconel. The windbox height is 150 mm and it was packed with 10 mm ceramic balls in order to improve the temperature uniformity. In order to achieve the desired operating temperature, the vessel is surrounded by two flexible ceramic heaters wrapped around the vessel, and capable of providing an operating temperature up to 900 °C. The two ceramic heaters covered 900 mm of the vessel height. To minimize heat losses and for safety reasons, the whole system was packed with two layers of 1.5 cm thick Super-wool, covered by a 7 cm thick layer of Rockwool wrapped with silver tape. A pressure tap is located above the distribution plate to measure the pressure drop across the bed as a function of the fluidizing gas velocity. Seven thermocouples were used to monitoring and controlling the temperature in the fluidized bed system. The temperature was controlled by three different PID controllers. The set temperatures in the experiments were 25, 100, 200, 300, 400 and 500 °C. The experimental apparatus was equipped with an X-ray facility, available in the Department of Chemical Engineering at University College. It is a non-intrusive tool which

allows qualitative and quantitative real-time information on the internal structure and on instantaneous changes in three dimensional systems. Further details are reported by Lettieri and Yates<sup>34</sup>. The X-ray unit consists of a generator, an X-ray source and an image intensifier, as shown in Figure 1. The X-ray source, or tube, and image intensifier are mounted on a twin column ceiling suspension unit. The two columns can be moved laterally and vertically allowing to change and adjust both the distance between the tube and the image intensifier and the height from the ground of the X-ray beam. All the system is motorized and can be remotely controlled from outside the room. The X-ray generation system provides X-ray pulses of variable width, down to 200 $\mu$ s, with an intensity up to 450mA at voltage variable in the range between 50kV and 150kV. The X-rays are detected on a 300 mm Industrial X-ray Image Intensifier, optically coupled to a 1024 x 1024 pixel high speed digital CCD camera. The camera is triggered by the control software, which itself is triggered by the X-ray generator at frame rates from 24 to 72 frames per second (fps). All X-ray operations are monitored and controlled from the main control console located outside the radiation proof room, hosting the experimental apparatus. The images are captured, displayed and stored using a powerful image acquisition software (SPS “iX-Control”). The software handles image processing, image corrections, lossless image storage and playback up to 72 fps in either real-time or frame by frame<sup>34</sup>.

**Figure 1** - Experimental apparatus and schematic of the X-ray Imaging technique<sup>34</sup>.

## 2.2 *Materials*

The experimental campaign was performed on ceramic powders provided by an industrial partner and described elsewhere <sup>33</sup>. In particular, the materials tested is obtained from the virgin material used in a fluidized bed reactor by sieving it in different samples. A small representative amount of each sample was used for characterization analyses, such as those for particle size distribution, shape and chemical composition. In addition, also thermal analyses, such as Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA), were performed.

**Table 1** - Characteristic sizes of the samples tested.

The physical properties of all materials prior to experiments are reported in Table 1. Results are reported in term of particle size distribution, relative diameter spread and Geldart classification. The samples span from Group B to Group C with particle density of 2330 kg/m<sup>3</sup> at ambient condition. The SEM images (Figure 2 <sup>33</sup>), show some similar features for all the size cuts analysed. In particular, it can be observed that large quantities of fines adhere on the surface of larger particles that appear as irregularly shaped particles with flat surfaces and sharp edges. Together with the SEM analysis also the EDX examination was performed. Most of the particle samples showed only the emission lines of the mother particles in the EDX diagram. However, some particles showed the presence of metals probably due to metallic impurities deriving from the ball milling process. Unfortunately, other details of the material cannot be provided for confidentiality reasons.

**Figure 2** - SEM pictures sample A5 (a, b), A3 (c, d) and A1 (e, f).

According with the results reported by Chirone et al.<sup>33</sup> DTA and TGA reveal a similar thermal behavior of the powder samples. The constant weight of the sample above 100 °C indicates that chemical reactions (e.g. oxidation) can be excluded in that range. The thermal behaviour observed for all the other samples was qualitatively similar.

### **2.3 Procedures**

The minimum fluidization velocity,  $u_{mf}$ , was experimentally measured at increasing temperature. At each temperature, the  $u_{mf}$  was graphically obtained from the fluidization curves, i.e. the diagrams of the pressure drop profile across the bed over the fluidizing gas velocity, as the intersection of diagonal line and the horizontal line obtained when decreasing the gas flow rate in Figure 3. Nitrogen was the fluidizing gas and its rate was controlled by calibrated rotameters. The fluidization curves were obtained first by increasing the gas flow rate from zero till the bed was well fluidized, and then by decreasing the flow rate to zero. Measurements were repeated, from 3 to 5 times, to increase the statistical significance of results and verify the internal consistency of the measurements. The experimental value of the pressure drops across the bed,  $\Delta P_m$ , was compared with the predicted,  $\Delta P_c$  ( $\Delta P_c = Mg/A_c$ , where M,  $A_c$  and g are the bed material weight, the cross-sectional area occupied by the material and the acceleration due to the gravity). The minimum fluidization velocity was measured from ambient temperature up to 500 °C, in steps of 100 °C. In order to guarantee a good mixing of particles the bed material was fluidized in bubble regime for around 20 minutes before any measurements was made.

The experimental values of  $u_{mf}$  were also compared with some of the available correlations used to predict the minimum fluidization condition. In particular, the experimental values

were compared with the Baeyens and Geldart <sup>35</sup> equation (1), the viscosity term of the Wen and Yu <sup>36</sup> equation (2) and the viscous flow term of the Ergun equation (3):

$$u_{mf} = \frac{0.0009 (\rho_p - \rho_g)^{0.934} g^{0.934} d_p^{1.8}}{\rho_g^{0.066} \mu^{0.87}} \quad \text{Eq. 1}$$

$$u_{mf} = \frac{(\rho_p - \rho_g) g d_p^2}{1650 \mu} \quad \text{Eq. 2}$$

$$u_{mf} = \frac{(\rho_p - \rho_g) g (\phi d_p)^2}{150 \mu} \frac{\varepsilon_{mf}^3}{1 - \varepsilon_{mf}} \quad \text{Eq. 3}$$

It is worth noting that while the Wen and Yu <sup>36</sup> and the Baeyens and Geldart <sup>35</sup> correlations do not require a value of the bed voidage, the Ergun equation, instead, include voidage. In this latter case, estimates will be carried out using for the voidage the tapped bed value,  $\varepsilon_{\text{tapped}}$ , measured before any fluidization experiments at ambient temperature.

**Figure 3** - Typical fluidization curves for powders belonging to the Group A of the Geldart <sup>3</sup> classification.

The bed expansion curve, i.e. the bed height as a function of the fluidizing gas rate, was obtained using the X-rays imaging technique. The bed material was initially vigorously fluidized to allow a good mixing of the particles, and then the expansion curves were obtained by slowly re-fluidizing the powder and recording the bed height at each gas velocity. Before recording the bed height, some time was allowed in order to stabilize the bed fluidization. It is also worth pointing out that the expansion profiles were obtained with several repeated

experiments. The expansion curves were calculated between ambient temperature and 500 °C. At each height, the corresponding average bed voidage was also calculated with the following equation.

$$\varepsilon = 1 - \frac{M}{Ac \rho_p H} \quad \text{Eq. 4}$$

### 3 RESULTS AND DISCUSSION

#### 3.1 *Experimental results: $u_{mf}$ and $\varepsilon_{mf}$*

Fluidization curves from ambient temperature up to 500 °C are reported in Figure 4 and Figure 5 for samples A5 and A4 in terms of  $\Delta P_m/\Delta P_c$  ratios as a function of the gas superficial velocity. In particular,  $\Delta P_m$  is the measured pressure drop and  $\Delta P_c$  is the theoretical value of pressure drop at fluidization. The geometry of the symbols identifies different operating conditions. The tests were repeated from three to five times in order to increase the validity of the measurement and the values plotted are the mean values. Furthermore, the error bars were reported only in case of poor repeatability. Figure 4a reports the pressure drop profile obtained decreasing the gas flow rate at all temperatures. Whereas Figure 4b reports the comparison between fluidizing and defluidizing pressure drop profiles. For gas flow rates above the minimum for fluidization, the  $\Delta P_m/\Delta P_c$  ratio was constantly equal to unity in the whole range of temperatures tested. This result indicates a good fluidization quality and a negligible effect of interparticle forces in the range of temperatures of interest. According to Figure 4 and Figure 5, the fixed bed branch of the fluidization curve moves towards the left with the temperature, indicating higher pressure drops through the bed at equal fluid velocity. Consequently, also the minimum fluidization condition, the velocity at which the bed is fully

supported by the gas, occurs at lower velocity and therefore, the experimental value  $u_{mf}$  decreases with increasing temperature for both samples.

**Figure 4** - Pressure drop as a function of fluidization velocity for Sample A5: a) defluidization experiments at changing temperature; b) fluidization and defluidization experiments at changing temperatures. Pressure drops are expressed in terms of the ratio of the measured values and the theoretical for fluidization.

**Figure 5** - Pressure drop as a function of fluidization velocity for Sample A4: a) defluidization experiments at changing temperature; b) fluidization and defluidization experiments at changing temperatures. Pressure drops are expressed in terms of the ratio of the measured values and the theoretical for fluidization.

Fluidization curves of samples A3 and A2 are reported in Figure 6 and Figure 7. Similarly, with these samples, for flow rates well above the minimum fluidization condition, the  $\Delta P_m$  value equals the theoretical fluidization value  $\Delta P_c$  at all the tested temperatures. In this case, the fluidization curves shift towards the left only up to temperatures of 400 °C and 300 °C for the sample A3 and A2 respectively. In fact, for sample A3 an increase of temperature above 400 has a limited effect on the fluidization curves (Figure 6b) that remains almost constant, and thus on the minimum fluidization condition, such as the  $u_{mf}$  value. Whereas for Sample A2, a further increase of temperature beyond 400 °C, caused an inversion of the curve shift with temperature and an increase of  $u_{mf}$  is observed (Figure 7b). It should also be noted that when increasing the temperature, the reproducibility of the experimental measurements became much lower, as it appears from the larger error bars.

**Figure 6** - Pressure drop as a function of fluidization velocity for Sample A3: a) defluidization experiments at changing temperature; b) fluidization and defluidization experiments at changing temperatures. Pressure drops are expressed in terms of the ratio of the measured values and the theoretical for fluidization.

**Figure 7** - Pressure drop as a function of fluidization velocity for Sample A2: a) defluidization experiments at changing temperature; b) fluidization and defluidization experiments at changing temperatures. Pressure drops are expressed in terms of the ratio of the measured values and the theoretical for fluidization.

While increasing the gas flow rate, four different stages can be identified for both samples A3 and A2:

- Stage 1: At low gas velocity,  $\Delta P$  increases almost linearly with the flow rate.
- Stage 2: Further increasing the gas velocity, the ratio  $\Delta P_m/\Delta P_c$  reaches its maximum value, larger than 1.
- Stage 3: At just larger gas velocities, small bubbles are seen breaking the surface and travelling through the bed in instable channelling. In the whole range of temperatures tested, the ratio  $\Delta P_m/\Delta P_c$  remains below 70-80% for sample A3 and below 70-50% for sample A2. Further increasing the gas flow rate, the pressure drop  $\Delta P_m$  approaches  $\Delta P_c$  as a consequence of the disruption of the formed channels (Figure 8).
- Stage 4: At the highest gas velocities tested, larger bubbles are seen all over the surface and the ratio  $\Delta P_m/\Delta P_c=1$

During stage 3, the fluidization behaviour was mainly characterized by unstable channelling fluidization, resulting in highly variable values of the ratio  $\Delta P_m/\Delta P_c$ , as shown in Figure 8.

To better explain the fluidization behaviour, Figure 9 reports an X-ray image of the inside of the reactor for sample A2. Images are taken at four different gas velocities, 0.12, 0.3, 0.4 and 0.8 cm/s. Inspection of the images suggests that the unstable pressure drop profile between 0.15 and 0.6 cm/s is due to irregular by-pass of the gas through the bed particles causing vertical channels. At  $u < u_{mf}$ , Figure 9a shows a fixed bed. Increasing the gas flow rate, the

pressure drop starts to fluctuate and, according with Figure 9b, a non-horizontal bed surface can be observed. In video sequences, corresponding to the depression of the bed surface, it is possible to observe local variations of bed density, visible as fluctuations of the image grey levels, and of the bed surface, that can clearly be attributed to high gas velocity in the region due to channelling. A further increase of the flow rate causes an expansion of the channel, a lower bed surface still non-horizontal (visible from the video sequences in the supplement material), with a consequent linear increase of the pressure drop (Figure 9c).

**Figure 8** - Pressure drop as a function of fluidization velocity for Sample A2 for fluidization and defluidization experiments at at 500 °C. Pressure drops are expressed in terms of the ratio of the measured values and the theoretical for fluidization.

**Figure 9** - X-rays images of the reactor for sample A2 at different flow rate at 500 °C.

For particular operating temperature and powder samples, it is also noticeable a pressure drop peak in the fluidization curve at increasing gas velocity close to the minimum for fluidization, corresponding to values of the ratio  $\Delta P_m/\Delta P_c$  significantly larger than 1. This overshoot can be an indication of some degree of cohesiveness of the bed particles. The values of the overshoot are reported in Figure 10 for both samples. The Figure shows an increase of the ratio  $\Delta P_m/\Delta P_c$  up to 300 °C. Instead between 300 and 500 °C the ratio is almost constant.

**Figure 10** - Effect of temperature on the overshoot, expressed with the ratio  $\Delta P_{\text{overshoot}}/\Delta P_{\text{fluidization}}$ , for sample A3 and A2.

Moreover, hysteresis phenomena were observed during fluidization and defluidization cycles. Hysteresis phenomena are more evident for sample A2, the most cohesive powder among those discussed above, at high temperatures (Figure 8).

The finest sample tested, A1, belongs to the Group C of the Geldart classification. This powder sample is characterized by a very high degree of cohesiveness. In fact, fluidization conditions could not be achieved at any temperatures between ambient and 500 °C, due to the dominant role of interparticle forces over hydrodynamic forces. Figure 11 and Figure 12 report the fluidization curves at ambient condition and the snapshots of the reactor at superficial gas velocities of 0, 0.9, 1.0, 2.2, 5.0 and 6.5 cm/s, respectively. The videos of the inside of the reactor in these conditions are available in the supplement material. From the X-rays images the structure of the bed can be observed. Inspection of Figure 12 indicates that channelling phenomena occur and, particularly at the higher flow rates, it becomes clear that the channels develop as horizontal cracks, such as those that, in similar cases, might lead to the phenomenon of solid plugs rising and breaking.

**Figure 11** - Pressure drop versus gas fluidization velocity for sample A1 at ambient condition.

**Figure 12** - Snapshot inside the reactor of sample A1 at ambient condition at different gas flow rates.

The bed voidage at the minimum velocity for fluidization,  $\varepsilon_{mf}$ , was estimated from the bed height measured with the X-ray images of the bed. In particular, the bed voidage was calculated using Eq. 4 and it is reported in Figure 13. All the samples show a steady increase of the bed voidage with temperature. A maximum value of the relative voidage increase was

observed for the finest sample A2 that was calculated to be 15% and around 7% for the other samples. The Ergun correlation (Eq. 3) was also used to calculate the particle sphericity,  $\phi$ , of each samples using the experimental values of  $u_{mf}$  and  $\varepsilon_{mf}$  at ambient temperature as suggested by Knowlton<sup>20</sup>. Unfortunately, the procedure led to unrealistic values of the sphericity between 1 and 1.2 that could not be used. Consequently, the shape factor of the particles was geometrically estimated using the SEM pictures and considering a parallelepiped shape of the particles. In particular, the prevalent dimension of the parallelepiped was considered. The results show values of  $\phi$  between 0.68 and 0.75. Thus, a constant value of  $\phi=0.7$  was considered and this value was used to estimate an effective fluid dynamic particle diameter  $d_{fd}$  also reported in Table 1.

**Figure 13** - Effect of temperature on the bed voidage at the minimum gas velocity for fluidization.

### ***3.1.1 Relationship between the pressure overshoot and the powder flow properties***

In cohesive powder systems, the tensile strength represents a fundamental mechanical property of a powder in handling issues<sup>37,38</sup>. Generally, it can be determinate indirectly from the yield locus by linear or curve extrapolation<sup>33,39,40</sup>. On the other hand, it can directly be measured with split cell tester<sup>41-43</sup> or lifting lid tester<sup>44</sup>. The main issue of these apparatus is the non-uniform stress distribution inside the powder sample that cause a poor reproducibility of the results in case of fine cohesive powders.

A fluidized bed system with a certain degree of particle cohesiveness generally shows some pressure overshoot during the fluidization branch of the pressure drop profile. The direct connection between the pressure overshoot and the powder flow properties is still a debated question. According to Castellanos et al.<sup>45</sup> the pressure overshoot, that is the difference

between the peak pressure and the theoretical fluidization pressure drop equals the tensile strength of the material that can withstand the overpressure only for values lower than those corresponding to the material break at the pressure peak.

$$\frac{\Delta P_{\text{overshoot}}}{\Delta P_c} = \frac{\sigma_t}{\rho(1-\varepsilon)gH} + 1 \quad \text{Eq. 5}$$

Where  $\sigma_t$  is the tensile strength at the base of the bed. Following this approach, it was possible to use the estimation of the tensile strength based on the measurement of powder flow properties made at ambient and high temperature and reported in a previous paper<sup>33</sup>, in order to verify if the change of interparticle forces with temperature can explain the changes observed in the overpressure.

The bed weight determines the powder consolidation at the bottom and therefore:

$$\sigma_1 = \rho(1 - \varepsilon)gH \quad \text{Eq. 6}$$

Zafar et al.<sup>46</sup> report experimental measurement results of the tensile strength of different powder samples determined by both direct, such as Sevilla Powder Tester and Raining Bed Method, and indirect techniques, extrapolated from the results of the Schulze Shear Cell. They found qualitatively similar results for the tested powders using different methods, concluding that it is fundamental to analyse in detail the conditions of powder flow for each application in order to choose the most appropriate test.

A simple model used to correlate the bulk material strength and the particle-particle properties was proposed by Rumpf<sup>47</sup> and Molerus<sup>48</sup> according to whom the following equation can be used to relate interparticle force with stresses and strength:

$$\sigma_t = \frac{F_{vdW}}{d_{sv}^2} \frac{1-\varepsilon}{\varepsilon} \quad \text{Eq. 7}$$

$$\sigma_1 = \frac{F_N}{d_{sv}^2} \frac{1-\varepsilon}{\varepsilon} \quad \text{Eq. 8}$$

The applicability of the model, especially for very low consolidated systems of particles, can be still considered debatable. However, in the past, the combined use of the tensile strength extrapolated from the yield locus and of Eq.7 was successfully used for several applications. Tomasetta et al.<sup>49</sup> found that Molerus equation (Eq.7) with the assumption of plastic deformation provides the correct order of magnitude values of tensile strength extrapolated from the powder yield locus and, more significantly, its dependence on consolidation. Furthermore, more accurate studies carried on ceramic powders demonstrated that, by using a reasonable value of the mean curvature radius at the contact points, the tensile strength and its dependence with the particle diameter, the applied consolidation and the system temperature are correctly predicted with the use of Eqs 7 and 8, together with the tensile strength extrapolated from a yield locus<sup>33</sup>. A direct confirmation of the appropriateness of the procedure was found by comparing the interparticle forces calculated by Chirone et al.<sup>33</sup> with the interparticle forces calculated from experiments of sound assisted fluidization on the same powders<sup>50</sup>. In particular, the results confirmed the applicability of both methodologies for the estimation of the interparticle forces under different consolidation state.

$$F_{vdW} = \frac{Ar}{12z_0^2} \frac{1 + \frac{2F_N}{\pi p_f r z_0}}{1 - \frac{A}{6\pi p_f z_0^3}} \quad \text{Eq. 9}$$

It was also found that in presence of a liquid phase, after a reasonable estimation of the capillary interparticle forces, Eqs 7 is able to correctly predict the order of magnitude of the

tensile strength extrapolated from the powder yield loci, as well as, its variations with temperature <sup>51</sup>. Other successful applications of the same approach used to relate the tensile strength of yield loci and interparticle forces with Eq. 7 as a function of consolidation forces estimated with Eq. 8 are reported by Macrì et al. <sup>52,53</sup> with reference to the flow properties of Titania powders at different temperatures, by Liu et al. <sup>54</sup> for ashes at different temperature and by Liu et al. <sup>55</sup> for coal. In this latter case a modified version of Eq. 7 was developed to account for wide particle size distribution of the particulate systems. Equation 7 and this latter modification were successfully used to relate the strength of interparticle connection with the material tensile strength in selective laser sintered artefact obtained by unimodal <sup>56</sup> and bimodal <sup>57</sup> powder samples, respectively. Independent proofs of the significance of the tensile strength of powder obtained from extrapolation from yield loci are provided by Barletta et al. <sup>58</sup> and by Barletta and Poletto <sup>59</sup> who were able, with that, to correctly predict the aggregates size of cohesive powders in the aerated discharge from hoppers and in gas fluidization assisted by mechanical vibrations, respectively.

Provided the above and, therefore, assuming that Eqs 5 to 8 as well as the extrapolation of the tensile strength from the yield locus and the pressure overshoot gas fluidization can be assumed valid with a reasonable degree of confidence, a linear relationship is adequate to relate  $F_{vdW}$  and  $F_N$

$$F_{vdW} = a + b F_N \quad \text{Eq. 10}$$

In <sup>33</sup> data of  $F_{vdW}$  and  $F_N$  estimated with Eqs. 7 and 8 from linear extrapolation of the tensile strength from powder yield loci and the corresponding values of  $\sigma_1$  were available for powders A2 and A3 at ambient temperature and at 500°C. These are reported in Figure 14 together with linear correlation function of the kind of Eq. 10.

**Figure 14** – Tensile Strength as function of the consolidation forces from in <sup>33</sup>.

Considering the same powders at the same temperature inside the fluidized bed, Table 2 reports the values of  $\sigma_1$  calculated according to Eq. 6,  $F_N$  values calculated according to Eq. 9. Furthermore  $F_{vdW}$  were calculated assuming that regression Eq. 10 with the coefficient values reported in Figure 14 apply in our fluidized bed. Finally, on these bases  $\sigma_1$  values were calculated using Eq. 8 and values of the ratios  $\Delta P_{overshoot}/\Delta P_c$  applying Eq. 5.

**Table 2** – Sample parameters for the mathematical estimation of the ratios  $\Delta P_{overshoot}/\Delta P_c$ .

The comparison of the calculated values of the pressure overshoots and the experimental ones is reported in Figure 15.

**Figure 15** – Pressure overshoots estimated from measured powder flow properties vs experimental pressure overshoots for sample A3 and A2.

The results show that the experimental overshoots at high temperature are much larger than those estimated from powder flow properties. Since the procedure adopted to estimate  $\sigma_1$  from powder flow properties uses a linear extrapolation of the yield locus on the traction side, it is known that it tends to somewhat overestimates values of the tensile strength<sup>42</sup>. The fact that, in spite of this theoretical overestimation, fluidization results provide larger overpressure suggests that the pressure overshoots in these experiments cannot be explained only by considering an increase of interparticle forces affecting the bed cohesion. Instead it is possible that other indirect effects of interparticle forces such as the bed adhesion on the column walls may play a significant role. This is likely in a fluidized bed system with a high ratio between the height and the diameter (in our experiments this ratio is around 2).

### 3.2 *Experimental result: bed expansion curves*

The bed expansion curves were determined from the X-ray imaging technique and following the experimental procedure described in the previous section. The expansion curves reported in the following are the result of an averaging procedure over several (3-4) repeated experiments. The bed expansion curves obtained for all the samples at each temperature are reported in Figure 16 and they show similar characteristics for all the samples tested. A maximum bed expansion value is obtained at temperatures around 300/400 °C. The results of the thermogravimetric analysis showed no weight loss in the temperature range of interest for all powder samples, thus this maximum cannot be justified with changes of the sample weight. Instead these temperature effects on the bed expansion it can be explained by the combined effects of temperature on both the gas properties and the particle compressive strength  $p_f$ <sup>60</sup>. In particular, for temperatures between 25 °C and 300 °C, it is likely that the temperature mainly affects the gas properties (density and viscosity), instead, for temperatures higher than 300 °C, the particles show a significant decrease of the compressive strength<sup>60</sup> with a relative increase of the interparticle forces. The gas velocity, at which the bed expansion starts, decreases with temperature, while the magnitude of the expansion increases with temperature and with decreasing average particle size of the sample, as shown in Figure 17.

**Figure 16** - Effect of temperature on bed expansion curves of the different samples: a) A5; b) A4; c) A3; d) A2.

**Figure 17** - Effect of temperature on the ratio  $h_{max}/h_0$  for all the materials.

A considerable increase of the bed expansion occurred for all the samples from 20 °C up to 300 °C: a 15% relative increase was observed for the A5 and A4 sample, about 24% for A3, and a relative increase of up to 50% was observed for A2.

Figure 18 shows the comparison of the bed height recorded while increasing and while decreasing the gas flow rate. Slight hysteresis phenomena can be observed at high temperature for samples A3 and A2.

**Figure 18** - Comparison fluidizing and defluidizing profile for sample a) samples A5; b) sample A4. c) sample A3; d) sample A2.

### ***3.2.1 The settled voidage of the bed***

Figure 19 reports the settled bed voidage calculated in slow and fast defluidization experiments as a function of temperature for all the tested powders. In both cases of slow and fast defluidization the starting conditions was a well-established bubbling condition. The slow defluidization experiment was achieved with small decremental steps of the gas flow rate. Whereas, the fast defluidization was obtained with a sudden cut off of the gas supply.

The settled bed voidage,  $\epsilon_s$ , was found to increase with temperature of about 9% in both cases of slow and fast defluidization experiments. The same trend with temperature was also found by Lettieri in experiments carried out on FCC powders <sup>21</sup>. The  $\epsilon_s$  values obtained from fast defluidization experiments were found to be a little larger for all the materials than those measured in slow defluidization experiments.

**Figure 19** - Effect of temperature of the settling procedure on the settled voidage of the bed. Slow settling procedure is obtained while slightly decreasing the flow rate and fast settling procedure is obtained when suddenly cutting off the gas supply.

### 3.2.2 *The bed expansion profile in Richardson-Zaki form*

The bed expansion in the range of homogenous fluidization was also investigated by using the Richardson-Zaki equation, Eq. 11 <sup>61</sup>.

$$u = u_t \varepsilon^n \quad \text{Eq. 11}$$

where  $u_t$  represents the terminal velocity of a single particle and  $n$  is an index that, according to Richardson and Zaki <sup>61</sup>, should depend on the system fluid dynamics. The values of  $u_t$  and  $n$  that were obtained by fitting Eq. 11 on the expansion curves are denoted as  $n^*$  and  $u_t^*$  and will be addressed to as experimental values. The fitting procedure was carried out by plotting the fluidizing velocity and the voidage, on logarithmic scales, on which Eq. 11 should appear as a line and a linear regression procedure on data can be adopted. Figure 20 shows the results of this fitting procedure on all the expansion curve.

**Figure 20** - Bed expansion in the Richardson-Zaki form profile for sample a) samples A5; b) sample A4. c) sample A3; d) sample A2.

For samples A5 and A4 a single slope line could be used to fit data in the whole expansion range of the bed, as shown in Figure 20a-b. The expansion profiles of samples A3 and A4 are better described by using two different lines to fit the data at low and large values of the bed expansion (the fitting equations are reported in Table 3). The values of the voidage,  $\varepsilon_{\text{changing slope}}$ , which identify the slope changes, are reported in Figure 21 and Table 3. An increase of  $\varepsilon_{\text{changing slope}}$  with temperature was observed. It can be argued that this parameter can identify

the point at which the interparticle forces and hydrodynamic forces change their relative significance. At values of  $\varepsilon < \varepsilon_{\text{changing slope}}$  the slope of the expansion curve is higher than at values of  $\varepsilon > \varepsilon_{\text{changing slope}}$ . Larger slopes in the lines of Figure 21 mean larger values of the exponent  $n$  of the Richardson and Zaki equation. These may suggest the presence of other forces affecting the bed expansion than purely fluid dynamic interaction. Interparticle forces may induce the formation of internal structures in the bed that support part of the bed weight, keep the bed expanded and, therefore, reduce the ability of the fluid velocity change to produce a significant change of the bed expansion, if referred to the case in which expansion is purely driven by only fluid dynamic forces. These structures are stable only at the lowest bed voidages and, perhaps, for  $\varepsilon < \varepsilon_{\text{changing slope}}$ . At higher bed expansion, for  $\varepsilon < \varepsilon_{\text{changing slope}}$ , the particles tend to be fluidized as separate particles and, therefore, the variation of bed height with fluidization velocity is less pronounced. It is consistent with this interpretation the fact that at higher temperatures, when interparticle forces become more important change in the slope are more significant.

**Table 3** – Linear regression fitting the data at low and large values of the bed expansion for sample A2 and A3.

Figure 22 and Figure 23 show the effect of temperature on the index  $n^*$  (slope of the line regression on Figure 20 for  $\varepsilon < \varepsilon_{\text{changing slope}}$ ) and the values of  $u_t^*$  (the line intercept at  $\varepsilon=1$ ). Both parameters decrease in the range of temperatures investigated. These results are in agreement with those reported by Lettieri et al. <sup>21</sup>. These experimental values were also compared with the predicted values of  $n$  and  $u_t$  obtained according to Richardson and Zaki <sup>61</sup>. In this case the values of  $u_t$  can be obtained from the theory of terminal velocity, the values of  $n$  from the empirical equations derived by Richardson and Zaki <sup>61</sup> for homogeneous fluidization governed by purely fluid dynamic interactions. The following relations were used to estimate the terminal velocity  $u_t$  and the index  $n$ :

$$Ga = 18Re_t \quad \text{for } Ga \leq 3.6$$

Eq. 12

$$Ga = 18Re_t + 2.7Re_t^{1.687} \quad \text{for } 3.6 \leq Ga \leq 500$$

$$n = 4.8 \quad Re_t \leq 0.2$$

$$n = 4.6Re_t^{-0.03} \quad 0.2 \leq Re_t \leq 1 \quad \text{Eq. 13}$$

$$n = 4.6Re_t^{-0.1} \quad 1 \leq Re_t \leq 500$$

where  $Re_t$  is the dimensionless Reynolds number referred to the terminal particle velocity and  $Ga$  is the dimensionless Galileo number.

Table 4 reports the values of  $n$  and  $u_t$  predicted according to Eqs. 12 and 13 and the corresponding experimental values obtained with the fitting procedure shown in Figure 20 for all sample tested and temperatures and for  $\varepsilon < \varepsilon_{\text{changing slope}}$ . Due to the small particle size that constrain the fluid particle system to the viscous regime, the predicted values for  $n$  are all 4.8. As expected for the viscous regime in which the effect on the terminal velocity is determined by the increase of the gas viscosity, the calculated values of  $u_t$  decrease with temperature. Similar trends are observed for the experimental values  $u_t^*$ , with the exception for the finest sample A2. Despite the similar trends, the calculated values of  $u_t$  are greater than the experimental values of  $u_t^*$  for samples A5 and A4, they are similar for sample A3, while they are smaller for the sample A2.

**Figure 21** - Effect of temperature on the voidage at which the slope changes for the R-Z equation.

**Figure 22** - Effect of temperature on the index  $n^*$  of the Richardson-Zaki equation.

**Figure 23** - Effect of temperature on  $u_t$  of the Richardson-Zaki equation.

**Table 4** - Comparison of the calculated and the experimental values for  $n$  and  $u_t$  of the R-Z equation.

#### 4 DISCUSSIONS

The experimental results show that the mean particle size affects significantly the fluidization behaviour of the materials investigated. In particular, significant differences were observed in the fluidization behaviour of the coarsest samples A5, A4 and the finest sample A3, A2. The sample A1, which exhibits the highest cohesion, was impossible to fluidize with an ordinary fluidized bed reactor. For all materials tested, the ratio  $\Delta P_m/\Delta P_c$  provided the very first indication on the influence of the HDFs and IPFs on the fluidization behaviour. The measured pressure drops across the bed,  $\Delta P_m$ , was within 1 or 2 percent of the theoretical value  $\Delta P_c$  for all fresh material tested, indicating that the bed material was relatively free from any dominant effect of the interparticle forces. However, an increase in the pressure deviation of the pressure drops with increasing temperature was observed to occur when the role of the IPFs was enhanced due to the increase of temperature. Hysteresis phenomena were observed in the pressure drop curves for the finest samples (A3 and A2) and for temperatures higher than 400 °C. Several researches found this phenomenon associated with fluidization of nanoparticles<sup>62,63</sup>. A theoretical explanation for this phenomenon is based on the role of contact or yield stresses and wall friction, which results in plugging of the nanoparticle agglomerates at low velocities<sup>63,64</sup>.

Different structures within the bed were found, as detected in the X-ray images. Vertical channels were seen to form into the bed of samples A3 and A2. Whereas, horizontal cracks were seen to form continuously within the bed of sample A1, causing the pressure drop to decrease and vary with time. This material sample was impossible to fluidize in ordinary conditions.

Regarding the effect of temperature on the minimum fluidization velocity, three different trends were found. Samples A5 and A4 show a decreasing experimental value of  $u_{mf}$  with increasing temperature. Sample A3 shows a weaker dependence of  $u_{mf}$  with temperature. Differently,  $u_{mf}$  values obtained for sample A2 decreased from 20 °C up to 200 °C as the fluidization behaviour is controlled by the HDFs,  $u_{mf}$  then suddenly increased between 300 and 500 °C when the IPFs started to become more dominant and to determine larger bed voidages. The experimental minimum fluidization velocity was compared with the Ergun equation (Eq. 3), considering the measured bed voidage from the X-ray observation at the minimum for fluidization at each temperature. In all the cases, the value of  $d_{fd}$  was used. The calculated values of  $u_{mf}$  are reported as a black solid line in Figure 24, where they can be compared with the experimental values reported as black dots. In the same plot also, the values of  $u_{mf}$  calculated from literature equations 1 to 3 are reported. As expected, since  $d_{fd}$  is obtained by fitting the Ergun equation on experimental data at ambient temperature, it can be seen that the Ergun equation, with the experimental values of voidage at the process conditions and  $d_{fd}$  values, do provide the best agreement between calculated values and experimental values of the  $u_{mf}$ . A sensitivity analysis on the effect of the value used for  $\epsilon_s$  in the prediction of the minimum fluidization velocity can be carried out using the predetermined values of  $\epsilon_{s,tapped}$  if in place of the experimental values determined on the basis of the bed height visualized with the X-ray set up. Figure 24 shows that for samples A5 and A4, the Baeyens and Geldart equation, the Wen and Yu equation and the Ergun equation with

the predetermined  $\epsilon_{s,tapped}$  well describe the effect of temperature on the minimum fluidization condition but underestimate the experimental values (black dotted lines). According to Table 5, the relative errors referred to the two materials for the different predictive equations not using experimental values for  $\epsilon_{mf}$  range between 24 and 78%. Whereas, for samples A3 and A2 the comparison indicates that all the predictions not using the experimental value of  $\epsilon_{mf}$  at the process conditions underestimate the experiments and are not even able to follow the trend of the experimental values of  $u_{mf}$  at the highest temperatures. According to Table 5, the relative errors referred to the two materials for the different predictive equations not using experimental values for  $\epsilon_{mf}$  vary from 50% to 66% for sample A3 and from 50% to 89% for sample A2. In all the cases the relative errors of the Ergun equation with the experimentally determined value of  $\epsilon_{mf}$  are within 15%. This finding suggests that for powders made of coarser particle the prevailing changes introduced by temperature are limited to the changes in the gas properties present in all model equation. Instead, for powders of finer particles there is also a significant effect of temperature on the bed voidage that has to be taken into consideration. It is likely, that this effect is determined by an increase of interparticle forces that allow the stability of looser beds of particles.

**Figure 24** - Comparison between experimental and predicted  $u_{mf}$  values with increasing temperature using equations 1-3: a) sample A5; b) sample A4; c) sample A3; d) sample A2.

**Table 5** - Averaged Relative errors for the different equations used to predict the Minimum fluidization velocity.

Furthermore, the experimental bed expansion curves reveal the greatest tendency to expand for beds made of the finest samples at high temperatures. Moreover, voidages of the settled

bed and at the minimum for fluidization were found to increase with temperature. Correspondingly to what has been observed with concern of fluidization pressure drops, bed expansion curves of systems made of A3 and A2 samples show important hysteresis phenomena. In particular, the higher height of the bed in the defluidizing branch of the expansion curve compared with the one in fluidizing branch at equal gas velocity, is due to changes the structure of the bed between the fluidization and the defluidization experiment, that lead to looser bed in this latter experiment. In fact, as the average particle size decreases, larger interparticle interactions stabilize the interparticle connections and result in a larger resistance of the particle bed to compact under its own weight. A similar behaviour was found by LaMarche et al. <sup>65</sup> in their experiments in presence of high air relative humidity, a situation that in a different way promotes the increase of the interparticle forces.

It was demonstrated that the bed expansion profiles plotted in the Richardson-Zaki form allowed to find best fitting values of  $n^*$  and  $u_t^*$  and that these values are quite different from  $n$  and  $u_t$  evaluated by using the Richardson-Zaki correlations and the theoretical values of the terminal Reynolds number calculated applying the Stokes drag. In the case of  $n^*$ , not only the values are different from  $n$  but also the trend with temperature is not the same of that found for  $n$ . Therefore, both the effect of temperature and of the particle size are quite different than those observed on the other parameters considered above like  $u_{mf}$  and  $\varepsilon_{mf}$ . This finding suggests that, in this case the discrepancies between experiment and calculations might not be exclusively attributed to the onset of interparticle forces, but perhaps also to the forced extension to homogeneous gas fluidization of the Richardson-Zaki correlations that were properly derived for liquids as fluidizing media.

## 5 CONCLUSIONS

A complete experimental characterization of the fluidization behaviour of powder samples of different particle sizes has been performed and some key conclusions can be drawn.

The results show that the mean size distribution affects significantly the fluidization behaviour of the materials investigated. In particular, significant differences were observed in the fluidization behaviour of the coarsest samples A5 and A4 and the finest sample A3 and A2. Sample A1, which exhibits the highest cohesive character, was impossible to be fluidized with an ordinary fluidized bed reactor.

For all materials tested, the fluidization curves provided the very first indication of the influence of the HDFs and IPFs on the fluidization behaviour. In fact, the measured pressure drops across the bed at full fluidization was within 1 or 2 percent of the theoretical value for gas suspensions for all the tested materials, indicating that the bed material was relatively free from any dominant effect of the interparticle forces in well fluidized conditions. Larger values of the pressure drop peak observed in the fluidization branch of the pressure drop profiles with the increasing operating temperature, highlights the role of temperature on the IPFs within the bed reactor. However, this result cannot be explained only by considering an increase of interparticle forces. Consistently, hysteresis phenomena were observed in the fluidization and defluidization branches of the fluidization curves obtained for the finest fluidizable samples (A3 and A2) and with increasing temperature. Different structures within the bed were detected with the X-ray images. In fact, the X-ray images enabled to identify the occurrence of channelling conditions. In this case it was possible to identify vertical or, in the case of the finest powder tested (A1) that could not be properly fluidized, horizontal channels in the bed.

Results suggest for fine particles a dominant role of IPFs over the HDFs when increasing temperature. The non-monotonic trend of  $u_{mf}$  with increasing temperature and consequent increase of  $u_{mf}$  for temperature higher than 300 °C cannot be explained only with the effects of temperature on the bed fluid dynamics, because both  $\varepsilon_{mf}$  and  $\varepsilon_s$  increase with temperature. Furthermore, the experimental expansion curves revealed a greatest tendency to expand for beds made of the finest samples at high temperatures.

The parameters of the Richardson-Zaki equation found with a fitting procedure on the experiments were found to be significantly different than the theoretical ones, predicted using the Richardson-Zaki correlations and the theoretical terminal velocity. Some of the experimental trends for the finest materials can be explained considering an active contribution of the IPFs in the particle systems, but the discrepancies between the fitting parameters and the model values perhaps should be attributed to breach of some model hypothesis.

#### ACKNOWLEDGEMENTS

Authors are grateful for the financial support provided by our industrial partner and wish to thank Mr Luciano Cortese of the IRC-CNR in Naples for his contribution in providing high quality SEM analyses.

## NOMENCLATURE

### Acronyms

TGA	Thermogravimetric analysis	-
DTA	Differential thermal analysis	-
SEM	scanning electron microscope	-
EDX	Energy Dispersive X-ray Analysis	-

### Symbols

$A_c$	cross-sectional area	$m^2$
$d_{43}$	volume weighted mean particle size	$\mu m$
$d_{50}$	size in correspondence of the 50 <sup>th</sup> of the PSD	$\mu m$
$d_{90}$	size in correspondence of the 90 <sup>th</sup> of the PSD	$\mu m$
$d_{fd}$	fluid dynamic particle diameter	$\mu m$
$d_{sv}$	Sauter mean diameter of the PSD	$\mu m$
$g$	Standard acceleration due to gravity	$\mu m$
$Ga$	dimensionless Galileo number	-
$H$	Height of the bed particle	$m$
$M$	Mass of the bed material	$kg$
$n$	Richardson and Zaki index	-
$n^*$	Experimental Richardson and Zaki index	-
$p_f$	particle compressive strength	$Pa$
$Re_t$	dimensionless Reynolds number	-

$u_{mf}$	Minimum fluidization velocity	cm/s
$u_t$	terminal velocity of a single particle	cm/s
$u_t^*$	Experimental terminal velocity of a single particle	cm/s

### Greek symbols

$\Delta P_c$	Theoretical value of the pressure drops for bed fluidization	Pa
$\Delta P_m$	experimental value of the pressure drops across the bed	$\mu\text{m}$
$\varepsilon$	porosity of the powder	-
$\varepsilon_{\text{changing slope}}$	values of the voidage at the slope changes	deg
$\varepsilon_{mf}$	Bed voidage at minimum fluidization condition	-
$\varepsilon_s$	settled bed voidage	-
$\mu$	Gas viscosity	$\text{Kg/m}\cdot\text{s}$
$\rho_{\text{mix}}$	Density of the mixture	$\text{kg/m}^3$
$\rho_p$	Particle density	$\text{kg/m}^3$
$\rho_g$	Gas density	$\text{kg/m}^3$
$\psi$	Particle shape factor	-
$\varphi$	angle of internal friction	deg

1

2 REFERENCES

- 3 1. Kunii D, Levenspiel O. *Fluidization Engineering*. Butterworth-Heinemann; 1991.
- 4 2. Molerus O. Interpretation of Geldart's type A, B, C and D powders by taking into  
5 account interparticle cohesion forces. *Powder Technol.* 1982;33(1):81-87.  
6 doi:10.1016/0032-5910(82)85041-9
- 7 3. Geldart D. Types of gas fluidization. *Powder Technol.* 1973;7(5):285-292.  
8 doi:10.1016/0032-5910(73)80037-3
- 9 4. Lettieri P, Yates JG, Newton D. The influence of interparticle forces on the fluidization  
10 behaviour of some industrial materials at high temperature. *Powder Technol.*  
11 2000;110(1-2):117-127. doi:10.1016/S0032-5910(99)00274-0
- 12 5. Chirone R, Massimilla L, Russo S. Bubble-free fluidization of a cohesive powder in  
13 an acoustic field. *Chem Eng Sci.* 1993;48(1):41-52. doi:10.1016/0009-2509(93)80281-  
14 T
- 15 6. Lettieri P, Newton D, Yates JG. High temperature effects on the dense phase properties  
16 of gas fluidized beds. *Powder Technol.* 2001;120(1-2):34-40. doi:10.1016/S0032-  
17 5910(01)00344-8
- 18 7. Girimonte R, Formisani B. The minimum bubbling velocity of fluidized beds operating  
19 at high temperature. *Powder Technol.* 2009;189(1):74-81.  
20 doi:10.1016/j.powtec.2008.06.006
- 21 8. Yates JG. Effects of temperature and pressure on gas-solid fluidization. *Chem Eng Sci.*  
22 1996;51(2):168-205.

- 23 9. Quintanilla MAS, Valverde JM, Castellanos A. Adhesion force between fine particles  
24 with controlled surface properties. *AIChE J.* 2006;52(5):1715-1728.  
25 doi:10.1002/aic.10770
- 26 10. Valverde JM, Castellanos A, Mills P, Quintanilla MAS. Effect of particle size and  
27 interparticle force on the fluidization behavior of gas-fluidized beds. *Phys Rev E.*  
28 2003;67(5):051305. doi:10.1103/PhysRevE.67.051305
- 29 11. Mutsers SMP, Rietema K. The effect of interparticle forces on the expansion of a  
30 homogeneous gas-fluidized bed. *Powder Technol.* 1977;18(2):239-248.  
31 doi:10.1016/0032-5910(77)80014-4
- 32 12. Rietema K, Piepers HW. The effect of interparticle forces on the stability of gas-  
33 fluidized beds – I. Experimental evidence. *Chem Eng Sci.* 1990;45(6):1627-1639.
- 34 13. Hou QF, Zhou ZY, Yu AB. Micromechanical modeling and analysis of different flow  
35 regimes in gas fluidization. *Chem Eng Sci.* 2012;84:449-468.
- 36 14. Donsì G, Massimilla L. Bubble-free expansion of gas-fluidized beds of fine particles.  
37 In: *Bubble-Free Expansion of Gas-Fluidized Beds of Fine Particles.* Vol 19. ; 1973:41-  
38 53. doi:10.1002/aic.690190604
- 39 15. Massimilla L, Donsì G, Zucchini C. The structure of bubble-free gas fluidized beds of  
40 fine fluid cracking catalyst particles. *Chem Eng Sci.* 1972;27(11):2005-2015.  
41 doi:10.1016/0009-2509(72)87059-3
- 42 16. Lettieri P, Macrì D. Effect of Process Conditions on Fluidization. *KONA Powder Part*  
43 *J.* 2016;33(October):86-108. doi:10.14356/kona.2016017
- 44 17. Grewal NS, Gupta A. Total and gas convective heat transfer from a vertical tube to a

- 45 mixed particle gas-solid fluidized bed. *Powder Technol.* 1989;57:27-38.
- 46 18. Geldart D. Estimation of basic particle properties for use in fluid-particle process  
47 calculations. *Powder Technol.* 1990;60:1-13.
- 48 19. Fletcher J, Deo M, Hanson F. Re-examination of minimum fluidization velocity  
49 correlations applied to Group B sands and coked sands. *Powder Technol. Powder  
50 Technol.* 1992;69:147-155.
- 51 20. Knowlton TM. Pressure and temperature effects in fluid-particle systems. In: *Pressure  
52 and Temperature Effects in Fluid-Particle Systems.* ; 1992:27–46.
- 53 21. Lettieri P, Newton D, Yates JG. Homogeneous bed expansion of FCC catalysts,  
54 influence of temperature on the parameters of the Richardson–Zaki equation. *Powder  
55 Technol.* 2002;123(2-3):221-231. doi:10.1016/S0032-5910(01)00463-6
- 56 22. Coltters R, Rivas AL. Minimum fluidization velocity correlations in particulate  
57 systems. *Powder Technol.* 2004;147:34-48.
- 58 23. Formisani B, Girimonte R, Mancuso L. Analysis of the fluidization process of particle  
59 beds at high temperature. *Chem Eng Sci.* 1998;53(5):951-961.
- 60 24. Siegell JH. Early studies of magnetized-fluidized beds. *Powder Technol.*  
61 1989;57(3):213-220. doi:10.1016/0032-5910(89)80077-4
- 62 25. Piepers H, Cottaar E, Verkooijen A, Rietema K. Effects of pressure and type of gas on  
63 particle-particle interaction and the consequences for gas—solid fluidization  
64 behaviour. *Powder Technol.* 1984;37:55-70.
- 65 26. Cottaar E, Rietema K. A theoretical study on the influence of gas adsorption on  
66 interparticle forces in powders. *J Colloid Interface Sci.* 1986;109(1):249-260.

- 67 27. Rietema K, Cottaar E, Piepers H. The effects of interparticle forces on the stability of  
68 gas-fluidized beds—II. Theoretical derivation of bed elasticity on the basis of van der  
69 Waals forces between. *Chem Eng Sci.* 1993;48(9):1687-1697.
- 70 28. Formisani B, Girimonte R, Pataro G. The influence of operating temperature on the  
71 dense phase properties of bubbling fluidized beds of solids. *Powder Technol.*  
72 2002;125:28-38.
- 73 29. Geldart, D., Wong ACY. Fluidization of powders showing degrees of cohesiveness—  
74 II. Experiments on rates of de-aeration. *Chem Eng Sci.* 1985;40:653-661.
- 75 30. Lin, C.L., Wey, M.Y., You SD. The effect of particle size distribution on minimum  
76 fluidization velocity at high temperature. *Powder Technol.* 2002;126:297-301.
- 77 31. Zhou T, Li H. Estimation of agglomerate size for cohesive particles during fluidization.  
78 *Powder Technol.* 1999;101(1):57-62. doi:10.1016/S0032-5910(98)00148-X
- 79 32. Agbim JA, Nienow AW, Rowe PN. Inter-particle forces that suppress bubbling in gas  
80 fluidised beds. *Chem Eng Sci.* 1971;26:1293-1294. doi:10.1016/0009-2509(71)87015-  
81 X
- 82 33. Chirone R, Barletta D, Lettieri P, Poletto M. Bulk flow properties of sieved samples of  
83 a ceramic powder at ambient and high temperature. *Powder Technol.* 2016;288:379-  
84 387. doi:10.1016/j.powtec.2015.11.040
- 85 34. Lettieri P, Yates JG. New Generation X-ray Imaging for multiphase systems. *Fluid*  
86 *XIV.* 2013:641-648.
- 87 35. Baeyens J, Geldart D. An investigation into slugging fluidized beds. *Chem Eng Sci.*  
88 1974;29(1):255-265. doi:10.1016/0009-2509(74)85051-7

- 89 36. Wen CY, Yu YH. A generalized method for predicting the minimum fluidization  
90 velocity. *AIChE J.* 1966;12:610-612.
- 91 37. Nedderman RM, Cambridge University Press. *Statics and Kinematics of Granular*  
92 *Materials*. Cambridge University Press; 1992.
- 93 38. Schulze D. *Powders and Bulk Solids*. (Springer Science & Business Media, ed.).  
94 Berlin, Heidelberg: Springer Berlin Heidelberg; 2008. doi:10.1007/978-3-540-73768-  
95 1
- 96 39. ASTM International. *ASTM D6773-02, Standard Shear Test Method for Bulk Solids*  
97 *Using the Schulze Ring Shear Tester*. West Conshohocken, PA: ASTM International;  
98 2008. doi:10.1520/D6682-08
- 99 40. Peleg M, Normand MD, Corradini MG. Interactive software for calculating the  
100 principal stresses of compacted cohesive powders with the Warren-Spring equation.  
101 *Powder Technol.* 2010;197(3):268-273. doi:10.1016/j.powtec.2009.10.003
- 102 41. Schwedes J. Review on testers for measuring flow properties of bulk solids. *Granul*  
103 *Matter.* 2003;5(1):1-43. doi:10.1007/s10035-002-0124-4
- 104 42. Ashton MD, Cheng DCH, Farley R, Valentin FHH. Some investigations into the  
105 strength and flow properties of powders. *Rheol Acta.* 1965;4(3):206-218.  
106 doi:10.1007/BF01969257
- 107 43. Pierrat P, Agrawal DK, Caram HS. Effect of moisture on the yield locus of granular  
108 materials: Theory of shift. *Powder Technol.* 1998;99(3):220-227. doi:10.1016/S0032-  
109 5910(98)00111-9
- 110 44. Kamiya H, Kimura A, Yokoyama T, Naito M, Jimbo G. Development of a split-type

- 111 tensile-strength tester and analysis of mechanism of increase of adhesion behavior of  
112 inorganic fine powder bed at high-temperature conditions. *Powder Technol.*  
113 2002;127(3):239-245. doi:10.1016/S0032-5910(02)00117-1
- 114 45. Castellanos A, Valverde JM, Quintanilla MAS. The Sevilla Powder Tester: A Tool for  
115 Characterizing the Physical Properties of Fine Cohesive Powders at Very Small  
116 Consolidations. *KONA Powder Part J.* 2004;22(22):66-81.  
117 doi:10.14356/kona.2004011
- 118 46. Zafar U, Hare C, Calvert G, et al. Comparison of cohesive powder flowability  
119 measured by Schulze Shear Cell, Raining Bed Method, Sevilla Powder Tester and new  
120 Ball Indentation Method. *Powder Technol.* 2015;286:807-816.  
121 doi:10.1016/j.powtec.2015.09.010
- 122 47. Rumpf H. Zur Theorie der Zugfestigkeit von  
123 Agglomeraten bei Kraftübertragung an Kontaktpunkten. *Chemie Ing Tech.* 1970;42:538-  
124 540.
- 125 48. Molerus O. Theory of yield of cohesive powders. *Powder Technol.* 1975;12(3):259-  
126 275. doi:10.1016/0032-5910(75)85025-X
- 127 49. Tomasetta I, Barletta D, Poletto M. Correlation of powder flow properties to  
128 interparticle interactions at ambient and high temperatures. *Particuology.*  
129 2014;12(1):90-99. doi:10.1016/j.partic.2013.02.002
- 130 50. Chirone R, Raganati F, Ammendola P, Barletta D, Lettieri P, Poletto M. A comparison  
131 between interparticle forces estimated with direct powder shear testing and with sound  
132 assisted fluidization. *Powder Technol.* 2018;323:1-7.  
133 doi:10.1016/j.powtec.2017.09.038

- 134 51. Chirone R, Barletta D, Poletto M, Lettieri P. Detection and estimation of capillary  
135 interparticle forces in the material of a fluidized bed reactor at high temperature by  
136 powder flow characterization. *Powder Technol.* 2018;330:371-385.  
137 doi:10.1016/j.powtec.2018.02.024
- 138 52. Macrì D, Poletto M, Barletta D, Sutcliffe S, Lettieri P. Analysis of industrial reactive  
139 powders flow properties at high temperature. *Powder Technol.* 2017;316:131-138.  
140 doi:10.1016/j.powtec.2016.10.064
- 141 53. Macrì D, Barletta D, Lettieri P, Poletto M. Experimental and theoretical analysis of  
142 TiO<sub>2</sub> powders flow properties at ambient and high temperatures. *Chem Eng Sci.*  
143 2017;167:172-190. doi:10.1016/j.ces.2017.03.057
- 144 54. Liu Y, Lu H, Barletta D, et al. Bulk flow properties of fly ashes at ambient and high  
145 temperature. *Particuology.* 2018;38:113-125. doi:10.1016/j.partic.2017.04.013
- 146 55. Liu Y, Lu H, Poletto M, Guo X, Gong X, Jin Y. Flow properties and inter-particle  
147 forces in fuel powders. *Particuology.* 2017;34. doi:10.1016/j.partic.2016.10.007
- 148 56. Sofia D, Barletta D, Poletto M. Laser sintering process of ceramic powders: The effect  
149 of particle size on the mechanical properties of sintered layers. *Addit Manuf.*  
150 2018;23:215-224. doi:10.1016/j.addma.2018.08.012
- 151 57. Sofia D, Chirone R, Lettieri P, Barletta D, Poletto M. Selective laser sintering of  
152 ceramic powders with bimodal particle size distribution. *Chem Eng Res Des.*  
153 2018;136:536-547. doi:10.1016/j.cherd.2018.06.008
- 154 58. Barletta D, Donsi G, Ferrari G, et al. Solid flow rate prediction in silo discharge of  
155 aerated cohesive powders. *AIChE J.* 2007;53(9):2240-2253xxxx.  
156 doi:10.1002/aic.11212

- 157 59. Barletta D, Poletto M. Aggregation phenomena in fluidization of cohesive powders  
158 assisted by mechanical vibrations. *Powder Technol.* 2012;225:93-100.  
159 doi:10.1016/j.powtec.2012.03.038
- 160 60. Domnich V, Aratyn Y, Kriven WM, Gogotsi Y. Temperature dependence of silicon  
161 hardness: Experimental evidence of phase transformations. *Rev Adv Mater Sci.*  
162 2008;17(1-2):33-41.
- 163 61. Zaki WN, Richardson JF. Sedimentation and fluidisation: Part I. *Trans Inst Chem Eng.*  
164 1954;32:35-53.
- 165 62. Zhu C, Yu Q, Dave R, Pfeffer R. Gas fluidization characteristics of nanoparticle  
166 agglomerates. *AIChE J.* 2005;51(2):426-439.
- 167 63. Loezos PN, Costamagna P, Sundaresan S. The role of contact stresses and wall friction  
168 on fluidization. *Chem Eng Sci.* 2002. doi:10.1016/S0009-2509(02)00421-9
- 169 64. Tsinontides SC, Jackson R. The mechanics of gas fluidized beds with an interval of  
170 stable fluidization. *J Fluid Mech.* 1993;255(1):237. doi:10.1017/S0022112093002472
- 171 65. LaMarche CQ, Miller AW, Liu P, Hrenya CM. Linking micro-scale predictions of  
172 capillary forces to macro-scale fluidization experiments in humid environments.  
173 *AIChE J.* 2016;62(10):3585-3597. doi:10.1002/aic.15281