STUDY OF DEFLUIDIZATION BEHAVIOUR OF INDUSTRIAL REACTIVE PARTICLES

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I, Domenico Macri’ confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
The overall objective of this research is to assess the effect of high temperature on the flow properties and fluidization behaviour of mixtures of petroleum coke and different titanium ores. To this end, a twofold approach based on fundamental fluidization and rheological measurements was followed with the aim of evaluating how the particle-particle interactions change with temperature.

On the one hand, the fluidization behaviour of every single component of the mixture and of the mixture itself have been studied at process temperatures ranging from ambient up to 500 °C in a specially designed heated fluid-bed reactor. Experiments were carried out under different fluidization conditions, where the carbon combustion causes defluidization, varying the amount of coke and its size distribution present in the bed. The latter is particularly important as coke particles are prone to promote ores particles’ sintering and thus leading to poor mixing and segregation.

Fundamental fluidization tests were performed using the unique X-ray Imaging technique available at UCL, which enabled to visualise the internal flow pattern inside the reactor and to obtain quantitative information on voidage distribution, bed expansion, mixing and segregation within the fluidized bed. Simultaneous measurements of local temperatures and pressure drop across the bed were carried out in order to detect possible aggregation and sintering phenomena. The tests showed that combination of operative conditions and coke characteristics have a significant role on the formation of the aggregates and on their properties. The resulting lumps of aggregated particles were collected and systematically characterized by performing specific analysis aimed at investigating their mechanical properties and the chemical compositions of the sintered bonds formed.

On the other hand, the unique heated annular shear cell available at the University of Salerno has been used to assess the changes of the bulk flow
properties of the different types of titanium ores at ambient and with increasing temperature. These experiments highlighted a significant increase with temperature of the macroscopic bulk flow properties, such as unconfined yield strength and cohesion, which resulted in a lower flowability of the samples. In parallel, two different models were used to correlate the experimental results with the microscopic interparticle interaction forces. Such outcomes provided an indication of the ability of the powders to flow and underpinned the link between the fluidization and the rheological behaviour below the minimum fluidization conditions: the capability of the powders to fail under a certain load was directly correlated to their capability to attain fluidization.
The Chemical Industry Association reports that 90% of all chemical products currently in production involve the use of particles at some stage in the manufacturing process. Particle science and technology are essential to the future of industry because of their potential to improve many types of consumer products (including electronics, paints, polymers, cosmetics, food and healthcare) and tackle most contemporary grand challenges, such as in advanced manufacturing, global health, water purification, sustainable energy, waste treatment and food preservation.

This research aimed at delivering fundamental understanding of multiphase and particulate processes by tackling a number of challenges still open on the prediction of the flow behaviour of dense multiphase reactive industrial powders that can be applied to design, scale-up, operate and control of innovative and sustainable particulate processes more reliably and efficiently.

Fluidization technology is employed in a wide range of industrial processes that operate at extreme conditions and it is also recognised to be the most promising technology to optimise the available potential of renewable energy. The knowledge developed in this research has therefore the potential to lead to a transformative impact on the commercial sector by providing industry with the underpinning science from which to develop innovative future technologies in the manufacturing, process engineering and energy sector.
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1 GENERAL INTRODUCTION

A general overview on the phenomenon of fluidization and its different regimes is given in this chapter with the aim of outlining the rationale behind the study conducted. The objectives of this project are also presented and the experimental approaches are discussed thereafter. The chapter concludes with a brief outline of the thesis.

1.1 A BRIEF OVERVIEW TO FLUIDIZATION

Fluidization is the operation by which solid particles are transformed into a fluid-like state through suspension in a gas or liquid [1]. It can be described as a random upward motion of stationary solid particles caused by an upward-flowing fluid with lower density. In particular, the particle become buoyant and free to move as soon as the combined drag and body forces exerted on the particle by the fluid exceed the gravitational force holding them assembled. The condition at which this occurs is termed incipient or minimum fluidization. Further increase of the fluid velocity causes the discrete particles to expand and the void fraction to increase.

In liquid-solid systems, a further increase in flow rate above minimum fluidization results in a smooth and progressive expansion of the bed, the so-called homogeneously fluidized bed. In gas-solid systems, this kind of behaviour is observed only under special conditions and it depends on the nature of the particles. To this end, Geldart classified fluidizable particles into four groups (namely A, B, C and D) according to their particle size and density as shown in Figure 1.1 [2].

For Group A particles, increasing the fluidizing gas velocity above the minimum fluidization velocity (u\text{mf}) causes the bed to expand uniformly in the same way as a liquid-solid system up to a gas velocity at which part of the fluid start to pass through the bed in the form of bubbles. These rise through the bed at
a velocity proportional to their size and burst as soon as they reach the bed surface. This type of bed is called *bubbling fluidized bed* and the velocity at which the first bubble forms is called minimum bubbling velocity (\(u_{mb}\)). For Group B particles, which are typically bigger in size than Group A particles, bubbles form once the gas velocity exceeds \(u_{mf}\). This kind of behaviour is known as *aggregative fluidization*. Group C particles are normally very fine and they easily tend to be cohesive and hard to fluidize, while Group D particles are relatively large, dense and prone to spouting rather than fluidizing.

![Figure 1.1 – Geldart’s powder classification diagram at ambient condition [2].](image)

Once the bubbling regime has been established in systems with Group A and B materials, bubbles coalesce and grow as they rise. In a bed with high enough aspect ratio (height to diameter ratio) they may eventually become large enough to spread across the vessel, at this point the bed is said to be *slugging*. For fine particles the above change is observed as axial slugs, whereas for coarse particles it is observed as flat slugs. Further increases of gas velocity above the terminal velocity of the particles (\(u_t\)) cause the transition to *turbulent regime* first and then to *fast fluidization* and *pneumatic conveying*. A schematic of the various regimes is shown in Figure 1.2.

The intimate interaction between solid particles and gas provides an ideal environment for rapid heat and mass transfer, good mixing of solids and fast chemical reaction inside the fluidized bed. These features enable fluidized beds to be widely applied in industry. Whenever a chemical reaction employing a particulate solid as a reactant or as a catalyst requires reliable temperature control,
a fluidized bed reactor is often the choice for ensuring nearly isothermal conditions by suitable selection of the operating conditions.

Fluidization was created as an industrial operation in the Winkler process for the gasification of lignite and the Ignifluid process for the combustion of coal, but it is only with the introduction in the 1940s of the fluid catalytic cracking (FCC) process that its true potential became apparent. Since then, a number of different fluid-bed industrial applications have been developed in several areas such as combustion, gasification, catalytic conversions and polymerization.

![Diagram of different regimes of fluidization](image)

Figure 1.2 – Different regimes of fluidization [3].

Fluidized beds are now decisively recognized as a major unit operation in the processing industries [4] and they can be considered one of the most powerful method to handle a variety of particulate solid materials [5]. They are widely used in different industrial processes thanks to their temperature uniformity generated by the frequent particle collisions and the good solid mixing. For example, they have been for several decades a key technology in the petroleum industry, specifically in fluid catalytic cracking process to make gasoline [5–7]; in catalytic chemicals synthesis processes, such as the partial oxidation of ammonia to
acrylonitrile to prepare acrylic resin and the production of melamine, maleic and phthalic anhydrides and ethylene dichloride [6,8]; in fluidized bed combustion and gasification of solid fuels (coal, wastes and biomass) to generate steam for boilers, syngas, chemicals or fuels [9–11]; in waste incineration of solids and sludge [5]; in metals and oxides production such as iron for steelmaking, titanium oxide by chloride process, aluminium fluoride synthesis, alumina calcination and ore roasting [5,6,8]; in gas phase polymerization processes of polyethylene and polypropylene [5,8]; in the chlorination process of metals such as silicon for purification in the semiconductor industry [5,8]; and in other operations including granulation process for the pharmaceutical industry, drying, flue gas cleaning, powder coating and thermal treatment of metals by hot or cold sands [5,6,12,13].

Table 1.1 lists some key industrial applications of fluidized beds, highlighting the main operating conditions generally employed, i.e. the range of temperatures, pressures and the proportion of fines.

<table>
<thead>
<tr>
<th>Process</th>
<th>Examples</th>
<th>Process conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>480-550 1-3</td>
</tr>
<tr>
<td>Acrylonitrile synthesis</td>
<td>Acrylonitrile (SOHIO Process) [1]</td>
<td>400-500 1.5-3 20-40</td>
</tr>
<tr>
<td></td>
<td>Melamine (Borealis Agrolinz Melamine GmbH) [6]</td>
<td>400 &gt;1</td>
</tr>
<tr>
<td></td>
<td>Maleic Anhydride (Mitsubishi Chemical Industries) [8]</td>
<td>410-420 1-5 25-55</td>
</tr>
<tr>
<td></td>
<td>Maleic Anhydride (DuPont) [8]</td>
<td>360-420 &lt;5</td>
</tr>
<tr>
<td></td>
<td>Ethylene dichloride [8]</td>
<td>220-245 2.5-6 30</td>
</tr>
<tr>
<td></td>
<td>Phthalic Anhydride [8]</td>
<td>345-385 2.7 28</td>
</tr>
<tr>
<td></td>
<td>Polyethylene (UNIPOL) [8]</td>
<td>75-105 20-25</td>
</tr>
<tr>
<td>Metallurgical industry</td>
<td>Iron (Finex process) [6]</td>
<td>850 3.5</td>
</tr>
<tr>
<td></td>
<td>AlF3 synthesis [8]</td>
<td>530 1</td>
</tr>
<tr>
<td></td>
<td>Alumina calcination [8,14]</td>
<td>800-1200 1</td>
</tr>
<tr>
<td></td>
<td>Limestone calcination [14]</td>
<td>770 1 Variable</td>
</tr>
<tr>
<td></td>
<td>Gold roasting (Lurgi process) [8]</td>
<td>650 1</td>
</tr>
<tr>
<td></td>
<td>SO2 from pyrite, zinc blende and other sulphide ores roasting [1]</td>
<td>650-700 1</td>
</tr>
<tr>
<td></td>
<td>Pyrite roasting (BASF) [1]</td>
<td>660-920 1</td>
</tr>
</tbody>
</table>
|                                | FeS2 from sulphide ores roasting [14]                                     | 650-1100 1 < 3
| Drying of solids              | Inorganic materials [14]                                                 | 60-110 1 Variable  |
|                                | Pharmaceuticals [14]                                                     | 60 1 Variable      |
| Semiconductor Industry        | SiHCl3 production from metallurgical-grade silicon (Union Carbide – Osaka Titanium process) [1,14] | 300 1 100          |
|                                | Silicon production (MEMC process)[8]                                     | 600-800 ~1         |
| Nuclear Industry              | Separation of U-235 from U-238[1]                                        | 450 - -            |
In parallel with the industrial development, significant academic research has been undertaken aimed at providing a theoretical framework to underpin the subject. The first examples are the two phases theory postulated by Toomey and Johnstone [15] in 1952, largely used over the years ahead, and the pioneering studies of bubble motion in fluidized beds by Davidson and Harrison in the early ‘60s [16,17]. In addition, there are also the work on the mechanics of the fluidized bed by Jackson in 1963 [18], the mathematical investigation on fluidization by Murray in 1965 [19] and the Geldart’s empirical classification of fluidizable powders into four groups in 1973 [2]. Some years later, in 1984, Foscolo and Gibilaro developed the particle-bed model [20] which is considered the main theoretical advance in the ‘80s [21]. In the next decade, the 1990s, computational fluid dynamics (CFD) was introduced for numerically simulate the fluidized bed hydrodynamics and, since then, its use has grown increasingly as a useful modelling tool.

During the years, several experimental techniques were adopted for investigating the hydrodynamics of fluidized bed such as capacitance probes, first introduced by Morse and Ballou in 1951 [22], X-ray attenuation, used for the first time by Grohse in 1955 [23] and optical sensor which were suggested by Yasui and Johanson in 1958 [24]. Starting from the early 1990s, the sophistication of the experimental methods for the study of the fluidized beds increased notably. Examples of such methods are electrical capacitance tomography, positron emission particle tracking (PEPT), laser Doppler velocimetry, X- and gamma-ray tomography, acoustic sensing and different typologies of probes. Details of these and other methods have been comprehensively reviewed in several works [25–27].

As highlighted by Yates and Lettieri [21] in their recent book on fluidized bed reactors, the field of fluidization continues to attract academic and applied research and major advances have been achieved in some areas, but much remains to be done before fluidized beds can be designed and scaled up with total confidence.
1.2 Research Objectives

The main focus of this research is on the experimental investigation of the effect of operative conditions, and high temperature in particular, on the fluidization behaviour of industrial reactive powders. The project is in part sponsored by Venator (formerly Huntsman Pigment), which is a leading manufacturer of titanium dioxide and coloured pigments.

This project addresses problems in the production of titanium tetrachloride where a bubbling fluidized bed is used for extracting titanium from naturally occurring ores. The process commonly entails numerous steps, with a high temperature fluid-bed chlorinator operated between 800 and 1100 °C being at the heart of the first process step, namely the carbo-thermal chlorination of the titanium rich ores to produce titanium tetrachloride. Titanium dioxide is firstly reduced with carbon (coke) and then oxidised again by a chlorine gas bubbling through the particles bed.

The typical carbo-chlorination reaction feedstock are natural and synthetic rutiles with a particle size distribution that depends on the source mineral. Nowadays, most titanium ore feedstock are prepared through a smelting process where the titanium-rich slag (e.g. from ilmenite - FeTiO₃) is milled to a generally larger size that it is more suitable for efficient fluid bed chlorination. However, it is more angular and therefore generally more abrasive on plant equipment and it tends to contain lighter elements as impurities. The chloride process was first commercialized in 1958 in the United States and nowadays there are a few different industrial process designs, although their operating principle remains the same.

Because of the differences in size, density and thermo-physic properties of all the reactants and the fluidization regime close to incipient conditions there are industrial concerns about the pervasiveness of dead zones within the fluidized bed which is mainly caused by powder caking, i.e. detrimental particles aggregation and agglomeration [28]. The direct effect of the above is the transition from a readily free-flowing powder to a coherent solid which leads to the reduction of the reaction volume due to the segregation of the aggregates at the bottom, as well as
to the substantial reactor clog and defluidization. The latter represents a significant cost for chlorinator operation as it requires lengthy reactor outages for cooling, unclogging and replenishment of the damaged reactor. It will thus be of great importance to gain a better understanding of the defluidization behaviour of such industrial reactive systems.

The overall objective of this PhD work is to understand the factors that affect fluidization at different regimes through a systematic study of variables such as the size and the morphology of the coke present, as well as the associated defluidization behaviour under a range of combustion conditions. More to the point, the various objectives of this thesis are as follows:

1. Characterize the rheological and fluidization behaviour of each particulate material at ambient and high temperature;
2. Find a possible link between the powders’ performance when fluidized and their rheological properties;
3. Investigate the fluidization performance of different mixtures of titanium ores and coke in the regimes where carbon combustion causes defluidization due to particles aggregation;
4. Systematically characterize the resulting lumps of aggregated particles by performing specific analysis aimed at investigating the factors responsible for their formation;
5. Provide a reliable analysis tool for the prediction of the defluidization phenomenon in the investigated systems.

1.3 THE INVESTIGATION APPROACH

It is important to note that the theories mentioned above, as well as the Geldart’s breakthrough classification of powders, are based on observations made under ambient conditions, hence the fluidisation behaviour needs to be extrapolated to higher temperatures and pressures by considering the effect of the physical properties on the drag laws.

The effects of process conditions on fluidization are still not entirely understood. Even the modern design criteria and performance predictions for fluid
bed units working at high temperature have been largely based on fluid-dynamic models and correlations established from tests developed at ambient temperature. Extrapolating to elevated temperature results and relationships available at ambient conditions can lead to misleading prediction of the fluid bed performance. Drastic changes can occur in the fluidization behaviour between low and high temperatures, due to possible modifications induced by temperature in the structure of the fluidized bed. In order to understand the factors responsible for such changes in fluidization behaviour, the role of the interparticle forces (IPFs) and the hydrodynamic forces (HDFs) has been studied, but much controversy still remains to define their relative importance.

Within this framework, powder rheology represents an interesting tool to evaluate indirectly the effects of the IPFs on fluidization. A great deal of research has been carried out over the last sixty years in order to define and measure rheological parameters apt to characterize and predict the flow properties of solid materials. To this end various approaches have been undertaken, including both static measurements and dynamic tests.

![Figure 1.3 – Schematic representation of the investigation approach of the work.](image)

In order to tackle the problem of assessing the defluidization behaviour of powders at high temperature, a twofold approach has been adopted in this study, as schematically reported in Figure 1.3. On the one hand, the fluid-dynamic and rheological characterization of the investigated powders (mono-component
systems); on the other hand, the assessment of the defluidization due to sintering of mixtures of rutile, slag and coke under a range of coke particles size and combustion conditions (multi-components systems). The first challenge of the project was to find a possible link between the rheological measurements to the corresponding defluidization behaviour of the powders in order to achieve a physical understanding of the effect of process conditions on fluidization. The second challenge was to provide a sound foundation for the understanding of the factors responsible for the formation of the aggregates in order to reliably predict the defluidization phenomenon.

The materials which have been used in this investigation are natural and synthetic rutile, slag from ilmenite smelting and petroleum coke particles provided by Venator.

The effect of temperature on the fluidization behaviour of each single material was studied by ranging the temperature from ambient to 500 °C. The fundamental fluidization parameters were measured with increasing temperature using a 14.6 cm diameter x 100 cm tall heated gas fluid-bed, fully described in the Section 3.3. The parameters measured included the minimum fluidization velocity \( u_{mf} \), the bed expansion profiles, the settled bed voidage \( \varepsilon_s \), the voidage at minimum fluidization \( \varepsilon_{mf} \) and the collapsing properties from bed collapse test. These tests were applied to the multi-components systems as well. In order to study the effect of changing the size distribution of the coke fraction, several cuts of coke were created by sieving and then blended with the others components in different proportions. This is very important as coke particles are substantially larger than the titanium based ones and they can thus dominate the fluidisation behaviour.

Early stages of the sintering process were experimentally simulated in the fluidization rig for the mixtures of coke, rutile and slag by blowing air into the fluidized bed for a certain time. The effects of high temperature and air flowrate were investigated systematically in different fluidization regimes. Fundamental fluidization tests were also carried out on the spent systems (i.e. after combustion and cooled down to ambient conditions) and compared to the fresh ones. The reactor was then emptied and the aggregates collected for further off-line examinations.
The rheological part of the work was carried out using a high temperature annular shear cell (HT-ASC), which is a modified Schulze shear cell specially designed and built at the University of Salerno, Italy. The cell allows the evaluation of the interparticle interactions at high temperature, by measuring the flow properties of the samples, namely static angle of internal friction, cohesion, unconfined yield strength and tensile strength. In addition, some theoretical modelling procedures were proposed and discussed with the aim of relating the micro-scale interparticle interactions to the measured macro-scale bulk flow properties.

1.4 Structure of this thesis

Chapter 1 introduces the fundamental aspects of fluidization along with the objectives of this thesis and the investigation approach adopted. Chapter 2 presents a survey on the state of the art in the field of fluidization and powder rheology, with special attention being paid to the main factors that cause defluidization. Chapter 3 reports the descriptions of the experimental apparatuses and methodologies used during this work. The materials and their main properties are reported as well. Chapters 4 and 5 are dedicated to the results obtained for mono-component and multi-components systems, respectively. Conclusions and Future Works are outlined in Chapters 6. The photographs of various aggregates collected during this work, the MATLAB scripts used for the X-ray images analysis and some numerical results are reported in the appendices.
2 Literature Survey

This chapter reviews the experimental and theoretical research on the effect of process conditions on fluidization of single and multi-components system, as well as the works concerning powder flowability measurements tests.

The survey begins by reviewing the classification of the powder behaviours during fluidization and the forces acting among particles in the micro scale range, with special focus to sintering phenomena. The influence of temperature on fundamental parameters of gas-solid fluidization, such as minimum fluidization, bed expansion and voidage are then reported. The survey will then address the main techniques used for the characterization and the prediction of the flow properties of powders. These include the standard bed collapse test and the various rheological tests. The chapter will conclude by reviewing the joint works done at University College London and University of Salerno on linking rheological measurements to fluidization tests, in the attempt to quantify the role of the interparticle forces on the fluidization behaviour of different industrial powders.

2.1 Classification of Powders

One of the first pioneering classification of the different fluidization behaviours of powders was proposed by Geldart in 1973 [2] and since then it has been widely used by chemical engineers. His empirical classification divides fluidizable particles into four groups (A, B, C and D) according to their particle size and density as shown in Figure 1.1.

The main features of each group behaviour have been briefly discussed in section 1.1 and further information are summarized in Table 2.1. However, it is important to note that Geldart’s classification of powder was originally intended to predict the behaviour of beds fluidized by dry air at ambient conditions only. Because of this, Rietema [29] pointed out that it would be more appropriate to
Literature Survey

speak only in terms of Geldart A, B, C or D-powder behaviour rather than classifying powders as A, B, C or D-powders since different types of fluidization behaviour may be exhibited by the same powder when changing the operative conditions.

Table 2.1 – Geldart’s classification of powders

<table>
<thead>
<tr>
<th>Properties</th>
<th>Geldart’s Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>$d_p$ (μm)</td>
<td>~20</td>
</tr>
<tr>
<td>$\rho_p$ (kg/m³)</td>
<td>-</td>
</tr>
<tr>
<td>Example</td>
<td>Flour</td>
</tr>
<tr>
<td>Phases Mixing</td>
<td>Very low</td>
</tr>
<tr>
<td>Bed Expansion</td>
<td>Low when channelling</td>
</tr>
<tr>
<td></td>
<td>High when fluidised</td>
</tr>
<tr>
<td>Deaeration rate</td>
<td>Very slow</td>
</tr>
<tr>
<td></td>
<td>Exponential trend</td>
</tr>
<tr>
<td>Bubble</td>
<td>No bubbles</td>
</tr>
<tr>
<td></td>
<td>- Channels</td>
</tr>
</tbody>
</table>

Over the years, some authors revised the Geldart’s classification by extending it with new features mostly related to boundaries between the different groups. For instance, in 1986, Grace [30] proposed a dimensionless plot (Figure 2.1) which included new boundaries between groups A and B and between groups B and D powder classification scheme. The former was altered by taking into account data available on the effects of pressure, high temperature and gases other than air. The latter was modified on the basis of the investigation on the relative magnitude of inertial to viscous acting forces.

In 2013, Valverde [31] revised the Geldart’s classical diagram in order to predict the possible transition between various types of fluidization behaviour for fine and ultra-fine powders. In his work, the author adapted the semi-empirical equations formulated to analyse the behaviour of granular materials fluidized by liquids to the gas-fluidization of fine powders. His diagram is shown in Figure 2.2, where the Geldart’s C region is transformed in a more complex one. When fluidized, the fine particle can exhibit two different scenarios according to their density and particle size: the system can transit from a solid-like to fluid-like and
then to a bubbling regime (SFB behaviour) or directly to elutriation (SFE behaviour).

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Figure 2.1 – Modified Geldart’s diagram by Grace [30]. Regions in which industrial reactors operate are also shown.

Figure 2.2 – Modified Geldart’s diagram by Valverde [31] showing the boundaries between the types of expected fluidization for fine particles.
2.2 **INTERPARTICLE FORCES**

The overall interaction processes between fluidizing fluid and particles are governed by the forces acting on individual particles. At minimum fluidization conditions a bed of powder is completely supported by the upward fluid flow, and the drag force exerted by the fluid on the particles, which is proportional to the global pressure drop across the bed, is balanced by the buoyant weight of the suspension. Therefore, the pressure drop across the bed associated to the buoyant weight of the suspension can be expressed according to Eqn. (2.1).

\[ \Delta P = (\rho_p - \rho_f)(1 - \varepsilon_{mf})gH \]  \hspace{1cm} (2.1)

where \( \rho_p \) and \( \rho_f \) are the particle and fluid density, \( \varepsilon_{mf} \) is the bed voidage at minimum fluidization and \( H \) is the height of the bed.

Several theoretical studies of the pressure drop through packed beds were conducted treating the packed bed region as analogous to flow in individual straight tubes. Among these, the Ergun equation [32] is one of the most often used:

\[ \Delta P = 150 \frac{\mu H u_{mf}}{(\phi d_p)^2} \left( \frac{1 - \varepsilon_{mf}}{\varepsilon_{mf}^3} \right)^2 + 1.75 \frac{\rho_f H u_{mf}^2}{\phi d_p} \left( \frac{1 - \varepsilon_{mf}}{\varepsilon_{mf}} \right) \]  \hspace{1cm} (2.2)

where \( d_p \) is the particle mean diameter, \( \phi \) is the particle sphericity and \( \mu \) is the viscosity of the fluid.

The velocity of minimum fluidization can be predicted by using Eqn. (2.2) as long as the value of the bed voidage at minimum fluidization is known. The experimental method used to measure \( u_{mf} \) is described in section 3.3.1.1.

As discussed in the introduction of this thesis, at minimum fluidization conditions the pressure drop across the bed becomes constant and it equals the buoyant weight of the particles when only hydrodynamic forces are present. The different types of fluidization behaviour at fluid velocities higher than \( u_{mf} \) have been introduced with respect to Geldart’s classification, namely homogenous expansion (Group A), bubbling or slugging (Group A and B), spouting (Group D) and channelling (Group C).

However, it is important to note that only the first three types of behaviour can be properly described as fluidization, because the bed of particles is fully supported
by the pressure drop. On the other hand, spouting and channelling cannot be described as proper fluidization since the pressure drop during these types of behaviour is less than that required to support the bed.

In the case in which additional forces are present, the pressure drop across the bed can also be higher than the buoyant weight. These forces hold the particles of the bed together making difficult their free movement and causing a poor fluidized state. For instance, it is commonly accepted that the reason for Group C powders being very difficult to fluidize is the dominance of surface forces. Moreover, it is well established in the literature that interparticle forces also exist in Group A and B powders, especially when high temperature is involved. Despite this, the importance of the IPFs as compared to the body forces is not yet unequivocally defined, mainly due to the difficulty in identifying the nature of the particle-particle interactions and in quantifying their effect on the fluidization behaviour. It is therefore necessary at this point to review the types and the nature of the interparticle forces which might be encountered.

Interparticle forces have been the subject of many studies over the years, but the first exhaustive investigation of the effect of interparticle adhesive forces on fluidization appeared for the first time in 1966 thanks to Baerns [33]. Several reviews on the different molecular and particle adhesive mechanisms that might be at the origin of the IPFs can be found in literature, as for instance the extensive analysis reported by Israelachvili [34] and Kendall [35], as well as the works of Visser [36], Matsusaka and Masuda [37] and Pollock et al. [38]. These can be divided in two different macro-groups: IPFs which arise without material bridges, namely van der Waals forces, electrostatic forces, magnetic forces and hydrogen bonding, and the ones that arise with material bridges, i.e capillary forces (or liquid bridges) and solid bridges caused by sintering. The forces belonging to the second macro-group are also the main causes for powder caking that, as previously discussed, represents a serious threat for the process profitability.

Electrostatic forces are only relevant when particles with electric charges interact to each other. Particle adhesion due to static electricity is generated by the movement of electric charges on the surface of the particles at contact. These forces can be attractive or repulsive, in spite of the charge of particles, and they
depend on a number of variables difficult to evaluate, such as particle local geometry, surface roughness, presence of impurities, humidity and moisture. Magnetic forces become important only for ferromagnetic and magnetisable materials. Hydrogen bonding and capillary forces need to be acknowledged if the operative environment is in some way affected by the presence of moisture or humidity. However, due to the characteristics of the examined systems, these forces have been considered not relevant to this work.

Regardless of the bonding mechanism, the key parameters that affect the interparticle force are the size and the undergoing transformation of the contact area. Tomas [39–42] and Seville et al. [43] extensively reported on this topic. An insight of the different contact mechanisms and deformations is developed in section 2.4.2.

2.2.1 VAN DER WAALS FORCES

The recipient of the 1910 Nobel Prize in physics, J. D. van der Waals, was the first to point out that deviations from the ideal-gas law at high pressures could be explained by assuming that molecules in a gas attract each other [44]. Therefore, the so-called van der Waals intermolecular forces arise from random motion of the electrons in the molecules surface that leads to an universal attraction between macroscopic bodies [45].

However, it is important to distinguish between intermolecular and interparticle forces as the former interacts with the adjacent molecules producing an attractive force proportional to \(z_0^7\), where \(z_0\) is the distance between molecules, while the latter decay as \(z_0^{-2}\) [21].

In order to scale up the van der Waals forces for macroscopic bodies having sizes larger than the molecular dimension, the microscopic theory of Hamaker [46] can be applied. The main assumption of this theory is that the interaction energies between the isolated molecules are additive and non-interacting, so the net energy can be calculated by integrating the molecular interactions over the entire body. This makes the calculations dependent on the shape of the objects. Considering two spherical and rigid particles with diameters \(d_1\) and \(d_2\), the attraction force \((F_H)\) is:
where $C_H$ is the material-related Hamaker constant. Values for the Hamaker constant can be found in Israelachvili [34] and they are significantly reduced for interaction across water. The Hamaker theory considers only pairwise additively and it neglects interactions between molecules and atoms in the presence of other atoms, known as many-body interactions.

The attractive Van der Waals forces are essentially contact forces as they operate at very short range and decay rapidly with distance. It can be seen that, according to Eqn. (2.3), the attractive force increases when the distance between particles decreases and theoretically it would go to infinity when the distance is reduced to zero. In other words, the attractive force would be infinite on contact but at very small distances repulsive interaction forces would start to be significant and balance attraction forces. Therefore, it was postulated that there is a minimum distance at which the attractive force reaches a maximum. Generally, when operating in air, values of the Hamaker constant around $10^{-20}$ J [47] and $z_0 = 0.4$ nm [48] are considered.

Rietema et al. [49] calculated the minimum molecular separation distance $z_0$ by considering the net force between repulsive and attractive forces ($F_{\text{attractive}} - F_{\text{repulsive}}$). They found the value of 0.223 nm as optimum and they also estimated the cohesion force due to van der Waals forces for two perfectly spherical and rigid particles having diameters and density of a typical Geldart Group A material. The result was several orders of magnitude greater than the gravitational force. They also suggested a fairly complicated model to account for particle deformation when evaluating the cohesive force between particles.

Massimilla and Donsi [50] used Eqn. (2.3) to estimate the van der Waals forces acting between two rigid particles, as well as Eqn. (2.4), previously developed by Molerus [51–53], for accounting for particle deformation:

$$F_H = \frac{C_H d_1 d_2}{12 z_0^2 (d_1 + d_2)} \left(1 + \frac{C_H}{6 \pi z_0^3 H_v} \right) R$$

(2.4)

where $H_v$ represents the material hardness and $R$ is the radius of curvature, generally calculated as for Eqn. (2.3), i.e. $d_1 d_2 / (d_1 + d_2)$. 

The calculated values increased by several hundred times when Eqn. (2.4) was used. Thus, the authors stated that the second term in the latter equation has to be neglected for materials with hardness values greater than $10^7$ Pa. They also investigated the particles’ surface with the aim of establishing the correct values for local radius of curvature $R$ to take into account. They observed the presence of asperities in the form of sub-particles on the surface and stated that such asperities are the real sites at which the contact takes place. Therefore, the contact forces between solids are smaller by several orders of magnitude depending on the ratio between sub-particles diameter and particle size. By accounting for surface irregularities the attractive force can be reduced by about two orders of magnitude [21]. For these reasons, Schubert [54] introduced the mean curvature radius at the contacting surface ($\delta$) to Eqn. (2.3):

$$F_H = \frac{C_H}{12z_0^3} \delta$$  \hspace{1cm} (2.5)

### 2.2.2 SOLID BRIDGES: SINTERING

Several materials are vulnerable to changes in operative conditions that may lead to bulk powder caking. As reported by Zafar et al. [28], the amount of caked material varies from large and weak lumps, which can be easily broken up when stressed, to irreversible fused aggregates that no longer represent the original system. Cleaver [55] pointed out that powder caking is still a very challenging topic because there are many reported mechanisms that may lead to powder transformation, but few studies which have undertaken a holistic view of the subject.

It is well established, however, that many factors need to be accounted when dealing with caking phenomena. Both material properties (i.e. particle size, flowability, elasticity, yield stress etc.) and environmental factors such as temperature, humidity and stress rate may influence caking behaviour. Simons [56] reported on the agglomerating phenomena and he identified solid bridges as the main cause for the formation of strong and tough aggregates.

In contrast to van der Waals forces, solid bridges form a continuous solid connection and they usually arise when particles come into contact at temperatures high enough to cause the softening of the particle surface and
formation of interparticle bonds. The temperature at which softening occurs is called minimum sintering temperature ($T_s$) and this is often lower than the fusion temperature of the bulk of the material. Other mechanisms for solid bridge formation are crystallization, chemical reaction, deposition of colloidal material and solidification of a binder [57].

As previously reported (see Table 1.1), fluidized bed processes are often operated at high temperature. Therefore, it is necessary to understand the mechanisms which enhance the adhesion forces due to sintering in order to predict the possible effects and reliably operate industrial processes at high temperatures.

2.2.2.1 SINTERING MECHANISMS

The sintering process is characterised by the coalescence of particles driven by the system minimising the surface free energy and thus reducing the surface area [35]. As reported by Siegell [58], this can occur at temperatures well below the normal melting or softening point of the bed particles, and it has been encountered in several processes including coal conversion, ores reduction and cement manufacture. The author categorised four different mass transport mechanisms: surface diffusion, volume diffusion, viscous flow and vaporization. Depending on the material and on the operative conditions, more than one mechanism can occur simultaneously. Sintering by diffusion is typical of crystalline and metallic materials, while polymeric, amorphous and non-metallic materials sinter by viscous flow mechanism. Among the cited mechanisms, vaporization can be considered negligible in defluidization phenomena [21].

According to Siegell [58], sintering by diffusion involves the movement of individual atoms from high to low density regions and consequently migration of lattice vacancies from regions of high to low vacancy concentration. At the bond zone between the two particles a concave surface is formed in which there is a greater lattice vacancy concentration than throughout the rest of the particle. Diffusion can occur both at the surface (surface diffusion) and through the bulk of the material (volume diffusion). Sintering by surface diffusion usually happens in the early stages of the sintering process as direct cause of the initial adhesion between particles, which leads to the formation of agglomerates. Volume diffusion follows surface diffusion leading to the densification of the material.
Kendall [35] gave a detailed insight into the mechanism of diffusion by suggesting the five significant steps that play a role in particle sintering and cake formation: gas phase transport, liquid layer transport, surface diffusion, grain boundary diffusion and solid-state diffusion (or volume diffusion). These are summarised in Figure 2.3.

![Figure 2.3](image)

Figure 2.3 – A summary of the steps of diffusion mechanism for particle sintering. Adapted from [28]

Herring [59] demonstrated that each step has a different response to the process time (t) and the particle size (d). Eqn. (2.6) was suggested as scaling rule among the steps [28]:

$$\frac{t_{i+1}}{t_i} = \left(\frac{d_{i+1}}{d_i}\right)^n$$  \hspace{1cm} (2.6)

where the index i refers to the various steps and the index n depends on the step mechanism: 1 for viscous flow, 3 for bulk diffusion and 4 for grain boundary diffusion.

As opposed to the movement of single atoms which occurs in the diffusion mechanism, the mass transfer mechanism by viscous flow is based the movement of entire planes of lattice. Thus, the growth of the bond area is faster when sintering occurs by viscous flow and the agglomerates which are formed are much more strongly bonded than those caused by a diffusion mechanism. This mechanism is the most important in caking and defluidization because of its rapidity [21]. The surface forces producing the viscous flow depend on the surface tension of the material and the radius of curvature of the surface at the contact zone. Frenkel [60,61] reported on sintering in viscous regime by suggesting Eqn. (2.7) to describe the increase in contact area during sintering, i.e. the time evolution of the neck size. According to his model, the sintering rate (or the neck
size $L_n$ as a function of time) is dependent on the surface tension ($\Gamma$), the viscosity of the melted material ($\eta$), the sintering process time ($t$) and the original particle size ($d_0$):

$$L_n^2 = \frac{3 \Gamma d_0}{2 \eta}$$

(2.7)

It then states that sintering proceeds faster for materials with a higher surface tension, lower viscosity and smaller particle size. However, this model assumes that the particle size remains nearly constant and, therefore, it can be valid only for the initial stage of the sintering, when the neck length is much smaller than the particle size.

Pokluda et al. [62] modified the model proposed by Frenkel in order to take into account also the effects of geometric and physical arrangements on the coalescence rate. They develop a sintering model based on the balance of the work of surface tension and the viscous dissipation (all the other forces, including gravity, are neglected) which describes the complete sintering process of two spherical particles. The shape evolution of the interacting particles develops as shown in Figure 2.4 and it can be mathematically expressed as follows:

$$L_n = d_0 \sin \theta \left( \frac{4}{(1 + \cos \theta)^2(2 - \cos \theta)} \right)^{\frac{1}{3}}$$

(2.8)

where $\theta$ represents the angle of the intersection of the neck, which evolution with time $t$ can be described according to Eqn. (2.9).

$$\frac{d\theta}{dt} = \frac{\Gamma 2^{-\frac{2}{3}} \cos \theta \sin \theta (2 - \cos \theta)^{\frac{1}{3}}}{d_0 \eta (1 - \cos \theta)(1 + \cos \theta)^{\frac{1}{3}}}$$

(2.9)

Figure 2.4 - Microscopic particles’ shape evolution during sintering, according to Pokluda et al. [63] model.
2.2.2.2 SINTERING TESTS AND DEFLUIDIZATION PHENOMENA

Defluidization of a fluidized bed takes place when the bonds between particles caused by sintering cannot be broken apart by the kinetic motion inside the bed [21]. As previously discussed, tough aggregates are caused by densification of the bond zone, which is not only a function of the temperature but also of the sintering mechanism. Siegel [58] observed that friable aggregates are formed during sintering by diffusion and that this mechanism does not modify the original shape of the particles. Agglomerates formed by viscous flow are, instead, more strongly bonded and the particles undergo considerable deformation in the contact area.

In order to predict the defluidization behaviour of a fluidized bed it is necessary to determine the initial sintering temperature of the particles. Siegel [58], Compo et al. [64] and Lettieri [65] measured the minimum sintering temperature of a range of materials using dilatometry analysis and they all combined such measurements with defluidization experiments.

In particular, Compo et al. [64] and Lettieri [65] used thermomechanical analysis (TMA) to determine the expansion/contraction mechanisms taking place when heating up different samples in order to relate changes in the thermomechanical properties to the fluidization behaviour with increasing temperature. Compo et al. [64] also correlated dimensionless excess velocity \( \frac{u-u_{\text{mfs}}}{u_{\text{mfs}}} \) with the dimensionless excess temperature \( \frac{T-T_s}{T_s} \), where \( u_{\text{mfs}} \) is the minimum fluidization velocity at the minimum sintering temperature \( T_s \) calculated from the value at ambient conditions using the Ergun equation (Eqn. (2.2)). Their results indicated that the behaviour of the materials is strongly affected by their constituents’ arrangement: amorphous materials (for which a sharp contraction occurred at \( T_s \)) showed exponential increase of the defluidization curve, while crystalline materials (which formed relatively weak aggregates) showed a slight increase.

Tardos et al. [66] developed a predictive theoretical model for the limiting gas velocity which is necessary to break the largest agglomerate in the bed and thereby to keep the bed continuously fluidized at temperatures above the minimum sintering temperature. Their model is based on a force/stress balance on
the aggregate (considered cylindrical in shape and non-freely buoyant) which was assumed to occupy the entire cross-section area of the bed. The magnitude of the forces acting on the agglomerate, mainly due to the passage of bubbles, were estimated as a function of the excess fluidizing gas velocity, i.e. $u-u_{mf}$. The forces were then related to the pressure ($\sigma$) acting on the agglomerate and the failure of the aggregate was predicted to occur when the pressure exceeded the maximum value $\sigma_{\text{max}}$ defined as:

$$\sigma_{\text{max}} = A \sigma_t \left( \frac{h_1}{h_2} \right)^2$$  \hspace{1cm} (2.10)

where $h_1$ and $h_2$ are the geometrical dimensions of the aggregate, $A$ is a mathematical coefficient ($A\sim8$) and $\sigma_t$ is the yield strength of the agglomerate that can be obtained on the basis of the theory of Rumpf [67], see Eqn. (2.36).

Seville et al. [68] also investigated the phenomenon of defluidization caused by particles sintering. They modelled the sintering phenomenon by comparing the characteristic residence time in which the particle motion is relatively small ($t_{bb}$) to the characteristic time necessary for the growth of sintered necks ($t_s$). Their model is based on the idea that, when the particles are fluidized, they can be considered to remain in quiescent zones with relatively little movement until they are disturbed by the passage of bubbles. If the residence time in the quiescent zones is sufficiently long for the sintering to occur, then the necks reach a critical size making the aggregates strong enough that cannot be broken by the passage of the bubbles. At this point, the defluidization starts occurring. According to this theory, the time spent in the quiescent zone can be considered the average time between the passage of bubbles of diameter $d_b$ and it can be calculated as a function of the excess fluidizing velocity:

$$t_{bb} = \frac{2}{3} \frac{d_b}{u_{mf} - u_{mf}}$$  \hspace{1cm} (2.11)

With regards to the critical time for sintering ($t_s$), a modified version of Frenkel Eqn. (2.7) was suggested by introducing a factor $k_T$ dependent on both materials’ properties and environmental conditions (including temperature):

$$t_s = \left( \frac{L_n}{d_0} \right)^2 \frac{\eta}{k_T}$$  \hspace{1cm} (2.12)
As previously discussed, solid bridges formation is one of the principal causes of bulk powder caking (and following defluidization) in fluidized beds. However, the dynamics of this phenomenon have not still fully understood. Zafar et al. [28] pointed out that the majority of the studies currently available in the literature are based only on constant environmental conditions and, therefore, they neglect the effects of heat and mass transfer within the bulk material and between the materials and its surroundings. According to the authors, a full knowledge of temperature and mass concentrations profiles is necessary to properly analyse and characterize the powder caking phenomenon.

Several caking test methods are available and they range from simplistic approach to more complex techniques. Cleaver [55] and Zafar et al. [28] extendedly reported on the different test methods and their reliability. However, they concluded that despite of the existing number of testing methods (very useful for empirical understanding of caking phenomenon) their predictive ability still needs to be improved. Flowability assessments by mean of shear cell testing is at the moment one of the best candidate for predictive and reliable caking tests [28]. This topic is analysed in detail in the next sections.

Bartels at al. [69] also reviewed the agglomeration and aggregation phenomena in fluidized beds at high temperature, reporting on their mechanisms, detection and counteraction strategies. However, the review focused only on thermo-chemical solid fuel conversion carried out in fluidized beds, such as biomass and waste treatments.

### 2.3 Effects of Temperature on Fluidization

Several studies have been carried out on the influence of operating temperature on fluidization, but the findings are still controversial and a satisfactory understanding of the phenomena which cause differences between ambient conditions and high temperature processes has not yet been achieved [4,70–78]. Operating temperature influences the operation of fluid-particle systems because it mostly affects gas density and viscosity. Most predictions of fluidization behaviour at high temperatures have been based solely on considering such
changes in the gas properties. However, this approach is valid under the condition that only hydrodynamic forces control the fluidization behaviour.

Temperature can have a considerable effect on particle adhesion, enhancing the role of the interparticle forces on the fluidization quality, especially if the system is operated at temperatures close to the minimum sintering temperature of the particles [77,79]. In addition, the increase of temperature may enhance the Hamaker constant and therefore Van der Waals attractive forces [77]. As reported by Lettieri et al. [74], the effect of temperature on a fluidized bed is also strongly dependent on particle size, which in turn defines the type of particle-particle and fluid-particle interaction, thus determining the stronger or weaker role of the IPFs.

Much theoretical debate is reported in the literature on the role of the interparticle forces on the fluid-bed behaviour and a sound knowledge of the factors which control changes in fluidization behaviour at high temperature has not yet been accomplished.

2.3.1 MINIMUM FLUIDIZATION CONDITIONS

The minimum fluidization velocity is a fundamental parameter when designing fluidized-bed systems. It can be calculated experimentally by means of measurements of the pressure drop across a bed of particles as a function of the gas velocity, and it can also be estimated on the basis of the Ergun equation (Eqn. (2.2)) for the pressure drop through a packed bed [32].

Several correlations can be found in the literature to predict $u_{mf}$ and some of the most used are reported in Table 2.2. However, they are not necessarily reliable when applied to high temperature conditions as it is often required to extrapolate results to the conditions of interest and, in addition, it overlooks possible changes induced by temperature on the structure of the fluidized bed, that can in turn cause drastic alterations in flow behaviour and powder stability [74,80].

Despite this, the Ergun equation is one of the most often used to evaluate the effect of temperature on minimum fluidization conditions. Its dimensionless version is reported in Eqn. (2.13), by considering the Archimedes dimensionless number ($Ar$) and the Reynolds number at minimum fluidization conditions ($Re_{mf}$), defined by Eqns.(2.14) and (2.15):
\[
Ar = 150 \left( 1 - \epsilon_{mf} \right) \frac{Re_{mf}}{\phi^2 \epsilon_{mf}^3} + 1.75 \frac{Re_{mf}^2}{\phi \epsilon_{mf}^3}
\]  
\[Ar = \frac{d_3^2 \rho_g (\rho_p - \rho_g) g}{\mu^2} \] 
\[Re_{mf} = \frac{d_p u_{mf} \rho_g}{\mu} \]  

(2.13)
(2.14)
(2.15)

Table 2.2 - Selected equations for the calculation of minimum fluidization velocity

<table>
<thead>
<tr>
<th>Authors</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carman [82]</td>
<td>( u_{mf} = \left( \frac{\phi_d p}{180} \right)^2 \left( \frac{\rho_p - \rho_g}{\mu} \right) g \left( \frac{d_3^2 \rho_g}{\phi^2 \epsilon_{mf}^3} \right) )</td>
</tr>
<tr>
<td>Miller and Logwinuk [83]</td>
<td>( u_{mf} = 1.25 \times 10^{-3} \frac{d_3^2 (\rho_p - \rho_g)}{\rho_g^2} \epsilon_{mf}^{0.04} )</td>
</tr>
<tr>
<td>Leva et al. [84]</td>
<td>( u_{mf} = 7.39 \frac{d_3^2 \rho_{g dp}^{0.94}}{\epsilon_{mf} \phi^2} )</td>
</tr>
<tr>
<td>Goroshko et al. [85]</td>
<td>( u_{mf} = \frac{\mu_g}{\rho_g dp} \left( \frac{Ar}{1400 + 5.2 Ar} \right) )</td>
</tr>
<tr>
<td>Leva [86]</td>
<td>( u_{mf} = 8.1 \times 10^{-3} \frac{d_3^2 (\rho_p - \rho_g)}{\rho_g^2} )</td>
</tr>
<tr>
<td>Riba et al. [87]</td>
<td>( u_{mf} = \frac{\mu_g}{\rho_g dp} \left( 1.54 \times 10^{-2} \left( \frac{d_3^2 \rho_{g dp}}{\mu_g} \right)^{0.66} \left( \frac{\rho_p - \rho_g}{\rho_g} \right)^{0.7} \right) )</td>
</tr>
<tr>
<td>Doichev and Akhmakov [88]</td>
<td>( u_{mf} = \frac{\mu_g}{\rho_g dp} \left( 1.08 \times 10^{-3} \frac{Ar^{0.947}}{\rho_g} \right) )</td>
</tr>
<tr>
<td>Wu and Baeyens [89]</td>
<td>( u_{mf} = \frac{\mu_g}{\rho_g dp} \left( 7.33 \times 10^{-5} \times 10^{\sqrt{\frac{24 \log_{10} Ar - 0.81}{}} } \right) )</td>
</tr>
</tbody>
</table>

Although the unknown voidage at minimum conditions may be a problem in applying this equation, numerous predictive correlations for \( u_{mf} \) are based on a modified Ergun equation. For instance, Wen and Yu [81] showed that the voidage and shape factor functions in the original Ergun equations can be approximated as:

\[
\frac{1 - \epsilon_{mf}}{\phi^2 \epsilon_{mf}^3} \approx 11
\]
\[
\frac{1}{\phi \epsilon_{mf}^3} \approx 14
\]

And they proposed the following modified form of Eqn. (2.13):

\[
Ar = 1650 Re_{mf} + 24.5 Re_{mf}^2
\]

(2.26)

That may be rearranged to the general formula:

\[
Ar = A Re_{mf} + B Re_{mf}^2
\]

(2.27)

Or, if \( a = \frac{A}{2B} \) and \( b = \frac{1}{B} \) are considered:

\[
Re_{mf} = \sqrt{a^2 + b Ar} - a
\]

(2.28)

The two constants \( a \) and \( b \) in the original Wen and Yu correlation were 33.7 and 0.0408, but several other sets of values are reported in the literature (see Table
2.3. It is important to note that predictions using Eqn. (2.26) do not take into account possible changes in the voidage which may occur with increasing temperature, as it will be discussed later.

Table 2.3 - Values for the constants a and b in Eqn.(2.28)

<table>
<thead>
<tr>
<th>Authors</th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wen and Yu (1966) [81]</td>
<td>33.70</td>
<td>0.0408</td>
</tr>
<tr>
<td>Bourgeois and Grenier (1968) [90]</td>
<td>25.46</td>
<td>0.0382</td>
</tr>
<tr>
<td>Saxena and Vogel (1977) [91]</td>
<td>25.28</td>
<td>0.0571</td>
</tr>
<tr>
<td>Babu et al. (1978) [92]</td>
<td>25.25</td>
<td>0.0651</td>
</tr>
<tr>
<td>Richardson and Jerónimo (1979) [93]</td>
<td>25.70</td>
<td>0.0365</td>
</tr>
<tr>
<td>Grace and Hetsonri (1982) [94]</td>
<td>27.20</td>
<td>0.0408</td>
</tr>
<tr>
<td>Chitester and Kornosky (1984) [95]</td>
<td>28.70</td>
<td>0.0494</td>
</tr>
<tr>
<td>Thonglimp et al. (1984) [96]</td>
<td>31.60</td>
<td>0.0425</td>
</tr>
<tr>
<td>Lucas and Arnaldos (1986) [97]</td>
<td>25.20</td>
<td>0.0672</td>
</tr>
<tr>
<td>Bin (1993) [98]</td>
<td>27.31</td>
<td>0.0386</td>
</tr>
<tr>
<td>Reina et al. (2000) [99]</td>
<td>48.00</td>
<td>0.0450</td>
</tr>
</tbody>
</table>

Pattipati and Wen [100] reported that the Wen and Yu correlation is capable of predicting changes in \(u_{mf}\) when temperature increases for some sand materials. They did not observe important changes with temperature in the voidage at minimum fluidization and they found a good matching between experimental and predicted \(u_{mf}\) values.

Generally, the experimental findings on Geldart’s Group B and D particles confirmed the trend predicted by the Wen and Yu equation. Nevertheless, absolute values did not always match with experiments. Knowlton [73] stated that one of the reasons lies in the evaluation of the correct mean particle size and shape factor. He suggested that this could be back-calculated from the Ergun equation using previously measured values of \(u_{mf}\). Doing so, an effective value for the particle size and shape factor would be found.

Botterill et al. [101] reported in 1982 experimental verification of the temperature effect on \(u_{mf}\) for some Group B and D powders. They observed a decrease of \(u_{mf}\) with increasing temperature for Group B materials, due to the consequent increase in gas viscosity. They compared their results with predictions from the Wen and Yu equation and noted that the decrease was less than that predicted since a change in \(\epsilon_{mf}\) had occurred. This is not in agreement with the results of Pattipati and Wen [100]. For Group D powders, they observed an
increase in \( u_{mf} \), because of the decrease of gas density. They also found that \( \varepsilon_{mf} \) for the Group D materials did not change with temperature. Their experimental data matched predictions obtained from the Ergun equation, using the values of \( \varepsilon_{mf} \) measured at the corresponding operating temperatures, and using also an appropriate value of the shape factor, back calculated from the Ergun equation for a given experiment.

Fletcher et al. [72] in 1992 reported that applying Eqn. (2.28) can introduce a significant error into the prediction of \( u_{mf} \), mainly because the \( a \) and \( b \) constants are functions of shape factor and voidage at minimum fluidization conditions, which are difficult to measure experimentally. They proposed different correlations for the prediction of \( R_{emf} \) at ambient temperature on the basis of the shape of the particles, see Table 2.4.

Table 2.4 - Correlations for the prediction of \( R_{emf} \) at ambient temperature [72]

<table>
<thead>
<tr>
<th>Type of sand</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Round</td>
<td>( R_{emf} = \frac{Ar}{1400+5\sqrt{Ar}} ) (( Ar \geq 1480 )) ( (2.29) ) ( R_{emf} = \frac{Ar}{1400} ) (( Ar &lt; 1480 ))</td>
</tr>
<tr>
<td>Moderately sharp</td>
<td>( R_{emf} = \frac{Ar}{1170+\sqrt{Ar}} ) ( (2.30) )</td>
</tr>
<tr>
<td>Very angular</td>
<td>( R_{emf} = \frac{Ar}{790+7\sqrt{Ar}} ) ( (2.31) )</td>
</tr>
</tbody>
</table>

Coltters and Rivas [78] in 2004 proposed a new equation to estimate the minimum fluidization velocity without having to experimentally determining the bed voidage and shape factor. They tested their correlation against 189 experiments’ results reported in the literature on about 90 different materials, and their outcomes showed a good agreement with the experimental data. In parallel, Delebarre [102] proposed a revisited Wen and Yu equations for the prediction of \( u_{mf} \) without the dependency on the voidage and shape factor.

The relative role of the hydrodynamic and interparticle forces on the minimum fluidization conditions at elevated temperature for Group A and C powders has been analysed by various authors. Lucas et al. [103] in 1986 reported that changes with temperature in \( \varepsilon_{mf} \) can be explained on a hydrodynamic basis, contrary to Raso et al. [104] and Formisani et al. [105] who later related such changes to a variation of IPFs with temperature.
Lucas et al. [103] explained the variation of $\varepsilon_{mf}$ with temperature in terms of a change in the flow pattern inside the bed. They analysed the variation of $\varepsilon_{mf}$ as a function of $Re_{mf}$ and observed that under flow regimes with $Re_{mf}$ less than 0.75, $\varepsilon_{mf}$ remains constant, while it decreases when this value is exceeded, becoming constant again for $Re_{mf}$ higher than 2. They explained that at low $Re_{mf}$ a sucking effect is produced in the particle boundary layer, which increases the closeness of the particles and causes $\varepsilon_{mf}$ to decrease. At higher values of $Re_{mf}$ the attractive forces between the particles decrease and $\varepsilon_{mf}$ gradually increases up to an approximately constant value. From this theory, a powder classification scheme based on the nature of the boundary layer around a particle was elaborated by Mathur and Saxena [106], and validated with data on $u_{mf}$ and $\varepsilon_{mf}$ at high temperatures obtained by Botterill et al. [101] and Lucas et al. [103].

In agreement with Raso et al. [104], Yamazaki et al. [107] reported that the role of the IPFs should not be ignored when trying to explain changes in $\varepsilon_{mf}$ with temperature. They showed that variations in bed voidage depend both on the physical properties of the fluidizing fluid, i.e. density and viscosity, and on changes in the physic-chemical properties of the particles. In particular, they studied the effect of adsorbed water onto the surface of silica particles with increasing temperature. At low temperatures, they observed a decrease in $\varepsilon_{mf}$ as humidity was raised, while at higher temperatures higher values of $\varepsilon_{mf}$ were found for the same humidity. They explained such changes in terms of the amount of water adsorbed onto the surface of the silica, and concluded that variation of the $\varepsilon_{mf}$ with temperature is caused by a change in the adhesion forces, which at velocities as low as $u_{mf}$ can cause formation of clusters, making the bed settle with a relatively looser structure.

Formisani et al. [105] and Lettieri et al. [74,75] also reported on the effect of temperature on minimum fluidization conditions and they stated that both the Ergun equation and the Wen and Yu correlation are capable of predicting changes in the minimum fluidization velocity with temperature if, in addition to changes of gas density and viscosity, the dependence of $\varepsilon_{mf}$ on temperature is also accounted for.
Formisani et al. [105] observed a linear increase of $\varepsilon_{\text{mf}}$ for various Group A, B and D powders and a linear increase of the voidage of the fixed bed with temperature (Figure 2.5). They performed their experiments in a transparent quartz column equipped with a stainless steel porous plate able to provide a homogeneous gas distribution; a video camera was used to record the experiments. The total pressure drop across the particle bed was measured with a pressure tap located just above the gas distributor level; a graduated scale was used to determine the bed height at each temperature, the average bed voidage was subsequently determined from the values of the bed height. The authors reported that bed heights measurements were affected by a 0.5 mm approximation, which caused uncertainty in the bed voidage evaluations of around 1%. They attributed the increase of the fixed bed voidage to an increase of the interparticle forces which was thought to stabilize the structure of the fixed bed state, in the total absence of a gas flow. They found a close similarity between the slope of the fixed bed voidage, $\varepsilon_0$, and $\varepsilon_{\text{mf}}$ and so they concluded that the increase of $\varepsilon_{\text{mf}}$, and in turn changes in $u_{\text{mf}}$ with temperature, are not due only to changes in the properties of the fluidizing gas but also to changes in packing properties. The authors attributed the capability of the bed to form a looser structure due to an increase of the van der Waals forces with temperature. Their results confirmed the findings reported by Raso et al. [104] on a 2D fluidized-bed.

![Figure 2.5 - Effect of temperature on the fixed bed voidage (left-side) and the bed voidage at minimum fluidization (right-side) for glass ballotini and silica sand particles of different size [105].](image-url)
Lettieri et al. [74,75] reported experimental observations on the effect of temperature on the fluidization of three fresh and an equilibrium (E-cat) FCC catalysts tested at ambient pressure and at temperatures up to 650 °C. Where changes in fluidization at high temperature were observed, the factors responsible were investigated via thermo-mechanical analyses. They also tested a porous silica powder, belonging to Group A, by deliberately changing its physical properties in order to highlight under which conditions the fluidization behaviour is dominated by the IPFs. The results demonstrated how temperature can increase the effect of IPFs, causing a Group A material to behave in a similar manner to a Group C material. Figure 2.6 shows the effect of temperature on the fluidization at minimum fluidization conditions for the same silica catalyst doped with different amounts of potassium acetate (KOAc). Figure 2.6 shows that prediction and experimental values of $u_{mf}$ match only for the catalyst sample doped with 1.7 % wt. of KOAc. Values of $u_{mf}$ obtained for the doped samples with 7% and 10% wt of KOAc were found to be higher than the predicted ones at ambient temperatures. The authors explained that during the drying process some potassium acetate might have migrated to the mouth of the pores from within, making this responsible for the higher values of $u_{mf}$, hence reflecting the influence of the IPFs on the fluidization behaviour.

![Figure 2.6 - $u_{mf}$ vs temperature for a silica catalyst doped with increasing values of KOAc, comparison of experiment with prediction [74].](attachment:image)

Significant changes in the fluidization quality of the sample with 10% wt of potassium acetate occurred with increasing temperature. The ratio between the
measured and calculated pressure drop across the bed of material is plotted against gas velocity in Figure 2.7, as temperature is increased. Fluidization behaviour of this material significantly changed when the bed temperature was about 200°C. A rapid decrease of the pressure drop was noted and channels were seen on the X-ray images. This material exhibited a typical cohesive Group C behaviour. Good fluidization at 200°C could be achieved only when operating the system at a higher velocity, thus causing the channels and rat holes to be broken down. When the bed was cooled back to 150°C good fluidization was obtained again at low velocities.

Lettieri et al. [74] explained that on increasing temperature the potassium acetate contained within the catalyst pores became mobile and migrated to the surface of the particles due to decreases in the surface tension and viscosity. The presence of potassium acetate on the surface of the catalyst caused the material to become sticky and therefore to channel. On the other hand, as the bed temperature decreased, re-absorption of the potassium acetate into the catalyst pores may have occurred, thus allowing good fluidization of the material to be re-established.

![Graph](image)

**Figure 2.7 - \( \Delta P_m/\Delta P_c \) vs bed velocity, as a function of temperature, for a silica catalyst doped with 10 %wt. of KOAc [74].**

As seen, several correlations have been derived for the prediction on the minimum fluidization conditions at high temperature, but these are however case specific. The debate of the phenomena causing changes in behaviour with increasing temperature remains controversial with still much disagreement on the role of the hydrodynamic and interparticle forces.
2.3.2 BED EXPANSION AND MINIMUM BUBBLING CONDITIONS

Many attempts have been made to describe the fluid dynamic properties of fluidized beds, with special attention paid to the transition between the particulate and bubbling regime of Geldart’s Group A powders. These materials are those which exhibit a stable region of non-bubbling expansion between minimum fluidization velocity and minimum bubbling velocity, $u_{mb}$.

The phenomenon of uniform expansion, or delayed bubbling, has been the subject of much research since it has a strong bearing on the difference between gas and liquid-fluidized beds and on the reasons for the formation of bubbles in the one but not in the other. The mechanism of bubble free expansion in gas-fluidized beds has been assumed by some researchers to be the same as the homogeneous expansion in a liquid fluidized bed to which the Richardson and Zaki [108] equation applies:

$$u = u_t \varepsilon^n$$  (2.32)

where $u$ is the liquid velocity of the suspension, $u_t$ is the terminal fall velocity and $n$ is a parameter that depends on the free fall particle Reynolds number and normally has values between 4.65 (viscous regime) and 2.4 (turbulent regime).

However, the validity of this comparison has not always been accepted. Massimilla et al. [109,110] made some experimental observations on the bubble free expansion of gas fluidized beds of fine particles and described the expansion mechanism as due to the nucleation and growth of cavities which they assumed occurring because of a broad distribution of interparticle forces.

The phenomenon of delayed bubbling is not only limited to fine Geldart’s Group A powders, it has also been observed with larger particle fluidized under high pressure conditions [4] and also with magnetised large particles, as reported by Agbim et al.[111] and later by Siegell [112].

The limiting condition for the uniform expansion of gas fluidized beds is defined by the voidage at minimum bubbling, $\varepsilon_{mb}$, whose determination has been at the centre of much theoretical controversy, due to the ill-defined role of the HDFs and IPFs. Mathematical models have been developed by various authors to predict the transition between particulate and bubbling regime. Two different approaches have been considered. On the one hand, criteria have been developed
based on the assumption that hydrodynamic forces are the controlling factor. The main contributors were Jackson [113], Verloop and Heertjes [114] and Foscolo and co-workers [20,115–117]. On the other hand, interparticle forces were considered to play a dominant role over the hydrodynamic forces. Rietema and co-workers [49,118–120] were the main supporters for this theory and formulated a physical model which accounted for additional forces to the fluid-dynamic forces and gravitational weight. They assumed that the interparticle forces between cohering particles give rise to a powder structure with a certain mechanical strength even in the expanded state of homogeneous fluidization. However, whereas models based on HDFs, such as Foscolo and Gibilaro’s ones, provide explicit formulation for the minimum bubbling condition, the formulation proposed by Rietema and co-workers cannot be used to make a priori predictions.

The effect of temperature on the transition between particulate to bubbling fluidization was investigated by Rapagna’ et al. [121] who demonstrated the capability of the Foscolo and Gibilaro criterion to predict $\varepsilon_{mb}$ for FCC powders with mean particle sizes of 65 and 103 $\mu$m in a 50 mm ID column, from ambient conditions up to 900 °C. They used a fast responding pressure transducer connected to an oscilloscope to detect the passage of bubbles in the bed. They observed a decrease in the average bubble size and a delay of the onset of bubbling with increasing temperature for both FCC powders. This corresponded to an increase in the voidage at minimum bubbling with temperature. Moreover, a larger increase in $\varepsilon_{mb}$ was observed for the finer materials, a comparison of their experimental values for $\varepsilon_{mb}$ with those predicted by the Foscolo and Gibilaro fluid-bed model showed good agreement for both powders at ambient and high temperatures (Figure 2.8).

Xie and Geldart [122] investigated the role of the IPFs on the bubbling conditions with increasing temperature by measurements of the voidage. They observed virtually no change in $\varepsilon_{mb}$ as temperature increased for any of the FCC catalysts investigated, in contrast with the results of Rapagna’ et al. [121]. They also reported that predictions of $\varepsilon_{mb}$ given by Foscolo and Gibilaro [20] and by Jean and Fan [123] matched with their experiments at ambient temperature for FCC powders larger than 60 $\mu$m. However, both models over-predicted $\varepsilon_{mb}$ values
at ambient temperatures for the finer powders, and they also predicted significant changes in $\varepsilon_{mb}$ with temperature, in contrast to the experimental results reported. Failure of the hydrodynamic models to predict correctly the transition between the particulate and bubbling regime was assumed to be the result of ignoring the interparticle forces.

![Figure 2.8](image)

Figure 2.8 - Experimental and calculated values of bed voidage at minimum bubbling condition as a function of temperature for sample smaller FCC particles (left side) and larger ones (right side) [121].

The onset of bubbling was also studied by Formisani et al. [105]. They measured changes in the minimum bubbling velocity of FCC catalysts and silica sand with increasing temperature from ambient up to 800 °C in a 55 mm ID quartz column. They relied on visual observation to determine the commencement of bubbling. For all the tested material they observed an increase of $u_{mb}$ with increasing temperature with a trend very similar to the increase observed for $u_{mf}$. Unlike Rapagna’ et al. [121], they observed a very small bed expansion increase with increasing temperature.

Lettieri et al. [75] in 2001 investigated the fluid-bed stability, i.e. the capability to maintain a uniform expansion, of three fresh FCC catalysts both experimentally and theoretically as a function of increasing temperature. Values of the voidage at minimum bubbling conditions were obtained from 20°C up to 650°C, and compared with predictions given by the Foscolo and Gibilaro’s particle bed model. Predicted $\varepsilon_{mf}$ values were found to disagree with what observed experimentally (Figure 2.9).
Such a disagreement was related to the large discrepancy between the values of $n$ and $u_t$ in the Richardson and Zaki equation, obtained from the experimental bed expansion profiles and the calculated ones. For all FCC catalysts, the highest values of the experimental $n$ and $u_t$ were found at ambient conditions. In order to correctly apply the particle-bed model to these particle systems, they generalized the expression of the drag force given by Foscolo and Gibilaro for the viscous flow regime. Consequently, they re-examined the procedure followed to obtain the Foscolo and Gibilaro stability criterion and proposed a generalized expression of their criterion. Predicted $\varepsilon_{mb}$ values obtained with the generalized expression of the Foscolo-Gibilaro criterion were within 5% for all FCC catalysts. Although the particle-bed model was originally developed on the assumptions that the hydrodynamic forces govern the fluid-bed stability, the results presented by Lettieri et al. [75] suggested that contribution of the interparticle forces to the bed stability of the materials studied cannot be ruled out.

As a follow up study, in 2008 Lettieri and Mazzei [124] analysed the effect of temperature on the fluid-bed stability of the same three FCC catalysts used in Lettieri’s previous work, but this time through considerations on the fluid-bed elasticity. They reported experimental findings on the effect of temperature on the elasticity modulus at minimum bubbling conditions, calculated according to the theory of Foscolo and Gibilaro [20] and also adopting the criterion of Mutsers and Rietema [118]. In accordance with the theoretical postulation of Mutsers and
Rietema, the results from bed expansion presented by Lettieri and Mazzei [124] and previously by Lettieri at al. [76], showed that the role played by the IPFs can affect the stability of Group A powders. However, the sensitive analysis carried out by Lettieri and Mazzei [124] on the parameters which dominate the elasticity modulus revealed that the gas viscosity was the dominant factor which defined its variations with temperature, as shown in Figure 2.10. This highlighted the importance of both HDFs and IPFs on the stability of Group A powders and the need for a correct and complete description of both contributions.

![Figure 2.10 - Influence of temperature and gas viscosity on the elasticity modulus at ε_{mb} according to Mutsers & Rietema criterion, for all fresh FCC [124]](image)

In line with Lettieri et al. [75], Valverde and co-workers [125] emphasized the importance of the interparticle forces on the settling and particulate fluidization of fine powders. They proposed an extension of the Richardson and Zaki empirical correlation and the theoretical Mills-Snabre [126] model, originally developed for the settling of non-cohesive spheres, to predict the settling of aggregates which may form when the interparticle forces exceed by several orders of magnitude the particle weight. Valverde et al. [127] extended the previous study investigating, from both macroscopic and local measurements, the transition between the solid-like, fluid-like, and bubbling fluidization of gas-fluidized fine powders. They showed that the transition between the solid-like and the fluid-like regimes takes place along an interval of gas velocities in which transient active regions alternate with transient solid networks. Using optical probe local measurements, they showed the existence of meso-scale pseudo-turbulent structures and short-lived voids, in the fluid-like state, which make the prediction of the transition between the different regimes a complex task.
Castellanos [128] observed that the onset of fluidization of fine and ultrafine powders was characterized by the presence of agglomerates which give place to a highly expanded state of uniform fluid-like fluidization. In an attempt to unify the above observations, Valverde and Castellanos [129] proposed in 2008 an extension of the Geldart's classification of powders to predict the gas-fluidization behaviour of cohesive particles which reconciles the role of the interparticle and hydrodynamic forces on the existence of a non-bubbling regime. In the new phase diagram proposed by Valverde and Castellanos, the boundaries between the different types of fluidization are defined as a function of fluid viscosity, particle density, the fractal dimension of the agglomerates and the powder’s compaction history, as reported in 2006 by the same authors [130].

Girimonte and Formisani [131] reported in 2009 on the influence of operating temperature on the transition to the bubbling regime for samples of FCC, silica and corundum sands, at temperatures ranging from 30 to 500 °C. They determined the minimum bubbling velocity using four different methods and obtained different results for $u_{mb}$ with increasing temperature. The first method was based on the direct observation of the velocity at which the first bubble erupted on the free surface of the bed. The second method was based on the measurement of the pressure drop across the whole bed, and $u_{mb}$ was taken at the point where a shallow minimum of the $\Delta P$ vs. $u$ curve occurred. The last two methods were derived from the analysis of the “fluidization map”, namely the examination of the expansion behaviour of the bed over a range of fluidization velocities from the fixed bed state to the bubbling regime. They demonstrated that the optical method and the method based on the detection of the pressure drop minimum were unreliable for correctly determining the starting point of bubbling. They stated that only the analysis of bed expansion as a function of the fluidization velocity allows reconstructing the succession of phenomena through which a stable flow of bubbles across the solid mass ensues. More recently, they reported on new experiments on the effect of temperature on the fluidization of FCC particles [132]. They used a non-invasive optical technique for acquiring images of bubbles’ eruption at the free surface and results from bed collapse tests. Their experiments showed that high temperature influences the quality of bubbles.
producing a smoother regime of bubbling, which they attributed to the thermal enhancement of IPFs that leads to higher porosity and lower interstitial flow in the emulsion phase.

In summary, high temperature clearly affects the expansion of fluidized beds of Group A powders; well established theories and models fail to predict correctly the voidage at minimum bubbling with increasing temperature. Models corrected on the basis of experimental data are capable to reproduce correct trends; however a priori predictions of the fluid bed stability with increasing temperature are yet to be achieved. The challenge here is still in the ability to describe the forces that determine the transition from particulate to bubbling fluidization. Hence, some kind of quantification of the effects of the IPFs on fluidization is needed in order to advance the understanding of fluidization at high temperature.

2.4 **CHARACTERIZATION AND PREDICTION OF POWDER FLOW PROPERTIES**

A great deal of research has been carried out over the last sixty years in order to define and measure, by means of simple tests, parameters apt to characterize and predict the flow properties of particulate materials. To this end various approaches have been undertaken and are presented in this section. These include rheological measurements and the bed collapse test technique.

2.4.1 **POWDER RHEOLOGY**

As discussed before, the flow behavior in multi-particles systems is strictly connected to the interparticle interactions. Moreover, the nature of the IPFs involved in fluidized system is still unclear and the need of measuring them still need to be accomplished. Within this framework, powder rheology represents an appealing tool to evaluate indirectly the effects of the IPFs on fluidization.

The macroscopic rheological behaviour of powders can be assessed by means of two different investigating approaches. The first approach is based on the measurement of the interactions between a single particle and the ones surrounding it and to the subsequent integration to the whole population of
particles. However, this approach is considerably problematic as many factors, which are difficult to properly evaluate, such as particles’ size distribution, shape and surface properties, need to be taken into account. The second approach is instead based on the direct parallelism between the rheological behaviour of the powders with the more well-known bulk solids. According to this approach, the theories developed for bulk solid materials can be extended to particulate solids.

The flow behaviour of solid materials is commonly described by using a continuum mechanics approach. In particular, the stress distribution inside a bulk solid is usually described by combining both yield locus and Mohr circles analysis. The first one is aimed at determining the limiting shear stresses under any normal stress when failure occurs or, in the case of particulate solids, incipient flow. In several applications it is assumed that the powder behaves like a solid at failure, therefore the local state of stresses can be represented in the normal-shear stresses plane (σ-τ plane) by Mohr circles tangent to the yield locus. The major principal stress named σ₁ is the one occurring during consolidation. It is usually considered that the Mohr circle representing the state of stress during the material consolidation in the critical state shear closes the yield locus on the consolidation side. Therefore, σ₁ is estimated from the largest intercept on the σ axis of the Mohr Circle tangent to the yield locus and passing through the consolidation point. The unconfined yield strength fₑ is the material strength under unconfined uniaxial compression and, therefore corresponds to the finite intercept on the σ axis of the Mohr Circles which is tangent to the yield locus line and passes through the origin of σ-τ plane. The unconfined yield strength represented as a function of the major principal stress is the so called “flow function”.

Other significant flow properties for particulate materials are the tensile strength, (σₜ), the material cohesion (C) and the static angle of internal friction (φᵢ). σₜ represents the resistance stress necessary to separate two layers of materials by means of an isostatic tensile strain. Despite its direct experimental measurement, which is not standardized, the tensile strength is represented by the intersection between the negative side of the σ-axis and the yield locus. When dealing with powders, a finite value of the tensile strength is possible only if interparticle attractive interactions are present. Cohesion is defined as the shear
stress necessary to deform a consolidated powder in absence of a normal stress. The static angle of internal friction is defined as the minimum angle at which the internal stress has to be inclined with respect to the normal direction in order to mobilize the material.

The analysis that, starting from the experimental shear data, allows to estimate all the above mentioned flow properties can be conducted by using two different approaches (see Figure 2.11).

The first one is the Mohr-Coulomb analysis, in which the yield conditions are represented by a straight line in the $\sigma$-$\tau$ plane:

$$\tau = \tan \phi \sigma + C = \left(\frac{C}{\sigma_t}\right) \sigma + C \quad (2.33)$$

where the cohesion and the tensile strength are the line intercepts on the $\tau$ and the $\sigma$ axis and the angle of internal friction is the slope angle of the line.

In the second approach, the yield locus can be described by a convex curved line expressed by the Warren-Spring equation in which the curvature index is represented by a dimensionless parameter of $n$ ($1 \leq n \leq 2$) [22, 23]:

$$\tau = C \left(1 + \frac{\sigma}{\sigma_t}\right)^{-\frac{1}{n}} \quad (2.34)$$

Figure 2.11 – Example of yield locus plots: linear and curved.

The possibility to adapt the curvature of the Warren-Spring equation improves the ability of yield locus curve fitting procedure to follow the experimental data. Furthermore, according to the experiments proposed by Ashton et al. [134] the estimation of the tensile strength obtained with the application of this equation is quite close to the directly measured experimental values. Unfortunately due to its
non-linearity, the regression procedure for the Warren Spring equation is much more complicated than for the Coulomb equation.

2.4.1.1 RHEOLOGICAL MEASUREMENT TESTS

In order to estimate the powder stress distribution several rheological tests were proposed over the years. These include static measurements, shear tests and viscometers. Static measurements (angle of repose, Hausner ratio, etc.) have been proposed as simple tests to predict the flowability of bulk powders. The shear cell type tests, first introduced by Jenike in 1953, are performed on powders in a compressed state where the shear measurements are used to obtain the yield locus. Viscometer type tests, whose study was initiated by Schugerl in the late 1960s, are instead based on the analogy between fluidized beds and liquids and in particular on the idea that in a fluidized bed a resistance against flow exists, just as in liquids. This resistance is a kind of internal friction between the particles in the suspension forming the dense phase and resembles the concept of viscosity used in describing the rheology of liquids.

Powder flowability is strictly related to the type and the magnitude of the interactions between particles acting at the microscopic scale [135–137]. In fact, many studies have highlighted the significant role of physical and mechanical properties of powder [39,41,51,138–141] and realistic process conditions on the powder flow behaviour, such as high temperature [142–145] and loose compacted conditions [146–148].

2.4.1.1.1 STATIC MEASUREMENTS

In 1965, Carr developed a classification system to predict the flow characteristics of particulate solids [149]. In Carr’s method, a numerical value is assigned to the results of several tests and it is summed to produce a relative flowability index for that particular bulk material. The method was further discussed in 1970 [150], when the author defined for the first time some of the main parameters used in his method: the angle of repose, the angle of fall, the angle of difference, the angle of spatula, the angle of internal friction and the cohesion. The latter have been already introduced in the previous section.
The angle of repose is defined as the constant angle to the horizontal assumed by a cone like pile of the material. It is a direct indication of the potential flowability of a material: materials with good flowability are characterized by low angles of repose. The angle of fall is determined by dropping a small weight on the platform on which an angle of repose has been formed. The fall causes a decrease of the angle of repose that is called angle of fall. The more free-flowing is the material the lower is the angle of fall. The angle of difference is the difference between the angle of repose and the angle of fall. The greater this angle, the better the flow. The angle of spatula is a quick measurement of the angle of internal friction. It is the angle that a material assumes on a flat spatula that has been stuck into the dry material and then brought up and out of it. A free flowing material will have formed one angle of repose on the spatula’s blade. A cohesive material will have formed several angles of repose on the blade; the average of these is taken. The higher the angle of spatula of the material, the worse is its flowability. The cohesion test consists of passing the material through three vibrating sieves in series. The material left on each sieve is weighted and a cohesion index is determined from the relative amounts retained.

In addition, the Hausner Ratio (HR) and the compressibility are also used to define the cohesiveness and thus the flowability of a material [14,151]. The Hausner Ratio is the ratio between the loose and the packed bulk density and is used as an indication of the cohesiveness of the materials [151]. The loose bulk density is measured by gently pouring a sample of powder into a container through a screen, whereas the packed or tapped bulk density is determined after settling and deaeration of the powder has occurred due to tapping of the sample. The powder compressibility is expressed as the percent variation between the packed bulk density and the loose bulk density.

The main advantage of these tests is their simplicity, that makes them an attractive tool to determine powders flowability and it explains their wide use in industry and academia. However, these tests are scarcely reproducible and their procedures are very difficult to standardise [152]. Furthermore, Bruni [14] pointed out that the link between the fluidization behaviour and static properties is not at all straightforward, due to the uncertain relationship between the IPFs and the
HDFs involved when gas is passed through a bed of particles. The use of static methods to predict the fluidization behaviour of powders, despite being widely employed, is therefore questionable, especially when the fluidization behaviour needs to be assessed at process conditions.

2.4.1.1.2 Shear Tests

Shear cell type tests are performed on the powder in a compressed state where the shear measurements are used to obtain a yield locus that represents the limiting shear stresses under any normal stress when failure, or to be precise flow, occurs. The shape of the obtained yield locus is related to the material cohesiveness.

Many conventional testers are available for the measurement of the flowability and they can be distinguished between direct (translational and rotational) and indirect (uniaxial, biaxial and triaxial) shear testers [153]. Some examples of translation direct testers are Jenike’s shear cell and Casagrande’s shear tester, while some of the most important rotational direct testers are the torsional and the ring shear testers.

Shear cell measurements are widely used to assess the flowability of powders for applications that involve powder discharge. Most of the principles of such tests have their origin in soil mechanics and in bunkers designing, but they have become increasingly useful for general characterisation of particulate materials. However, as for the static tests, a direct link between the failure properties of the material measured with a shear cell and the corresponding fluidization behaviour is not straightforward.

Shear testers are known to be very useful to predict the solid flow from a tall silo, in which the relatively high loading pressure of the solids is prevailing. However, due to the very small or zero loads on the bulk of a fluidized powder, standard shear testers are unlikely to provide an accurate characterization of fluid bed behaviour, as values of the failure properties need to be extrapolated from data at higher loads. Barletta and co-workers overcame this problem in their modified Peshl shear cell by introducing a cinematic chain to counterbalance the weight of the lid of the cell and therefore allow measurements under low normal stresses [147,154–156].
Furthermore, existing Shear Cells are not designed to operate at high temperature, because applications involving powder discharge are run at ambient temperature. Therefore, shear cells are not capable of detecting possible changes in the settled bed packing with increasing temperature. Few studies available in the literature have addressed the experimental evaluation of powder flow properties at high temperature. The first attempt was carried out in 1997 by Smith et al. [157] who preheated powder samples of MgSO$_4$ and CaSO$_4$ up to 750°C and moved them into a Jenike shear cell and performed shear tests immediately without any control of the temperature. Experimental results for consolidation stresses in the range 40–200 kPa showed an increase of the unconfined yield strength with increasing temperature for all the analysed powders. This was explained with the aid of SEM observations and X-ray diffraction measurements which showed the formation of agglomerates during the preheating of the sample. The lack of a proper measurement of the temperature during the shear tests was to some extent overcome by some authors who placed the shear cell inside a heated chamber with temperature control [142,145].

In 2010, Ripp and Ripperger [158] designed a temperature controlled annular shear cell for the Schulze shear tester operating from 80°C to 220°C. For this purpose, an electric heater was placed inside the lid while the vertical walls and the bottom of the cell were provided with a double casing through which a heating or a cooling medium could flow.

Recently, Tomasetta and co-workers [159,160] modified a Schulze shear cell to perform measurements of the powder flow properties of powders up to 500°C. Electric heaters were introduced below the bottom of the cell and on the lid to efficiently heat up the cell and the powder sample contained in it. A covering insulating material was placed around the body of the cell and above the lid in order to reduce the heat flux from the external surface of the cell and then to minimise the temperature gradient within the sample. They evaluated the yield loci at room temperature and at 500 °C for different samples: FCC powder, fly ashes, glass beads, natural corundum and synthetic porous α-alumina. Furthermore, in order to simulate the formation of liquid bridges deriving from the melting of one of the phases and to verify the role of capillary forces on the
flow properties of bulk solids at high temperature, a sample of glass beads was mixed with some (1% of the total weight) high-density polyethylene (HDPE), which has a relatively low melting point. The results showed that whereas no significant effect of the temperature in the range 20–500°C was revealed on the shear flow of FCC powder, fly-ashes, corundum powder and alumina. On the other hand, a small but significant increase of cohesion and, therefore, of the unconfined yield strength was observed with temperature for glass beads.

More recently, Chirone et al. [161,162] used the shear cell modified by Tomasetta et al. to characterize the flow properties of five ceramic powder samples with different particle size distributions between ambient temperature and 500°C. A model based on the multiscale approach proposed by Rumpf [67] and Molerus [51] was also used to predict the effect of temperature on the tensile strength of the powder samples. They observed a significant increase of powder cohesion at 500°C for different cuts of the same powder with a particle size larger than 20 μm. This resulted in a lower flowability of the samples. Thermal analysis on the powder samples revealed that the temperature effect on the powder flow properties was only due to van der Waals forces.

2.4.1.1.3 VISCOMETER TYPE TESTS

Particles fluidized by a gas can be treated as a continuum at length scales much larger than the particle diameter. The rheology of such a continuum results from a cumulative effect of microscopic (at length scale of the particles) forces due to the interaction between particles, such as van der Waals, capillary, electrostatic and hydrodynamic drag forces. Rheological properties, in the form of flow constitutive equations, are thus an essential component of the averaged continuum equations for flow of fluidized particles.

Fluid bed viscosity represents an extremely attractive parameter to characterise fluid bed behaviour, but the results obtained in many of the works available in literature are not consistent at all with each other, as reported by Newton et al. [163]. They reviewed the results of the available studies and reported that different orders of magnitude for the bed viscosity were obtained using the various methods.
It should be noted that the bed viscosity is influenced by the shape of the particles, the voidage of the bed, the fluidizing velocity and the fluidizing gas viscosity. Moreover, according to Rietema making measurements in a freely bubbling bed is pointless because when a bubble collides with the measuring device the shear stress will locally approach zero [164]. Therefore, only the measurement of the viscosity of the dense phase seems to be meaningful.

Various measuring devices have been employed to determine the viscosity of powders. Conventional type viscometers are those where the material is sheared by a rotating element (Stormer, Brookfield and Couette) and the resistance to the rotation is measured. Other methods are the floating and falling ball and the torsion pendulum. In the method developed by Grace [165] the measurement of the shape of rising bubbles is used to indirectly calculate the bed viscosity. All these methods are in some ways “intrusive”, as an external object is immersed in the bed in all cases. An indirect method is the quasi-solid emulsion viscosity method developed by Kono et al. [166], where the viscosity is measured indirectly through the measurement of fluidization parameters.

Whether a fluidized bed has to be considered a Newtonian or a non-Newtonian fluid is also a controversial question. In the early studies of gas fluidized beds rheology, an implicit assumption was that the fluidized beds behave as a Newtonian fluid [167–172]. In 1991 Kai et al. [173] assumed Newtonian behaviour for the fluidized bed that they modelled. Others authors, instead, described fluidized beds using a non-Newtonian viscoplastic model, in particulate a Bingham fluid model [174,175].

Gibilaro et al. [176] and Colafigli et al. [177] also reported on the apparent viscosity of a fluidized bed and they proposed theoretical models and experimental analysis in order to evaluate such a property on the base of the analogy between fluidized beds and fluids.

2.4.2 MECHANICS OF PARTICLE ADHESIONS: MODELLING APPROACHES

In order to relate the measured bulk flow properties to the microscopic interparticle forces, models based on Rumpf-Molerus [51–53,67] and Tomas [39–42] theories for steady-state flow criterion of fine and cohesive particulate solids
can be followed. Such theories are based on the possibility to relate consolidation and non-rapid flow of particulate solids with adhesion forces in particles contacts, and they include the failure hypotheses of Tresca and Coulomb-Mohr, the yield locus concept developed by Jenike [178,179] and the Warren-Spring model [134,180–183].

First of all, according to Tomas it is important to consider which kind of mechanical deformation occurs when an external compressive normal force ($F_N$) acts on particles that are very close to each other. There are four main different kinds of mechanical interactions, which are influenced by particle material characteristics and that can be identified as follows [41]:

1. Reversible elastic, in which deformation rate and consolidation do not bear time effects, these are generally valid for all particulate solids at least in a limited portion of the interparticle approach;

![Figure 2.12 – Particle contact approaching, deformations and removing. Adapted from Ref. [40]](image)

Figure 2.12 – Particle contact approaching, deformations and removing. Adapted from Ref. [40]
2. Irreversible plastic, in which deformation rate and consolidation are time invariant, these are typical for mineral powders;

3. Reversible viscoelastic, in which deformation rate and consolidation change with time, these are distinctive for cut post-consumer waste particles;

4. Irreversible viscoplastic, in which deformation rate and consolidation change with time, these apply to fine particle fusion.

Tomas [40] reported a schematic diagram (Figure 2.12) of what happens when an external compressive normal force $F_N$ is acting on isotropic, stiff, linear elastic and monodisperse spherical particles, highlighting how the contact point deforms to a contact area and how the adhesion force between the particles increases.

In this work, both Rumpf-Molerus and Tomas microscale modelling approaches were followed. These models are based on the following assumptions [42,160]:

1. Particles are organised in a randomly packed assembly and the packing structure is assumed to be isotropic with uniform porosity ($\varepsilon$) in any cross-sectional areas as well as in the powder bulk;

2. Particles are spherical and monodisperse and thus the contact points are uniformly distributed over the particle surface with equal probability;

3. The contact areas are small in comparison to the characteristic particle size, therefore these may be considered as contact points;

4. The transmission of an isostatic state of compressive stress with three equal principal stresses is assumed.

These hypotheses are the basis of the equation derived by Molerus [51] for the relationship between stresses and contact forces ($F_C$) for monodisperse particles with characteristic particle size $d$ and assembly porosity $\varepsilon$:

$$\sigma = \frac{F_C}{d^2} \frac{1 - \varepsilon}{\varepsilon}$$

Eqn. (2.35) can be used to relate the IPFs acting in a real bulk solid ($F_H$) to the isostatic tensile strength $\sigma_t$ extrapolated from the powder experimental yield locus, i.e. the tensile stress at which the contact separation equals the adhesive interparticle forces $F_H$ at the contact point:
\[ \sigma_t = \frac{F_H 1 - \varepsilon}{d_{sv}^2 \varepsilon} \quad (2.36) \]

In which \( d_{sv} \) is the particle Sauter mean diameter; this should be used as the characteristic particle size for size distributed powders because it provides the best estimate of the ratio between particle surface and volume and it gives the most accurate volumetric concentration of the interparticles contact points, which is the key variable to relate stresses to average interparticle forces values [160].

In order to define the adhesive forces, the equation proposed by Tomas [41] and Schubert [184] and later adopted by Tomasetta et al. [160] can be used if the contact point is considered to deform only elastically (Figure 2.12b):

\[ F_H \approx \frac{C_{H,sfs} r_{el}}{12 z_0^2} \quad (2.37) \]

where \( C_{H,sfs} \) is the Hamaker solid-fluid-solid constant, \( r_{el} \) is the mean curvature radius at the contact point (which is not necessarily related to the particle size because of the surface can have some local curvatures and asperities) and \( z_0 \) is the characteristic molecular separation distance between touching and non-continuous solids, that amounts to about 0.3-0.4 nm [48].

Combining Eqn. (2.36) and (2.37) a theoretical value for the tensile strength can be estimated. Such a value depends only on the changes in the number of contact points per unit volume, which are related to the changes in the powder porosity during the consolidation step. Furthermore, the pure elastic model does not take into account any change in the particle structure due to the consolidation stage. Instead, if at the contact point the particle can be considered as a solid that is subjected to a plastic and irreversible deformation, then the extent of the particle flattening at the contact point that occurs during consolidation must be taken into account in order to make a proper assessment of the adhesion forces. To this end, both Rumpf and Molerus proposed the same model equation for the adhesion forces, considering that the external normal force \( F_N \) flattens the particle contact to a plate-plate contact:

\[ F_H = F_0 + \kappa_{pl} F_N \quad (2.38) \]

in which \( F_0 \) is the adhesion force without any consolidation (\( F_N =0 \)), intrinsically present in fine powders and related to their cohesive nature. \( F_N \) is the compressive normal force transmitted at the contact during the consolidation stage and \( \kappa_{pl} \) is
the plastic repulsion coefficient. Such a coefficient is defined as a dimensionless ratio of the attractive van der Waals pressure \( p_{VdW} \) for a plate-plate model to the repulsive particle micro-hardness \( p_f \), i.e. the resistance against plastic deformation expressed as the plastic compressive yield strength of the material.

\[
\kappa_{pl} = \frac{p_{VdW}}{p_f} \approx \frac{C_{H,sls}}{6\pi p_f z_0^3 \left(1 - \frac{C_{H,sls}}{6\pi p_f z_0^3}\right)}
\]

Molerus proposed the following expression for the definition of \( F_0 \) [52]:

\[
F_0 = \frac{C_{H,sls} r_p}{12 z_0^2 \left(1 - \frac{C_{H,sls}}{6\pi p_f z_0^3}\right)}
\]

Thus, Eqn. (2.38) results in the following expression:

\[
F_H = \frac{C_{H,sls} r_p}{12 z_0^2 \left(1 - \frac{C_{H,sls}}{6\pi p_f z_0^3}\right)} + \frac{C_{H,sls}}{6\pi p_f z_0^3 \left(1 - \frac{C_{H,sls}}{6\pi p_f z_0^3}\right)} F_N
\]

The normal stress at consolidation \( \sigma_N \) was used to estimate the normal contact force \( F_N \) with Eqn. (2.35), assuming a uniform distribution of powder consolidation at contact points:

\[
F_N = \sigma_N \frac{d_y^2}{1 - \varepsilon}
\]

This assumption could be criticised by arguing that not all of the contact points are equally loaded, but as reported and demonstrated by Tomasetta et al. [160], a non-uniform distribution of consolidation forces at contact points does not introduce variations in the estimates of the tensile strength \( \sigma_t \) with the procedures discussed below.

According to the theory developed by Tomas [39–42,141], to describe the failure/flowability conditions of bulk powders, an elastic-plastic particle contact model should be used rather than a perfect plastic or perfect elastic model as suggested by Molerus. His theory is inspired by the Rumpf and Molerus approach, but it also takes into account the theory proposed by Schubert [185] to combine the elastic and plastic contact strains using the annular elastic \( A_{el} \) and the circular plastic \( A_{pl} \) contact area (Eqn. (2.43)), as well as the mathematical model developed by Thornton [186] for the stick/bounce behaviour of adhesive and elastic-plastic particles:
\[ F_H = F_{H0} + \frac{\pi \sigma_{vdw} r_c^2}{p_f \left(1 + \frac{2 A_{el}}{3 A_{pl}}\right)} F_N \] (2.43)

Tomas developed a normal force-displacement model starting from the particle contact force equilibrium between attraction and elastic/plastic repulsion (\(r_c\) contact radius and \(r\) coordinate of annular elastic contact area):

\[ F_{H0} + \pi \sigma_{vdw} r_c^2 + F_N = \frac{\pi p_f r_c^2}{r_{pl}} + 2 \pi \int_{r_{pl}}^{r_c} p_{el}(r) r \, dr \] (2.44)

This delivers to a linear force-displacement model for particles with height of flattening equals to \(h_c\) (see Figure 2.12c) [40,42]:

\[ F_{H0} + F_N = \frac{\pi}{4} d_{fr} (\kappa_A - \kappa_p) h_c \] (2.45)

where \(\kappa_p\) is the plastic repulsion coefficient and \(\kappa_A\) is the elastic-plastic contact area coefficient representing the ratio of plastic particle deformation area \(A_{pl}\) to the total contact deformation area, which includes the contact area affected by elastic displacement \(A_c = A_{pl} + A_{el}\). They can be estimated as:

\[ \kappa_p = \frac{C_{H,sls}}{6 \pi p_f z_0^3} \] (2.46)

\[ \kappa_A = \frac{2}{3} + \frac{1}{3} \frac{A_{pl}}{A_c} = 1 - \frac{1}{3} \sqrt{\frac{h_{cf}}{h_c}} \] (2.47)

in which \(h_{cf}\) is the height of flattening for incipient yielding at \(p = p_f\) that can be defined as function of particle size and the Hertz modulus of elasticity \(E^*\) (\(\nu\) Poisson ratio and \(E\) Young’s modulus):

\[ h_{cf} = d \left(\frac{\pi p_f}{2 E^*}\right)^2 \] (2.48)

\[ E^* = \frac{E}{1 - \nu^2} \] (2.49)

Starting from Eqn. (2.45), Tomas obtained a general non-linear adhesion force model, in which the interparticle adhesive force \(F_H\) depend on the normal force applied \(F_N\), the adhesion force \(F_{H0}\) without any consolidation and contact flattening, the extent of elastic-plastic deformation that is taken into account by an elastic-plastic consolidation coefficient \(\kappa\), the radius of surface curvature \(r_c\) and the modulus of elasticity \(E^*\):

\[ F_H = F_{H0} + \kappa (F_N + F_{H0}) - \pi r_c^2 \sigma_{vdw} \left[ \frac{3 F_N + F_{H0}}{2 r_c^2 E^*} \left(1 + \frac{F_H - F_{H0}}{F_N + F_{H0}}\right) \right]^2 \] (2.50)
He observed, in agreement with the experimental evidences in powder handling [178,187], that the slope of the adhesion force is reduced with increasing contact radius. Furthermore, he proposed the following linearized form of Eqn. (2.50):

\[
F_H = \frac{\kappa_A}{\kappa_A - \kappa_p} F_{H0} + \frac{\kappa_p}{\kappa_A - \kappa_p} F_N = (1 + \kappa) F_{H0} + \kappa F_N
\]  

Eqn. (2.51) can be interpreted as a general linear particle contact constitutive model or, indeed, linear in forces and non-linear concerning material characteristics.

The elastic-plastic consolidation coefficient \(\kappa\) describes the influence of plastic contact deformation and so it is a measure of irreversible particle contact stiffness or softness. As shown in Eqn. (2.51), it can be defined as:

\[
\kappa = \frac{\kappa_p}{\kappa_A - \kappa_p}
\]  

It is therefore given by the slope of the linear relationship between the interparticle adhesive force \(F_H\) and the normal force \(F_N\): a small slope \((F_H \approx F_{H0})\) stands for low adhesion level because of stiff particle contacts, while a large inclination means soft contacts and a resulting cohesive flow behaviour.

The theories proposed by Molerus and Tomas promote therefore the estimation and the characterization of flow properties of fine powders using plastic repulsion coefficient \((\kappa_{pl})\) and elastic–plastic contact consolidation coefficient \((\kappa)\), which are both related to the particles material characteristics. Thus, for a softer material and for fine particles, the contact consolidation coefficient will be higher in magnitude \((\kappa_{pl} \rightarrow 1)\) as compared to those for a harder material and for coarser particles \((\kappa_{pl} \approx 0)\). Similarly, the elastic–plastic contact consolidation coefficient is expected to increase with increasing interparticle adhesive forces. As a result, values of these coefficients estimated by means of powder shear tests can be used to understand the flow behaviour of powders.

With the aim of analysing the powder flowability, Tomas proposed to estimate the material characteristic parameters using the concept of stationary yield locus (SYL), which is completely described by the parameters shown in Figure 2.13:

- Angle of internal friction \((\phi_I)\);
- Steady-state angle of internal friction \((\phi_{st})\);
• Isostatic tensile strength of unconsolidated powder ($\sigma_0$);
• Centre ($\sigma_{M,\text{st}}$) and radius ($\sigma_{R,\text{st}}$) of the Mohr circle for the steady-state flow

![Figure 2.13 – Evaluation of steady-state yield locus and associated parameters](image)

Whereas the standard yield loci (YL) describe the limits of incipient plastic deformation during consolidation and flow, the stationary yield locus (SYL) is the envelope of Mohr circles for steady-state flow with a certain negative intersection of the abscissa $\sigma_0$. This steady-state yield locus is expressed in radius stress-centre stress coordinates as follows:

$$\sigma_{R,\text{st}} = \sin \phi_{\text{st}} (\sigma_{M,\text{st}} + \sigma_0) \quad (2.53)$$

The steady-state angle of internal friction is related to the increase in adhesive forces as a result of elastic–plastic contact deformation of particles ($\phi_{\text{st}} - \phi_i$). The larger difference between these friction angles entails the softer particle contacts and consequently the more cohesive powder. The centre and radius of the Mohr circle for the steady-state flow are invariants of the state of stress and are related to the pre-consolidation state and thus to the powder bulk density. They are calculated using the major and minor principal stresses ($\sigma_1$ and $\sigma_2$) from experimental yield loci data at each consolidation levels:

$$\sigma_{M,\text{st}} = \frac{\sigma_1 + \sigma_2}{2} \quad \sigma_{R,\text{st}} = \frac{\sigma_1 - \sigma_2}{2} \quad (2.54)$$

Both $\phi_{\text{st}}$ and $\sigma_0$ can be estimated from the experimental flow function data [141]:

$$f_c = \frac{2(\sin \phi_{\text{st}} - \sin \phi_i)}{(1 + \sin \phi_{\text{st}})(1 - \sin \phi_i)} \sigma_1 + \frac{2 \sin \phi_{\text{st}} (1 + \sin \phi_i)}{(1 + \sin \phi_{\text{st}})(1 - \sin \phi_i)} \sigma_0 \quad (2.55)$$

The contact consolidation coefficient $\kappa$ can be then evaluated using Eqn. (2.56):

$$\kappa = \frac{\tan \phi_{\text{st}}}{\tan \phi_i} - 1 \quad (2.56)$$
The isostatic tensile strength $\sigma_0$ of an unconsolidated powder having characteristic diameter $d$ and without any particle contact deformation is related to the adhesion force $F_{H0}$ by Eqn. (2.57):

$$\sigma_0 = \frac{F_{H0}}{d^2} \frac{1 - \varepsilon_0}{\varepsilon_0}$$  \hspace{1cm} (2.57)

The initial porosity $\varepsilon_0$ of loose packing needs to be considered. In order to estimate it Tomas proposed a relationship between powder bulk density and applied normal stresses introducing a compressibility index $n$ by extending analogies to the adiabatic gas law for isentropic compression. In particular, he proposed a differential equation for isentropic compresibility of a powder, where the total pressure includes the particle interaction $p = \sigma_0 + \sigma_{M, st}$:

$$dS = 0 \rightarrow \frac{dp_b}{\rho_b} = n \frac{dp}{p} = n \frac{d\sigma_{M, st}}{\sigma_0 + \sigma_{M, st}}$$  \hspace{1cm} (2.58)

If particles are considered to be interacting without an external consolidation stress (i.e. $\sigma_{M, st} = 0$), Eqn. (2.58) can used to obtain the loose powder packing density $\rho_{b,0}$ and the initial porosity $\varepsilon_0$ according to Eqns. (2.59) and (2.60), respectively. The compressibility index $n$ lies between $n = 0$, i.e. incompressible stiff bulk material, and $n = 1$, i.e. the ideal (gas) compressibility index. Therefore, the author suggested the semi-empirical estimated values for $n$ for $\sigma_1 = 1$-100 kPa reported in Table 2.5.

$$\rho_{b,0} = \rho_b \left( \frac{\sigma_0}{\sigma_0 + \sigma_{M, st}} \right)^n$$  \hspace{1cm} (2.59)

$$\varepsilon_0 = \frac{\rho_p - \rho_{b,0}}{\rho_p}$$  \hspace{1cm} (2.60)

<table>
<thead>
<tr>
<th>$n$ index</th>
<th>Evaluation</th>
<th>Example</th>
<th>Flowability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 0.01</td>
<td>Incompressible</td>
<td>Gravel</td>
<td>Free flowing</td>
</tr>
<tr>
<td>0.01 – 0.05</td>
<td>Low compressibility</td>
<td>Fine sand</td>
<td>Free flowing</td>
</tr>
<tr>
<td>0.05 – 0.1</td>
<td>Compressible</td>
<td>Dry powder</td>
<td>Cohesive</td>
</tr>
<tr>
<td>0.1 – 1</td>
<td>Very compressible</td>
<td>Moist powder</td>
<td>Very cohesive</td>
</tr>
</tbody>
</table>

Tomas proposed also a relationship between $\kappa$, the Jenike flowability factors $f_c$ [179] and the angle of internal friction $\phi_i$ in order to extend the use of the coefficient $\kappa$ for powder flowability characterization:

$$\kappa = \frac{1 + (2 f_c - 1) \sin \phi_i}{\tan \phi_i (2 f_c - 1 + \sin \phi_i)} \left[ \frac{1}{1 - \left( \frac{1 + (2 f_c - 1) \sin \phi_i}{2 f_c - 1 + \sin \phi_i} \right)^2} - 1 \right]$$  \hspace{1cm} (2.61)
Table 2.6 shows directly the correlation between flowability and elastic-plastic contact consolidation coefficient for a typical angle of internal fraction of 30°. However, as reported by Medhe et al. [141], the use of Eqn. (2.56) to evaluate $\kappa$ instead of calculating it from Jenike’s flow function and $\phi_i$ directly using Eqn. (2.61) is necessary to avoid any dependence on consolidation levels.

<table>
<thead>
<tr>
<th>Flowability factors $ff$</th>
<th>$\kappa$ value</th>
<th>$\phi_i$ ['°]</th>
<th>Evaluation</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 – 10</td>
<td>0.01 – 0.107</td>
<td>30.3 – 33</td>
<td>Free flowing</td>
<td>Dry fine sand</td>
</tr>
<tr>
<td>4 – 10</td>
<td>0.107 – 0.3</td>
<td>33 – 37</td>
<td>Easy flowing</td>
<td>Moist fine sand</td>
</tr>
<tr>
<td>2 – 4</td>
<td>0.3 – 0.77</td>
<td>37 – 46</td>
<td>Cohesive</td>
<td>Dry powder</td>
</tr>
<tr>
<td>1 – 2</td>
<td>0.77 – ∞</td>
<td>46 – 90</td>
<td>Very cohesive</td>
<td>Moist powder</td>
</tr>
<tr>
<td>&lt; 1</td>
<td>∞</td>
<td>-</td>
<td>Non flowing</td>
<td>Hydrated powder</td>
</tr>
</tbody>
</table>

### 2.4.3 BED COLLAPSE TEST TECHNIQUE

The bed collapse test (BCT) was first introduced in 1967 by Rietema [188] and was subsequently used by Sutton and Richmond [189] in 1973 to test the capacity of a powder bed to retain aeration gas. Since then, BCT has been used in a great deal of research over the last sixty years with different aims. Such a test consists of suddenly turning off the gas supply to a vigorously bubbling fluidized bed and recording the deflation of the bed with time.

It has been adopted to compare Geldart Group A and C powder behaviour [190], to assess the effects of fines distribution [191–193], to evaluate changes in catalyst properties and to help diagnose commercial operational problems [194], but mostly to characterize dense phase properties [74,75,105,132,188,193,195–198], namely the dense phase voidage $\varepsilon_d$, the dense phase collapse rate $U_{de}$, the bubble escape rate $U_b$, the standardised collapse time SCT and the bed expansion ratio BER.

When the fluidizing gas is suddenly shut off, the bed material exhibits different collapse profiles depending on the powder properties. Figure 2.14 reports typical collapse profiles for a gas-solid system with different Geldart group powders, in which three main stages can be observed (as also highlighted in Figure 2.15).

The already mentioned dense phase properties (or collapse parameters) are very helpful for the analysis of the capability of the powder to retain the aeration gas. In particular, the dense phase collapse rate ($U_{de}$) is a useful parameter for the
measurement of how quickly the bed loses its interstitial aeration gas, whereas the 
standardised collapse time (SCT), introduced for the first time in 1985 by Geldart 
and Wong [190], takes into account that the time required for the powder to 
daerate depends on both the collapse rate and the height through which the bed 
surface has to fall. The latter is normalised with respect to the height of the settled 
bed, and then it accounts for possible changes in the packing of the settled bed due 
to changes in the IPFs. Therefore, it is a good indicator for the detection of 
changes happening in the bed when changing operative conditions, e.g. 
temperature, initial gas velocity and PSD of the powder.

Figure 2.14 - Typical collapse profiles for different Geldart group powders

For type A powders, in the first stage a rapid initial collapse occurs when the 
bubbles leave the bed (bubble escape stage). An intermediate stage follows, where 
the dense phase collapses linearly with time until the bed approaches the height at 
incipient fluidization (hindered sedimentation stage) and a final consolidation of 
the solid materials is then observed (solid consolidation stage).

From the BCT curve the following parameters can be calculated:

\[
\varepsilon_d = 1 - \frac{M}{\text{XSA} \, \rho_p \, H_d}
\]

(2.62)

\[
U_{de} = \frac{H_d - H_s}{t_s - t_0}
\]

(2.63)

\[
U_b = \frac{H_0 - H_b}{t_b - t_0}
\]

(2.64)

\[
\text{BER} = \frac{H_d - H_s}{H_s} \times 100
\]

(2.65)

\[
\text{SCT} = \frac{\text{BER}}{U_{de}} = \frac{t_s - t_0}{H_s} \times 100
\]

(2.66)
where \( t_0 \) is the time when the gas supply to the fully bubbling bed is cut off and \( t_s \) is the time when the collapse is complete and the bed is completely settled. \( H_s \) is the height of the settled bed, whereas \( H_d \) is the extrapolated value of the dense phase height at time \( t_0 \).

\[
\begin{align*}
U_{de} & = \frac{188 \rho_g^{0.089} \mu^{0.371} e^{(0.508 F_{45})}}{d_p^{0.568} \rho_g^{0.663} H_s^{0.244} (\rho_p - \rho_g)^{0.663}} \\
\text{SCT} & = \frac{1.27 \times 10^6 \rho_g^{0.19} \mu^{0.785} e^{(1.074 F_{45})}}{d_p^{1.2} \rho_g^{1.4} (\rho_p - \rho_g)^{1.4}}
\end{align*}
\]

where all the parameters and dimensional constants have units according to International System of Units (MKS) and \( F_{45} \) is the fraction of fines under 45 microns.

Figure 2.15 – Stages in the bed collapse process

Geldart and co-workers [151,199] reported that the BCT parameters can be influenced by the starting fluidizing velocity and they found that in beds of Group A powders the voidage is strongly affected by particle density and size distribution, as well as by variations in gas viscosity and density. They also developed a correlation to predict \( U_{de} \) and SCT at ambient temperature:

\[
\begin{align*}
U_{de} & = \frac{188 \rho_g^{0.089} \mu^{0.371} e^{(0.508 F_{45})}}{d_p^{0.568} \rho_g^{0.663} H_s^{0.244} (\rho_p - \rho_g)^{0.663}} \\
\text{SCT} & = \frac{1.27 \times 10^6 \rho_g^{0.19} \mu^{0.785} e^{(1.074 F_{45})}}{d_p^{1.2} \rho_g^{1.4} (\rho_p - \rho_g)^{1.4}}
\end{align*}
\]
For Group B and D powders, which show aggregative fluidization for gas velocities above $u_{mf}$, the bed collapse curve shows a sharp sedimentation stage as the particles reach the final static bed height as soon as the bubbles are expelled. For these systems, in which $u_{mb}/u_{mf} = 1$, the dense phase may be not expanded at all and, therefore, the consolidation stage may not appear. As consequence, their collapse rate is much faster than for Group A materials. In these cases, the collapse parameters defined for Group A powders need to be revised as there is not a clear distinction between $H_0$ and $H_b$ and the extrapolation of $H_d$ may be pointless. The overall collapse rate $U_c$, the standardised collapse time $SCT$ and the bed expansion ratio $BER$ can be defined as follow:

$$U_c = \frac{H_0 - H_s}{t_s - t_0}$$  \hspace{1cm} (2.69)

$$BER = \frac{H_0 - H_s}{H_s} \times 100$$ \hspace{1cm} (2.70)

$$SCT = \frac{BER}{U_c} = \frac{t_s - t_0}{H_s} \times 100$$ \hspace{1cm} (2.71)

Group C materials display a different collapse curve for either A or B and D powders. There is not a hindered sedimentation stage, but only consolidation. Geldart and co-workers reported that Group C bed expansion is caused by the presence of cavities and cracks [190,200]. They observed that when the gas is switched off, the largest cracks close up rapidly and further collapse proceeds more slowly, and then the rate of collapse is controlled by the rate at which gas can escape from vertical channels. In addition, they reported that the bed height decreases exponentially with time.

Barreto et al. [196] found good agreement between the results for the dense phase voidage in bubbling beds obtained using the BCT technique and those directly observed with the X-rays absorption technique.

Lettieri at al. [74,75,79] and Formisani et al. [105,132,198] used the bed collapse technique to investigate the influence of temperature on the dense phase properties of various solid materials. Lettieri and collaborators observed that, despite the sensitivity of the fluidization parameters on the initial gas velocity, it did not affect the trends of these parameters with increasing temperature. This finding suggests that as long as the experiments are carried out in a consistent
fashion, i.e. at the same initial fluidizing velocity, a meaningful assessment of the influence of process conditions can be achieved. They found a good agreement between Eqn. (2.17) and the experimental values for $U_{de}$ measured for FCC catalysts (Group A) at temperatures ranging from ambient to 650 °C. Within this range of temperatures, they reported a decrease of 25-50% at high temperatures. In addition, they found that the SCT was the most discriminating parameter to distinguish between systems of powders dominated by the interparticle forces or the hydrodynamic forces. The SCT increased with increasing temperature for those powders dominated by the HDFs (the fresh FCC catalysts), while it decreased with increasing temperature for those materials for which the increasing influence of the IPFs caused formation of aggregates within the bed.

Formisani and co-workers highlighted the significant influence of operating temperature on the quality of bubbling and in particular on the “bubble hold-up”, i.e. the deviation of the bed height in bubbling regime with respect to the extrapolated dense phase height. Their results indicated that the bubble hold-up increases with increasing temperature, because of the decrease in the gas velocity through the dense phase and in the bubble diameters. The authors linked these phenomena to the thermally induced IPFs, which enhanced the cohesiveness of the dense phase, making the behaviour of the bed very similar to that typical of the beds of fine particles fluidized at room temperature.

### 2.5 Link Between Rheological Measurements and Fluidization

In this section, previous investigations on the relationship between the rheological properties of powders and the corresponding fluidization behaviour are discussed. Such researches were aimed at understanding and quantifying the effect of the interparticle forces on fluidized powders.

In 1992, Reiling [201] explored the link between the apparent viscosities of fine catalyst powders and the bubble size. He studied the effects on viscosity of adding ultrafine silica cuts to the bed of catalyst, using a Brookfield paddle
viscometer. The author questioned the validity of the instability/wave perturbation theory elaborated by Rice and Wilhem [202] and Romero and Johanson [203] according to which low viscosity and low density fluid beds should promote the suppression or destruction of large bubbles and, thus, contain smaller bubbles than beds of high viscosity or high density. The experimental data reported by the author did not support this conclusion. The addition of ultrafine silica had a large effect on the dense phase voidage but only a small effect on the viscosity of the fluidized bed. Therefore, Reiling concluded that the link between bubble size and apparent viscosity is not supported by a viscous mechanism.

Newton and co-workers also tried in 1999 to relate the bubble size and bubble number to the bed viscosity [163]. They used a ball dropping technique in order to measure the viscosity of a bed of Geldart group B polymer powder with increasing temperature (17 – 96 °C). They reported that the effect of increasing temperature on the polymer cohesiveness and stickiness was demonstrated by the significant changes observed on the mean bubble size and bubbles number. However, the viscosities measured through the ball dropping technique did not show dramatic changes with increasing temperature. The authors, in line with the findings of Reiling, concluded that viscosity effects do not explain bubble sizes in the case of the tested powder and that they could not assign a viscosity to the dense phase.

Kai et al. [173] related the apparent bed viscosity to the bubble diameter and to pressure fluctuation measurements. The authors, in disagreement with Reiling and Newton, found that the bubble diameter increased with increasing viscosity. They also carried out experiments with increasing temperature, but they did not clearly state what trend they found for the apparent viscosity with such a parameter. However, they showed that the experimental data for the bubble diameter and the viscosity at high temperatures followed the same relationship found at ambient temperature. They obtained similar results plotting experimental data obtained at high pressure by Weimer and Quarderer [204]. The authors also proposed an empirical correlation to predict the variation of apparent bed viscosity with operating temperature.
Khoe et al. [191] analysed the fluidization and the rheological behaviour of sets of powders differing in PSD and fines content. According to the method described by Molerus, they used shear tests measurements and experimental values of $\varepsilon_{mf}$ and mean particle diameter $d_{sv}$ to derive an expression for the average adhesive force per contact, $F$. The method assumes each powder as a semi-continuum and derives the average tensile strength, from which the average $F$-value at the contact points between monosized particles of diameter $d_{sv}$ is calculated. Khoe et al. found that the adhesive force per contact correlated very well with the ratio $(\varepsilon_{mb} - \varepsilon_{mf})/\varepsilon_{mf}$ obtained from experiments. In particular, they found that $F$ increases when the maximum dense phase expansion increases. The authors used the $F$ values obtained from the shear cell measurements also to question the commonly accepted assumption that at the minimum bubbling velocity the average adhesive forces counterbalance the overall hydrodynamic forces. They developed a model to calculate a theoretical $\Delta F$ which would be needed to reach the minimum bubbling without expanding the bed, and compared it with the measured values of $F$. They found that $\Delta F << F$ and thus they stated that the energy needed to reach minimum bubbling without expanding the bed is much smaller than the average interparticle bond strength. Khoe et al. also concluded that vertically elongated microcavities are responsible for premature weakening of the bed structure, allowing bubbling to start at a much lower value of the hydrodynamic force than $F$. This result was in agreement with findings of Donsì and Massimilla [110], who also observed cavities and microchannels in the homogeneous expansion of Geldart group A powders.

Kono et al. [146] performed several fluidization tests on powders differing in size, shape, density, chemical properties and surface characteristics, but all fluidizable and free from any agglomeration or segregation phenomenon. They used spent FCC, glass beads, carbon black and various starch powders with sizes ranging from 15 to 70 μm. For each powder the fracture strength and the plastic deformation were evaluated at ambient temperature and, for the FCC experiments, were calculated at temperatures up to 500 °C as well. The authors suggested a linear relationship between the two parameters, which held true for all the experimental data, regardless of the type of powder, properties or operating
temperature. They interpreted this line as a flow characteristic line, where all powders characterised by smooth fluidization should fall. This idea was supported by the fact that, when powders forming agglomerates were fluidized or wall effects were significant, the two above-mentioned parameters could not be related using their correlation. Furthermore, a qualitative correspondence was found between the measured rheological parameters and the observed fluidization behaviour. The smaller were the values of the plastic deformation and/or of the fracture strength at minimum bubbling condition, the larger was the expansion of the dense phase at $u_{mb}$ and the smaller were the values of bubble size observed in a 2-D fluidised bed.

Moreover, as pointed out by Lettieri [79], moving along the linear relationship suggested by Kono, different degrees of flowability among fluidizable powders could be predicted. In particular, points obtained with increasing temperature systematically shifted along the line towards the small values of the rheological parameters, which was in agreement with the widely reported positive effect of temperature on the fluidization behaviour of free flowing materials.

Quintanilla et al. [125] investigated the correlation between bulk stresses and adhesion forces in fine powders. They presented measurements of the tensile strength as a function of the consolidation stress for a set of very fine cohesive powders (i.e. xerographic toners) of 12.7 µm particle size and with a range of concentration of submicron fumed silica as flow control additive. In 2002, Castellanos et al. [205] investigated the dynamics of fine cohesive powders inside rotating drums with the aim to study the transition from rigid-plastic flow to gas-fluidized regime. They performed experimental measurements on the bed expansion as a function of the rotation velocity, using drums of different diameters and fine powders with different cohesiveness. They demonstrated that the onset of fluidization in the rotating drum is determined by the ratio of the powder kinetic energy per unit volume to its tensile strength, and that once the powder is completely fluidized the average interstitial gas velocity increases proportionally to the rotation velocity. Subsequently, in 2004 Castellanos et al. presented the so called Sevilla Powder Tester (SPT), a 4.45 cm diameter, 17 cm high cylinder placed on a shaker to help fluidization of cohesive materials [206].
The SPT showed the interdependence between the consolidation stresses, the tensile yield stress and the particle volume fraction for powders with different levels of surface additives which were used to vary the powders’ degree of flowability.

Bruni and co-workers investigated the effects of adding different fines cuts on the fluidization and the rheological behaviour of an alumina powder [14,147,156,207,208]. To this end, they followed a two-fold approach to establish a link between the two aspects of the work. On the one hand, the fluidization behaviour of the alumina was studied at process temperatures ranging from ambient to 400°C and by adding to the material previously deprived of fines two fine sub-cuts of nominal size 0-25 and 26-45 μm respectively. Fluidization experiments were carried out changing the total fines content from 22% to 30% by weight. On the other hand, a new mechanically stirred fluid-bed rheometer (the msFBR, 15cm in diameter and 30cm tall) was designed and built to determine the rheological behaviour at ambient temperature of the powders containing different fines sub cuts. Rheological experiments were carried out at different rates of aeration and impeller depths (Figure 2.16).

A model was developed, based on the failure properties of the materials, to determine the stress distribution corresponding to any given rate of aeration in the msFBR. This allowed a true comparison to be made between the rheological behaviours of different powders, aiding the assessment of the effect of fines size distribution on powder rheology. Moreover, the model allowed the prediction of the torque measured with the msFBR and the assessment of the effect of aeration on powder rheology.

The interpretation of the failure properties of the materials provided an indication of the capability of the powders to flow and underpinned the link between the fluidization and the rheological behaviour below the minimum fluidization conditions, interpreted as the capability of the powders to fail under a certain load and their capability to attain fluidization. In particular, for all materials tested, measurements of the torque at different impeller depths and different levels of aeration showed that the torque reaches a plateau, similar to a normal stress profile in silos observed by Janssen [209]. The effect of increasing the aeration
rate was to linearly decrease the torque needed to stir the materials. These trends were explained considering that the stress distribution in the bed changes with changing aeration, as shown in Figure 2.16. Thus, at a constant impeller depth and when the aeration rate is increased, the normal load on the impeller will decrease, due to the additional upward drag force exerted by the gas on the powder. This reduces the apparent gravity and reduces the local state of stress that is responsible of the measured torque.

![Graph showing the effect of impeller depth and aeration rate on torque](image)

Figure 2.16 - Effect of impeller depth (ID) and aeration rate (ΔP/ΔPc) on torque, alumina with fines sub-cut 26-45 μm [14]

On the basis of the above results, Bruni and co-workers developed a model to estimate the state of stress by varying impeller depth, following Janssen’s approach for silo design, and modified to take into account the aeration of the bed and the possible cohesiveness of the material. The model uses properties such as the dynamic and the wall yield loci of the powders used, which were estimated with a Peschl shear cell modified for small loads. The comparison between the experimental and predicted values for the torque demonstrated that the torque is
defined by the plastic deformation of the powders and can be explained within a simple Mohr–Coulomb approach to powder flow.

In 2012, Tomasetta and co-workers re-examined the model and performed a sensitivity analysis on the wall failure properties and on some of the original model assumptions regarding the active and passive state of stress in the fluid-bed rheometer [210]. They also proposed a novel procedure for the inverse application of the model in order to assess the powder flow properties from the torque measurements. The application of this procedure provided good results in terms of effective angle of internal friction and was deemed promising for the ability of the system to explore powder flow at very low consolidation states.

### 2.6 Chapter Remarks

The literature survey has demonstrated the important role that both the material properties (i.e. particle size, flowability, yield stress etc.) and the process conditions (i.e. environmental factors such as temperature and humidity) play on the fluidization behaviour of gas-solids fluidized beds.

Process conditions influence fundamental parameters describing the minimum fluidization conditions, bed expansion and contraction, and the transition from particulate to bubbling fluidization. The analysis of the influence of elevated temperatures on fluidization highlights the enhanced role that the interparticle forces can play on the fluidization quality over the hydrodynamic forces, emphasizing the need for a quantification of the effects of these forces.

To this end, the multidisciplinary approach based on linking rheology and fluidization is promising. Further work is, however, needed; the challenge lies in the difficulty to relate the different rheological measurements to fluidization, mostly due to the variety of techniques employed, which makes standardisation of rheological tests very difficult. A more systematic assessment of the independent and the combined effects of real process conditions on fluid bed rheology and fluidization still need to be accomplished. A twofold approach based on fundamental fluidization and rheological measurements is used in this thesis with
the aim of evaluating how the particle-particle interactions change with temperature. This will be tackled in this thesis.

Moreover, the literature review on agglomeration and aggregation phenomena that can lead to defluidization at high temperature have highlighted the complexity of identifying the factors that are responsible for the onset of sintering, making it difficult to find a unique solution or prediction strategy that will suit all powders and conditions. For this reason, this is an area that needs to be further investigated to better understand the evolution of solid bridging forming between the particles.
3 MATERIALS AND EXPERIMENTAL METHODS

This chapter reports on the powders and particle characterization techniques used to classify the materials employed in this work. Particle properties such as particle size distribution, mean diameter, particle density and surface characteristics are reported. Scanning electron microscope (SEM) was used to investigate surface properties. This chapter also details fluidization tests and the rheological measurements used to investigate the flow properties of the materials at the different operative conditions. The materials used include natural, synthetic and slag rutile as well as three different sizes of petroleum coke particles. All the materials were supplied by Venator.

3.1 MONO-COMPONENT SYSTEMS

3.1.1 PARTICLES PROPERTIES

Sauter mean diameters (SMD or \(d_{sv}\)), particle size distributions (PSD) and relative diameter spread (RDS) were determined by sieve analysis in an external laboratory upon request of Venator. For each material, the sieve test was repeated three times and average values were taken. Sauter diameter is defined as follows:

\[
SMD = d_{sv} = \frac{1}{\sum_i x_i d_{pi}}
\]  \hspace{1cm} (3.1)

where \(x_i\) is the weight fraction of particles in each size range \(d_{pi}\).

RDS is defined according to Geldart [211] by using the 16th, the 50th and the 84th percentile sizes (\(d_{16}, d_{50}\) and \(d_{84}\) respectively) obtained from sieve analysis. It is used to compare the width of the size distribution of the powders provided for this work:

\[
RDS = \frac{1}{2} \frac{d_{94} - d_{16}}{d_{50}}
\]  \hspace{1cm} (3.2)
The classification proposed by Geldart [211], reported in Table 3.1, was used to elucidate the type of size distribution corresponding to the relative diameter spread.

The main physical properties of all the investigated materials are reported in Table 3.2. It also includes particle densities, bulk densities and assembly porosities at ambient temperature, which were calculated from data supplied from the Schulze apparatus used for the shear testing.

### Table 3.1 - Width of PSD based on RDS, adapted from [211].

<table>
<thead>
<tr>
<th>Number of sieves on which the middle 70% (approx.) of the powder is found</th>
<th>RDS</th>
<th>Type of distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Very narrow</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>Narrow</td>
</tr>
<tr>
<td>3</td>
<td>0.17</td>
<td>Fairly narrow</td>
</tr>
<tr>
<td>4-5</td>
<td>0.25 – 0.33</td>
<td>Fairly wide</td>
</tr>
<tr>
<td>6-7</td>
<td>0.41 – 0.48</td>
<td>Wide</td>
</tr>
<tr>
<td>9-11</td>
<td>0.60 – 0.70</td>
<td>Very wide</td>
</tr>
<tr>
<td>&gt;13</td>
<td>&gt;0.80</td>
<td>Extremely wide</td>
</tr>
</tbody>
</table>

### Table 3.2 – Main physical properties of the investigated materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_p$ [kg/m$^3$]</th>
<th>$\rho_b (25^\circ)$ [kg/m$^3$]</th>
<th>$\varepsilon (25^\circ)$ [-]</th>
<th>$d_{16}$ [μm]</th>
<th>$d_{50}$ [μm]</th>
<th>$d_{84}$ [μm]</th>
<th>$d_{sv}$ [μm]</th>
<th>RDS [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Rutile (SR)</td>
<td>3200</td>
<td>1500</td>
<td>0.53</td>
<td>122</td>
<td>162</td>
<td>212</td>
<td>145</td>
<td>0.28</td>
</tr>
<tr>
<td>Natural Rutile (NR)</td>
<td>4200</td>
<td>2320</td>
<td>0.45</td>
<td>117</td>
<td>202</td>
<td>379</td>
<td>155</td>
<td>0.65</td>
</tr>
<tr>
<td>Titania Slag (TS)</td>
<td>4200</td>
<td>2160</td>
<td>0.48</td>
<td>169</td>
<td>356</td>
<td>686</td>
<td>234</td>
<td>0.73</td>
</tr>
<tr>
<td>Small Pet Coke (SPC)</td>
<td>1350</td>
<td>870</td>
<td>0.36</td>
<td>322</td>
<td>620</td>
<td>1205</td>
<td>520</td>
<td>0.71</td>
</tr>
<tr>
<td>Medium Pet Coke (MPC)</td>
<td>1350</td>
<td>760</td>
<td>0.44</td>
<td>1840</td>
<td>2290</td>
<td>2720</td>
<td>2290</td>
<td>0.19</td>
</tr>
<tr>
<td>Large Pet Coke (LPC)</td>
<td>1350</td>
<td>650</td>
<td>0.52</td>
<td>2920</td>
<td>3440</td>
<td>4240</td>
<td>3690</td>
<td>0.19</td>
</tr>
</tbody>
</table>

A Scanning Electron Microscope (SEM), i.e. a special type of electron microscope that uses a beam of electrons to generate a magnified image of the sample, was used to observe the samples’ surface topography. In this work, SEM magnifications of all the fresh materials have been performed by the staff of the EIL – Electrochemical innovation Lab at UCL and by the staff of the Istituto di Ricerche sulla Combustione (IRC-CNR) in Naples (Italy).

Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were performed by a SDT-Q600 (TA Instruments) available at the University of Salerno (Italy) with the aim of assessing the occurrence of phase transitions or chemical reactions in the temperature range of interest. TGA is a technique through which changes in physical and chemical properties of materials...
are measured as a function of temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The analysis provides information about both physical phenomena including vaporization, sublimation, absorption and chemical phenomena such as desorption, chemisorptions, desolvation, decomposition, and solid-gas reactions (e.g., oxidation or reduction). Generally, TGA is used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (e.g. moisture). DTA is instead a technique that measures the energy necessary to maintain a nearly zero temperature difference between a specific sample and an inert reference material. The two materials experience identical thermal regimes in an environment heated or cooled at a controlled rate. The differential temperature is registered and plotted over the temperature. Thus, physical or chemical transformations, such as glass transitions, crystallization, melting and sublimation, can be detected comparative to the inert sample, for either exothermic or endothermic processes.

3.1.2 Shear Tests: Apparatus and Procedures

3.1.2.1 High Temperature-Annular Shear Cell

A Schulze Ring Shear Tester RST-01 [212] was used as a reference apparatus to characterize the flow properties of the materials at ambient and high temperature. A standard type S cell was used at ambient temperature, while, to perform measurements of the powder flow properties at high temperature the cell modified by Tomasetta et al. [144,159,160] was used. The materials used for the construction of the High Temperature-Annular Shear Cell (HT-ASC) allow a safe operation of the system up to 500 °C. In this work, experiments were performed at 500 °C. The main design data of the two cells used in the present case study are listed in Table 3.3. Some pictures and a schematic of the apparatus are reported in Figure 3.1.

The HT-ASC apparatus operates on the original workbench developed by Schulze for shear tests at room temperature and it has the same internal geometrical characteristics of the SV10 cell. Its external part has, instead, been redesigned to allow the introduction of two electrical resistances aimed at heating
up the cell and the powder sample contained in it during the measurements: in particular, one of the resistances was placed below the cell bottom and the other one was installed above the lid.

Table 3.3 – Main design data of the shear cells

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>HT-ASC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bottom ring</td>
<td>Lid</td>
</tr>
<tr>
<td>Internal volume, cm³</td>
<td>95</td>
<td>204</td>
</tr>
<tr>
<td>Inner diameter, mm</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>Outer diameter, mm</td>
<td>120</td>
<td>118</td>
</tr>
<tr>
<td>Nominal height, mm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating power, W</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Two thick layers of insulating material cover the bottom ring and the lid in order to reduce the heat flux to the surrounding environment and then minimise the temperature gradient within the sample. The base of system is equipped with a metal cooling plate that uses running water. The high thermal conductivity of the metal promotes the heat exchange between the bottom insulation layer and the coolant, keeping the cell base at a temperature close to the water stream temperature and preventing damage to the instrument gears.

The temperature uniformity inside the powder sample is verified and controlled by two separate PID temperature control loop: one for the base and the other for the lid. Each of them uses thermocouples (J types) placed inside the sample and entering the cell through purposely bored channels. A third J thermocouple enters radially through a third channel at an intermediate height inside the sample to verify temperature homogeneity.

Figure 3.1 – A schematic and some pictures of the HT-ASC apparatus [144].

The experimental procedure used to evaluate the flow properties of the material follows the standard shear tests procedure proposed by Schulze [213]. After filling
the bottom ring of the cell and positioning it on the desk of the Ring Shear Tester, thermocouples and cooling system were set and the lid and the weights for consolidation were placed. In order to achieve the desired operating temperature, before starting the shear experiment, heaters were activated and steady-state temperature conditions at the set level were reached. Tomasetta et al. [159] demonstrated the equivalence of the experimental measurements performed by the modified and the original Schulze shear cell.

3.1.2.2 Experimental Yield Locus Construction

Once the cell is loaded with the powder specimen, the Schulze tester is switched on: the lid is held in place by two tie-rods while the bottom ring rotates determining a shear plane inside the material. Two load cells measure the torque necessary to keep the lid in place. A normal stress to the shear plane is applied by loading the lid with a certain weight through a hanger connected to the crossbeam. The weight of the lid, crossbeams and hanger is balanced by a counterbalance system. Therefore, the normal stress is calculated as the weight loaded defined by the cell surface. The shear stress is determined by the torque necessary to keep the lid in place and the surface of the shear plane. This is calculated as average forces measured by the two load cells.

For each sample, the shear test was repeated with four different consolidation loads to obtain four different yield loci and then a flow function with four points. Each yield locus can be obtained by following two measurement steps. The first step, known as pre-shear or consolidation step, consists of applying a horizontal shear within the sample by moving forward the ring while a specific normal consolidation stress $\sigma_{\text{pre}}$ is applied on the sample. This lasts until steady state conditions are reached and then a constant value of shear stress $\tau_{\text{pre}}$ can be detected. The second step, known as shear step, consists in applying again a shear within the sample with a normal stress on the shear plane lower than the normal stress used in the previous step: the maximum value of the registered shear stresses indicates the shear stress for incipient flow, i.e. the yield shear stress $\tau_{\text{sh}}$. The yield stress is a function of the applied normal stress and it is parametric in the consolidation stress applied during the pre-shear step. The normal stress and corresponding yield shear stress can be represented by a point in the $\sigma$-$\tau$ plane.
Repetitions of these steps in series with decreasing normal stresses during shear steps allow evaluating the internal yield locus relevant to the powder consolidation attained in the pre-shear phase [159]. A typical shear stress chart and the derived yield locus, corresponding to a specific consolidation stress, is schematically presented in Figure 3.2.

Figure 3.2 - Determination of Yield Locus through shear stresses measurements

The interpolation of all the experimental points leads to the construction of the yield locus. It is worth pointing out that the choice of the normal stresses used in the shearing phases can be arbitrary as all the points obtained in the shearing phases will belong to the same yield locus provided that the same consolidation stress is applied in the pre-shearing phase and that its value is consistent with the measurement purpose. In the present case study, the tests were carried for normal stresses below 1 kPa. Such low values were chosen in order to approach a consolidation state relevant to fluidised powders. For all the tests, at least 4 shear points were registered to obtain a yield locus and a software application developed in the LabVIEW environment (National Instrument) was used to acquire, visualize and record the main data measured during the shear experiments. Each measurement was repeated at least thrice at every temperature and load, in order to increase the statistical significance of the results in terms of yield loci.

The combination of the interpolated yield loci and of the linked Mohr circles allows a detailed description of the stress distribution inside a bulk solid, as reported in section 2.4.1.1. The major principal stress $\sigma_1$ is estimated from the largest intercept on the $\sigma$ axis of the Mohr Circle tangent to the yield locus and passing through the consolidation point ($\sigma_{pre}$). The unconfined yield strength $f_c$
corresponds to the finite intercept on the σ axis of the Mohr Circles which is tangent to the yield locus line and passes through the origin of σ-τ Plane.

Yield loci obtained at different consolidation stresses provide different couples of values (σ₁, f_c) that can be plotted on the σ₁-f_c plane in order to obtain the so-called material flow function. As reported by Jenike [179], the plane σ₁-f_c is divided into five regions corresponding to different classes of flowability and bounded by lines corresponding to constant values of the ratios σ₁/f_c, known as flow factor (ff_c).

As previously discussed, the tensile strength σ_t is represented by the intersection between the tensile side of the σ-axis and the yield locus and it can estimated by using two different approaches:

1. Mohr-Coulomb analysis or linear yield locus, according to Eqn. (2.33)
2. Warren-Spring equation or curved yield locus, according to Eqn. (2.34)

Due to its non-linearity, the regression procedure for the Warren Spring equation is much more complicated than for the Coulomb equation. In order to understand and evaluate the possible advantages of using the Warren Spring equation, a purpose-built MATLAB App was developed and presented in the next section.

3.1.2.3 Development of a MATLAB App for the Analysis of Bulk Flow Properties from Shear Tests

A systematic procedure was developed to programmatically estimate the best fitting parameters of both the linear and the curved yield locus.

The best fitting straight line through the experimental data is estimated by using the MATLAB routine polyfit which enables the coefficients of a generic polynomial P(X) of specific degree N that best fits the input data in a least-squares sense to be found. In the case when N = 1 the output coefficients P(1) and P(2) are considered. All the linear yield locus parameters expressed by Eqn. (2.33) can be calculated as function of the polynomial coefficients:

\[ C = P(2) \]  
\[ \sigma_t = \frac{P(2)}{P(1)} \]  
\[ \phi_t = \arctan(P(1)) \]
Regarding the curved yield locus, expressed by Eqn. (2.34), the best fitting function through the experimental data is estimated by minimizing the root mean square error (RMSE method). In order to perform the RMSE, the MATLAB routine `fmincon` is used. This routine is based on the method of Lagrange multipliers, which enables to solve general minimization problems subjected to constraints. In this case, the problem consists in finding the values of the parameters appearing in the Warren-Spring equation, which are able to provide the minimum value for RMSE. This problem is subjected to one constraint only in the space of the curve parameters, i.e. the curvature index, n, must be in the range $1 \leq n \leq 2$. Final values of the non-linear regression procedure may depend on the initial values adopted for the calculation. In all the cases the latter were set to the values found assuming a linear Yield Locus, namely $n=1$.

In order to compare the results in terms of the most significant flow properties, in both the regression cases, the major principal stress during consolidation $\sigma_1$ is calculated by the intersection of the $\sigma$-axis and the Mohr circle tangent to the yield locus and passing through the point representative of the pre-shear stresses. The tangent point between the Mohr circle and the yield locus, as well as the Mohr circle radius ($R$) and centre ($M$), are calculated according to tangency condition between a line and a circle. In particular, the first-order Taylor series approximation of the Warren-Spring curve about the tangent point is used to obtain a linear function.

Similarly, the unconfined yield strength, $f_c$, representing the state of stress in the unconfined material at yield, is estimated by the intersection of the $\sigma$-axis and the Mohr circle tangent to the yield locus in the point and passing through the origin of the axis.

The solution script was coded in the MATLAB software, using the Graphical User Interface Design Environment (GUIDE) and a specific MATLAB App was created. The app, named cYield, is freely downloadable and available for use in every MATLAB environment at `uk.mathworks.com/MATLAB central/fileexchange/60998-cyield`. Figure 3.3 and Figure 3.4 present the code structure and the view of the Graphical User Interface (GUI). There are three sub-
processes within the general code process, identified by the push button bearing the corresponding names:

1. **Linear YL** – It generates a linear yield locus, the related consolidation Mohr circle and unconfined yield Mohr circle starting from experimental data.

2. **Warren-Spring** – It generates the curved yield locus, the consolidation Mohr circle and the unconfined yield Mohr circle starting from experimental data.

3. **Compare** – It compares the results obtained by the two previous approaches.

![Figure 3.3 - GUI general view](image-url)
Figure 3.4 - Structure of the general code process

Figure 3.5 and Figure 3.6 report the structure of the two yield loci regression sub-processes procedures. Each sub-process needs all the sets of experimental couples made by the \((\sigma, \tau)\) shear data points and \((\sigma_{\text{pre}}, \tau_{\text{pre}})\) pre-shear data points. These values are used as input data for the sub process that returns the main bulk flow properties and the statistics data as output. In particular, the coefficient of determination (R-squared), the root-mean-square error (RMSE) and the Pearson’s coefficient are reported as statistical indexes of the fitting process.

As discussed earlier, the fitting procedure for the Warren-Spring yield locus is more complex than the linear case, and data from linear fitting are used as starting point for the analysis.

A similar approach to the one presented above was proposed by Peleg et al. [133]. They realised an interactive software for calculating the principal stresses of compacted cohesive powders with the Warren-Spring equation. In their application, however, they forced the contact point between the yield locus with the major Mohr circle to be coincident with the pre-shear representing point \((\sigma_{\text{pre}}, \tau_{\text{pre}})\). Instead, in this work, the pre-shear representing point \((\sigma_{\text{pre}}, \tau_{\text{pre}})\) is considered to belong to the yield locus only in the case in which the resulting model value for the yield locus \(\tau\) at \(\sigma_{\text{pre}}\) is larger than the experimental value \(\tau_{\text{pre}}\). Such an approach is well described by Salehi et al. [214] and it is also highlighted in Figure 3.5 and Figure 3.6 where hyphenated lines report the repeated procedure applied in case the above mentioned condition on \(\tau_{\text{pre}}\) is met.
Figure 3.5 – Linear YL sub-process structure
Figure 3.6 – Warren-Spring sub-process structure
3.2 MULTI-COMPONENT SYSTEMS

3.2.1 MIXTURES PROPERTIES

Table 3.4 reports the compositions and some physical properties of the systems of ternary mixtures that have been investigated in this work. Two different systems have been obtained by mixing synthetic rutile or natural rutile with titania slag and pet coke. Each system was then investigated by varying the pet coke sizes, since coal particles, and in particular fines, are prone to promote sintering at high operative temperature leading to poor mixing and segregation. Three distinct subsystems were then considered on the basis of the pet coke particle sizes. Specification and nomenclature are reported in Table 3.4. The ratio between the mean diameter of the pet coke and the rutile component is also reported. It is worth noting that the size ratios are similar for both the investigated systems.

Table 3.4 – Ternary mixtures investigated

<table>
<thead>
<tr>
<th>System</th>
<th>Subsystem</th>
<th>General Ref.</th>
<th>Composition [wt.%]</th>
<th>( \rho_b ) [kg/m³]</th>
<th>( \frac{d_{PC}}{d_{RUT}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST</td>
<td>M</td>
<td>STM</td>
<td>SR, TS, SPC</td>
<td>1630</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>STL</td>
<td>SR, TS, LPC</td>
<td>1530</td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>STS</td>
<td>SR, TS, SPC</td>
<td>1760</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>STM</td>
<td>SR, TS, MPC</td>
<td>1590</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>STL</td>
<td>SR, TS, LPC</td>
<td>1530</td>
<td>25.4</td>
</tr>
<tr>
<td>NT</td>
<td>M</td>
<td>NTM</td>
<td>NR, TS, SPC</td>
<td>1760</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>NTL</td>
<td>NR, TS, LPC</td>
<td>1680</td>
<td>23.8</td>
</tr>
</tbody>
</table>

The choice of using a fixed composition (i.e. 45% wt. rutile, 30% slag material and 25% pet coke) was made upon suggestion of Venator in order to make it consistent with the composition used during the real industrial process.

3.2.2 COKE COMBUSTION AND SINTERING TESTS

Early stages of the sintering process were experimentally simulated in the fluidization rig described in the section 3.3. The effects of high temperature and air flowrate were investigated systematically in different fluidization regimes:

1. Below minimum fluidization conditions
2. Close to incipient fluidization conditions
3. In well-fluidized bed conditions.
For each fluidization regime, the bed was firstly filled with 3 kg of mixture and then fluidized at a high superficial gas velocity for 15 minutes in order to ensure it was perfectly mixed. Afterwards, the fluidizing gas was shutoff and the fundamental fluidization tests were carried out (namely minimum and complete fluidization velocities, bed expansion and collapse tests) according to the procedures described in sections 3.3.1.1, 3.3.1.2 and 3.3.1.3.

The bed was then heated up to 500 °C using nitrogen as fluidizing agent in order to avoid any combustion reactions during this stage. Such a temperature value was chosen because it is above the small and medium coke ignition temperature and close to the large coke one, according to the experimental outcomes proposed by Mi et al. [215]. A timing factor was also taken into account as the experimental setup required around 4 hours to reach 500 °C from ambient conditions.

At this point, the gas feed was switched to air and the flowrate adjusted to the desired testing value. After 50 minutes the air flow was shutoff and the system let cooling down to ambient conditions. Time evolutions of pressure drop and temperatures were monitored and recorded on a computer. In particular, the temperatures inside the bed, outside the reactor and below the disengaging area were recorded as illustrated in Figure 3.9. Typical temperature profile recorded inside the bed during the entire experimental test is reported in Figure 3.7.

Fundamental fluidization tests were also carried out on the spent systems and compared to the fresh ones. The reactor was then emptied and the aggregates collected for characterization and further examinations.

Figure 3.7 - Typical schematic temperature profile inside the bed during sintering test
3.2.3 AGGREGATES CHARACTERIZATION

The technique used for the assessment of the mechanical and chemical properties of the lumps of aggregated particles collected after combustion are illustrated in this section.

The mechanical strength of the aggregates was measured in terms of friability, i.e. their tendency to break into smaller pieces under stress. Following the procedure proposed by Turchiuli et al. [216], the friability was measured as the time for the aggregates to break by passing through a 4.5 mm sieve during shaking on a vibration plate (*Endecotts Minor* with electromagnetic drive motion and fixed wave amplitude to ~ 1.6 mm). A sieve with a nominal aperture size of 4.5 mm has been used in order to ensure the sifting of every single particle, including the large coke particles that are up to 4 mm in diameter.

The presence, the size and the chemical composition of sintered bridges among particles were inspected by Scanning Electron Microscope (SEM) and Energy Dispersion X-ray (EDX) analysis. The latter is an analytical technique used for the elemental analysis and chemical characterization of the materials. It is based on an interaction between the X-ray excitation and the material sample and its working principle is based on the fact that each element has a unique atomic structure corresponding to a unique set of peaks on its electromagnetic emission spectrum. By reading the resulting spectrum it is then possible to measure the elemental composition of the analysed specimen.

In this work, SEM/EDX magnification and analysis on the aggregates have been performed by Venator R&D division of Duisburg, Germany.

3.3 FLUIDIZATION TESTS AND EXPERIMENTAL RIG

The experimental rig used for this study was designed by Prof. Paola Lettieri and then built and commissioned at BP Chemicals Ltd, Sunbury for a previous PhD study on the influence of temperature on the flow behaviour of Group A particles [79]. The fluidized reactor and the associated instrumentation, i.e. piping, valves and controllers, are mounted together on a wheeled trolley, see Figure 3.8.
A 14.6 cm diameter x 100 cm tall Inconel vessel with a wall thickness of 3mm is used for testing the powders at ambient pressure and for temperatures up to 950°C. The wall thickness was chosen to be as low as possible to reduce the amount of X-ray absorption by the material of the vessel. The vessel is fitted with a very fine (i.e. pore size of 20µm) stainless steel sintered distributor plate to ensure a high pressure drop and therefore a good and even fluidization in the bed. The Inconel plenum chamber below the distributor plate (also known as windbox) has a height of 150mm and packed with several 10mm ceramic balls to improve heat transfer. A 2.5 kW powered preheater (10 cm diameter x 30.5 cm length) is installed on the gas feeding line; it is able to provide an operating temperature up to 500 °C.

Figure 3.8 – Experimental Rig and X-ray facility (rear view on the right side and front view on the left side).

The upper disengaging section fitted on top of the vessel is made of stainless steel, 50 cm height with a freeboard diameter of 25 cm. A 3.8 cm diameter stainless steel pipeline is connected to the top centre of the disengaging section,
through flanges, to vent the fluidizing gas out of the bed. To reduce the loss of any elutriated fine material a removable stainless steel filter is installed on the vent line inside the disengaging section. The filter is a cylinder having 5mm diameter holes on the surface, around which a 45 μm stainless steel mesh is wrapped twice. The fine material which escaped from the system was eventually recovered in a filter bag fitted at the other end of the vent line.

A second 38.1mm diameter stainless steel pipeline is connected to the disengaging section on the side, and acted as a pressure relief valve. Any pressure built up in the fluidized bed is released, through this pipeline, into a stainless steel cylindrical tank (170 cm tall x 13 cm diameter) containing water. This container is filled with water to give a pressure drop of 150 cm H_2O (14.7 kPa), the maximum pressure drop across the fluidized bed was about 70 cm H_2O (6.9 kPa). A schematic drawing of the system is presented in Figure 3.9, for a detail flow and control diagram please refer to [79].

![Schematic drawing of the fluidization rig](image)

**Figure 3.9 – Schematic layout of the fluidization rig**

Fluidizing gas, air or nitrogen, is measured with rotameters before being preheated while passing through the preheater and the windbox section, which is wrapped with 800 W heating tape. High temperatures in the vessel are achieved
and maintained by means of two flexible ceramic heaters wrapped around the vessel, and capable of providing an operating temperature up to 1250°C. The two ceramic heaters cover 90 cm of the vessel height. Since this material is not transparent to X-rays, they are fitted to leave a vertical window, 7 cm wide, on both sides of the vessel, to let X-rays through. The hot surfaces are perfectly insulated using two layers of 1.5 cm thick super-wool, covered by a 7 cm thick layer of rockwool wrapped with silver tape.

A Rosemount, Model 1151, differential pressure transducer is used to measure the pressure drop profile as a function of the fluidizing gas velocity to determine the experimental minimum fluidization velocity. A system of thermocouples allows temperature monitoring in various spots of the system, including inside and outside the reactor, the windbox and the feeding line. Indicators for temperatures in the bed, high temperature alarms, bed pressure drop, are displayed on a panel external to the electrical control box and directly linked to a data acquisition board (DAQ) that enables real time information to be visualised and recorded on a computer. A specific software application was developed on purpose in the LabVIEW environment (National Instrument).

Two solenoid valves are fitted on the rig: SV1, for cutting the air supply to the bed, and SV2, for venting the air trapped in the windbox section. The inlet valve SV1 is installed on a 3.8 cm pipeline connecting the rotameters to the windbox. The outlet valve SV2 is installed on a 3.8 cm pipeline connecting the vent line to the bottom of the windbox. Such a system of solenoid valves is used during bed collapse experiments and it is operated remotely from outside the room hosting the fluidized bed. The two valves have been synchronized to guarantee a simultaneous operation: when the fluidizing gas is shut off by closing valve SV1, SV2 is opened allowing trapped gas in the windbox to be vented.

### 3.3.1 Fluidization Tests

#### 3.3.1.1 Minimum and Complete Fluidization Velocity

The minimum and complete fluidization velocity, namely $u_{mf}$ and $u_{cf}$ were obtained in this study from the diagrams of the pressure drop profile across the bed over the fluidizing gas velocity. The fluidizing gas flowrate, air or nitrogen,
was controlled via calibrated rotameters and the bed pressure drop recorded through a DAQ board connected to a pressure transducer.

The pressure drop profiles were determined by firstly increasing the gas flow rate until the bed was entirely fluidized and then by decreasing the flow rate until the bed was completely settled down: the so-called “fluidization” and “defluidization” curves were then plotted.

The experimental minimum fluidization velocity was determined from the intersection of the horizontal fully fluidized bed line and the inclined packed bed line, obtained when decreasing the gas flow rate, as shown in Figure 3.10 where a typical pressure drop profile for Geldart group A and B powders is shown. The experimental complete fluidization velocity was determined from the “defluidization” curve as the first velocity value at which the plateau in the pressure drop is reached. Measurements were repeated at least three times in order to verify the reproducibility and the consistency of the outcomes.

![Diagram showing pressure drop profiles](image)

Figure 3.10 – Typical pressure drop for a Geldart group A and B powders

The experimental pressure drop profile represents a powerful tool to discriminate between powders in terms of cohesiveness and flowability. For systems that are easy to fluidize, and which are free from any dominant effect of interparticle forces, the experimental pressure drop at minimum fluidization conditions should be equal to the predicted one, $\Delta P_c$. The latter is calculated
according to Eqn (3.6), where M is the bed material weight, g is the gravitational acceleration and XSA is the cross-section area occupied by the material.

\[ \Delta P_c = \frac{M g}{XSA} \]  

(3.6)

Minimum bubbling velocity, \( u_{\text{mb}} \), was determined as the velocity at which the first bubble appearance was visualised by means of the X-ray technique (that also corresponds to the maximum bed height of the homogeneous expansion). However, this method did not appear very reliable because of the poor contrast generated by the particulate materials employed. For this reason experimental values of \( u_{\text{mb}} \) are not presented in this thesis.

### 3.3.1.2 Bed Expansion and Bed Voidage

Bed expansion profiles were obtained using the X-rays imaging technique described in section 3.4. The bed height \( H \) was recorded for both fluidization and defluidization stages and plots of \( H \) versus \( u \) were therefore produced for increasing and decreasing gas velocities. From each bed height the corresponding bed voidage \( \varepsilon \) was evaluated considering the particle density \( \rho_p \) and the reactor cross sectional area XSA by means of Eqn.(3.7):

\[ \varepsilon = 1 - \frac{M}{XSA \rho_p H} \]  

(3.7)

In addition, voidage was also calculated from the optical computer-aided analysis of X-ray frames and by following the methodology reported in section 3.4.2.

### 3.3.1.3 Bed Collapse Tests

In the present work, the bed collapse tests were run using the system of two solenoid valves (dual-drainage method) described in details in the introduction to section 3.3. When the solenoid valves operate simultaneously, the fluidizing gas trapped in the windbox section is vented out as the gas supply to the bed is cut off. This method ensures measurements of correct values for the dense phase voidage and velocity, as highlighted by Park et al. [217]. Moreover, by using the dual-drainage configuration, the measured parameters do not need any correction due to gas leakage from the windbox, as suggested by some researchers for the single-drainage method [199,218].
3.4 X-ray Technique and Image Analysis

The X-ray system is a non-intrusive analysis tool which can provide a detailed insight into the flow patterns and general hydrodynamic characteristics of multiphase systems, as long as a sufficiently powerful radiation dose is used.

X-rays are electromagnetic waves generated using an X-ray tube, namely a vacuum tube across which electrons released from a hot cathode are accelerated by means of an imposed high voltage. High-energy photons are then released due to collisions of the high velocity electrons with the anode.

The X-ray facility used in this work and described below is available in the Department of Chemical Engineering at University College London. It has been widely used for both academic and industrial works to assess the flow phenomena and fluid-particle interactions in dense multiphase systems, to study the bubble dynamics, and to investigate how the operative conditions influence the reactor performance, efficiency and scale-up.

The analysis of the X-ray images provides data that allows quantifying the bed height, the average fluid-bed voidage and the voidage distribution around bubbles. The detailed analysis of bubble dynamics and bubble hold-up, along with expansion and de-aeration profiles can be performed as well.

3.4.1 X-ray Facility

The X-ray equipment is housed in a radiation proof room which contains the X-ray tube (1) and the image intensifier (2) mounted on a twin column ceiling suspension unit (3), see Figure 3.8 and Figure 3.11. The suspension unit allows the columns to be moved along the length of the room. Each column can be moved in the horizontal plane to adjust the distance between the tube and image intensifier, and in the vertical plane either independently or synchronized as a pair. The motion is motorized and can be remotely controlled from outside the room.

The X-ray generation system has been specially design by Genvolt Ltd., Bridgnorth - UK and it is capable to provide high-energy cone-shaped pulsed X-ray beams down to 200µs width with an intensity of up to 450mA at a voltage variable from 50kV to 150kV.
Figure 3.11 - X-ray facility: source and image intensifier

The system enables to record images with a frequency of up to 72 frames per second (fps) and to capture details with high resolution, visualizing objects smaller than 100 microns. Such a system is coupled to a special rotating anode X-ray source with a capacity of up to 1 million heat units and 68kW peak loading, which allows several minutes of operation.

The X-ray pulses are synchronised with an image detecting device (Image intensifier + Video Camera) and pass through the reactor vessel as schematically show in Figure 3.12. X-rays passing through a solid material are attenuated by processes of absorption, scattering and reflection. The extent of the attenuation is strongly dependent on the chemical nature of the solid and on the quantity of material layers in the path of the beam.

The image capturing device is a standard 30cm Industrial X-ray Image Intensifier and it consists of a scintillator input window, a photocathode, electron optics, a luminescent screen and an output window. The image intensifier is able to detect and amplify the radioactive beam emerging from the vessel, which is then converted into a grayscale image and recorded by a 1024 x 1024 pixel high-speed charge coupled device (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 fps. 8-bit digital images are then sent optically to a workstation for storage and analysis. Both the X-ray source and the intensifier come with motorised X-ray masking (or shutters) to ensure the best quality images and reduce the level of scattering.
The voltage applied between the anode and the cathode determines the acceleration of the electrons, and therefore the energy spectrum of the X-ray beams. The voltage needs to be chosen adequately for each system depending on its geometry and the physical characteristics of the materials present. Low voltages might result in poor-quality images as the X-ray beam will have insufficient power to penetrate the column and the bed of particles. On the other hand, extremely high voltages might lead to poor-contrast images, with consequential lack of details, due to insufficient attenuation of the X-ray beam. The brightness and the resolution of the images also depend on the applied current, which is characterized by the amount of electrons hitting the anode.

Figure 3.12 - Schematic of the X-ray Imaging Technique and the fluid bed system
3.4.2 **IMAGE RECORDING AND ANALYSIS**

The images captured by the video camera are displayed and stored on a computer using a custom version of the *SPS iX-Control* software. The software allows the acquisition, the display and the general handling of the frames, as well as the images post-processing and images play back up to 72 fps in either real time or frame by frame. It comes with an extensive set of analysis tools that allows also the off-line data analysis and measurements.

Furthermore, different algorithms for image analysis were developed and implemented in *MATLAB*. In particular, the collected raw images need to be post-processed in order to be able to perform any quantitative hydrodynamic analysis. Among all, the main factors that need to be considered are:

- **Pincushion distortion.** Due to the intrinsic curvature of the X-ray image intensifier and to the diverging conical shape of the X-ray beam (as shown in Figure 3.13) that introduce a non-linear magnification across the image. The image magnification increases with the distance from the optical axis. The visible effect is that lines that do not pass through the centre of the image are bowed inwards, towards its centre.

- **Penumbra formation at the edge of the image.** Due to the limited size of the focal spot, that is defined as the area of the anode on which electrons impinge. The smaller is the focal spot, the smaller will be the penumbra (and then the better will be the image resolution). However, it is important to note that there is a trade-off between obtaining a small focal spot and the X-ray power, since concentrating a high power beam into a small area may lead to the anode melting.

Such factors can be manipulated by acting on object-to-intensifier distance (OID) and source-to-intensifier distance (SID), see Figure 3.13. In particular, the pincushion distortion can be reduced by decreasing OID and increasing SID, as well as the size of the penumbra can be reduced by increasing SID.

The values of current and voltage employed in this specific analysis were chosen on the basis of visual inspection of the images for fluidized beds operating at different superficial gas velocities: 140kV voltage and 300 mA current.
To correct the image pincushion distortion, a global correction method applying a barrel distortion with an appropriate distortion parameter has been employed to each single image [219, 220]. The script used is available online at the MathWorks authorized “File Exchange” portal [221] and it required the knowledge of a distortion parameter that depends on the specific source-to-intensifier distance and object-to-intensifier distance. Considering the geometry of the system, a perforated plate with holes of 2 mm diameter arranged on a 10 mm square pitch was used as system to calibrate and get the pincushion distortion parameter [222].

Source-to-intensifier and object-to-intensifier distances were also chosen (SID = 80 cm, OID = 15 cm) in order to optimize the quality/intensity of the resulting images by limiting the effects of pincushion distortion and penumbra formation.

![Figure 3.13-Top view of the X-ray Imaging Technique and the fluid bed system](image)

The basic procedure adopted for the images analysis is reported in Figure 3.14, where two X-ray raw images of a reactor filled with natural rutile powder are used as examples: one for the settled bed and one for a well-fluidized bed. Examples of pincushion correction are also shown, with a grid highlighting the correction effects. The settled bed image are usually used to calibrate the distances. To this end, a square lead marker (1x1 cm) has been placed to a known height and then used as reference by determining the settled bed height. A region of interest (ROI) is then accurately selected in order to include all the parts of the system needed for the subsequent analysis.
Figure 3.14 – Examples of basic images analysis procedures

Figure 3.15 – Examples of image processing: bed height and voidage distribution.
Specific scripts for quantitative analysis of bed height, average fluid-bed voidage and voidage distribution, as well as of the frames from bed collapse tests, have been developed by using different built-in MATLAB functions. An open access Java package, called MIJ [223], was also used in order to link MATLAB potentialities with a more advanced imaging software, namely ImageJ/Fiji [224]. The scripts are reported and briefly explained in the appendix of this thesis.

Figure 3.15 reports examples of images analysis starting from the selected ROI. For the bed height calculation each gray-level frame is firstly reduced to a binary image by using the MATLAB / MIJ inbuilt feature based on Otsu's method [225,226]. Such a feature allows to automatically perform adaptive clustering-based image thresholding. The binary images are then segmented in order to easily distinguish the interface between particles bed and freeboard. The values of the two areas identified by the boundary interface are measured by implementing the inbuilt feature MIJ.RUN (“ANALYSE PARTICLES/AREAS…”). These values are then used to calculate the bed height starting from the already known fixed bed conditions, namely the fixed bed height, $H_s$, and the area occupied by the particles bed, $A_s$, according to Eqn. (3.8). This method also allows to take into account the possible irregularities of the boundary lines obtained from the processed images.

$$H = H_s \frac{A_f}{A_s} \quad (3.8)$$

With particular regard to the bed voidage evaluation, the procedure extendedly reported by Yates and co-workers [25,227–231] has been used. Such a procedure is based on the Beer–Lambert relationship between the attenuation of X-ray beam and the resulting image intensity:

$$I = I_0 e^{-\mu_m c L} \quad (3.9)$$

where $I$ represents the transmitted intensity, $I_0$ the incident intensity, $\mu_m$ the attenuation coefficient of the particulate material, $c$ its concentration and $L$ the path length of the X-ray beam. Eqn. (3.9) can be expanded to its linear form since the second and higher order terms in the exponential may be neglected. Such an approximation was justified by Yates et al. to be accurate with a linear correlation coefficient of 0.997 [25,227,230,231].

$$I = I_0 - I_0 (\mu_m c L) \quad (3.10)$$
Since the attenuation of X-rays by ambient air is negligible, the concentration, \( c \), can be expressed in terms of the solids fraction of the fluidized bed through which the beam passes, considering \( \varepsilon \) as the average voidage of the bed material along the path length.

\[
I = I_0 - I_0 \mu_m (1 - \varepsilon)L \tag{3.11}
\]

Once a reference image of the packed bed with known voidage is acquired, the average voidage corresponding to each path length can be obtained [229]. Eqn. (3.11) applied to the packed bed image provides the coefficient \( \mu_m L \) for the specific particulate material, which can then be used to obtain the voidage for the spatial gray-scale intensity distribution associated with each snapshot.
4 MONO-COMPONENT SYSTEMS RESULTS

This chapter reports on the experimental results of rheological and fluidization tests performed on all the mono-component powders. At first, the analytical results in terms of chemical composition, SEM and thermal analyses are presented. The characterization of the single materials laid the basis for a better understanding of the behaviour of the powders when operated in the fluidized bed reactor, as well as their performance when mixed together. Rheological experimental results are then critically analysed in order to assess the macroscopic bulk flow properties of the tested materials. Two different theoretical models are proposed and implemented with the aim to relate the measured properties to the microscopic interparticles forces acting on the system. Finally, the results from fluidization tests are reported and discussed in order to link the observed changes in the powders’ fluidization behaviour with their rheological properties.

4.1 ANALYTICAL RESULTS

The chemical and mineralogy analysis of the titanium based materials has been performed by the supplier (Venator) and shared with University College London for the aim of this research. The results are reported in Table 4.1.

The composition of the petroleum coke is 96.7 %wt. of free carbon, 3%wt. of ash, 0.2% of moisture and 0.1% of volatiles and according to the safety data sheet attached to the material it consists of granules of calcined petroleum coke (CPC) identified by EC number 265-210-9. The European Inventory of Existing Commercial chemical Substances (EINECS) states: “it is a complex combination of carbonaceous material including extremely high molecular weight hydrocarbons obtained as a solid material from the calcining of petroleum coke at temperatures in excess of 1000°C. The hydrocarbons present in calcined coke have a very high carbon-to-hydrogen ratio” [232].
Mono-component Systems Results

Using the scanning electron microscopes presented in section 3.1.1, the surface morphology of all the fresh materials under investigation have been observed and photographs taken. SEM photographs of the synthetic, natural and slag rutile are reported from Figure 4.1 to Figure 4.3. Analysis of the synthetic rutile shows rounded particles, while irregularly angular shaped particles with flat surfaces and sharp edges can be observed for the natural and slag rutile.

Table 4.1 – Chemical analysis of the titanium based materials

<table>
<thead>
<tr>
<th>Component</th>
<th>SR %wt.</th>
<th>NR %wt.</th>
<th>TS %wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (Ti₂O₃)</td>
<td>91.0 (8.5)</td>
<td>95.0 (1.2)</td>
<td>89.5 (28.5)</td>
</tr>
<tr>
<td>FeO (Fe₂O₃)</td>
<td>4.6 (-)</td>
<td>- (1.2)</td>
<td>7.5 (-)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.3</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>MnO</td>
<td>1.1</td>
<td>0.0</td>
<td>0.4</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.2</td>
<td>0.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.3</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>-</td>
<td>0.2</td>
<td>0.2</td>
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<tr>
<td>ZrO₂</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.1 - SEM images of a synthetic rutile (SR) sample.
Figure 4.2 - SEM images of a natural rutile (NR) sample.

Figure 4.3 - SEM images of a slag (TS) sample.
Figure 4.4 reports some SEM images of a coke sample. It can be observed that the shape of the particles is quite irregular and several internal pores are clearly visible.

Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were performed by a SDT-Q600 (TA Instruments) at the University of Salerno with the aim of assessing the occurrence of phase transitions or chemical reactions in the temperature range of interest. The analysis were performed in air and nitrogen atmospheres, and the adopted temperature program ensured a linear increase of the temperature rate, 10 °C/min, from 25 °C to 1200 °C. Unfortunately, it was not possible to calibrate the heat signal for the DTA, whose response in terms of heat exchanged has to be considered qualitatively.

Figure 4.5 shows the heat flow (the continuous line) and the sample weight (the dashed line) as a function of temperature for synthetic, natural and slag rutile samples. The three materials show very similar results. The perfectly flat curve of the sample’s weight excludes the presence of significant vaporization phenomena due to phase change or chemical reactions. The heat flux curve is in the negative side of the diagram, indicating that all heat fluxes are negative and that it
corresponds to heat absorption. Phase changes should be visible with fluxes larger in modulus as negative peaks. Apart from the peak at about 100 °C corresponding to the release of small amounts of condensed water, inspection of the heat flow plot reported in the figure reveals that melting or solid phase transitions do not occur in the temperature range investigated. An increase of the required heat flux towards the sample at higher temperatures, as shown by more negative values of heat fluxes, indicates an increase of the sample heat capacity with temperature. Moreover, a weight loss lower than the 1% occurred at around 500 °C, due to the loss of moisture present in the sample. Given the very limited weight changes, a constant weight of the sample can be reasonably considered and it allows excluding the occurrence of chemical reactions (e.g. oxidation).

TGA analysis were performed also on a coke sample in nitrogen atmosphere only. The adopted temperature program ensured a linear increase of the temperature rate, 10 °C/min, from 25 °C to 950 °C. Similarly to the other materials, no important weight variations were observed.

Figure 4.5 - TGA analysis for synthetic, natural and slag rutile samples. Solid line is for heat flow and dotted line is for the weight variation.
4.2 SHEAR TESTING RESULTS AND DISCUSSION

4.2.1 EXPERIMENTAL RESULTS

The linear yield loci and the flow functions of the three tested materials at ambient and high temperatures are reported from Figure 4.6 to Figure 4.10. The main results in terms of major ($\sigma_1$) and minor ($\sigma_2$) principal stresses, consolidation stress ($\sigma_N$), angle of internal friction ($\phi_i$), cohesion (C) and tensile strength ($\sigma_t$) are listed in Table 4.2.

Table 4.2 - Results of the shear test performed with the Schulze apparatus

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>Cell Type</th>
<th>YL</th>
<th>$\sigma_1$ (Pa)</th>
<th>$\sigma_2$ (Pa)</th>
<th>$\sigma_N$ (Pa)</th>
<th>C (Pa)</th>
<th>$\phi_i$ (°)</th>
<th>$\sigma_t$ (Pa)</th>
<th>$f_c$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Rutile (SR)</td>
<td>25</td>
<td>S</td>
<td>1</td>
<td>986</td>
<td>261</td>
<td>571</td>
<td>4</td>
<td>35.2</td>
<td>5.7</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>1200</td>
<td>310</td>
<td>696</td>
<td>5</td>
<td>35.9</td>
<td>6.9</td>
<td>19</td>
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<td></td>
<td></td>
<td></td>
<td>3</td>
<td>1409</td>
<td>369</td>
<td>820</td>
<td>5</td>
<td>35.5</td>
<td>7.0</td>
<td>21</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>4</td>
<td>1633</td>
<td>431</td>
<td>944</td>
<td>6</td>
<td>35.3</td>
<td>8.5</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>HT</td>
<td>1</td>
<td>982</td>
<td>263</td>
<td>564</td>
<td>31</td>
<td>32.5</td>
<td>48.7</td>
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<td>688</td>
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<td>34.0</td>
<td>48.9</td>
<td>126</td>
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<td>1689</td>
<td>414</td>
<td>936</td>
<td>40</td>
<td>35.2</td>
<td>56.7</td>
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<tr>
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<td>603</td>
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</tr>
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<td>12.2</td>
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<td>3</td>
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<tr>
<td></td>
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<td>590</td>
<td>16</td>
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<td>61</td>
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<td>1502</td>
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<td>27.4</td>
<td>79</td>
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<tr>
<td>Titania Slag (TS)</td>
<td>25</td>
<td>S</td>
<td>1</td>
<td>1230</td>
<td>209</td>
<td>597</td>
<td>69</td>
<td>39.6</td>
<td>83.4</td>
<td>292</td>
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<td>1441</td>
<td>257</td>
<td>722</td>
<td>71</td>
<td>39.3</td>
<td>86.7</td>
<td>299</td>
</tr>
<tr>
<td></td>
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<td>1666</td>
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<td>846</td>
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</tr>
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<td></td>
<td></td>
<td></td>
<td>4</td>
<td>1917</td>
<td>353</td>
<td>970</td>
<td>82</td>
<td>39.3</td>
<td>100.2</td>
<td>348</td>
</tr>
</tbody>
</table>

The shear tests on the synthetic rutile powder were performed at low consolidation levels corresponding to major principal stresses in the range of approximately 1000–1700 Pa. The corresponding yield loci at different levels of consolidation for tests at ambient and high temperatures are reported Figure 4.6 (A) and (B), respectively. A slight change in the cohesion and therefore in the tensile strength were observed with increasing consolidation stress, both at ambient and high temperature. A slight upward shift in the yield loci was instead observed from ambient to high temperature for a given consolidation level. Such a shift corresponds to an increase of C from 5 ± 1 to about 34.8 ± 3 Pa and of $\sigma_t$ from 7 ± 1 to 51 ± 3 Pa.
The tests on the natural rutile were performed at low consolidation levels as well, which correspond to the same range for major principal stresses of synthetic rutile. The corresponding yield loci at different levels of consolidation for tests at ambient and high temperatures are reported in Figure 4.6(C) and (D), respectively. Yield loci measured at ambient and high temperatures for each level of consolidation are shown in the Figure 4.8. Also for this powder, slight changes in the cohesion and in the tensile strength were observed with increasing consolidation stress, both at ambient and high temperature. Similarly to synthetic rutile, a slight upward shift in the yield loci was observed increasing the temperature: C values increased from 10 ± 1 to about 18 ± 2 Pa and σ_s values from 12 ± 1 to 25 ± 2 Pa.

Figure 4.6 – Yield loci measured with the Schulze apparatus at ambient and high temperature and at different levels of consolidation. (A) and (B) synthetic rutile at 25 °C and 500 °C respectively. (C) and (D) natural rutile at 25 °C and 500 °C respectively. Large dots: experimental pre-shear data; other symbols: experimental shear data.
Figure 4.7 – Yield loci measured with the Schulze apparatus at ambient and high temperatures for synthetic rutile at different levels of consolidation: (A) $\sigma_1 \approx 980$ Pa, (B) $\sigma_1 \approx 1200$ Pa, (C) $\sigma_1 \approx 1400$ Pa, (D) $\sigma_1 \approx 1650$ Pa. Large dots: experimental pre-shear data; other symbols: experimental shear data.

Figure 4.8 – Yield loci measured with the Schulze apparatus at ambient and high temperatures for natural rutile at different levels of consolidation: (A) $\sigma_1 \approx 1100$ Pa, (B) $\sigma_1 \approx 1300$ Pa, (C) $\sigma_1 \approx 1500$ Pa and (D) $\sigma_1 \approx 1700$ Pa. Large dots: experimental pre-shear data; hollow symbols: experimental shear data.
With concern to the shear tests on titania slag, only tests at ambient temperature could be performed because of the larger particles size and particular shape, which prevented the measurements and did not allow the use of the high temperature annular shear cell. This was maybe caused by the comparable sizes of the particles and the bars in the lower side of the lid. The corresponding yield loci at different levels of consolidation for tests at ambient temperature are reported in Figure 4.9. Slight changes in the cohesion and in the tensile strength were observed with increasing consolidation stress.

Figure 4.9 - Yield loci measured with the Schulze apparatus at ambient and high temperature and at different levels of consolidation for titania slag sample. Filled symbols: experimental pre-shear data; other symbols: experimental shear data.

Figure 4.10 reports the flow functions of the three tested powder samples, according to Jenike’s standard form and classification. The inspection of the figure shows how the powders flowability is slightly influenced by temperature in the range explored.

Figure 4.10 – Flow functions of the three tested powders measured with the Schulze apparatus at ambient and high temperatures.
4.2.2 MODELS RESULTS

With the aim to correlate the macroscopic powder flow properties with the forces that act between the particles and to give an interpretation of the particle–particle contact mechanics, a quantitative evaluation was performed. Both theoretical models described in section 2.4.2 were implemented for this purpose.

4.2.2.1 RUMPF-MOLERUS MODELS RESULTS

The model proposed by Rumpf and Molerus and previously described was applied to the tested materials. This approach, however, showed problems related to the difficulty in identifying the accurate physical and mechanical properties of the materials at the different conditions investigated, such as the Hamaker constant, the compressive yield strength and the mean local curvature radius at the contact point.

A unique value of the Hamaker constant and of the characteristic molecular separation distance $z_0$ were instead assumed for all samples and temperatures, according to the value reported by Tomas for titanium dioxide [40]. Although, due to the thermal expansion and the thermal effects on mechanical properties of the particle material, different values of Young’s modulus $E$ [233,234], particle densities $\rho_p$ [235] and compressive yield strength $p_f$ [40,236] were adopted at 25°C and 500°C, as well as of samples porosities and bulk densities, measured during shear tests with HT-ASC. The average main materials properties adopted in the present case study are listed in Table 4.3.

With regard to the compressive yield strength $p_f$, it is necessary to consider that the local plastic deformation occurs under hindered conditions because of the surrounding material at the contact point. Hence, such a parameter is larger than the compressive yield strength usually measured under unhindered deformation conditions ($\sigma_f$) and reported in the literature. According to the theoretical works of Hencky [237] and Ishlinsky [238] and as also reported by Tomasetta et al. [160], the correct value for $p_f \approx 3 \sigma_f$ should be considered. Moreover, $\sigma_f$ values at high temperature are hard to find in the literature and the reported values are often ambiguous and controversial. As observed for similar materials [239–241], the
compressive yield strength was considered to decrease with temperature and it was estimated as:

\[ p_{T500} = \alpha p_{T25} \] (4.1)

where \( \alpha \) is a proportional constant varying in the range 0.1-1 that relates \( p_f \) at high temperature with the one at ambient temperature.

In the present case study two approaches were followed:

- at first the value for the \( p_f = 400 \) MPa at 25 °C as reported by Tomas [40] and an average values of \( \alpha = 0.6 \) were used;
- secondly, the Vickers Hardness (HV) of polycrystalline TiO\(_2\) reported by Guermazi et al. [236] as a function of temperature was considered for the compressive yield strength.

The sample porosity \( \varepsilon \) was estimated from Eqn. (4.2), using the values of particle densities (from the powders’ data sheets) and the bulk densities measured with the Schulze cell, both reported in Table 4.3.

\[ \varepsilon = 1 - \frac{\rho_b}{\rho_p} \] (4.2)

Table 4.3 - Samples main average properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [°C]</th>
<th>( \rho_p ) [kg/m(^3)]</th>
<th>( \rho_b ) [kg/m(^3)]</th>
<th>( \varepsilon ) [-]</th>
<th>( C_{H,v0} ) [10(^{-20}) J]</th>
<th>( z_0 ) [nm]</th>
<th>E [GPa]</th>
<th>ν [-]</th>
<th>( \sigma_f ) [MPa]</th>
<th>HV [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR25</td>
<td>25</td>
<td>3200</td>
<td>1500</td>
<td>0.53</td>
<td>12.6</td>
<td>0.336</td>
<td>284.2</td>
<td>0.28</td>
<td>130</td>
<td>10</td>
</tr>
<tr>
<td>SR500</td>
<td>500</td>
<td>3120</td>
<td>1385</td>
<td>0.56</td>
<td>12.6</td>
<td>0.336</td>
<td>270.8</td>
<td>0.28</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>NR25</td>
<td>25</td>
<td>4200</td>
<td>2320</td>
<td>0.45</td>
<td>12.6</td>
<td>0.336</td>
<td>284.2</td>
<td>0.28</td>
<td>130</td>
<td>10</td>
</tr>
<tr>
<td>NR500</td>
<td>500</td>
<td>4120</td>
<td>2050</td>
<td>0.50</td>
<td>12.6</td>
<td>0.336</td>
<td>270.8</td>
<td>0.28</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>TS25</td>
<td>25</td>
<td>4200</td>
<td>2160</td>
<td>0.48</td>
<td>12.6</td>
<td>0.336</td>
<td>284.2</td>
<td>0.28</td>
<td>130</td>
<td>10</td>
</tr>
</tbody>
</table>

This assessment is however affected by some inaccuracies, because of the leakage of the powder from the cell during shear testing, as observed by Tomasetta et al. [160]. This leakage may entail in an overestimation of the effective mass of the sample, and a resulting underestimation of the relevant porosity, which is calculated from the bulk density (i.e., the ratio between the initial sample mass and the current sample volume). Moreover, the estimated porosity is an averaged value and is not necessarily representative of the local porosity in the shear zone, which is more relevant to the measured stresses. In fact, powder dilation in the shear zone makes the local porosity value larger than
the sample average. However, as reported by Tomasetta et al. [160], changes in this parameter slightly affect the model results.

In order to overcome the problem of identifying the accurate value of the compressive yield strength, the following procedure was followed:

- The model was first fitted with experimental values at both ambient and high temperature to determine the mean curvature radius \( r \) (that is considered constant with temperature) at the reference properties reported in Table 4.3;
- Sensitivity analysis was then performed to assess the effect of changes in the compressive strength.

Experimental values of cohesion and angle of internal friction were used to calculate the powder tensile strength \( \sigma_t \) according to Eqn. (2.33). Such values were compared with the tensile strength values obtained with the application of the theoretical models \( \sigma_t^* \).

For each sample, the value of the mean curvature radius \( r \) that best fits the estimated tensile strengths to the experimental value was calculated for both elastic \( (r_{el}) \) and plastic \( (r_{pl}) \) deformation hypothesis. For the elastic case, the values of \( \sigma_t \) determined from experimental data were used to evaluate the adhesion forces by Eqn. (2.36). These values were then used to evaluate the mean curvature radius \( r_{el} \) at the contact point by Eqn. (2.37). For the case of plastic deformation at the contact point, the value of \( r_{pl} \) for each sample was estimated by minimizing the mean square error (MMSE method) between the tensile strength evaluated from the experimental data and the predicted values calculated by combining Eqns. (2.36) and (2.41), using data for each consolidation level.

The value for the normal consolidation force \( F_N \) in Eqn. (2.41) was estimated by Eqn. (2.42) using the normal stress for pre-shear phase as consolidation stress, i.e. \( \sigma_N = \sigma_{pre} \). This assumption permits to extend Eqn. (2.42) to a real consolidation state for stress, which is generally applied for an isostatic state of stress.

The results obtained by the application of the Rumpf-Molerus mathematical model for each material with the reference properties reported in Table 4.3 are reported in Table 4.4. They indicate an increasing mean curvature radius for the three samples, with the NR powder having the smallest value and the TS sample...
the largest one. Although they seem to agree with the features observed with the optical microscope imaging, they are dependent on both the contact model and the reference $p_f$ value.

**Table 4.4 - Mean curvature radii obtained by application of the Rumpf-Molerus model**

<table>
<thead>
<tr>
<th></th>
<th>$p_f = 400 \text{ MPa, } \alpha = 0.6$</th>
<th>$p_f = H_V \approx 10 \text{ GPa, } \alpha = 0.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR</td>
<td>SR</td>
</tr>
<tr>
<td><strong>Elastic hypothesis, $r_{el} [\mu m]$</strong></td>
<td>4.8</td>
<td>8.1</td>
</tr>
<tr>
<td><strong>Plastic hypothesis, $r_{pl} [\mu m]$</strong></td>
<td>$0.6 \times 10^{-6}$</td>
<td>$0.7 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The solution of the model for plastic deformation hypothesis was implemented by performing the MMSE analysis using the MATLAB routine `fmincon`. In this case, the problem consists in finding the value of $r_{pl}$ which corresponds to the minimum value for MSE. This problem is subjected to one constraint only: the value of the local curvature radius must be greater than zero and less than the mean particle radius, i.e. $d_{50}/2$.

The model results also confirmed the expectations on the low local curvature radii compared to the particle size. In particular for the SR powder, the curvature radius at the contact point was expected to be of the order of the particle roughness [242,243]. Results in terms of interparticle forces, tensile strength and other model parameters are reported in Table 4.5, where the values for the plastic hypothesis obtained with the two different approaches are also presented.

The tensile strength values obtained by the application of the model $\sigma_t^*$ are compared with the tensile strength values calculated from experimental data $\sigma_t$ in Table 4.6. It can be clearly seen that Rumpf-Molerus model do not fit properly with the experimental data in the cases of elastic deformation and plastic deformation hypothesis in which the value of $p_f$ proposed by Tomas is taken into account. In the first case, the discrepancy is probably due to the simplicity of the modelling equations. In fact, the related equations cannot take appropriately into account the effect of changes in consolidation load and temperature. In the second case, instead, the model shows great discrepancies with the experimental evidence, perhaps because of the wrong value of the compressive strength considered. In fact, as discussed earlier, this is one of the key parameters in the Rumpf-Molerus modelling approach and reported values at both ambient and high
temperatures are not only difficult to find but are often ambiguous and controversial. On the other hand, the model based on plastic deformation hypothesis, in which $p_f = H_V$, gives reasonable estimates of the tensile strength values at both the investigated temperatures for all the samples. These results confirmed that such a model approach might provide a correct order of magnitude relationship between experimental tensile strength and its theoretical prediction if reasonable values for the compressive yield strength and the curvature of the particle surface are taken into account.

Table 4.5 - Main results of the Rumpf-Molerus mathematical models

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F_s$ [μN]</th>
<th>Elastic hypothesis</th>
<th>Plastic hypothesis with $p_f$ from Tomas [40]</th>
<th>Plastic hypothesis with $p_f$ from Guermazi et al. [236]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F_H$ [μN]</td>
<td>$\sigma_t^*$ [Pa]</td>
<td>$\kappa_{pl}$</td>
<td>$F_0$ [pN]</td>
</tr>
<tr>
<td>SR25</td>
<td>13.99</td>
<td>0.76 30.8</td>
<td>0.79 0.115</td>
<td>11.0 449.6</td>
</tr>
<tr>
<td></td>
<td>16.54</td>
<td>0.76 31.8</td>
<td>13.0 548.1</td>
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<tr>
<td></td>
<td>19.59</td>
<td>0.76 31.6</td>
<td>15.4 645.7</td>
<td>0.55 22.9</td>
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<tr>
<td></td>
<td>22.33</td>
<td>0.76 32.0</td>
<td>17.6 743.4</td>
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<tr>
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<td>2.76 0.241</td>
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<tr>
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<td>50.3 1900.8</td>
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<td>58.9 2243.4</td>
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</tr>
<tr>
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<td>0.44 22.5</td>
<td>0.79 0.103</td>
<td>9.4 474.8</td>
</tr>
<tr>
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<td>14.17</td>
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<td>11.2 573.3</td>
<td>0.25 13.1</td>
</tr>
<tr>
<td></td>
<td>16.36</td>
<td>0.44 23.1</td>
<td>12.9 670.9</td>
<td>0.29 15.3</td>
</tr>
<tr>
<td></td>
<td>18.98</td>
<td>0.44 23.7</td>
<td>14.9 768.6</td>
<td>0.34 17.6</td>
</tr>
<tr>
<td>NR500</td>
<td>14.50</td>
<td>0.44 18.1</td>
<td>2.76 0.217</td>
<td>40.1 1630.1</td>
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<tr>
<td></td>
<td>17.33</td>
<td>0.44 18.3</td>
<td>47.9 1972.7</td>
<td>0.63 26.1</td>
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<tr>
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<td>20.06</td>
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<td>55.4 2315.3</td>
<td>0.73 30.6</td>
</tr>
<tr>
<td></td>
<td>23.29</td>
<td>0.44 18.3</td>
<td>64.4 2657.9</td>
<td>0.85 35.2</td>
</tr>
<tr>
<td>TS25</td>
<td>31.41</td>
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<td>0.79 0.980</td>
<td>24.7 470.1</td>
</tr>
<tr>
<td></td>
<td>37.12</td>
<td>4.68 91.0</td>
<td>29.2 568.5</td>
<td>4.59 89.2</td>
</tr>
<tr>
<td></td>
<td>13.99</td>
<td>4.68 91.6</td>
<td>34.0 666.2</td>
<td>4.69 91.9</td>
</tr>
<tr>
<td></td>
<td>16.54</td>
<td>4.68 92.2</td>
<td>38.8 763.8</td>
<td>4.80 94.7</td>
</tr>
</tbody>
</table>

As previously reported, the sensitivity of the model to the compressive yield strength at both ambient ($p_{f,25}$) and high temperature ($p_{f,500}$) was carried out. In particular, values for $p_{f,25}$ in the range between 0.08 and 31.6 GPa and different values for the parameter $\alpha$ in Eqn. (4.1) have been considered.

The results for the SR sample are shown in Figure 4.12 where the ratio $\sigma_t^*/\sigma_t$, i.e. the ratio between the tensile strength obtained from Rumpf-Molerus model and the one calculated from experimental data, is reported as function of the compressive yield strength. The sensitivity analysis suggests relevant effect on the
ratio $\sigma_t^*/\sigma_t$ for variations of both $p_{f,25}$ and $\alpha$. It can be seen that such a ratio is closer to 1 for values of compressive strength at ambient temperature higher than the reference ones and for values of $\alpha$ lower than 0.6. In particular, the best fitting between model and experimental data is obtained when the value of $\alpha$ is in the range 0.1 - 0.2 and if values for $p_{f,25}$ from 15 to 20 GPa are considered. Furthermore, the tensile strengths of yield loci at high temperature are less influenced by changes in $p_{f,25}$ and $\alpha$ than the ones of yield loci at ambient temperature.

Table 4.6 - Comparison of tensile strength values obtained from Rumpf-Molerus models versus values obtained from experimental data: (EL) elastic hypothesis; (PL-T) plastic hypothesis with $p_f$ value reported by Tomas [40]; (PL-G) plastic hypothesis with $p_f$ value reported by Guermazi et al. [236].

<table>
<thead>
<tr>
<th>$T$ [°C]</th>
<th>Synthetic Rutile</th>
<th>Natural Rutile</th>
<th>Titania Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_t$ [Pa]</td>
<td>$\sigma_{t,EL}$ [Pa]</td>
<td>$\sigma_{t,PL-T}$ [Pa]</td>
</tr>
<tr>
<td>25</td>
<td>5.7  30.8 449.6 18.2</td>
<td>11.0 22.5 474.8 10.8</td>
<td>83.4 89.0 470.1 85.2</td>
</tr>
</tbody>
</table>

The results for the NR and the TS samples are shown in Figure 4.13 and Figure 4.11 respectively. The sensitivity analysis suggests major effects on the tensile strength for both samples. For the natural rutile powder, the ratio $\sigma_t^*/\sigma_t$ follows similar trends as those for the synthetic rutile. The best fitting between model and experimental data is obtained when $p_{f,25}$ is in the range 10 - 20 GPa and if values of $\alpha$ from 0.30 to 0.60 are considered. On the other hand, for the titania slag powder the analysis shows a sharply decline for the ratio $\sigma_t^*/\sigma_t$ from values higher than 10 to 1 when the compressive yield strength increases from 0.08 to about 1.5. Then, for values of $p_{f,25}$ higher than 1.5 GPa there is no influence on the tensile strength.

Thus, the sensitivity analysis shows that the Rumpf-Molerus model approach might provide a good estimate for the theoretical tensile strength if a reasonable value for the compressive yield strength is taken into account. Furthermore,
considering accurate changes in $p_f$ with temperature, it can explain the temperature effects on the tensile strength observed during the experiments. In fact, a change in the adopted value of $\alpha$ (and then of $p_{f,500}$) could improve the fitting of the model data with the experimental ones for all evaluated temperatures.

Figure 4.11 - Scatter plot of the ratio between the tensile strength obtained from Rumpf-Molerus model and the tensile strength calculated from experimental data versus changes in compressive strength for TS sample: sensitivity analysis for $p_f$ at ambient temperature.
Figure 4.12 – Scatter plot of the ratio between the tensile strength obtained from Rumpf-Molerus model and the tensile strength calculated from experimental data versus changes in compressive strength for SR sample: sensitivity analysis for $p_f$ at ambient temperature (on the abscissas axis) and for $p_l$ at high temperature (graphs parametric with $\alpha$).
Figure 4.13 - Scatter plot of the ratio between the tensile strength obtained from Rumpf-Molerus model and the tensile strength calculated from experimental data versus changes in compressive strength for NR sample: sensitivity analysis for $p_f$ at ambient temperature (on the abscissas axis) and for $p_f$ at high temperature (graphs parametric with $\alpha$).
4.2.2.2 Tomas Model Results

The results obtained from the application of the mathematical model proposed by Tomas are reported in Table 4.7, in which interparticle forces, mean tensile strength and models parameters are presented.

The $\kappa$ values obtained from the application of Eqn. (2.51), as slope of the linear relationship between experimental $F_H$ and $F_N$, are also reported and compared with the values obtained from Eqn. (2.56). The material characteristic parameters of SYL that allowed the estimation of $\kappa^*$ from Eqn. (2.56) are presented as well. They were estimated combining Eqns. (2.53) - (2.55) as shown in the flowchart in Figure 4.14.

Despite the significant number of simplifying assumptions that were considered, the model gives reasonable estimates of $\kappa$ values at both investigated temperatures. It is also important to note that the estimation of $\kappa^*$ and $\sigma_t^*$ is independent of the compressive yield strength. More details about the fitting analysis on the experimental $F_H$ vs. $F_N$ data are reported in Table 4.8.

Information on the quality of the linear fit test are reported in terms of descriptive statistics such as $R^2$ coefficient, residual sum of squares (RSS) and Pearson’s coefficient.

The parameters for the evaluation of initial porosity $\varepsilon_0$ according to Eqn. (2.60) are reported in Table 4.9.

The compressibility index $n$ was estimated according to Tomas suggestions reported in Table 2.5. This index was related to the flowability assessments discussed in Table 2.6 for $\kappa$ values. In the present case study, the $\kappa$ values for all the samples are in the range of $0.01 – 0.107$, therefore a value of $n$ of 0.01 was used.
Figure 4.14 – Flowchart showing the calculation process for $\kappa^*$ and $\sigma_0$. 

- **Input data:**
  - experimental $f_c$
  - experimental $\sigma_1$

- Diagram $f_c$ vs. $\sigma_1$

- **Experimental $\Phi_i$**

- **Intercept $f_{c0}$**

- **Initial estimate:**
  - $\sigma_0 = \sigma_1$
  - $\Phi_{st} = \Phi_i/2$

- **Solution of system of Eqs. (2.53) and (2.55)**

- $\sigma_0$

- $\Phi_{st}$

- $\kappa^* = \frac{\tan(\Phi_{st})}{\tan(\Phi_i)} - 1$

- $\kappa^*$
### Table 4.7 - Main results of the Tomas mathematical models

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F_N$ [nN]</th>
<th>$\kappa$ [-]</th>
<th>$F_{H0}$ [nN]</th>
<th>$F_H$ [nN]</th>
<th>$\sigma_1$ [Pa]</th>
<th>$\phi_{st}$ [°]</th>
<th>$\sigma_0$ [Pa]</th>
<th>$\sigma_{M,st}$ [Pa]</th>
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</thead>
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<tr>
<td>SR25</td>
<td>13987</td>
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<td>26</td>
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<td>16543</td>
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<td>25</td>
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<td>0.91</td>
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### Table 4.8 - Output data from linear fitting

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<tr>
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<th>Slope</th>
<th>Statistics</th>
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<tr>
<td>Value</td>
<td>Stand. Error</td>
<td>Value</td>
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<td>4.74E-08</td>
<td>2.72E-08</td>
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<td>1.89E-07</td>
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<tr>
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<td>7.96E-08</td>
</tr>
<tr>
<td>TS25</td>
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<td>2.63E-07</td>
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</tbody>
</table>

### Table 4.9 - Valuation of bulk powders initial conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [°C]</th>
<th>$\kappa$ value</th>
<th>n</th>
<th>$\epsilon_0$ [-]</th>
<th>$\rho_{b,0}$ [kg/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Rutile</td>
<td>25</td>
<td>0.010</td>
<td>0.01</td>
<td>0.56</td>
<td>1398</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.048</td>
<td>0.01</td>
<td>0.57</td>
<td>1336</td>
</tr>
<tr>
<td>Natural Rutile</td>
<td>25</td>
<td>0.013</td>
<td>0.01</td>
<td>0.47</td>
<td>2207</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.022</td>
<td>0.01</td>
<td>0.52</td>
<td>1965</td>
</tr>
<tr>
<td>Titania Slag</td>
<td>25</td>
<td>0.068</td>
<td>0.01</td>
<td>0.50</td>
<td>2103</td>
</tr>
</tbody>
</table>
Figure 4.15 shows the comparison between the tensile strength values obtained by the application of the model and the experimental values. Even though the model seems to overestimate the tensile strength value by 20%, quite a good match is reached between model and experimental values.

![Parity plot of tensile strength values](image)

Figure 4.15 – Parity plot of tensile strength values obtained from Tomas model versus values obtained from experimental data.

The κ values were also evaluated according to Eqn. (2.52) and reported in Table 4.10, along with the calculated displacement $h_c$. To this end, the coefficients $\kappa_P$ and $\kappa_A$ were estimated by Eqns. (2.46) and (2.47) and material properties reported in Table 4.3. The calculation process for $\kappa^{**}$ and $h_c$ is schematically shown in the flowchart in Figure 4.16.

As for Rumpf-Molerus model, the Tomas approach for the calculation of the deformation displacement is strongly dependent on the value of the compressive yield strength considered. In the present analysis, both Tomas [40] and Guermazi et al. [236] approaches for $p_f$ were firstly considered, while a sensitivity analysis on such parameters was then carried out.

The sensitivity analysis on the elastic-plastic consolidation coefficient as function of $p_{f,25}$ for materials at ambient temperature is reported in Figure 4.17, while the effects of $p_{f,25}$ and $\alpha$ on $\kappa^{**}$ for materials at high temperature are instead described in Figure 4.18.
As shown in Figure 4.17, the sensitivity analysis for the samples at ambient temperature suggests relevant effect on the consolidation coefficient for variations of \( p_{f,25} \). It shows that \( \kappa^{**} \) is closer to \( \kappa^* \) and \( \kappa \) when values of compressive strength different from the reference ones are used. In particular, for SR and NR, the best fitting is achieved if values of \( p_{f,25} \) higher than 18 GPa are considered; while for TS, the best fitting is obtained when \( p_{f,25} \) is considered to be in the range 2-5 GPa.
### Table 4.10 - First evaluation of $\kappa^\ast$ values according to Eqn. (2.52)

<table>
<thead>
<tr>
<th>Sample</th>
<th>YL</th>
<th>$p_t$ from Tomas [40]</th>
<th>$p_t$ from Guermazi et al. [236]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\kappa_P$</td>
<td>$\kappa_A$</td>
</tr>
<tr>
<td>SR25</td>
<td>1</td>
<td>0.441</td>
<td>0.726</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.441</td>
<td>0.737</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.441</td>
<td>0.748</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.441</td>
<td>0.757</td>
</tr>
<tr>
<td>SR500</td>
<td>1</td>
<td>0.734</td>
<td>0.872</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.734</td>
<td>0.877</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.734</td>
<td>0.882</td>
</tr>
<tr>
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<td>4</td>
<td>0.734</td>
<td>0.886</td>
</tr>
<tr>
<td>NR25</td>
<td>1</td>
<td>0.441</td>
<td>0.705</td>
</tr>
<tr>
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<td>2</td>
<td>0.441</td>
<td>0.718</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.441</td>
<td>0.728</td>
</tr>
<tr>
<td></td>
<td>4</td>
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<td>1</td>
<td>0.734</td>
<td>0.865</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.734</td>
<td>0.871</td>
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<tr>
<td></td>
<td>3</td>
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<td>4</td>
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<td>0.880</td>
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<tr>
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<td>0.441</td>
<td>0.742</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.441</td>
<td>0.753</td>
</tr>
<tr>
<td></td>
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<tr>
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<td>4</td>
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<td>0.770</td>
</tr>
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</table>

**Figure 4.17 – Sensitivity analysis on $\kappa^\ast$ as function of $p_t$**

---

**Mono-component Systems Results**
The results for the SR and the NR at high temperature suggest major effects on the elastic-plastic consolidation coefficient for variations of both $p_{f,25}$ and $\alpha$. The sensitivity analysis shows that the coefficient $\kappa^{**}$ follows the same trend in both cases regarding changes of $p_{f,25}$ and $\alpha$: it decrease with increasing compressive yield strength and $\alpha$ values.

However, the best fitting between the values of the three consolidation coefficients depends on the material used. In the case of synthetic rutile, the analysis shows different matches between $\kappa^{**}$ and $\kappa^{*}$ and between $\kappa^{**}$ and $\kappa$ in relation to the values of $p_{f,25}$ and $\alpha$ considered. In particular, the match between $\kappa^{**}$ and $\kappa^{*}$ ranges from 4 to 20 GPa for $p_{f,25}$ and from 0.2 to 1 for $\alpha$. Whereas, the
match between $\kappa^{**}$ and $\kappa$ is achieved for $p_{f,25} = 10 - 30$ GPa and $\alpha = 0.4 - 1$. On the other hand, for the natural rutile the analysis suggests as best match with $\kappa^*$ $p_{f,25} = 8 - 30$ and $\alpha = 0.3 - 1$; and with $\kappa p_{f,25} = 15 - 30$ and $\alpha = 0.5 - 1$.

Therefore, as similar as to the theoretical model proposed by Rumpf and Molerus, the sensitivity analysis shows that the Tomas modelling approach might provide good estimates for the consolidation coefficient and theoretical tensile strength, if reasonable values for the compressive yield strength are taken into account. Moreover, the changes in $p_f$ with temperature might explain the temperature effects observed during the experiments. In fact, a change in the adopted values of $p_f$ and $\alpha$ could improve the fitting of the model data with the experimental ones for all the evaluated temperatures.

### 4.2.3 Experimental and Modelling Analysis using the Warren-Spring Approach

The experimental results were analysed with the help of the MATLAB App presented in section 3.1.2.3. Table 4.11 reports the main flow properties (namely, cohesion $C$, unconfined yield strength $f_c$ and major principal stress $\sigma_1$) obtained for the SR and NR samples at the various consolidation levels. They are presented as function of the yield locus model and the operating temperature. Moreover, values of the extrapolated isostatic tensile strength $\sigma_{t,EXP}$ and of the Warren-Spring coefficient $n$ are reported as well.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (°C)</th>
<th>Pre-Shear Load (g)</th>
<th>Linear Yield Locus</th>
<th>$C$ (Pa)</th>
<th>$f_c$ (Pa)</th>
<th>$\sigma_1$ (Pa)</th>
<th>$\sigma_{t,EXP}$ (Pa)</th>
<th>$C$ (Pa)</th>
<th>$f_c$ (Pa)</th>
<th>$\sigma_1$ (Pa)</th>
<th>$\sigma_{t,EXP}$ (Pa)</th>
<th>$n$ (-)</th>
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<td>0.2</td>
<td>1266</td>
<td>0.01</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>17.72</td>
<td>70.5</td>
<td>1502</td>
<td>23.9</td>
<td>0.07</td>
<td>0.5</td>
<td>1510</td>
<td>0.04</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>700</td>
<td>18.76</td>
<td>74.0</td>
<td>1726</td>
<td>25.6</td>
<td>0.15</td>
<td>0.8</td>
<td>1730</td>
<td>0.11</td>
<td>1.07</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.19 and Figure 4.20 present some examples of the application of the MATLAB App for both the linear and the curved cases. They allow visualizing the differences between the two yield locus models and the related flow properties. Figure 4.21 reports the flow functions for all the samples, in which the results obtained with the two different model yield loci are compared.

Figure 4.19 – Top side: SR25 with pre-shear load 500g; Bottom side: SR500 with pre-shear load 600g.
Figure 4.20 – Top side: NR25 with pre-shear load 500g; Bottom side: NR500 with pre-shear load 600g.

The flow function of the material is significantly affected by the choice of the yield locus model because of the significantly different values of the cohesion and of the resulting unconfined yield strength due to the extrapolation of the curve towards the \( \tau \) axis. Also the comparison between the values of the extrapolated tensile strength \( \sigma_t \) shows great differences in the two cases. It has to be recognized that the extrapolation in the traction plane of the yield locus is a rather strong assumption as it is not possible to consider shear data in the traction half-plane. Indeed, such an extrapolation does not necessarily reflect the reality, as it may estimate an incorrect value of the tensile strength: in the case of linear yield locus such a value is typically overestimated, while the use of the Warren Spring equation leads to considerable low - and in some cases even unrealistic [162] -
values of $\sigma_t$. However, in this case, the estimated ones using the Warren Spring equation seem to be quite unreasonable, probably because of the low cohesive nature of the selected samples.

![Figure 4.21 – Comparison between the flow functions evaluated with the two different model yield loci](image)

In order to analyse the quality of the experimental outcomes from a statistic point of view, the values of the coefficient of determination ($R^2$) and of the root-mean-square error (RMSE) are reported in Figure 4.22: similar quality of the descriptive statistical analysis was observed in the two cases as the values of $R$-square and RMSE were comparable.

![Figure 4.22 – $R^2$ and RMSE values for the investigated samples](image)
The Rumpf-Molerus theoretical model earlier described was implemented with the aim to correlate the macroscopic powder flow properties to the forces acting among particles in the microscopic scale.

The main materials properties adopted in the present case study are listed in Table 4.3. Due to the difficulties in finding consistent values of the compressive yield strength \( p_f \) in the literature, the values suggested in the sensitivity analysis performed earlier were considered: \( p_f = 15 \text{ GPa} \) for SR and NR at 25 °C, \( p_f = 3 \text{ GPa} \) for SR at 500 °C and \( p_f = 6 \text{ GPa} \) for NR at 500 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [°C]</th>
<th>FN [μN]</th>
<th>( r_{pl} ) [-]</th>
<th>( r_{pl} ) [μm]</th>
<th>( F_0 ) [μN]</th>
<th>( F_H ) [μN]</th>
<th>( \sigma_{t,MOD} ) [Pa]</th>
<th>( r_{pl} ) [μm]</th>
<th>( F_0 ) [μN]</th>
<th>( F_H ) [μN]</th>
<th>( \sigma_{t,MOD} ) [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR</td>
<td>25</td>
<td>13.99</td>
<td>0.012</td>
<td>0.185</td>
<td>7.5</td>
<td>0.166</td>
<td>6.8</td>
<td>15.09</td>
<td>0.030</td>
<td>0.492</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>16.54</td>
<td>0.215</td>
<td>10.5</td>
<td>8.4 x10^4</td>
<td>0.942</td>
<td>35.2</td>
<td>14.17</td>
<td>0.012</td>
<td>0.427</td>
<td>23.29</td>
<td>0.758</td>
</tr>
<tr>
<td></td>
<td>19.59</td>
<td>0.251</td>
<td>12.0</td>
<td>1.137</td>
<td>0.197</td>
<td>8.3</td>
<td>16.36</td>
<td>0.012</td>
<td>0.427</td>
<td>23.29</td>
<td>0.758</td>
</tr>
<tr>
<td></td>
<td>22.33</td>
<td>0.284</td>
<td>12.0</td>
<td>1.137</td>
<td>0.233</td>
<td>9.8</td>
<td>18.98</td>
<td>0.012</td>
<td>0.427</td>
<td>23.29</td>
<td>0.758</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>15.09</td>
<td>0.062</td>
<td>0.961</td>
<td>1.156</td>
<td>43.7</td>
<td>8.3 x10^3</td>
<td>0.019</td>
<td>1.349</td>
<td>20.06</td>
<td>0.660</td>
</tr>
<tr>
<td></td>
<td>18.22</td>
<td>1.156</td>
<td>51.4</td>
<td>8.3 x10^3</td>
<td>1.330</td>
<td>50.7</td>
<td>17.33</td>
<td>0.030</td>
<td>0.577</td>
<td>17.33</td>
<td>0.577</td>
</tr>
<tr>
<td></td>
<td>21.31</td>
<td>1.534</td>
<td>59.2</td>
<td>8.3 x10^3</td>
<td>1.515</td>
<td>58.4</td>
<td>20.06</td>
<td>0.030</td>
<td>0.577</td>
<td>17.33</td>
<td>0.577</td>
</tr>
<tr>
<td></td>
<td>24.28</td>
<td>1.534</td>
<td>59.2</td>
<td>8.3 x10^3</td>
<td>1.515</td>
<td>58.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td>25</td>
<td>11.91</td>
<td>0.012</td>
<td>0.194</td>
<td>9.8</td>
<td>0.142</td>
<td>7.2</td>
<td>14.17</td>
<td>0.012</td>
<td>0.427</td>
<td>23.29</td>
</tr>
<tr>
<td></td>
<td>16.36</td>
<td>0.221</td>
<td>12.8</td>
<td>9.3 x10^4</td>
<td>0.195</td>
<td>10.1</td>
<td>18.98</td>
<td>0.012</td>
<td>0.427</td>
<td>20.06</td>
<td>0.660</td>
</tr>
<tr>
<td></td>
<td>17.33</td>
<td>0.278</td>
<td>14.3</td>
<td>9.3 x10^4</td>
<td>0.226</td>
<td>11.6</td>
<td>20.06</td>
<td>0.030</td>
<td>0.577</td>
<td>17.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>14.50</td>
<td>0.030</td>
<td>0.492</td>
<td>20.0</td>
<td>0.439</td>
<td>17.9</td>
<td>20.06</td>
<td>0.030</td>
<td>0.577</td>
<td>17.33</td>
</tr>
<tr>
<td></td>
<td>20.06</td>
<td>0.660</td>
<td>27.6</td>
<td>8.9 x10^3</td>
<td>0.607</td>
<td>25.4</td>
<td>23.29</td>
<td>0.035</td>
<td>0.758</td>
<td>23.29</td>
<td></td>
</tr>
</tbody>
</table>

Experimental values of shear and normal stresses were used to estimate the powder tensile strength for the linear yield locus case and the curved one according to Eqns. (2.33) and (2.34) respectively. For each sample, the value of \( r_{pl} \) that best fits the estimated tensile strengths to the experimental value was calculated. It was estimated by minimizing the mean square error (MMSE method) between the tensile strength evaluated from experimental data and the values calculated for each consolidation level by combining Eqns. (2.36) and (2.41). The MATLAB routine \texttt{fmincom} was used to perform the MMSE analysis with the aim of finding the value of \( r_{pl} \) which corresponds to the minimum value for MSE. In fact, since the radius of the contact point is a geometrical parameter of the material particles it should be independent of both the consolidation load.
and of the system temperature. Only two constraints on the possible value of $r_{pl}$ were set. Namely these were: 1) the value of the local curvature radius needed to be positive and 2) it had to be lower than $d_{so}/2$.

The results obtained by the application of the Rumpf-Molerus mathematical model in terms of interparticle forces, tensile strength and other model parameters for each material are reported in Table 4.12 where they are named $\sigma_{t,\text{MOD}}$. The same table reports the corresponding values of $r_{pl}$ for each material and each yield locus model used to extrapolate $\sigma_{t,\text{EXP}}$. The tensile strength values obtained by the application of the model $\sigma_{t,\text{MOD}}$ are compared with the tensile strength values calculated from experimental data $\sigma_{t,\text{EXP}}$ in Figure 4.23.

Figure 4.23 - Parity plot of tensile strength values obtained from Rumpf-Molerus model versus values obtained from experimental data.

In the case of linear yield locus and for each of the two tested materials, it is clearly shown that it is possible to find a single value of $r_{pl}$ that gives reasonable estimates of tensile strength values at both investigated temperatures and at all the tested consolidation conditions. Instead, in the Warren-Spring case, in spite of the possibility to change the value of $r_{pl}$, even the best fitting value of this parameter provides values of $\sigma_{t,\text{MOD}}$ greatly differing from the corresponding values of $\sigma_{t,\text{EXP}}$. This finding might perhaps be due to the unsuitable value for the compressive strength considered that, as already discussed above, represents a key factor for
the Rumpf-Molerus modelling approach. Unfortunately, there is not a better estimate to date of the compressive strength than the values adopted in the calculation.

These results suggest that a simple linear Coulomb yield locus might deliver an estimate of the experimental tensile strength with the correct order of its theoretical prediction based on the particle contact mechanics. Moreover, the results confirm that non-cohesive powders, such as the tested ones, do not exhibit curved yield loci towards lower shear stresses; therefore the Warren Spring yield locus model might lead to inaccurate results if used to extrapolate data towards zero or even negative normal stresses.

4.2.4 SUMMARY OF THE SHEAR TESTS

Experimental examinations with a Schulze shear cell were carried out in order to assess the rheological behaviour of the materials at ambient conditions and with increasing temperature. Shear experiments highlighted a significant increase of the unconfined yield strength with temperature, which means that a higher force is required to deform or break the material when it is not confined by a container. From the particulate material perspective, it means that a higher force is required to fail a consolidated mass of material to initialize flow. This resulted in a lower flowability of the samples.

Theoretical models based on the particle–particle approaches of Rumpf and Molerus and of Tomas were used to correlate the isostatic tensile strength of powders with the interparticle interaction forces. The comparison between experiments conducted at ambient and high temperatures and the theoretical model suggests that the proposed approaches give correct predictions for the tensile strength if the proper values for the material physical and mechanical properties, in particular for the compressive yield strength, are used at both ambient and high temperature. In fact, as highlighted by the sensitivity analysis, different values for \( p_f \) may yield a better fit between experimental data and predictions.
4.3 Fluidization Results and Discussion

Previous chapters have outlined how the operating temperature may affect the flow behaviour of solid particles. In particular, shear-testing experiments highlighted a significant increase of unconfined yield strength with temperature, which means that a higher force is required to deform or break the material when it is not confined by a container. From the particulate material perspective, it means that a higher force is required to fail a consolidated mass of material to initialize flow. This resulted in a lower flowability of the samples.

In this chapter, the fluidization results carried out on the same materials and at the same temperatures of the shear experiments are reported and discussed. The aim of this work was to provide a better understanding of the factors responsible for changes in the fluidization behaviour between ambient and high temperature, highlighting the conditions under which either HDFs or IPFs dominate and control the fluidization behaviour.

4.3.1 Pressure Drop Measurements

The minimum and complete fluidization velocities were measured at ambient and high temperature (500 °C) for the three titanium ores components, namely synthetic rutile (SR), natural rutile (NR) and slag (TS). In order to guarantee a good mixing of particles, the bed material was fluidized in bubble regime for around 20 minutes before making any measurement. As described in section 3.3.1.1, the fluidization curves were obtained from measurements of the pressure drop profiles across the bed in experiments with increasing gas velocity first and with decreasing gas velocity then. Coke material exhibited a spouting behaviour and it made the pressure drop measurements impossible to perform. The signal was too noisy and instable due to the irregular mixing of the particles. This behaviour is typical for Geldart Group D (and boundary B/D) particles, which coke materials belong to.

The pressure drops profiles from Figure 4.24 to Figure 4.26 are plotted for each sample at the different operative temperatures as the ΔP_m/ΔP_c ratio, where ΔP_m is the experimentally measured pressure drop and ΔP_c is the calculated pressure drop when full bed support is achieved, as defined by Eqn. (3.6).
Figure 4.24 – Pressure Drop profiles for SR sample at ambient and high temperature

Figure 4.25 – Pressure Drop profiles for NR sample at ambient and high temperature

Figure 4.26 – Pressure Drop profiles for TS sample at ambient and high temperature
The minimum fluidization velocities obtained along with the related voidage values \( \varepsilon_{mf} \) are reported in Table 4.13. \( u_{mf} \) values show a decreasing trend with increasing temperature for all materials, in agreement with findings in literature [4,77]. The complete fluidization velocities \( (u_{cf}) \), the initial settled bed heights \( (H_s) \) and the related voidage \( (\varepsilon_s) \), calculated from Eqn. (3.7), are reported as well. For all the powders investigated in this work, the voidage of the settled bed was not affected by the temperature in a significant way; this was in disagreement with the findings reported by Botterill et al. [101] and Raso et al. [104] regarding the increases with temperature of voidage of the settled bed \( (\varepsilon_s) \) for Group A and B materials.

It is worth mentioning that, as reported in section 3.3, the fluidizing gas is measured with rotameters before being preheated while passing through the preheater and the windbox. Therefore, the notable variations of the pressure drops curves from ambient to high temperature reported from Figure 4.24 to Figure 4.26 are also due to the changes, with the increase of the temperature, of the physical properties of the fluidizing gas. Indeed, if an isobaric process without chemical reaction is assumed, the increment in volume of an ideal gas is directly proportional to the increment of the temperature.

### Table 4.13 – Experimental results from fluidization curves

<table>
<thead>
<tr>
<th>Sample</th>
<th>( u_{mf} ) (cm/s)</th>
<th>( \varepsilon_{mf} ) (-)</th>
<th>( u_{cf} ) (cm/s)</th>
<th>( H_s ) (cm)</th>
<th>( \varepsilon_s ) (-)</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Rutile (SR)</td>
<td>2.3 0.6 0.560 0.572 3.0 1.2 12.5 12.7 0.552 0.560 0.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Rutile (NR)</td>
<td>2.7 0.9 0.470 0.483 5.1 1.8 15.8 16.0 0.460 0.467 0.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slag (TS)</td>
<td>5.3 2.0 0.482 0.506 14.0 4.2 9.4 9.7 0.470 0.487 0.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The experimental \( u_{mf} \) values were compared with predictions obtained from some of the correlations reported in section 2.3.1, namely:

- Carman correlation, Eqn. (2.16)
- Wu and Baeyens correlation, Eqn. (2.23)
- Wen and Yu correlation, Eqn. (2.28)
- Ergun correlation, Eqn. (2.13)

In the Carman and Ergun correlations, the experimental values of \( \varepsilon_{mf} \) were used and the particle sphericity \( \phi \) of each powder was back-calculated from the Ergun equation using the experimental values of \( u_{mf} \) and \( \varepsilon_{mf} \) at ambient conditions, as
suggested by Knowlton [73] and later applied by Lettieri et al. [74,79] and Bruni et al. [14] to different materials fluidized at high temperature. The values of $\phi$ so obtained and reported in Table 4.13 were then kept constant for higher temperatures. The results are reported in Figure 4.27 and they show a good match between the experimental and the predicted data.

Figure 4.27 – Comparison between experimental and predicted $u_{mf}$ values with increasing temperature.
4.3.2 BED EXPANSION AND BED VOIDAGE

The bed material was at first vigorously fluidized to allow good mixing of the particles, then the gas flow rate was slowly decreased until the bed settled. The expansion profiles were obtained by slowly increasing the gas velocity at first and by slowly decreasing it afterwards. Recordings of the bed height at various gas velocities were performed by means of X-ray facility. At each gas velocity the bed was allowed to stabilize before recording the X-ray images. The bed expansion and bed voidage profiles were obtained at ambient and high temperature (500 °C) for the three titanium ores components according to what reported in sections 3.3.1.2 and 3.4.2.

Bed expansion and bed voidage profiles are reported in Figure 4.28 in terms of deviation from the settled bed height (Hs). The profiles obtained for all the three materials showed similar characteristics: at ambient conditions expansion is significantly lower and the deviation from fluidization to defluidization stage is less evident.

Differently to what reported by Lettieri [79] and Bruni [14] in similar investigations on Geldart A type powder, the bed expansion profiles do not level off to a certain height value. This suggests that the powders used for this study easily reach conditions of slugging or turbulent regime, in line with the characteristic of sand-like Group B materials.

A comparison between the expansion profiles of the SR sample for the two tested temperatures is shown in Figure 4.29, which reports the normalised deviation from the settled bed height (similar to the bed expansion rate, BER, defined by Eqn. (2.70)) as function of the gas velocity. Expansion appeared to change as a function of temperature, in particular the rate of expansion increased with increasing the operating temperature. Similar results have been obtained for NR and TS samples. The effect of temperature on the bed expansions for such powders is shown in Figure 4.30 and Figure 4.31 respectively.

Similarly to what reported for the influence of temperature on the pressure drop measurements, it is important to mention that also the bed expansion curves are affected by the temperature dependence of the fluidising gas physical properties.
With regards to the bed voidage, this was also calculated from the optical computer-aided analysis of the X-ray frames according to the methodology presented in section 3.4.2. The fluidization maps obtained from the snapshots of the fluidized beds at different gas velocity for SR, NR and TS samples at both ambient and high temperatures are reported from Figure 4.32 to Figure 4.34. 72 X-ray frames (i.e. 2 seconds of recording) have been used for every single snapshot.

It is important to point out that, due to the limited size of the window left between the ceramic heaters (7cm wide), the voidage distribution in the x-direction has been considered constant and only variations in the y-direction have been reported. This approach allows the analysis of the axial bed voidage.
distribution for the different fluidization regimes, from settled conditions to a fully fluidised bed. As already reported, it can be also helpful to investigate on possible dead zones in the reactor and the bubble distribution within the bed. However, the physical characteristics of the particles (high density) caused a large attenuation of the X-ray beam, reducing the contrast of the image produced. This prevented a more detailed analysis of the structure of the bed, i.e. visualising the bubbles formation, the bubbled size, etc. For these reasons, the X-ray parameters have been set to enhance the quality of the images around the boundary between the particles bed and the freeboard. From the following figures, it can be seen how the voidage in the bed/freeboard boundary region matches with the average values reported in Figure 4.28.
Figure 4.29 – Effect of temperature on bed expansion for SR sample

Figure 4.30 - Effect of temperature on bed expansion for NR sample

Figure 4.31 - Effect of temperature on bed expansion for TS sample
Figure 4.32 – Fluidization maps of the bed at different gas velocity for SR samples at ambient (SR25) and high temperature (SR500).
Figure 4.33 – Fluidization maps of the bed at different gas velocity for NR samples at ambient (NR25) and high temperature (NR500).
Figure 4.34 – Fluidization maps of the bed at different gas velocity for TS samples at ambient (TS25) and high temperature (TS500).
4.3.3 **BED COLLAPSE TESTS**

The bed collapse technique was used as quantitative test for the characterization of the aeratability of the tested powders at both ambient (25 °C) and high (500 °C) temperature. The parameters presented in the section 2.4.3 have been determined from experimental data and discussed in this section.

4.3.3.1 **INITIAL GAS VELOCITY CHOICE**

The influence of the initial fluidizing velocity \( u_i \) on the bed collapse profiles has been investigated for both the operating temperatures. For each sample, different initial gas velocities were used. Such values were determined by considering different gas excess fluidizing gas velocity from minimum fluidization, according to the following equation:

\[
 u_i = (1 + \nu)u_{mf}
\]

where \( \nu \) represents the excess percentage and it has been varied between 0.25 and 3.5. In order to compare the collapse parameters obtained for the various samples with each other, the same values of gas excess were employed in this work. This allows us to operate in similar fluidization regimes and then to produce meaningful and comparable results. The values used for the operating gas velocities are summarised in Table 4.14.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( u_{mf} )(cm/s)</th>
<th>0.25</th>
<th>0.50</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
<th>3.00</th>
<th>3.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR25</td>
<td>2.3</td>
<td>2.9</td>
<td>3.5</td>
<td>4.6</td>
<td>5.8</td>
<td>6.9</td>
<td>9.2</td>
<td>10.4</td>
</tr>
<tr>
<td>SR500</td>
<td>0.6</td>
<td>0.8</td>
<td>0.9</td>
<td>1.2</td>
<td>1.5</td>
<td>1.8</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>NR25</td>
<td>2.7</td>
<td>3.4</td>
<td>4.1</td>
<td>5.4</td>
<td>6.8</td>
<td>8.1</td>
<td>10.8</td>
<td>12.2</td>
</tr>
<tr>
<td>NR500</td>
<td>0.9</td>
<td>1.1</td>
<td>1.4</td>
<td>1.8</td>
<td>2.3</td>
<td>2.7</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td>TS25</td>
<td>5.3</td>
<td>-</td>
<td>8.0</td>
<td>10.6</td>
<td>13.3</td>
<td>15.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TS500</td>
<td>2</td>
<td>-</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.35 shows the bed collapse profiles of the SR sample obtained at ambient temperature for different initial fluidizing gas velocities ranging from 2.9 to 10.4 cm/s, i.e. for values increased by the 25 to 350% more than the minimum fluidization velocity. In the figure, the bed height is plotted against the operating time in seconds. The negative values of time indicate the moment before the fluidizing gas is suddenly shut off.
It can be qualitatively observed that the bed collapse parameters are affected by the initial gas velocity: apart from the obvious initial height value, also the rate of the sedimentation stage increased with increasing gas velocity. Results obtained for SR sample at high temperature are shown in Figure 4.36, in which similar outcomes can be observed.

The experimental data were fitted by means of the following mathematical relationship between bed height and time:

\[
H = \frac{H_0 - H_s}{1 + e^{t/t_B}} + H_s
\]  

(4.4)

where \(H_0\) and \(H_s\) are the initial and the settled bed height respectively, \(t_c\) is the time at which the bed start to consolidate (from a mathematical prospective it is the inflection point of the function) and \(\tau_B\) is a time constant. More details about the fitting analysis will be discussed in the next section.

![Figure 4.35](image)

Figure 4.35 – Collapse profiles at 25 °C for SR sample at different initial gas velocities
The same technique was used also on the other two material, i.e. the NR and TS sample at both ambient and high temperature. The results were very similar to the ones obtained for the SR samples and they are plotted from Figure 4.37 to Figure 4.40.
Figure 4.38 - Collapse profiles at 500 °C for NR sample at different initial gas velocities

Figure 4.39 - Collapse profiles at 25 °C for TS sample at different initial gas velocities
4.3.3.2 Bed collapse test parameters and discussion

The output parameters from non-linear fitting of the experimental data through Eqn. (4.4) are reported in Table 4.15 for the three investigated materials at different initial gas velocities and operating temperatures.

Information on the quality of the fit test are also reported in terms of descriptive statistics, such as $R^2$ coefficient and residual sum of squares (RSS). According to the findings, i.e. values of $R^2$ close to 1 and low values of RRS, the chosen model give an accurate fitting of the experimental data.

The overall collapse rate ($U_c$), the bed expansion ratio (BER) and the standardised collapse time (SCT) were determined from the bed collapse profiles according to what reported in section 2.4.3 for Geldart Group B particles. In particular, $U_c$ was analytically determined as the slope of the sharp sedimentation curve. The values of the three parameters are summarised in Table 4.16 for the three investigated materials at the different operating conditions.
### Table 4.15 - Eqn. (4.4) fittings parameters for all the samples

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Table 4.16 – Collapse parameters

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In Figure 4.41, the trends of the three parameters at both ambient and high temperature are plotted for the SR sample. It can be observed that in all the cases $U_c$ and BER increase with increasing the initial gas velocity, but with some differences between ambient and high temperature. The overall collapse rate ($U_c$) does not seem to be strongly affected by the operating temperature for low initial gas velocities (low decreases have been observed in these cases), whereas it decreases by an average 45% for the higher gas velocities. However, the trend of $U_c$ is in agreement with the Abrahamsen and Geldart [199] correlation for the dense phase collapse rate, Eqn. (2.17), which predicts a slower collapse rate as temperature rises. On the other hand, the bed expansion ratio (BER) does not show significant changes with the operating temperature for all the initial gas velocities investigated.

Similar trends for $U_c$ and BER parameters are observed for the NR samples with respect to both the initial gas velocity and the operating temperature, as reported in Figure 4.42. The trend observed for the SCT is instead very interesting as, in both cases, it significantly increases with increasing temperature for low initial gas velocities, whereas the deviation attenuates for higher velocities. This means that an increase in temperature improves the ability to retain aeration gas
when the fluidization gas velocity is less than $2xu_{mf}$. Therefore, unlike $U_c$ and BER, the SCT showed to be more sensitive to changes in operating conditions. This behaviour might indicate a more important role of the IPFs in fluidization regimes close to the incipient conditions.

Figure 4.41 – Effect of temperature on the collapse parameters for SR sample

Figure 4.42 – Effect of temperature on the collapse parameters for NR sample
In order to support the physical interpretation of the collapse tests, as well as to better understand the role played by the IPFs during the bed collapses, the dimensionless Bond number ($Bo$) is introduced. Such a number, also known as Eötvös number ($Eo$), is usually used in fluid dynamics for measuring the importance of the interparticle forces over the gravitational forces. Valverde et al. [127] defined the granular Bond number for packed beds ($Bo$) as the ratio of interparticle van der Waals force $F_{vdW}$ to particle weight $F_g$:

$$Bo = \frac{F_{vdW}}{F_g}$$  \hfill (4.5)

The outcomes from shearing tests, reported in section 4.24.1, were used for defining $F_{vdW}$ according to Rumpf–Molerus theory [51], whereas the particle weight $F_g$ was evaluate as follows:

$$F_{vdW} = \frac{\sigma \varepsilon^2}{1 - \varepsilon}$$  \hfill (4.6)

$$F_g = \frac{\pi}{6} \rho_p g d_p^3$$  \hfill (4.7)

However, it is important to point out that the interparticle forces have been determined in a fixed bed condition, i.e. a condition in which the particles are in a consolidation state far different from the one in a fluidised system. To this end, the degree of dispersion of the system should be taken into account in the IPFs estimation and a modified Bond number $Bo^*$ can therefore be defined as follows.

$$Bo^* = \frac{NC F_{vdW}}{F_g}$$  \hfill (4.8)

where NC is the coordination number of the particles bed at the initial fluidization conditions and the isostatic tensile strength $\sigma_0$ of the unconsolidated powder, that is a reasonable estimation of the consolidation conditions inside a fluidized bed, is used for defining $F_{vdW}$. The coordination number NC, defined as the number of contacts of a given particle with the surrounding particles, has been calculated as $NC \approx \frac{\pi}{\varepsilon}$ [244,245].

The modified Bond number can be useful to estimate the importance of to the interparticle forces over the hydrodynamic forces in a fluidized particles bed at different fluidization conditions. Table 4.17 reports the values of the calculated dimensionless $Bo^*$ and $Bo_s$ numbers. The latter is the Bond number calculated for the fixed bed. The two values are compared to the SCT results from bed collapse...
tests in Figure 4.43 for SR and NR samples. It can be observed that the greater the deviation of $\text{Bo}^*$ from $\text{Bo}_s$, the smaller is the variation of SCT with temperature. This means that when the system is more dispersed (i.e. higher fluidization velocity) the IPFs have a lower effect on the fluidization behaviour.

Table 4.17 – Bond number estimations for settled and fluidized beds

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</tr>
</tbody>
</table>

Furthermore, it can be observed that the time constant $\tau_B$ from fitting analysis reported in Table 4.15 is slightly affected by the initial fluidization conditions, suggesting that it might be a specific property of the powder, although it seems to be temperature dependent.

Figure 4.43 – Comparison of SCT values to the deviation of $\text{Bo}^*$ from $\text{Bo}_s$.

Figure 4.44 presents the collapse parameters for TS sample at both ambient and high temperature. They are in line with what observed for the others powders, but
the SCT variations for low initial gas velocities are less marked than the previous cases. Because of the missing rheological properties of TS sample for high temperature, this material has been excluded from the discussion on the link between fluidization and rheological findings for the investigation of the relative role of IPFs over HDFs.

Figure 4.44 - Effect of temperature on the collapse parameters for TS sample

### 4.3.4 SUMMARY OF THE FLUIDIZATION TESTS

The results obtained from the fluidization tests showed a typical Group B behaviour, in particular:

- aggregative fluidization (bubbles form once the gas velocity exceeds the minimum fluidization velocity);
- relatively small bed expansion and bed expansion profiles that do not level off to a certain height value;
- bed collapse curve showing a sharp sedimentation stage and then a very fast deaeration rate.

The bed collapse test was found to be a discriminating technique, able to highlight the changes in the powders’ aeratability with temperature. For all the materials tested, the overall collapse rate \( U_c \) and the bed expansion ratio (BER)
increased with increasing the initial gas velocity, but with some differences between ambient and high temperature. \( U_c \) does not seem to be strongly affected by the operating temperature for low initial gas velocities, whereas it decreases by 45% on average for the higher gas velocities. Instead, BER does not show significant changes with the operating temperature for all the initial gas velocities investigated.

On the other hand, the standardised collapse time (SCT) showed to be very sensitive to the changes in operating conditions: initial gas velocity and related bed expansion in particular. SCT increased significantly with increasing temperature for low initial gas velocities, whilst such a deviation decreased at higher velocities. This suggested that higher temperature improves the ability to retain aeration gas only when the fluidization gas velocity was less than \( 2x u_{mf} \).

4.4 CHAPTER REMARKS

This chapter reported on the experimental results obtained from rheological and fluidization tests performed on all of the mono-component powders. The findings for each of the materials investigated laid the basis for a better understanding of the behaviour of the powders when operated in the fluidized bed reactor, as well as their performance when mixed together (that will be investigated in the next chapter).

Experimental shear tests’ results were critical to assess the macroscopic bulk flow properties of the materials tested. These were related to the microscopic interparticles forces by means of two different theoretical models. Shear experiments, carried out at ambient and with increasing temperature, highlighted a significant increase of the unconfined yield strength with increasing temperature, which meant that the flowability of the samples lessened.

The results from fluidization tests were discussed in order to link the observed changes in the powders’ fluidization behaviour with their rheological properties. All the powders showed a typical Group B behaviour: aggregative fluidization, small bed expansion and bed collapse curve showing a sharp sedimentation stage.
The results from the bed collapse test were related to the rheological behaviour of the materials tested; the dimensionless Bond number (Bo, which is commonly used in fluid dynamics for measuring the importance of the interparticle forces over the gravitational forces) was used to support the physical interpretation of the results. The standardised collapse time (SCT) showed to be the most sensitive parameter obtained from the bed collapse test to the changes in both the initial gas velocity and the operating temperature. SCT increased significantly with increasing temperature for low initial gas velocities, whilst such a deviation decreased at higher velocities. This suggested that higher temperature improves the ability to retain aeration gas only when the fluidization gas velocity was less than a certain value (namely twice \( u_{mf} \)). This behaviour was explained as a function of the role played by the IPFs, enhanced by the increasing temperature, on the fluidization regimes close to incipient conditions. The analysis showed that the greater the deviation from the settle bed conditions, the less the variation in SCT with temperature, meaning that the IPFs had a lower effect on the fluidization behaviour at higher fluidizing velocities.
5 Multi-component Systems Results

In this chapter the results obtained on the multi-components systems are reported. At first, the results of the fundamental fluidization tests for each fresh mixture are presented and discussed. Then, the outcome from the experimental study of the early stages of the sintering process are analysed by systematically investigating the effect of high temperature, air flowrate and coke particle size distribution for different fluidization regimes. The results of the fundamental fluidization tests and bed collapse test on the spent mixtures (i.e. the mixtures resulting after combustion processes) are reported and compared to the fresh ones.

Detailed information on the characterization of the aggregates found in the spent mixtures are reported in section 5.3.2, where the SEM/EDX analysis and the friability tests results are presented and discussed. Special attention has been paid to the analysis of the sintered bonds observed between particles.

5.1 Fundamental Fluidization Tests on Fresh Mixtures

The so-called “fluidization” and “defluidization” curves were obtained by measuring the pressure drop profiles across the bed at different superficial gas velocities as described in section 3.3.1.1. In order to guarantee a good mixing of particles, the bed material was fluidized in bubble regime for around 20 minutes before making any measurement.

The measured minimum \( (u_{mf}) \) and complete \( (u_{cf}) \) fluidization velocities for all the fresh mixtures at both ambient and high temperature (500 °C) are reported in Table 5.1. Because of the complexity of the mixtures analysed, the procedure for determining the minimum fluidization velocity from pressure drop measurements, as presented in section 3.3.1.1, was found not to be reliable. As shown in Figure 5.1 and Figure 5.2, the pressure drop curves presented in some cases more than
Multi-component systems results

one slope in the packed bed regime; this prevented to find the intersection between the horizontal fully fluidized bed line and the inclined packed bed line. In order to overcome this problem, X-rays were used for estimating the minimum fluidization velocity by means of visual analysis of the images on a frame by frame basis and noting the velocity at which the first bubble was seen to break the bed surface.

The pressure drop profiles shown in Figure 5.1 and Figure 5.2 are plotted for each fresh mixture for 25 and 500 °C as the ΔP_m/ΔP_c ratio, where ΔP_m is the experimentally measured pressure drop and ΔP_c is the calculated pressure drop when full bed support is achieved, as defined by Eqn. (3.6). As expected, both the minimum and the complete fluidization velocities decreased with increasing temperature, in line with the results for the mono-component systems. Significant hysteresis were observed when fluidizing and defluidizing the bed both at ambient temperature and at 500 °C. In particular, the pressure drop in the packed bed region showed a fluctuating trend, indicating a certain difficulty of the mixtures to achieve complete fluidization. However, full bed support (i.e. ΔP_m/ΔP_c = 1) was eventually reached at both temperatures.

Table 5.1 – Experimental results from fluidization curves for fresh mixtures

<table>
<thead>
<tr>
<th>System</th>
<th>Mixture</th>
<th>u_mf (cm/s)</th>
<th>u_cf (cm/s)</th>
<th>ΔH_{MAX} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25 °C 500 °C</td>
<td>25 °C 500 °C</td>
<td></td>
</tr>
<tr>
<td>ST</td>
<td>STS-0</td>
<td>7.1 1.8</td>
<td>8.0 2.5</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>STM-0</td>
<td>10.6 2.5</td>
<td>10.0 3.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>STL-0</td>
<td>14.1 2.8</td>
<td>17.0 6.0</td>
<td>11.0</td>
</tr>
<tr>
<td>NT</td>
<td>NTS-0</td>
<td>10.8 2.6</td>
<td>15.5 3.5</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>NTM-0</td>
<td>13.0 3.0</td>
<td>16.5 4.0</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>NTL-0</td>
<td>13.8 4.0</td>
<td>16.0 5.2</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Bed expansion was investigated at ambient temperature by implementing the same procedure used for mono-component systems (see sections 3.3.1.2 and 4.3.2 for further information). Figure 5.3 and Figure 5.4 report the absolute bed heights for ST and NT fresh mixtures at different superficial gas velocities; measurements were performed by decreasing the gas velocity from well-fluidized conditions to complete settling. In all the cases, the bed expansion profiles do not level off to an exact height value and the maximum expansion registered is strongly dependent
on the particle size of the coke present in the mixture. This decreases with increasing coke size either when synthetic or natural rutile is used. A maximum increase equal to or greater than 20% is observed when small and medium coke is used, whereas it drops drastically when large particles of coke are used, namely to 11% for the STL mixture and to 13.5% for the NTL mixture.

Figure 5.1 – Pressure drops profiles for ST fresh mixtures at ambient and high temperature
Multi-component systems results

An important difference can be observed between the mixtures containing the synthetic rutile and those containing natural rutile with regards to achieving complete fluidization. The latter are not as sensitive as the former to the change in the coke particles size: the values of $u_{cf}$ for the NT mixtures are indeed very similar.

![Graph showing pressure drops profiles for NT fresh mixtures at ambient and high temperature](image)

Figure 5.2 - Pressure drops profiles for NT fresh mixtures at ambient and high temperature
Figure 5.3 – Bed expansion profiles for ST fresh mixtures at ambient temperature
Figure 5.4 – Bed expansion profiles for NT fresh mixtures at ambient temperature
5.2 COKE COMBUSTION TESTS RESULTS

The early stages of the sintering process were experimentally simulated according to the procedure reported in section 3.2.2. In particular, the effect of high temperature and air flowrate were investigated systematically at three different fluidization regimes, close to and well above the minimum fluidization conditions, as reported in Table 5.2.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Suffix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh mixtures</td>
<td></td>
</tr>
<tr>
<td>• see Table 3.4 for composition</td>
<td>-0</td>
</tr>
<tr>
<td>Spent mixture after test with air flowrate below minimum fluidization conditions</td>
<td>-1</td>
</tr>
<tr>
<td>• $u_{air} = 0.5x u_{mf}$</td>
<td></td>
</tr>
<tr>
<td>Spent mixture after test with air flowrate close to incipient fluidization conditions</td>
<td>-2</td>
</tr>
<tr>
<td>• $u_{air} = 0.5x (u_{mf} + u_{cf})$</td>
<td></td>
</tr>
<tr>
<td>Spent mixture after test with air flowrate in well-fluidized bed conditions</td>
<td>-3</td>
</tr>
<tr>
<td>• $u_{air} = 2x u_{cf}$</td>
<td></td>
</tr>
</tbody>
</table>

The temperature and pressure drop profiles recorded inside the bed during the coke combustion operations are reported from Figure 5.5 to Figure 5.11. The first three figures refer to the ST mixtures with coke having different particle size distribution: small (STS), medium (STM) and large (STL) respectively. The operating time was set to 50 minutes in order to keep the temperature within the rig below the maximum temperature allowed for safe operations, 1100 °C.

The temperature reached within the bed is strongly dependent on the air flowrate as this determines the bubble flow and hence the amount of oxygen present in the reaction environment. In all the cases, the value of the final temperature reached increases with the increasing of the air flowrate.

On the other hand, the final temperature seems weakly dependent on the coke particle size, apart from the case where the gas velocity is close to incipient fluidization. When the temperature increases, the minimum fluidization velocity decreases; hence, for the same gas flow, the bed may become more evenly fluidized at higher temperature, with better oxygen transfer across the bed. Such a
change is strongly related to the PSD of the mixtures and it can lead to higher final temperature in the bed.

It is worth mentioning that the recording of the temperature and the pressure drop during the combustion stage was not able to detect possible hot spots inside the bed which can cause defluidization. Moreover, it is important to point out that the tests were repeated three times to ensure the reliability of the measurements.

The pressure drop profiles obtained during the coke combustion stage showed little variation of the pressure drop inside the bed. This suggests that the aggregates did not form during this specific stage.

Figure 5.5 – Temperature and pressure profiles inside the bed during combustion stage for STS mixture at different fluidization conditions (see Table 5.2 for details).
Multi-component systems results

Figure 5.6 – Temperature and pressure profiles inside the bed during combustion stage for STM mixture at different fluidization conditions (see Table 5.2 for details).

Figure 5.7 – Temperature and pressure profiles inside the bed during combustion stage for STL mixture at different fluidization conditions (see Table 5.2 for details).
After combustion, the system was let to cool down to ambient temperature without any external aid (e.g. without injecting any cold air flow). The temperature profiles during the cooling stage are reported in Figure 5.8 for the ST mixtures and they show a very similar profile in all the tested cases, confirming that the cooling conditions do not differ from case to case.

![Temperature profiles for ST mixtures](image)

![Temperature profiles for NT mixtures](image)

![Temperature profiles for NTL mixtures](image)

Figure 5.8 - Temperature profiles inside the bed during cooling stage for all the tested ST mixtures (see Table 5.2 for details).

The next three figures refer to the NT mixtures with coke with different particle size distribution: small (NTS), medium (NTM) and large (NTL) respectively. Also for these mixtures the operating time was set to 50 minutes, but in most of the cases the maximum safe temperature (900-950 °C) was reached in a
Multi-component systems results

shorter time compared with the ST mixtures. This dictated an earlier shutdown of the gas inlet.

The final temperature reached (or similarly the time at which the maximum safe value is reached) for the NT mixtures is also strongly dependent on the fluidization regime and the coke particle size. The temperature profiles found for the NT mixtures were reasonably similar to those obtained for the ST mixtures: the final temperature increases with increasing the air flowrate. Some important differences in the bed pressure drop profiles for the NTM and NTL mixtures were observed when the superficial gas velocity is close to incipient fluidization. In both cases, there is a sudden and sharp decrease in the bed pressure drop towards the end of the test. This coincides with the onset of a sharp temperature increase, corresponding to a peak in the combustion rate, which triggers a greater consumption of the coke material, leading in turn to a reduction of the overall bed weight. This observation is further enhanced when larger particles of coke are used (blue lines in Figure 5.10 and Figure 5.11).

Figure 5.9 – Temperature and pressure profiles inside the bed during combustion stage for NTS mixture at different fluidization conditions (see Table 5.2 for details).
Multi-component systems results

Figure 5.10 – Temperature and pressure profiles inside the bed during combustion stage for NTM mixture at different fluidization conditions (see Table 5.2 for details).

Figure 5.11 – Temperature and pressure profiles inside the bed during combustion stage for NTL mixture at different fluidization conditions (see Table 5.2 for details).
Similarly to the ST mixtures, also for the NT mixtures the system was let to cool down to ambient temperature after combustion. The temperature profiles during this stage are reported in Figure 5.12 and they confirmed very similar cooling conditions for all the cases tested.

Figure 5.12 – Temperature profiles inside the bed during cooling stage for NT mixtures (see Table 5.2 for details).
5.3 Fluidization Tests on Spent Mixtures

5.3.1 Pressure Drop and Bed Height Measurements

The parameters determined from the pressure drop measurements and from inspection of the bed height obtained with the X-rays for the spent mixtures at ambient conditions are reported in Table 5.3.

Table 5.3 – Experimental results from fluidization curves for spent mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Spent condition</th>
<th>(u_{mf}) (cm/s)</th>
<th>(u_{cf}) (cm/s)</th>
<th>(H_s) (cm)</th>
<th>(\Delta H_{\text{MAX}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STS</td>
<td>STS-1</td>
<td>6.0</td>
<td>8.0</td>
<td>11.4</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>STS-2</td>
<td>5.7</td>
<td>9.0</td>
<td>10.7</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>STS-3</td>
<td>4.5</td>
<td>7.0</td>
<td>11.3</td>
<td>21.4</td>
</tr>
<tr>
<td>STM</td>
<td>STM-1</td>
<td>9.6</td>
<td>12.0</td>
<td>11.6</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>STM-2</td>
<td>7.7</td>
<td>10.0</td>
<td>11.0</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>STM-3</td>
<td>5.5</td>
<td>6.5</td>
<td>11.4</td>
<td>20.4</td>
</tr>
<tr>
<td>STL</td>
<td>STL-1</td>
<td>11.5</td>
<td>13.0</td>
<td>12.4</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>STL-2</td>
<td>10.9</td>
<td>12.0</td>
<td>12.6</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>STL-3</td>
<td>7.2</td>
<td>8.5</td>
<td>12.0</td>
<td>13.1</td>
</tr>
<tr>
<td>NTS</td>
<td>NTS-1</td>
<td>10.0</td>
<td>10.0</td>
<td>10.5</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td>NTS-2</td>
<td>8.5</td>
<td>11.0</td>
<td>10.2</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>NTS-3</td>
<td>8.7</td>
<td>10.0</td>
<td>10.3</td>
<td>22.3</td>
</tr>
<tr>
<td>NTM</td>
<td>NTM-1</td>
<td>12.0</td>
<td>14.0</td>
<td>10.7</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>NTM-2</td>
<td>11.0</td>
<td>15.0</td>
<td>10.7</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>NTM-3</td>
<td>10.0</td>
<td>16.4</td>
<td>10.3</td>
<td>11.8</td>
</tr>
<tr>
<td>NTL</td>
<td>NTL-1</td>
<td>11.0</td>
<td>14.5</td>
<td>10.5</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>NTL-2</td>
<td>10.5</td>
<td>17.0</td>
<td>10.5</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>NTL-3</td>
<td>9.8</td>
<td>12.0</td>
<td>10.0</td>
<td>18.8</td>
</tr>
</tbody>
</table>

The pressure drops profiles are reported from Figure 5.13 to Figure 5.15 for the ST mixtures and from Figure 5.19 to Figure 5.21 the NT mixtures. \(\Delta P_{mf}/\Delta P_{cf}\) values against the superficial gas velocity are compared to the results obtained for the fresh mixtures. Changes in both \(u_{mf}\) and \(u_{cf}\) were observed in comparison with the fresh mixtures’ results. The minimum fluidization velocity of the spent mixtures decreased in all the cases investigated and this was emphasized when larger particles of coke were used.

Significant hysteresis were observed between the “fluidization” and the “defluidization” curves for all the spent ST mixtures (see Figure 5.13 to Figure 5.15). The pressure drop in the packed bed region showed a fluctuating trend, indicating a certain difficulty of the mixtures to achieve complete fluidization. Moreover, the pressure drop measured in the packed bed of the spent mixtures
was found to be greater than that measured for the fresh mixtures (see the green areas highlighted in the figures). This indicates that the upward-flowing gas encounters more difficulty when passing through the bed, due to the presence of aggregates. These obstruct the gas flow, causing possible channelling and an increase in the pressure drop. As soon as the complete fluidization velocity is reached, the mixture of loose particles and small aggregates is suspended. This is substantiated by the experimental pressure drop at complete fluidization conditions which does not equal the predicted one: final values of $\Delta P_{mf}/\Delta P_c$ are always less than 1. This indicated that parts of the bed were not fully fluidised.

The spent mixtures obtained after combustion in well-fluidized bed conditions (i.e. STS-3, STM-3 and STL-3 mixtures—yellow curves in the figures) reached the complete fluidization at lower gas velocities than those measured for the fresh ones (see vertical lines in the figures). This suggested that the coke particles’ size, and in turn overall weight of the bed, was reduced to a greater extend during the combustion in well-fluidized conditions. This explained also the trends observed for the $u_{mf}$: the reduction of the particles size led to a lower minimum fluidization velocity. Moreover, mixtures with larger particles of coke were observed to be more sensitive to this reduction.

Bed expansion profiles for the ST mixtures were also investigated by implementing the same procedure used for the mono-component systems. The normalised deviation profiles from the settled bed height, as function of the gas velocity, are reported from Figure 5.16 to Figure 5.18.

In particular, the spent mixtures after combustion in well-fluidized conditions ($2x u_{cf}$) show always the higher bed height (see the yellow curves in the figures). In the other two cases, namely for the spent mixtures obtained after combustion with gas flowrates below and at incipient minimum fluidization (blue and red curves in the figures), the bed height is lower than the fresh mixtures’ one when small or medium coke is used, while it is higher when large particles of coke are used.
Figure 5.13 – Comparison between pressure drops profiles for STS spent mixtures and fresh one
Figure 5.14 – Comparison between pressure drops profiles for STM spent mixtures and fresh one
Figure 5.15 – Comparison between pressure drops profiles for STL spent mixtures and fresh one
Multi-component systems results

Figure 5.16 – Comparison between bed expansion profiles for STS spent mixtures and fresh one

Figure 5.17 – Comparison between bed expansion profiles for STM spent mixtures and fresh one
Multi-component systems results

Figure 5.18 – Comparison between bed expansion profiles for STL spent mixtures and fresh one

The pressure drop profiles of the spent NT mixtures also present important hysteresis between the “fluidization” and the “defluidization” curves (see Figure 5.19 to Figure 5.21). The pressure drop in the packed bed region showed a fluctuating trend, indicating a certain difficulty of the mixtures to achieve complete fluidization. A small overshooting in the pressure drop during “fluidization” is noticeable in two of the spent mixtures with small coke particles (i.e. NTS-2 and NTS-3), indicating the resistance of the bed to flow due to the presence of the aggregates.

The pressure drop measured in the packed bed region (see the green areas highlighted in the figures) follows the same trend observed for the ST mixtures when small and large coke particles are used (i.e. NTS and NTL mixtures - Figure 5.19 and Figure 5.21 respectively). When medium coke particles are used, the trend of the pressure drop of the spent mixtures is upturned: they are all lower than the values found for fresh mixtures (see Figure 5.20). However, similarly to the ST mixtures, the experimental pressure drop at complete fluidization conditions for all the spent mixtures do not equal the
predicted ones (final values of \( \Delta P_m/\Delta P_c \) are always less than 1); furthermore, these are always lower than the values found for the fresh mixtures, suggesting again presence of aggregates within the bed.

The complete fluidization condition is reached at lower gas velocity for most of the spent mixtures compared to the fresh ones (see vertical lines in the figures). This suggests that the combustion of coke particles is better promoted in the systems with natural rutile (NT mixtures) than in the ones with synthetic rutile (ST mixtures). This means that there is a considerable reduction of the overall bed weight, due to the burning and shrinking of the coke particles, which in turn causes a faster complete fluidization. The only exception is the NTL-2 mixture, which has a complete fluidization velocity higher than the fresh one. This indicates that less coke has been consumed. This observation is confirmed by the pressure drop measured at complete fluidization velocity: in this case, the value of \( \Delta P_m/\Delta P_c \) is very close to the one obtained for the fresh mixture.

The normalised deviation profiles from the settled bed height as function of the gas velocity are reported from Figure 5.22 to Figure 5.24. All the spent mixtures with small coke particles show bed height profiles similar to the ones of the fresh mixtures. The spent mixtures with medium coke particles show however lower values of the bed height when compared to the fresh mixtures; whereas, when large coke particles are used, the spent mixtures expand more than the fresh one. In this latter case, the spent mixture after combustion in well-fluidized conditions (NTL-3) show the greatest bed expansion.
Figure 5.19 – Comparison between pressure drops profiles for NTS spent mixtures and fresh one
Figure 5.20 – Comparison between pressure drops profiles for NTM spent mixtures and fresh one
Multi-component systems results

Figure 5.21 – Comparison between pressure drops profiles for NTL spent mixtures and fresh one
Multi-component systems results

Figure 5.22 – Comparison between bed expansion profiles for NTS spent mixtures and fresh one

Figure 5.23 – Comparison between bed expansion profiles for NTM spent mixtures and fresh one
Figure 5.24 – Comparison between bed expansion profiles for NTL spent mixtures and fresh one

5.3.2 BED COLLAPSE TESTS RESULTS

The bed collapse technique was used as a quantitative test for the characterization of the aeratability of the spent mixture in comparison with the fresh ones. The parameters presented in section 2.4.3 (namely the overall collapse rate, $U_c$, the bed expansion ratio, BER, and the standardised collapse time, SCT) have been determined from experimental data and are discussed in this section.

Figure 5.25 to Figure 5.27 report the collapse profiles of all the ST mixtures tested. The results in terms of initial and settled bed height ($H_0$ and $H_s$), consolidation time $t_c$ and time constant $\tau_B$ are reported in the appendix C. Two different initial gas velocities ($u_i$) were used in order to compare the collapse behaviour of the three tested mixtures, namely STS, STM and STL:

1. $u_i = 15$ cm/s in all the cases;
2. $u_i = (u_{\text{mf}} + 4$ cm/s) for each mixture.

These values allowed the comparison when the same gas velocity is used and also when the same deviation from the minimum fluidization condition is taken into account.
Figure 5.25 - Collapse profiles STS fresh and spent mixtures at different initial gas velocities
Figure 5.26 - Collapse profiles STM fresh and spent mixtures at \( u_i = 15 \, \text{cm/s} \)
Multi-component systems results

Figure 5.27 - Collapse profiles STL fresh and spent mixtures at different initial gas velocities
Table 5.4 summaries the resulting collapse parameters $U_c$, BER and SCT for ST mixtures at the different initial gas velocities. The variations of these parameters from fresh to spent conditions for each mixture are also highlighted from Figure 5.28 to Figure 5.30.

For instance, for the STS mixtures (see Figure 5.28), the overall collapse rate, $U_c$, of the spent mixtures appears always lower than the one of the fresh mixture when the initial gas velocity is 11 cm/s, while it oscillates when the gas velocity is increased to 15 cm/s. On the other hand, the bed expansion ratio, BER, of the spent mixtures follows the same trend when changing the initial gas velocity: mixtures STS-1 and STS-3 expand more than the fresh one, while STS-2 expands less the fresh mixtures. Finally, the standardised collapse time, SCT, shows a unique trend from fresh to spent mixtures: it is always higher for the spent mixtures. This means that the spent mixtures require more time to fully deaerate, perhaps due to the presence of aggregates within the bed.

Table 5.4 – Collapse parameters for ST mixtures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mixture</th>
<th>STS $u_i=11$ cm/s</th>
<th>STM $u_i=15$ cm/s</th>
<th>STL $u_i=18$ cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_c$ [cm/s]</td>
<td>-0</td>
<td>7.4</td>
<td>8.4</td>
<td>5.7</td>
</tr>
<tr>
<td>BER [%]</td>
<td>23.8</td>
<td>25.8</td>
<td>29.6</td>
<td>18.7</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>3.2</td>
<td>3.2</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td>$U_c$ [cm/s]</td>
<td>-1</td>
<td>6.6</td>
<td>9.8</td>
<td>6.7</td>
</tr>
<tr>
<td>BER [%]</td>
<td>24.7</td>
<td>30.4</td>
<td>32.6</td>
<td>21.0</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>3.7</td>
<td>3.3</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>$U_c$ [cm/s]</td>
<td>-2</td>
<td>5.8</td>
<td>4.1</td>
<td>6.1</td>
</tr>
<tr>
<td>BER [%]</td>
<td>20.9</td>
<td>18.2</td>
<td>20.9</td>
<td>26.5</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>3.6</td>
<td>3.4</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>$U_c$ [cm/s]</td>
<td>-3</td>
<td>6.2</td>
<td>9.0</td>
<td>5.6</td>
</tr>
<tr>
<td>BER [%]</td>
<td>24.8</td>
<td>32.1</td>
<td>25.7</td>
<td>31.4</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>4.0</td>
<td>3.5</td>
<td>4.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>
With regards to the mixtures containing medium coke particles (STM - Figure 5.29), it can be observed that the three parameters \( U_c \), BER and SCT oscillate for the different spent conditions. STM-1 shows higher values of \( U_c \) and BER than the fresh mixture, but slightly lower SCT. STM-2 displays lower values of \( U_c \) and BER than the fresh mixture, but considerably higher SCT. STM-3 shows instead the same SCT of the fresh mixtures, but higher values of \( U_c \) and BER.

The spent mixtures with the largest coke particles (STL - Figure 5.30) show higher values of BER than the fresh one, therefore they all expand more than the fresh mixture. The \( U_c \) variations are affected by the conditions of the combustion stage: the spent mixtures STL-1 and STL-2 (i.e. obtained after combustion below and at minimum fluidization condition) have higher collapse rates at the two gas velocities investigated, while the spent mixture STL-3 (i.e. combustion stage in well-fluidized condition) has collapse rate very similar to the fresh one.
Multi-component systems results

Figure 5.29 – Variation of collapse parameters for STM mixture from fresh to spent conditions.

Figure 5.30 – Variation of collapse parameters for STL mixture from fresh to spent conditions.
Figure 5.31 to Figure 5.33 show the collapse profiles of all the tested NT mixtures, both fresh and spent ones. The results in terms of initial and settled bed height ($H_0$ and $H_s$), consolidation time $t_c$ and time constant $\tau_B$ are reported in the appendix C. Different initial gas velocities, ranging from 13 to 20 cm/s, were used in order to compare the collapse behaviour of NTS, NTM and NTL mixtures.

Figure 5.31 - Collapse profiles NTS fresh and spent mixtures at different initial gas velocities
Multi-component systems results

Figure 5.32 - Collapse profiles NTM fresh and spent mixtures at different initial gas velocities
Multi-component systems results

Figure 5.33 - Collapse profiles NTL fresh and spent mixtures at different initial gas velocities
Table 5.5 summaries the collapse parameters $U_c$, BER and SCT for the tested NT mixtures at the different initial gas velocities. Variations of such parameters from fresh to spent conditions for each mixture are also highlighted from Figure 5.34 to Figure 5.36. Although all change for each mixture, no common trends have been found.

Table 5.5 – Collapse parameters for NT mixtures

<table>
<thead>
<tr>
<th>Mix</th>
<th>NTS $u_i$ (cm/s)</th>
<th>NTM $u_i$ (cm/s)</th>
<th>NTL $u_i$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>$U_c$ [cm/s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0</td>
<td>6.8</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td>BER [%]</td>
<td>22.0</td>
<td>28.5</td>
<td>-</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>3.2</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>$U_i$ [cm/s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>4.7</td>
<td>7.2</td>
<td>-</td>
</tr>
<tr>
<td>BER [%]</td>
<td>19.2</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>4.1</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>$U_i$ [cm/s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>6.6</td>
<td>7.3</td>
<td>-</td>
</tr>
<tr>
<td>BER [%]</td>
<td>23.8</td>
<td>26.0</td>
<td>-</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>3.6</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>$U_i$ [cm/s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>6.7</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td>BER [%]</td>
<td>22.3</td>
<td>28.2</td>
<td>-</td>
</tr>
<tr>
<td>SCT [s/cm]</td>
<td>3.4</td>
<td>3.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Focusing on the NTS mixtures (Figure 5.34), the overall collapse rate, $U_c$, of the spent mixtures appears always lower than the one of the fresh mixture. The bed expansion ratio, BER, of the spent mixtures remains similar to the one of the fresh one, apart from the case of spent mixture after combustion below minimum fluidization (namely NTS-1), in which it considerably decreases. The standardised collapse time, SCT, is higher in all the spent mixture than in the fresh one.

NTM mixtures show a clear trend for all the three parameters: $U_c$, BER and SCT decrease from fresh to spent conditions and the lowest values are registered by the spent mixture obtained after combustion in a well-fluidized bed. Moreover, the trend is slightly decreasing with the fluidization condition: the more the aeration inside the bed, the lower the values of $U_c$, BER and SCT. Therefore, when the system is more aerated during the combustion stage, the resulting mixture expand less and deaerate faster.

NTL mixtures also show some trends with regard to the single parameters: $U_c$ and BER increase from fresh to spent conditions, while SCT slightly decreases.
Focusing on the variations of the standardised collapse time, that is a useful index of the quality of the fluidization by assessing the capability of the bed to retain the aeration gas, it can be noticed that it is strongly affected by the coke particles size. This increases from fresh to spent NTS mixtures, but decreases for NTM and NTL mixtures. Therefore, smaller coke particles may lead to spent mixtures that are more able to retain air, whereas larger particles may lead to spent mixtures with higher velocity of deaeration. This observation is perhaps linked to the characteristics of the aggregates formed as a result of the combustion taking place inside the reactor. The investigation of the aggregates’ properties is carried out in the next section.

Figure 5.34 – Variation of collapse parameters for NTS mixture from fresh to spent conditions.
Multi-component systems results

Figure 5.35 – Variation of collapse parameters for NTM mixture from fresh to spent conditions.

Figure 5.36 – Variation of collapse parameters for NTL mixture from fresh to spent conditions.
5.4 AGGREGATES INVESTIGATIONS

Photographs of some of the aggregated particles found in the bed after the combustion tests are reported in Appendix A. Table 5.6 summarises the total weight of the aggregates collected after each test. The size and shape of the aggregates has been neglected in the analysis because they are strongly affected by the collection method: the loose particles are extracted with a vacuum cleaner and then the segregated lumps are removed from the reactor by means of a custom built scoop. The cases in which no lumps have been found are indicated as “-”.

Table 5.6 – Lumps total weight

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Spent condition</th>
<th>Total weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STS</td>
<td>STS-1</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>STS-2</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>STS-3</td>
<td>-</td>
</tr>
<tr>
<td>STM</td>
<td>STM-1</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>STM-2</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>STM-3</td>
<td>-</td>
</tr>
<tr>
<td>STL</td>
<td>STL-1</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>STL-2</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>STL-3</td>
<td>83</td>
</tr>
<tr>
<td>NTS</td>
<td>NTS-1</td>
<td>271</td>
</tr>
<tr>
<td></td>
<td>NTS-2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>NTS-3</td>
<td>-</td>
</tr>
<tr>
<td>NTM</td>
<td>NTM-1</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>NTM-2</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>NTM-3</td>
<td>-</td>
</tr>
<tr>
<td>NTL</td>
<td>NTL-1</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>NTL-2</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>NTL-3</td>
<td>-</td>
</tr>
</tbody>
</table>

Friability tests were performed on the samples retrieved from the bed. The results of these tests are shown in Figure 5.37, where the breaking times are reported for specimens of 11-12 g each. Both the coke PSD and the fluidizing regime seemed to affect the mechanical strength of the aggregates. These appeared more friable with increasing the coke particles size from small to medium to large, and with decreasing air flowrate during the combustion stage.

This can be explained by the fact that when the bed is not well fluidized, the likelihood of having a dead zone is higher. In these zones, there is weak gas permeability and hence a low heat transfer which prevents the formation of strong sintered bridges between the particles. On the other hand, larger particles of coke...
Multi-component systems results

may lead to the formation of weaker aggregates because of worse mixing conditions due to the difference in particle size between coke and rutile/slag; which could contribute to a less efficient heat transfer.

Some of the bond structures among the aggregated particles are presented in the SEM pictures from Figure 5.38 to Figure 5.41. Figure 5.38 shows some examples of the necks bonding between the particles within the sintered aggregates. Specific SEM images of each enlarged neck are then reported from Figure 5.39 to Figure 5.41.

![Figure 5.37 – Friability test results on samples of lumps of 11-12 g. MF: minimum fluidization](image)
Figure 5.38 – SEM pictures of aggregates: general views with some highlighted interparticles bonds
Figure 5.39 – SEM pictures of bonds between particles in mixtures with small and large coke.

Figure 5.40 – SEM pictures of the bonds between particles in STM-2 mixture. Upper and lower right bonds refer to general view in Figure 5.38.
EDX analysis were performed on the various samples and presented here. In order to aid the investigation of the bond, each sample was embedded in a special resin and part of its surface was ground away. Such a technique allowed visualising the internal cross section of the interparticles’ bonds.

Figure 5.42 reports the SEM picture of one of the bonds seen in STM-2 sample (namely the upper right bond showed in Figure 5.40) obtained after resin embedding and surface grinding. The EDX spectra reported at the bottom of the figure belong to the different marked areas in the SEM picture. In particular, the areas A and B refer to the internal body of the particle and the area C refers to the bond between the two particles. EDX spectra on areas A and B reveal high amounts of titanium and iron, whereas in the area C, silicon, aluminium and calcium are present in higher proportions. More specific details on the elemental composition of the areas marked in Figure 5.42 are reported in Table 5.7. These reveal that only the synthetic rutile and slag give place to the formation of the sintered neck, with a particular enrichment of Al-Si phase in the bond.

Table 5.7 – Elements composition from EDX spectra of the marked areas in Figure 5.42

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area A</td>
</tr>
<tr>
<td>O</td>
<td>35.33</td>
</tr>
<tr>
<td>Mg</td>
<td>1.16</td>
</tr>
<tr>
<td>Al</td>
<td>0.72</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>29.88</td>
</tr>
<tr>
<td>Mn</td>
<td>4.84</td>
</tr>
<tr>
<td>Fe</td>
<td>28.07</td>
</tr>
</tbody>
</table>
Some of interparticles’ necks seen in the NTS-1 and NTL-1 samples were analysed by means of EDX. Also in these cases, the results showed enrichment of the Al-Si phase in the bonds between the rutile and slag particles. Details of these observations are reported in Figure 5.43 and Figure 5.44. Similar results were obtained also for the other ST and NT samples and the possibility of bonds involving coke particles was explored as well.

Figure 5.45 shows the details of the investigation on some coke embedded in the STL-2 samples. SEM/EDX pictures of some typical interparticles contact areas have been magnified and they are shown in contrast of topography and composition to enable getting information regarding the physic-chemical structure of the bond. It can be observed that no relevant bonding structures involving the coke particles could be found. It is worth mentioning that the EDX analysis was performed on the areas marked by the yellow arrows, showing small ore-type particles scattered around the large coke particle. However, no clear bond structures could be identified.
Figure 5.43 – EDX analysis and spectra on NTS-1 sample necks

Figure 5.44 – EDX analysis and spectra on NTL-1 sample necks
Figure 5.45 – SEM pictures around coke particles in STL-2 sample
5.5 **Chapter Remarks**

The early stages of the sintering process were experimentally investigated on a small pilot scale fluidization rig for a number of three-component mixtures by changing the type of titanium ore and the size of the coke particles. In particular, mixtures of synthetic rutile, slag and coke were firstly studied; then, the synthetic rutile was replaced by a natural one. Three different cuts of coke particles were used during the tests: small, medium and large size.

The effects of temperature and air flowrate were investigated systematically at three different fluidization regimes: close to and well above the minimum fluidization conditions. The final temperature reached for all the mixtures was found to be strongly dependent on the fluidization regime and the coke particle size. In all the cases, the value of the final temperature increased with increasing the air flowrate, but it seemed weakly dependent on the coke particle size, apart from the case where the gas velocity is close to incipient fluidization.

The fluid-dynamic characteristic of the spent systems were assessed by means of pressure drop measurements, bed height inspections and bed collapse tests. Changes in both $u_{inf}$ and $u_{cf}$ were compared with the fresh mixtures’ results: $u_{inf}$ of all the spent mixtures decreased and this reduction enhanced when larger particles of coke were used. The systems with synthetic rutile presented some differences from the systems with natural rutile, with respect to the complete fluidization velocity. In the former, the complete fluidization condition was reached at lower gas velocity in the spent mixtures than in the fresh ones only when high gas flowrates were used during the combustion stage. In the latter, $u_{cf}$ was reached at lower gas velocity in mostly of the spent mixtures than in the fresh ones, regardless of the fluidization regime of combustion stage. This suggested that the combustion of coke particles was better promoted in the systems with natural rutile (NT mixtures) than in the ones with synthetic rutile (ST mixtures).

The inspections on the bed expansion of the spent mixtures also showed a number of differences between the systems with synthetic rutile and the ones with natural rutile, and between the different spent conditions. However, it was
observed that the spent mixtures with large coke particles after combustion in well-fluidized conditions expanded more than the fresh ones.

Similarly, the bed collapse parameters varied for each single mixture, but a common pattern was found for the standardised collapse time, SCT, between the systems with synthetic and with natural rutile. When small particles of coke were used (i.e. STS and NTS), the SCT increased; whereas it mostly decreased when medium or large coke particle were used. This suggested that small coke particles promoted the formation of spent mixtures more capable to retain air than the bigger particles, which, instead, led to spent mixtures with higher velocities of deaeration. This observation can be explained by the possible presence of bigger and heavier aggregates which cause the mixture to deaerate faster as the fluidizing gas is shut off.

Finally, friability tests and SEM pictures were performed with the aim of analysing the properties of the aggregates. The mechanical strength of the aggregates was found to be strongly dependent on the coke particles size and the fluidizing regime during the combustion stage. The aggregates appeared more friable with increasing the coke particles size from small to large, and with decreasing air flowrate during combustion. Two main factors were identified as possible causes for this:

1. when the bed was not well fluidized, there was a more likely chance to have dead zones within the bed, with weak gas permeability and low heat transfer that prevented the formation of strong sintered interparticles bridges;
2. larger particles of coke may have contributed to a less efficient heat transfer, leading to the formation of weaker aggregates because of the worse mixing conditions due to the difference in particle size between coke and rutile/slag.

The SEM/EDX analysis permitted the inspections of the bridges among particles and the assessment of the chemical composition of the sintered material. The results suggested that only particles of rutile and slag were involved in the formation of the sintered bridge (with a particular enrichment of Al-Si phase in the bond) and no relevant bonding structures involving coke particles were found.
Therefore, we can conclude that the coke particles do not affect particles aggregation per se, but they are only responsible for local increase in temperature due to exothermic combustion. This in turn might favour the sintering phenomena of rutile and slag particles.
6 CONCLUSIONS AND FUTURE WORK

The main focus of this research, which was defined in collaboration with Venator, was the experimental investigation of the effect of operating conditions on the defluidization behaviour of industrial reactive powders. To this end, a twofold approach has been adopted: experimental analyses were conducted on both mono-component and multi-components systems.

This thesis sought to address the following objectives:

1. Characterize the rheological and fluidization behaviour of each particulate material at ambient and high temperature;

2. Find a possible link between the powder’s performance when fluidized and their rheological properties;

3. Investigate the fluidization performance of different mixtures of titanium ores and pet coke in the regimes where carbon combustion initiates defluidization due to particles aggregation;

4. Systematically characterize the resulting lumps of aggregated particles by performing specific analysis on the samples aimed at investigating the factors responsible for their formation;

5. Provide a reliable analysis tool for the prediction of the defluidization phenomenon in the investigated systems.

The key findings of this work can be summarized as follows:

1. The rheological and fluidization behaviour of each particulate material was found to be influenced by the operative temperature. In particular, the flowability of the particles decreased with the increasing temperature and the fluidization tests revealed a typical Group B particles behaviour for all the material tested;
2. The fluidization behaviour of each powder was affected by the action of the IPFs, which were found to be more dominant under conditions close to and below incipient fluidization and with high operative temperature;

3. Inspections of the fluidization performance of different mixtures of titanium ores and coke showed that a number of factors are responsible for the onset of defluidization due to particles aggregation, such as rutile’s nature, coke particles size, operative fluidization regime, etc.;

4. The resulting aggregates were found to be more friable when larger particles of coke were used and when low air flowrates were employed during the combustion stage. Moreover, the SEM/EDX analysis showed that the titanium ores particles were the only ones involved in the formation of the sintered bridges, mostly made up of aluminium silicate compounds;

5. Achieving a fundamental understanding of the investigated industrial process and the prediction of the defluidization phenomenon has been addressed by reproducing and controlling the early stage stages of the sintering processes, as well as the formation of the aggregates and relating their characteristics to the various operative conditions.

As part of the investigation on the mono-component systems, a comparison was conducted between the rheological properties of the powders to the corresponding defluidization behaviour in order to achieve a physical understanding of the effect of process conditions on fluidization (Objective 1).

Experimental examinations with the modified Schulze shear cell were carried out in order to assess the rheological behaviour of the materials at ambient and with increasing temperature. Shear experiments highlighted a significant increase of unconfined yield strength with temperature, which means that a higher force is required to deform or break the material when it is not confined by a container. From the particulate material perspective, it means that a higher force is required to fail a consolidated mass of material to initialize flow. This resulted in a lower flowability of the samples. Theoretical models based on the particle–particle approaches of Rumpf-Molerus and Tomas were used to correlate the isostatic
tensile strength of powders with the interparticle interaction forces. The comparison between experiments conducted at ambient and high temperatures and the theoretical model suggested that the proposed approaches give correct predictions for the tensile strength if the proper values for the material physical and mechanical properties, in particular for the compressive yield strength, at both ambient and high temperature, are used. In fact, as highlighted by the sensitivity analysis, different values of $p_I$ may yield a better fit to the experimental data.

The results obtained from fundamental fluidization tests showed a typical Group B particles, as for instance aggregative fluidization (bubbles form once the gas velocity exceeds the minimum fluidization velocity), relatively small bed expansion and bed expansion profiles that do not level off to a certain height value. Furthermore, the bed collapse curve showed sharp sedimentation stages and then very fast deaeration rates. The bed collapse test was found to be a discriminating technique, able to highlight the changes in the powders’ aeratability with temperature. The collapsing parameters were related to the rheological behaviour of the materials examined.

For all the materials tested, the overall collapse rate ($U_c$) and the bed expansion ratio (BER) increased with increasing the initial gas velocity, but with some differences between ambient and high temperature. $U_c$ does not seem to be strongly affected by the operating temperature for low initial gas velocities, whereas it decreases by 45% on average for the higher gas velocities. Instead, BER does not show significant changes with the operating temperature for all the initial gas velocities investigated.

On the other hand, the standardised collapse time (SCT) showed to be very sensitive to the changes in operating conditions: initial gas velocity and related bed expansion in particular. SCT increased significantly with increasing temperature for low initial gas velocities, whilst such a deviation decreased at higher velocities. This suggested that higher temperature improves the ability to retain aeration gas only when the fluidization gas velocity was less than $2 \times u_{mf}$. This behaviour was explained as a function of the role played by the IPFs on the fluidization regimes close to the incipient conditions by introducing the dimensionless Bond number, which is commonly used in fluid dynamics for
measuring the importance of the interparticle forces over the gravitational forces (Objective 2). The analysis showed that the greater the deviation from the settle bed conditions (i.e. when the system was more dispersed due to the higher fluidization velocities), the less the variation in SCT with temperature, meaning that the IPFs had a lower effect on the fluidization behaviour at higher fluidizing velocities.

The second challenge of this PhD project was to provide a sound foundation for the defluidization behaviour caused by the formation of the aggregates in multi-components systems. A number of systems were investigated using different titanium ore types in mixtures with coke of various sizes (Objective 3). Early stages of the sintering process were experimentally simulated in a small-pilot scale fluidization rig for the different mixtures by blowing air into the fluidized bed for a certain time. The effects of high temperature, air flowrate and coke particle size distribution were then systematically investigated in three different fluidization regimes:

1. below minimum fluidization conditions, 0.5x $u_{mf}$
2. close to incipient fluidization conditions, 0.5x ($u_{mf} + u_{cf}$)
3. in well-fluidized bed conditions, 2x $u_{cf}$

The temperature profiles during combustion tests showed that, as expected, both the coke particle size and the operating regime affect the fluid-dynamics and heat distribution inside the bed and, therefore, the possible pervasiveness of dead zones in which the temperature control is quite difficult and hot spots are likely to be present. Standard fluidization tests were confirmed as a reliable indicator for anomalies within the fluidized bed. The comparison between the results of the spent and fresh systems clearly pointed out the presence of larger aggregates which the fluidizing gas could not suspend. Changes in both $u_{mf}$ and $u_{cf}$ have been observed in all the spent mixtures when compared to the fresh ones: $u_{mf}$ of all the spent mixtures decreases and this reduction is enhanced when larger particles of coke were used. In the systems with synthetic rutile, the complete fluidization condition was reached at lower gas velocity in the spent mixtures than in the fresh ones only when high gas flowrates are used during the combustion stage. In the systems with natural rutile, instead, $u_{cf}$ is reached at lower gas velocity in mostly
of the spent mixtures than in the fresh ones, regardless of the fluidization regime of combustion stage. This suggested that the combustion of coke particles was better promoted in the systems with natural rutile (NT mixtures) than in the ones with synthetic rutile (ST mixtures).

The inspections on the bed expansion of the spent mixtures also showed a number of differences between the systems with synthetic or natural rutile, and between the different spent conditions. However, it has been observed that the spent mixtures with large coke particles after combustion in well-fluidized conditions expand more than the fresh ones, highlighting a significant change in the bed characteristics, probably related to the properties of the aggregates formed.

Similarly, the bed collapse parameters varied for each single mixture, but an interesting common pattern was found for the standardised collapse time, SCT, between the systems with synthetic and with natural rutile. When small particles of coke were used (STS and NTS mixtures), the SCT increased; whereas it mostly decreased when medium or large coke particle were used. This suggested that small coke particles promoted the formation of spent mixtures more capable to retain air than the bigger particles, which, instead, led to spent mixtures with higher velocities of deaeration. This observation was explained by the possible presence of bigger and heavier aggregates which caused the mixture to deaerate faster as the fluidizing gas was shut off.

The mechanical properties of the aggregates collected after combustion were analysed by measuring their friability (Objective 4). Both the coke PSD and the fluidizing regime seemed to have an important role: the aggregates were more friable with increasing coke size and with decreasing air flowrate. Inspections of the bridges among particles were performed by SEM/EDX analysis with the aim of determining the chemical composition of the sintered material. For the majority of the collected samples, the results suggested that only particles of rutile and slag were involved in the formation of the sintered bridge, with a particular enrichment of Al-Si phase in the bond. Moreover, no relevant bonding structures involving coke particles were found.
To conclude, the basis for a fundamental understanding of the investigated industrial process has been delivered (Objective 5) by:

- Successfully reproducing the early stage stages of the sintering processes in a small pilot scale fluidized bed at temperature far below the real operative one;
- Being able to control the formation of the aggregates by varying the fluidization regime during the combustion stage and the particle size of the coke;
- Finding a clear relationship between the characteristics of the final aggregates and the operative conditions, e.g. the friability of the aggregated were related to the flowrate during combustion and the PSD of the coke used during the experiments;
- Identifying the titanium ores particles (synthetic and natural rutile, as well as slag) as the only ones involved in the sintering process.
- Excluding the coke from the particles aggregation per se, as it is only responsible for the local increase in temperature due to exothermic combustion, that in turn favour the sintering of the other particles present in the mixture.

6.1 Future Work

In light of the main findings, this thesis concludes by recommending some of the possible areas for future research work.

First of all, it is important to consider that the analysis presented was limited to some parameters such as constant mixtures composition (45% wt. rutile, 30% slag and 25% coke), fixed injected oxygen content and unique cooling conditions. For these reasons, there are several dimensions in which the study could be extended:

1. Investigate different mixtures with different proportions of slag over rutile, for instance by using a fixed amount of coke, while systematically varying the percentages of rutile and slag (Venator, for example, reported that
percentages of slag material above 60% have cause several processing difficulties in the past).

2. Vary the amount of air and the degree of fluidization. In this work only three well distinct fluidization regimes have been explored, but the extent of sintering under more and less aggressive fluidizing conditions could be of great importance. For instance, it would be interesting to explore more than one regime below minimum fluidization conditions by further discretizing the range of operating gas from 0 to umf.

3. The relationship between the degree of sintering and the time-temperature profiles during both combustion and cooling stages should be further analysed. Taking into account the temperature limitations of the experimental equipment, it would be worth exploring the effect of gas flowrate dilution on the temperature evolution. For instance, by mixing the air stream to a pure nitrogen one might reduce the combustion reaction rate and then allow longer operative times.

4. The gas distributor system was limited to a sintered plate distributor only, which gives a very even gas distribution. At large scale operations, multijet tuyere distributors are used and these cause partially fluidised beds within the tuyere jet region. This may play a role in the aggregates formation and distribution inside the reactor; thus it would be worth studying the effects of the gas distribution systems on such parameters.

5. Of course, all the above considerations will need to be related to the possible variations in the strength and the properties of the final aggregates. Particular attention will need to be paid on the particles bridges by perhaps implementing more advanced and more detailed testing methodologies, such as the X-ray Computed Tomography (CT) for visualizing the interior features of the aggregates and for obtaining digital information on their 3-D geometries and properties (e.g. neck size, porosity and pores size and arrangement, etc.).
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_f$</td>
<td>Area occupied by the particles bed during fluidization in the X-ray image analysis (m$^2$)</td>
</tr>
<tr>
<td>$A_i$</td>
<td>Area occupied by the particles in the settled bed in the X-ray image analysis (m$^2$)</td>
</tr>
<tr>
<td>BCT</td>
<td>bed collapse test</td>
</tr>
<tr>
<td>BER</td>
<td>bed expansion ratio (-)</td>
</tr>
<tr>
<td>$B_0$</td>
<td>Bond Number (-)</td>
</tr>
<tr>
<td>$B_0^*$</td>
<td>Bond Number defined for fluidized beds (-)</td>
</tr>
<tr>
<td>$C$</td>
<td>cohesion (Pa)</td>
</tr>
<tr>
<td>$C_{H,sfs}$</td>
<td>Hamaker solid-fluid-solid constant (J)</td>
</tr>
<tr>
<td>$d$</td>
<td>particle diameter (m)</td>
</tr>
<tr>
<td>$d_{sv}$</td>
<td>Sauter mean diameter (m)</td>
</tr>
<tr>
<td>$E$</td>
<td>Young modulus (N m$^{-2}$)</td>
</tr>
<tr>
<td>$E^*$</td>
<td>Hertz modulus of elasticity (N m$^{-2}$)</td>
</tr>
<tr>
<td>$f_c$</td>
<td>unconfined yield strength (Pa)</td>
</tr>
<tr>
<td>$ff_c$</td>
<td>flow factor (-)</td>
</tr>
<tr>
<td>$F_0$</td>
<td>adhesion force without any consolidation (N)</td>
</tr>
<tr>
<td>$F_C$</td>
<td>contact force between particles (N)</td>
</tr>
<tr>
<td>$F_H$</td>
<td>adhesion force (N)</td>
</tr>
<tr>
<td>$F_{H0}$</td>
<td>adhesion force without any consolidation and contact flattening (N)</td>
</tr>
<tr>
<td>$F_N$</td>
<td>compressive normal force (N)</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational acceleration (m s$^{-2}$)</td>
</tr>
<tr>
<td>$h_c$</td>
<td>height of flattening (m)</td>
</tr>
<tr>
<td>$h_{cf}$</td>
<td>height of flattening for incipient yielding at $p = p_f$ (m)</td>
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<tr>
<td>$H$</td>
<td>bed height (m)</td>
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<tr>
<td>$H_0$</td>
<td>initial bed height during bed collapse test (cm)</td>
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<tr>
<td>$h_s$</td>
<td>settled bed height during bed collapse test (cm)</td>
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<td>HDFs</td>
<td>Hydrodynamic forces</td>
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<tr>
<td>$H_V$</td>
<td>Vickers Hardness (Pa)</td>
</tr>
<tr>
<td>IPFs</td>
<td>Interparticle forces</td>
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<td>LYL</td>
<td>linear yield locus</td>
</tr>
<tr>
<td>$n$</td>
<td>Richardson-Zaki exponent</td>
</tr>
<tr>
<td>NR</td>
<td>natural rutile sample</td>
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<tr>
<td>$p_f$</td>
<td>compressive yield strength (Pa)</td>
</tr>
<tr>
<td>$p_{vdW}$</td>
<td>attractive van der Waals pressure (Pa)</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure (Pa)</td>
</tr>
<tr>
<td>PSD</td>
<td>particle size distribution</td>
</tr>
<tr>
<td>RDS</td>
<td>relative diameter spread (-)</td>
</tr>
<tr>
<td>$r_c$</td>
<td>contact radius (m)</td>
</tr>
<tr>
<td>$r_{el}$</td>
<td>mean curvature radius for elastic contact point (m)</td>
</tr>
<tr>
<td>$r_p$</td>
<td>mean curvature radius for plastic contact point (m)</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number (-)</td>
</tr>
<tr>
<td>$Re_{mf}$</td>
<td>Reynolds number at minimum fluidization (-)</td>
</tr>
<tr>
<td>SCT</td>
<td>standardized collapse time (s/cm)</td>
</tr>
<tr>
<td>SR</td>
<td>synthetic rutile sample</td>
</tr>
<tr>
<td>SYL</td>
<td>stationary yield locus</td>
</tr>
</tbody>
</table>
Nomenclature

\( t \)  
- time (s)

\( t_c \)  
- time at which the bed start to consolidate during BCT (s)

\( T \)  
- temperature (°C)

\( TS \)  
- titania slag sample

\( u \)  
- superficial velocity \((m \ s^{-1})\)

\( u_{cf} \)  
- complete fluidization velocity \((m \ s^{-1})\)

\( u_i \)  
- initial fluidization velocity during BCT \((m \ s^{-1})\)

\( u_{mb} \)  
- minimum bubbling velocity \((m \ s^{-1})\)

\( u_{mf} \)  
- minimum fluidization velocity \((m \ s^{-1})\)

\( u_t \)  
- terminal fall velocity \((m \ s^{-1})\)

\( U_c \)  
- Bed collapse rate \((m \ s^{-1})\)

\( WS \)  
- Warren-Spring

\( YL \)  
- yield locus

\( z_0 \)  
- characteristic molecular separation distance (m)

\( \alpha \)  
- ratio between \( p_t \) at high temperature and \( p_f \) at ambient temperature

\( \Delta H_{MAX} \)  
- maximum bed height expansion (°)

\( \Delta p \)  
- pressure drop (Pa)

\( \Delta p_c \)  
- calculated pressure drop (Pa)

\( \Delta p_m \)  
- measured pressure drop (Pa)

\( \delta \)  
- bubble hold-up (-)

\( \varepsilon \)  
- bed voidage (-)

\( \varepsilon_0 \)  
- fixed bed voidage (-)

\( \varepsilon_d \)  
- dense phase voidage (-)

\( \varepsilon_{mb} \)  
- minimum bubbling voidage (-)

\( \varepsilon_{mf} \)  
- minimum fluidization voidage (-)

\( \kappa \)  
- elastic-plastic consolidation coefficient (-)

\( \kappa_A \)  
- elastic-plastic contact area coefficient (-)

\( \kappa_p \)  
- plastic repulsion coefficient for Tomas model (-)

\( \kappa_{pl} \)  
- plastic repulsion coefficient for Rumpf-Molerus model (-)

\( \mu_g \)  
- gas viscosity (Pa s)

\( \nu \)  
- Poisson ratio (-)

\( \rho_b \)  
- powder bulk density (kg m\(^{-3}\))

\( \rho_g \)  
- gas density (kg m\(^{-3}\))

\( \rho_p \)  
- particle density (kg m\(^{-3}\))

\( \sigma \)  
- normal stress (Pa)

\( \sigma_0 \)  
- isostatic tensile strength of unconsolidated powder (Pa)

\( \sigma_1 \)  
- major principal stress (Pa)

\( \sigma_2 \)  
- minor principal stress (Pa)

\( \sigma_{M, st} \)  
- centre of the Mohr circle for the steady-state flow (Pa)

\( \sigma_N \)  
- normal stress at consolidation (Pa)

\( \sigma_{pre} \)  
- normal pre-shear stress (Pa)

\( \sigma_{R, st} \)  
- radius of the Mohr circle for the steady-state flow (Pa)

\( \sigma_t \)  
- tensile strength (Pa)

\( \tau \)  
- shear stress (Pa)

\( \tau_B \)  
- time constant in BCT profiles (s)

\( \tau_{pre} \)  
- tangential pre-shear stress (Pa)

\( \phi \)  
- shape factor (-)

\( \phi_i \)  
- angle of internal friction (deg.)

\( \phi_{st} \)  
- steady-state angle of internal friction (deg.)

\( \nu \)  
- gas excess percentage during BCT (-)
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A. LUMPS PHOTOGRAPHS

Figure A.1 - Photograms of the lumps collected for test STS-1
Figure A.2 - Photograms of the lumps collected for test STS-2
Figure A.3 - Photograms of the lumps collected for test STM-1
Figure A.4 - Photograms of the lumps collected for test STM-2
Figure A.5 - Photograms of the lumps collected for mixtures STL

Figure A.6 - Photograms of the lumps collected for test STL-1
Figure A.7 - Photograms of the lumps collected for test STL-2

Figure A.8 - Photograms of the lumps collected for test STL-3
Figure A.9 - Photograms of the lumps collected for test NTS-1
Figure A.10 - Photograms of the lumps collected for test NTM-1 (top) and NTM-2 (bottom)
Figure A.11 - Photograms of the lumps collected for test NTL-1 (top) and NTL-2 (bottom)
B. MATLAB SCRIPTS

BED HEIGHT DETERMINATION

close all
clc
clear all

folder_REF=(uigetdir('start_path','Choose the directory for FIXED BED REFERENCE IMAGES')); %Choose the work directory
cd(folder_REF);

%MIJ starting
javaaddpath 'C:\Program Files\MATLAB \R2017a\java\mij.jar'
javaaddpath 'C:\Program Files\MATLAB \R2017a\java\ij.jar'
MIJ.start;

dist_par=0.180; % Parameter for correcting pincushion distortion

%% IMAGE DISTANCES CALIBRATION // TO BE PERFORMED OFF-LINE %

im_ref_calibration=imread('File000000100.tif'); %Reference image for calibrating the image size (delta1 and pixel ratio)(externally)
im_ref_calibration=lensdistort(im_ref_calibration,dist_par,'border type','fit','padmethod','fill'); % Packed image

figure('NumberTitle', 'off', 'Name', 'SELECT ROI FOR DISTANCES CALIBRATION - TO BE PERFORMED OFF-LINE');
[ROI_cal,rect_cal]=imcrop(im_ref_calibration);
Img_calibration=imadjust(ROI_cal);
imwrite(Img_calibration,fullfile(cd,['Calibration Image','.tif']));

%% INPUT PARAMETERS %
prompt_pixels = 'What is the pixels/cm ratio?';
pix=input(prompt_pixels);
pix_s=['"distance"= num2str(pix) " known=1 pixel=1 unit=cm"'];
pix_ss=join(pix_s,'');
prompt_indicator = 'What is the height of the indicator (cm)?';
h_ind=input(prompt_indicator);
prompt_deltah1 = 'What is the "distance between the indicator and the fixed bed" array (cm)?';
deltaH1=input(prompt_deltah1);

im_ref=imread('File000000100.tif'); %Reference image for choosing the Region of Interest
im_ref=lensdistort(im_ref,dist_par,'bordertype','fit','padmethod','fill');
figure('NumberTitle', 'off', 'Name', 'SELECT ROI FOR HEIGHT CALCULATION');
[ROI,rect]=imcrop(im_ref); % Choose and Save the ROI

close all;
MIJ.createImage(ROI);
MIJ.run("Set Scale...", pix_ss);
MIJ.run("Set Measurements...", "area bounding redirect=None
decimal=3");
MIJ.run("Input/Output...", "jpeg=85 gif=-1 file=.csv use_file");
MIJ.run("Measure");
A_tot=MIJ.getResultsTable; %A_tot=[Area_tot BX BY W_tot H_tot]

cd('..'); %get back to the main folder
Area=zeros(30);
D = dir; % it is a struct ... first elements are '.' and '..' used
for navigation.
Np=length(D)-2;
Area=zeros(Np);
for kc = 3:length(D) % avoid using the first ones as they are '.'
and '..'
    currD = D(kc).name; % Get the current subdirectory name
cd(currD)
k=kc-2; %new index, as the first 2 values for kc are useless
    for j=75:105
        filename = sprintf('File%08d.tif', j);
        Img=imread(filename);
        Img=lensdistort(Img,dist_par,'bordertype',
'fit','padmethod','fill');
        ImgROI=imcrop(Img,rect); % region of interest based on the
selection done at the beginning
        ImgROI=imadjust(ImgROI);
        MIJ.createImage(ImgROI);
        MIJ.run("Set Scale...", pix_ss);
        MIJ.setThreshold(155,255);
        MIJ.run("Threshold");
        MIJ.run("Set Measurements...", "area redirect=None
decimal=3");
        MIJ.run("Input/Output...", "jpeg=85 gif=-1 file=.csv
use_file");
        MIJ.run("Analyze Particles...", "size=1.7-Infinity clear
include");
        res_b=MIJ.getResultsTable;
        if length(res_b)==1
            Area((j-74),k)=res_b;
        else
            Area((j-74),k)=sum(res_b);
        end
        MIJ.closeAllWindows
    end
    cd('..') %to get back
end

MIJ.exit;

h1=A_tot(5)*(1-Area/A_tot(1));
h1_fix=h1(:,1); %h1(:,1) is the fixed bed height (01pm)
h1_mean=mean(h1_fix,1);
h_fixedbed=h_ind-deltaH1;
h_hidden=h_fixedbed-h1_mean;
h_real=h1+h_hidden;

function I2 = lensdistort(I, k, varargin)
p = inputParser;
%   Make input string case independant
p.CaseSensitive = false;

%   Specifies the required inputs
addRequired(p, 'I', @isnumeric);
addRequired(p, 'k', @isnumeric);

%   Sets the default values for the optional parameters
defaultFtype = 4;
defaultBorder = 'crop';
defaultInterpolation = 'cubic';
defaultPadmethod = 'fill';

%   Specifies valid strings for the optional parameters
validBorder = {'fit', 'crop'};
validInterpolation = {'cubic', 'linear', 'nearest'};
validPadmethod = {'bound', 'circular', 'fill', 'replicate', 'symmetric'};

%   Function handles to determine wheter a proper input string has been used
checkBorder = @(x) any(validatestring(x, validBorder));
checkInterpolation = @(x) any(validatestring(x, validInterpolation));
checkPadmethod = @(x) any(validatestring(x, validPadmethod));

%   Create optional inputs
addParamValue(p, 'bordertype', defaultBorder, checkBorder);
addParamValue(p, 'interpolation', defaultInterpolation, checkInterpolation);
addParamValue(p, 'padmethod', defaultPadmethod, checkPadmethod);
addParamValue(p, 'ftype', defaultFtype, @isnumeric);

% Pass all parameters and input to the parse method
parse(p, I, k, varargin{:});

%------------------------------------------------------------------------------
% This determines wether its a color (M,N,3) or gray scale (M,N,1) image
if ndims(I) == 3
    for i=1:3
        I2(:,:,i) = imdistcorrect(I(:,:,i), k);
    end
elseif ismatrix(I)
    I2 = imdistcorrect(I, k);
else
    error('Unknown image dimensions')
end
% Nested function that performs the transformation

function I3 = imdistcorrect(I,k)
    % Determine the size of the image to be distorted
    [M N] = size(I);
    center = [round(N/2) round(M/2)];
    % Creates N x M (#pixels) x-y points
    [xi, yi] = meshgrid(1:N, 1:M);
    % Converts the mesh into a column vector of coordinates relative to
    % the center
    xt = xi(:) - center(1);
    yt = yi(:) - center(2);
    % Converts the x-y coordinates to polar coordinates
    [theta, r] = cart2pol(xt, yt);
    % Calculate the maximum vector (image center to image corner) to be used
    % for normalization
    R = sqrt(center(1)^2 + center(2)^2);
    % Normalize the polar coordinate r to range between 0 and 1
    r = r/R;
    % Apply the r-based transformation
    s = distortfun(r, k, p.Results.ftype);
    % un-normalize s
    s2 = s * R;
    % Find a scaling parameter based on selected border type
    brcor = bordercorrect(r, s, k, center, R);
    s2 = s2 * brcor;

    % Convert back to cartesian coordinates
    [ut, vt] = pol2cart(theta, s2);
    u = reshape(ut, size(xi)) + center(1);
    v = reshape(vt, size(yi)) + center(2);
    tmap_B = cat(3, u, v);
    resamp = makeresampler(p.Results.interpolation, p.Results.padmethod);
    I3 = tformarray(I, [], resamp, [2 1], [1 2], [], tmap_B, 255);
end

% Nested function that creates a scaling parameter based on the % 'bordertype' selected

function x = bordercorrect(r, s, k, center, R)
    if k < 0
        if strcmp(p.Results.bordertype, 'fit')
            x = r(1)/s(1);
        end
        if strcmp(p.Results.bordertype, 'crop')
            x = 1/(1 + k*(min(center)/R)^2);
        end
    elseif k > 0
        if strcmp(p.Results.bordertype, 'fit')
            x = 1/(1 + k*(min(center)/R)^2);
        end
    end
end
end
if strcmp(p.Results.bordertype, 'crop')
x = r(1)/s(1);
end
end

% Nested function that picks the model type to be used
function s = distortfun(r,k,fcnum)
switch fcnum
  case(1)
    s = r.*(1./(1+k.*r));
  case(2)
    s = r.*(1./(1+k.*(r.^2)));
  case(3)
    s = r.*(1+k.*r);
  case(4)
    s = r.*(1+k.*(r.^2));
end
end
BED VOIDAGE DISTRIBUTION

clear all
clc

folder_REF={uigetdir('start_path','Choose the work directory')};
%Choose the work directory
cd(folder_REF);

prompt = 'What is the number of frames to process?'; %insert only
the last numbers different than zeros
n_frames=input(prompt);
prompt_pixels = 'What is the pixels/cm ratio?';
pi=csat[prompt_pixels];
prompt_Hexp = 'What are the Boltzmann Function Fitting parameters
[H1 H2 tc TAU]?'; %[H1 H2](cm) %[tc TAU] (sec)
BtzFunct_exp=input(prompt_Hexp);

[m,q,e_fix,con,qr,I0]=imageVOIDAGE_calibration();
im_pack=imread('NewA0108.tif'); %Reference image for choosing the
Region of Interest
im_pack=im2double(im_pack);

%%
cont=0;
for j=1:n_frames %Loop for calculating the voidage in all of the
frames
    filename=sprintf('NewA%04d.tif', j);% nome del file
    Img=imread(filename);
    Img=im2double(Img);
    num=I0-im_pack;
    den=I0*(1-e_fix);
    epsilon_in=1-(I0-Img)./(I0*con);
    epsilon=m*epsilon_in+q;

    cont=cont+1;
    Eps_matrix(:,j,cont)=epsilon;
    eps_av_dy=mean(epsilon,2);
    E_dy(:,cont)=eps_av_dy;
end

sizeEps=size(Eps_matrix);
voidage_average=mean(Eps_matrix,3); %Time-average voidage
distribution

%% FIGURES %%
%TimeArray
tspan=1/36;
t(1)=0;
for i=1:n_frames
    t(i+1)=i*tspan;
end

H1=BtzFunct_exp(1); %cm
H2=BtzFunct_exp(2); % cm
tc=BtzFunct_exp(3); % sec
TAU=BtzFunct_exp(4); % sec

figure(1), imagesc(E_dy);
[X_fixed,Y_fixed]=getpts(figure(1));
H2_pix=round(mean(Y_fixed));
Y_pix=1:size(E_dy,1);
mm=-pix;
qq=H2_pix-mm*H2;
Y_cm=(Y_pix-qq)/mm; % Y axis from pixels to cm
close(figure(1));

figure(2), imagesc(t,Y_cm,E_dy);
set(gca,'YDir','normal');

t_tan=tc; % tangent point in the flexural point
H_tan=H2+(H1-H2)/(1+exp((t_tan-tc)/TAU));
m_tan=(H2-H1)/(4*TAU);
q_tan=H_tan-m_tan*t_tan;

td=(H1-q_tan)/m_tan;
ts=1.2*tc;
dH2dt=H2/(ts-td);
Pcc=2*pix; % 2 cm in the bottom of the image are excluded due to curvature of the images
H_min_pix=size(E_dy,1)-Pcc; % minimum H visible in the image
H_min=(H_min_pix-qq)/mm; % conversion to cm
H1_pix=round(mm*H1+qq); % from cm to Pixels

for j=1:n_frames
    Hv(j,1)=H2+(H1-H2)/(1+exp((t(j)-tc)/TAU));
    Hv_pix(j,1)=round(mm*Hv(j,1)+qq);
    eps_H1(j,1)=E_dy(Hv_pix(j,1),j);
    if t(j)<=td
        Hv2(j,1)=0;
        Hv2_pix(j,1)=round(size(E_dy,1)-Pcc);
    elseif t(j)<=t_min
        Hv2(j,1)=dH2dt*(t(j)-td);
        Hv2_pix(j,1)=round(size(E_dy,1)-Pcc);
    elseif t(j)<=ts
        Hv2(j,1)=dH2dt*(t(j)-td);
        Hv2_pix(j,1)=round(mm*Hv2(j,1)+qq);
    else
        Hv2_pix(j,1)=H2_pix;
    end
end
dHz1=E_dy([Hv_pix(j,1):Hv2_pix(j,1)],j);
dHz12=E_dy([Hv_pix(j,1):H2_pix],j);
Eps_L(j,1)=mean(dHz1); % Voidage in zone 1 considering a larger portion of bed
Eps_R(j,1)=mean(dHz12); % Voidage in zone 1 considering a reduced portion of bed
end
function [m, q, eps_pack, const, I0] = imageVOIDAGE_calibration()

im_pack0 = imread('NewA0108.tif');
rect_pack = [16 470 20 20];
rect_fb = [16 88 20 20];

[ROI_p] = imcrop(im_pack0, rect_pack); % Choose the ROI
ROI_p = im2double(ROI_p);
eps_pack = 0.45;

[ROI_fb] = imcrop(im_pack0, rect_fb); % Choose the ROI
ROI_fb = im2double(ROI_fb);
eps_fb = 0.999;

% I0 = 1; % I0 (Maximum intensity) was 255(uint8)== 1(double) in this case
ek = (1 - eps_pack) / (1 - eps_fb);
umk = (ROI_p - ek * ROI_fb);
denk = 1 - ek;
I01 = mean(mean(numk / denk));
I0 = mean([I01 max(ROI_fb)]);

num_ = I0 - ROI_p;% packed solid
den_ = I0 * (1 - eps_pack);
const0 = mean(num_ / den_);
const = mean(const0);

EC_pack = 1 - (I0 - ROI_p) ./ (I0 * const);
E_calc_pack = mean(mean(EC_pack));

EC_bubble = 1 - (I0 - ROI_fb) ./ (I0 * const);
E_calc_bubble = mean(mean(EC_bubble));

m = (E_calc_bubble - E_calc_pack) / (eps_fb - eps_pack);
q = eps_pack - m * E_calc_pack;
end
## C. Bed Collapse Tests Results for Fresh and Spent Mixtures

Table C.1 - Fittings parameters for ST samples from Eqn. (4.4)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Parameter</th>
<th>STS (u_i=11 cm/s)</th>
<th>STM (u_i=15 cm/s)</th>
<th>STL (u_i=18 cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0</td>
<td>H_0, cm</td>
<td>13.98</td>
<td>14.21</td>
<td>14.51</td>
</tr>
<tr>
<td></td>
<td>H_0, cm</td>
<td>11.29</td>
<td>11.30</td>
<td>11.19</td>
</tr>
<tr>
<td></td>
<td>t_c, sec</td>
<td>0.52</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>τ_B, sec</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.92</td>
<td>0.91</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>H_0, cm</td>
<td>14.08</td>
<td>14.74</td>
<td>15.52</td>
</tr>
<tr>
<td></td>
<td>H_0, cm</td>
<td>11.29</td>
<td>11.30</td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td>t_c, sec</td>
<td>0.52</td>
<td>0.51</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>τ_B, sec</td>
<td>0.09</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.92</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>-1</td>
<td>H_0, cm</td>
<td>12.93</td>
<td>13.58</td>
<td>12.88</td>
</tr>
<tr>
<td></td>
<td>H_0, cm</td>
<td>10.70</td>
<td>10.70</td>
<td>10.89</td>
</tr>
<tr>
<td></td>
<td>t_c, sec</td>
<td>0.54</td>
<td>0.52</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>τ_B, sec</td>
<td>0.04</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.90</td>
<td>0.91</td>
<td>0.88</td>
</tr>
<tr>
<td>-2</td>
<td>H_0, cm</td>
<td>13.96</td>
<td>14.72</td>
<td>14.66</td>
</tr>
<tr>
<td></td>
<td>H_0, cm</td>
<td>11.19</td>
<td>11.19</td>
<td>11.10</td>
</tr>
<tr>
<td></td>
<td>t_c, sec</td>
<td>0.57</td>
<td>0.54</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>τ_B, sec</td>
<td>0.09</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.93</td>
<td>0.91</td>
<td>0.95</td>
</tr>
<tr>
<td>-3</td>
<td>H_0, cm</td>
<td>14.06</td>
<td>14.70</td>
<td>14.06</td>
</tr>
<tr>
<td></td>
<td>H_0, cm</td>
<td>11.19</td>
<td>11.18</td>
<td>11.18</td>
</tr>
<tr>
<td></td>
<td>t_c, sec</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>τ_B, sec</td>
<td>0.09</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Note: STS, STM, STL stand for different sample configurations.
### Table C.2 - Fittings parameters for NT samples from Eqn. (4.4)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Parameter</th>
<th>NTS $u_i$ [cm/s]</th>
<th>NTM $u_i$ [cm/s]</th>
<th>NTL $u_i$ [cm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>0</td>
<td>$H_0$, cm</td>
<td>13.29</td>
<td>14.01</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>$H_s$, cm</td>
<td>10.90</td>
<td>10.90</td>
<td>10.30</td>
</tr>
<tr>
<td></td>
<td>$t_c$, sec</td>
<td>0.52</td>
<td>0.50</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>$\tau_B$, sec</td>
<td>0.05</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.97</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>-1</td>
<td>$H_0$, cm</td>
<td>12.52</td>
<td>13.02</td>
<td>11.69</td>
</tr>
<tr>
<td></td>
<td>$H_s$, cm</td>
<td>10.50</td>
<td>10.50</td>
<td>10.70</td>
</tr>
<tr>
<td></td>
<td>$t_c$, sec</td>
<td>0.53</td>
<td>0.50</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>$\tau_B$, sec</td>
<td>0.03</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.93</td>
<td>0.93</td>
<td>0.95</td>
</tr>
<tr>
<td>-2</td>
<td>$H_0$, cm</td>
<td>12.63</td>
<td>12.85</td>
<td>11.55</td>
</tr>
<tr>
<td></td>
<td>$H_s$, cm</td>
<td>10.20</td>
<td>10.20</td>
<td>10.70</td>
</tr>
<tr>
<td></td>
<td>$t_c$, sec</td>
<td>0.54</td>
<td>0.52</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>$\tau_B$, sec</td>
<td>0.04</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.98</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td>-3</td>
<td>$H_0$, cm</td>
<td>12.60</td>
<td>13.20</td>
<td>10.79</td>
</tr>
<tr>
<td></td>
<td>$H_s$, cm</td>
<td>10.30</td>
<td>10.30</td>
<td>10.30</td>
</tr>
<tr>
<td></td>
<td>$t_c$, sec</td>
<td>0.52</td>
<td>0.52</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>$\tau_B$, sec</td>
<td>0.05</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.96</td>
<td>0.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>
PUBLICATIONS


CONFERENCE ABSTRACTS


