UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II



SCUOLA POLITECNICA E DELLE SCIENZE DI BASE

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale

Dottorato in Ingegneria dei Prodotti e dei Processi Industriali

XXXV Ciclo

Hydrodynamics and mixing of dissimilar granular solids in dense gas-fluidized beds

Ph.D. Thesis

Candidate

Laura Molignano

Scientific Committee

Prof. Piero SalatinoUniversità degli Studi di Napoli Federico IIProf. Roberto SolimeneSTEMS-CNRProf. Jean-François JolyIFP Energies NouvellesDr. Sina TebianianIFP Energies Nouvelles

Contents

Abstract	5
List of Figures	7
List of Tables	10
1. INTRODUCTION	11
1.1 Relevance of bed hydrodynamics and solids mixing to chemical reaction engineering of fluidized bed converters	11
1.2 Hydrodynamics and mass transfer in dense gas-fluidized beds	14
1.2.1 Literature review	14
1.2.2 Diagnostics	20
1.3 Mixing of polydisperse solids in dense gas-fluidized beds	23
1.3.1 Literature review	23
1.3.2 Diagnostics	26
1.4 Scope of the thesis	29
2. CAPACITANCE PROBE DIAGNOSTICS	30
 2.1 Cupacitatice process operation principle, design and applications to dense fluidized beds	30 ope34
3. EXPERIMENTAL	39
3.1 Experimental apparatus	39
3.2 Materials	40
3.3 Experimental procedures and data analysis	42
3.3.1 Experiment 1: hydrodynamic characterization of gas-fluidized beds of monodisperse solids	42
3.3.2 Experiment 2: characterization of mass transfer between an active part and the fluidized bed	icle 48
3.3.3 Experiment 3: characterization of solids mixing in a fluidized bed of bidisperse granular solids	52
4. CHARACTERIZATION OF HYDRODYNAMICS AND MASS TRANSFE FLUIDIZED BEDS OF MONODISPERSE SOLIDS	R IN 55
4.1 Experiment 1	55
4.1.1 Bed voidage measurements by capacitance probes	55
4.1.2 Balance of superficial gas velocity at bed cross-section	68
4.2 Experiment 2: mass transfer-limited reaction experiments	72

5.	CHAR	ACTERIZATION OF PARTICLE MIXING IN BEDS OF BIDISPE	RSE
GRA	ANULA	R SOLIDS	_ 76
5.	1 E	xperiment 3	_ 76
	5.1.1	Study of the transient phase of mixing	_ 76
	5.1.2	Steady-state profiles of solid tracer concentration in the dense phase of t	he
	fluidize	ed bed	_ 78
6.	CONC	LUSIONS	_ 87
7.	ONGO	ING ACTIVITIES AND FUTURE PERSPECTIVES	_ 90
Non	nenclatu	ire	_ 92
Refe	erences _		_ 95
Sup	Supplementary material		108

Abstract

Gas-fluidized beds (FB) are frequently used as favorable reaction environments in many industrially relevant heterogeneous processes where intimate contact between a solid and a gas phase is required. Bed hydrodynamics strongly influence the course of heterogeneous and homogeneous reactions in gas-FBs as they affect mixing/segregation patterns of the fluidizing gas and of fluidized solids, as well as heat and mass transfer around active particles immersed in a bed of inert particles. Assessment of the mentioned phenomena is, therefore, a key prerequisite for successful design and operation of FB converters.

The *two-phase theory* is of fundamental importance as a conceptual framework of *aggregative* fluidization for freely bubbling FBs of materials belonging to groups B and D of Geldart classification. Despite the vast popularity of the two-phase theory, it has long been recognized as being inaccurate under certain conditions, often resulting in an overestimation of the actual visible bubble flow. There is ample experimental evidence that properties of the emulsion phase in a freely bubbling FB depart from bed properties at incipient fluidization conditions. Nonetheless, systematic and comprehensive modelling of the emulsion phase expansion at gas superficial velocities in excess of incipient fluidization is still largely lacking. The scenario becomes even more complex when two or more dissimilar solids are fluidized, and operating conditions must be optimized so as to promote a prescribed degree of solids mixing. Characterization of hydrodynamics and mixing of single and polydisperse granular solids in FBs requires the setup of appropriate diagnostic tools, combining lack of intrusiveness, good sensitivity and reproducibility, robustness with respect to a broad range of process conditions.

In the present PhD thesis, hydrodynamics and solids mixing in freely bubbling FBs of Geldart B/D particles are investigated. Home-made uncooled capacitance probes are purposely developed. Most of the study is based on experiments in a laboratory-scale unit, to pave the groundwork for ongoing research on a pilot-scale FB.

In a first experimental campaign, four different bed materials are investigated both at ambient temperature and 500 °C, by varying the gas superficial velocities. The major effort consists in the analysis and interpretation of the time series of capacitance probe

signals at different locations in the bubbling FB. Results provide clear evidence of the expansion of the emulsion phase of the bed, and of the possible presence of two previously unnoticed low- and high-voidage regions in the emulsion phase. The consequent increase in the associated superficial gas velocity with respect to minimum fluidization conditions is assessed through available correlations/balance equations, and interpreted in relation to the role of the bubble throughflow coefficient.

A second experiment, based on diffusion-limited oxidation of carbon monoxide on a solid catalyst, is directed to the assessment of the effect of emulsion phase expansion on mass transfer around active particles immersed in beds of inert solids. Very good prediction of the Sherwood number dependence on superficial gas velocity is attained. Better estimates of the active particle Sherwood number are obtained if the Frössling-type correlation is implemented using the actual voidage and superficial gas velocity of the expanded emulsion phase. Results also support the possible usage of the Richardson-Zaki correlation applied to the emulsion phase of gas bubbling FBs.

In a third experiment, capacitance probes are further employed, with a novel approach, to characterize mixing of dissimilar solids in gas FBs. Time-series of signals from capacitance probes are analyzed with the aim of assessing the transient dispersion of one solid component into the other. Steady-state spatially resolved profiles of the solids concentration are determined at different operating conditions of the gas FB. Results reveal advantages and limitations of the technique applied to bidisperse solids and show, for the investigated systems, a peculiar phenomenology, which resembles the *layer inversion*.

Altogether, results are intended to provide not only a step forward in the understanding of dense gas FBs phenomenology but also widen the capabilities in design, scale-up and optimization of FB reactors.

Keywords: Gas-solid fluidization, Bed expansion, Mass transfer, Mixing/Segregation, Capacitance probe.

List of Figures

Figure 1.1 Schematic diagram of gas distribution on a horizontal section of the freely bubbling fluidized bed. 16

Figure 2.1 Needle-type guarded capacitance probes designs: (a) uncooled one-channel probe; (b) water-cooled two-channel probe; (c) water-cooled combined capacitance/zirconia-cell probe. 31

Figure 2.2 Outline of the uncooled capacitance probe (needle-type cylindric design) electricallywired to the amplifier by a low-noise coaxial cable.35

Figure 2.3 The capacitance probe. (A) From left to right: needle-type central sensor, inner ceramic tube, guard tube, outer ceramic tube, ground tube; (B) needle-type central sensor and ceramic tube assembly; (C) guard tube addition; (D) complete assembly; (E) refractory glue addition. 35

Figure 2.4 Relationship between output voltage *V* and relative dielectric constant κ for the applied capacitance measuring instrument ($V_0 = 7.6$ [V], $\Sigma = 0.3$ [-], Gain = 21 [pF V]). 36

Figure 2.5 Characteristic curve of the capacitance measuring instrument (relationship between output voltage *V* and relative dielectric constant κ). Different effects of the same relative dielectric constant variation ($\Delta \kappa = 1$ -) on the measured voltage. 37

Figure 3.1 Laboratory-scale experimental apparatus. (1) Windbox; (2) electrical furnaces; (3) ceramic insulation; (4) gas distributor; (5) column lateral accesses (schedule 40: ID 12.4 mm); (6) thermocouple for oven PID controller; (7) bed solids; (8) fluidization column; (9) hood; PT: piezoresistive pressure transducer (operating range: 0-75 mbar); TC: K-type thermocouple. 39

Figure 3.2 SEM images of three out of four bed materials. From left to right: grey quartz sand after conditioning, silicon carbide after conditioning, γ -alumina–1. 41

Figure 3.3 Experimental apparatus equipped for experiments of hydrodynamic characterization of dense FBs. (1) Air compressor; (2) air flowmeter; (3) column lateral tubes for capacitance probes (CP) fitting. $H_1 = 0.06$ m, $H_2 = 0.1$ m, $H_3 = 0.14$ m represent the axial location of the capacitance probes in terms of distance from the distributor. PT: piezoresistive pressure transducer (operating range: 0-75 mbar); TC: K-type thermocouple. 43

Figure 3.4 Variation of the mean number of pulses per unit time in the voidage signal from grey quartz sand experiment run at ambient temperature and with an excess gas velocity $U - U_{mf} = 0.35$ m/s. Capacitance probe sensing volume located at H_2 and column center. 45

Figure 3.5 Probability Density Function (PDF) of time-resolved voidage signal from grey quartz sand experiment run at ambient temperature and with an excess gas velocity with respect to minimum fluidization conditions $U - U_{mf} = 0.005$ m/s. Capacitance probe sensing volume located at H_2 and column center. 46

Figure 3.6 Emulsion-phase signal resolved over a fictitious time from grey quartz sand experiment run at ambient temperature and with an excess gas velocity $U - U_{mf} = 0.35$ m/s. Capacitance probe sensing volume located at H_2 and column center. 47

Figure 3.7 Experimental apparatus for reactive experiments. (1) Gas cylinders; (2) gas flowmeters; (3) gas suction probe; (4) membrane pump; (5) gas analyzers. PT: piezoresistive pressure transducer (operating range: 0-75 mbar); TC: K-type thermocouple. 49

Figure 3.8 Identification of signal *changepoints* based on the evaluation of signal mean within each section. Operating conditions: bed axis, H_1 , T = 500 °C, U = 0.44 m/s. 53

Figure 4.1 Time-resolved voidage signals. Probe radial location: center, probe level: H_1 , T = 500 °C, $U - U_{mf} = 0.1$ m/s. 56

Figure 4.2 Time-resolved voidage signals. Probe radial location: center, probe level: H_1 , T = 500 °C, $U - U_{mf} = 0.4$ m/s. 57

Figure 4.3 Estimate of bed expansion by unrelated methods. (a) Results at ambient temperature; (b) results at 500 °C. 58

Figure 4.4 Probability density functions of the local voidage of grey quartz sand fluidized bed at ambient temperature for different excess gas superficial velocities and probe locations. 59

Figure 4.5 Probability density functions of the local voidage of grey quartz sand fluidized bed at 500 °C for different excess gas superficial velocities and probe locations. 62

Figure 4.6 (A) Sample of the time-resolved voidage signal. (B) Schematic pattern of the time resolved voidage associated with the passage of a bubble. (C) PDF of the time series. Operating conditions: ambient temperature, $U - U_{mf} = 0.2$ m/s, probe location: bed axis, H_2 . 63

Figure 4.7 Probability density functions of the local voidage of γ -alumina–1 fluidized bed at ambient temperature for different excess gas superficial velocities and probe locations. 64

Figure 4.8 Probability density functions of the local voidage of γ -alumina–1 fluidized bed at 500 °C for different excess gas superficial velocities and probe locations. 65

Figure 4.9 Probability density functions of the local voidage of γ -alumina–0.6 fluidized bed for different temperatures, excess gas superficial velocities and probe locations. 66

Figure 4.10 Plot of the normalized mode values in the PDFs of the emulsion-phase voidage for the four material samples, at 500°C, as function of $U - U_{mf}$. 67

Figure 4.11 Comparison of dimensionless emulsion-phase gas superficial velocities reported versus $U - U_{mf}$, obtained with the three different procedures, for the four bed materials. Room temperature. 70

Figure 4.12 Comparison of dimensionless emulsion-phase gas superficial velocities reported versus $U - U_{mf}$, obtained with the three different procedures, for the four bed materials. 500 °C.

71

Figure 4.13 Comparison between the measured visible bubble flow and the one predicted from the correlation of Fu *et al.* valid for Geldart B and D solids and reported on the x-axis. 72

Figure 4.14 Sherwood number as a function of excess gas superficial velocity. T = 450 °C; bed material: grey quartz sand. Frössling-type correlations: black continuous line, K = 0.70, $U_e = U_{mf}$, $\varepsilon_e = \varepsilon_{mf}$; black dashed line, K = 0.84, U_e obtained from Eq. 3, $\varepsilon_e = \varepsilon_e^{HV}$; red continuous line, K = 0.69 not used as fitting parameter, U_e obtained from Eq. 4 applied to the HV-phase, $\varepsilon_e = \varepsilon_e^{HV}$.

Figure 5.1 Moving average, computed on a time interval of 1 s, of time-resolved pressure signal recorded at 0.01 m above gas distributor. Operating conditions: T = 500 °C, U = 0.44 m/s; fluidized bed of γ -alumina–1 solids (0.486 kg), tracer batch of SiC solids (0.196 kg). Injection performed at about 120 s. 76

Figure 5.2 Time-resolved voltage signals recorded at bed axis with the probes sensing volume placed at H_1 (bottom) and H_3 (top). Operating conditions: T = 500 °C, U = 0.44 m/s; bed of γ -alumina–1 solids (0.486 kg), tracer batch of SiC solids (0.196 kg). Injection performed at about 120 s. t_{H1} and t_{H3} represent the times at which the batch crosses the sensing volume of the two probes, respectively. $t_{H1} > t_{H3}$.

Figure 5.3 PDFs of voltage signals recorded by capacitance probe with the sensing volume placed at bed axis and H_1 . Operating conditions: T = 500 °C, U = 0.44 m/s. f_{γ} is the local volume fraction of γ -alumina–1 in the emulsion phase of the fluidized bed. 79

Figure 5.4 PDFs of voltage signals recorded by capacitance probe with the sensing volume placed at bed axis and H_2 . Operating conditions: T = 500 °C, U = 0.44 m/s. f_{γ} is the local volume fraction of γ -alumina–1 in the emulsion phase of the fluidized bed. 80

Figure 5.5 PDFs of voltage signals recorded by capacitance probe with the sensing volume placed at bed axis and H_3 . Operating conditions: T = 500 °C, U = 0.44 m/s. f_{γ} is the local volume fraction of γ -alumina–1 in the emulsion phase of the fluidized bed. 81

Figure 5.6 Concentration profiles of silicon carbide in the emulsion phase of the fluidized bed of γ -alumina–1. Tracer volume fraction is represented versus superficial gas velocity, and parametric in the axial coordinate. 83

Figure 5.7 Concentration profiles of γ -alumina–1 in the emulsion phase of the fluidized bed of silicon carbide. Tracer volume fraction is represented versus superficial gas velocity, and parametric in the axial coordinate. 84

Figure 5.8 Concentration profiles of silicon carbide (a) and γ -alumina–1 (b) in the emulsion phase of the fluidized bed measured in complementary experiments. Tracer volume fraction is averaged over bed cross section (Eq. 28) at H_1 (circles), H_2 (diamonds), and H_3 (squares), and finally, averaged over bed height (dotted line).

List of Tables

Table 1. Properties of bed materials.	41
Table 2. Properties of catalyst particles.	42

Table 3. Characteristic times of the voidage time series. Operating conditions: ambient
temperature, $U - U_{mf} = 0.2$ m/s, probe location: bed axis, H_2 .63

1. INTRODUCTION

1.1 Relevance of bed hydrodynamics and solids mixing to chemical reaction engineering of fluidized bed converters

Gas-fluidized beds are frequently used as favorable reaction environments in many industrially relevant heterogeneous processes where intimate contact between a solid and a gas phase is required. If properly designed and operated, gas-fluidized beds offer several advantages relative to competing gas-solid contactors (fixed beds, moving beds, grate reactors, rotary kilns) [1]. Among them:

- The relatively low pressure drops across the bed limit the operating costs.
- Continuous agitation of the particulate phase results in higher heat and mass transfer coefficients.
- Dead zones, hot spots, inhomogeneities, and variability in the quality of the products are significantly mitigated, if not completely avoided.
- Gas-fluidized beds are scalable to very large sizes and capable of being operated in a wide gas flowrate range.
- Particles can be added and removed continuously, facilitating continuous operation.
- Wide particle size distributions can be adopted.

On the other hand, abrasion, and erosion on walls and immersed surfaces, high-amplitude pressure oscillations, structural vibrations hamper a full exploitation of the potential of this technology. Gas bypass, which appears as rising bubbles in the dense gas-fluidized bed (FB), is another issue. However, the presence of bubbles cannot be seen as a penalty since they are also the main driver of particulate-phase agitation and mixing mechanisms [2]. Nevertheless, confined fluidized beds have been raising increased interest as they prevent the formation of bubbles, being particularly suitable for operations in which maximization of the conversion of gaseous reactant is crucial [3]. Gas *back-mixing*, which causes large deviations from the plug-flow model in the dense phase, is another element that might be perceived as undesirable. In this context, staged-fluidized beds represent a promising solution to the stated problem [4]. It can be concluded that, in most situations, advantages of gas-fluidized beds are found to outweigh their drawbacks.

Typical chemical processes carried out in gas-fluidized beds at commercial scale span across the refining, petrochemical, energy, environmental, chemical synthesis, pharmaceutical, food, biochemical and biotechnological, cement and mineral industries. The intrinsic advantages of fluidized beds significantly contribute to the environmental sustainability of such processes, which is a hot topic nowadays. For example, the absence of hot spots in the operation of high temperature units limits the production of undesirable pollutant compounds. Their removal can be, either way, accomplished by in situ feeding of solid sorbents, as it is the case for desulfurization in FB combustion [5]. The possibility to handle diverse solid particulate materials also favors direct exploitation/valorization of biomasses through various thermochemical processes, such as conventional combustion, gasification and pyrolysis [6]. The ease in removing/adding particles continuously paves the way to chemical looping processes, headed by the early success of chemical looping combustion (CLC) [7]. In this novel perspective for solid fuel conversion, based on the use of solid oxygen carriers to prevent direct contact between fuel and air, CO₂ separation is inherent to the process, so that the energy penalty associated with gas separation is ruled out. The remarkable thermal properties of FBs associated with the inherent mobility of fluidized particles has strongly supported the implementation of solar-driven heterogeneous chemical processes [8]. Reduction of fine iron ores in FBs is extremely advised over the classic blast furnaces: among several advantages, SO_x, NO_x and dust emissions are reduced due to the elimination of two high-pollution and high-emission processes of coking and sintering [9]. These are only some of many other examples in which FBs demonstrate to be at the forefront for the sustainability of chemical processes.

The widespread application and potential of gas-fluidized beds along with the complexity of these multiphase systems stimulate intense research efforts, still dedicated to gaining new insight at the fundamental level. Aspects like the extent of emulsion-phase expansion – to which mass transfer around fluidized particles is related – visible bubble flow, bubble rise velocity and emulsion-bubble interphase mass transfer are key reaction engineering parameters. In this perspective, they are considered fundamental knowledge prerequisites for successful design and operation of fluidized bed converters. However, there are still broad areas of uncertainties regarding bed hydrodynamics, on which mixing, heat and mass transfer phenomena depend. Commonly used models on bed hydrodynamics are often oversimplified or based on experimental studies in which operating conditions are far from those of real units. An aspect which is sometimes overlooked is that temperature

increase may affect the gas-solid distribution in a way that cannot be simply predicted by accounting for gas properties variation (i.e., density and viscosity) [10,11]. Interparticle forces may play an important role under certain conditions, providing one key for the effect of temperature. Shabanian and Chaouki [12] extensively surveyed the literature regarding the effects of temperature, pressure and interparticle forces on the hydrodynamic behavior of Geldart A, B and D solids. Altogether, it is concluded that the effect of temperature on bed hydrodynamics is still poorly characterized and understood, and this may jeopardize design and operation of industrial-scale fluidized bed converters operated at moderate-to-high temperature. The reduced number of available diagnostics for high temperature applications is unquestionably one of the factors contributing to the paucity of investigations at moderate-to-high temperatures. And this is even more true when large-scale systems are considered.

If the hydrodynamics of a bed of monodisperse particles are more complex than the existing models suggested in literature, the fact that in real processes the bed is never truly monodisperse and is made up of, at least, two different types of solids kinds complicates matters further. A dense fluidized bed reactor is generally characterized by an inert bed material, acting as dispersing phase. Inert solids are in preponderant amount with respect to active solids, which undergo an evolution throughout the process in terms of size, shape, density, and chemical composition. This is the case for solid fuels dispersed in an inert bed of sand. In more complex cases, a third different solid material is present, which acts, for example, as a catalyst. Mixing/segregation between such solids strongly influences the performance of the process, as it regulates particle-particle interactions and gas-solid mass transfer, with consequences on heat transfer and reactants conversion. Even in circulating FBs, solids mixing in the bottom bed zone is determinant for the overall process [13].

Requirements about the level of mixing/segregation of active solids in the dense FB, both in axial and lateral direction, depend on the type of process. Conventional combustion of solid fuels relies on relatively intense solids mixing to ensure complete burn out of fuel and to minimize the number of fuel feeding ports. In allothermal gasifiers, characterized by two interconnected beds, the aim is to control the fuel mixing to give the fuel sufficient residence time within the gasifier. Too high lateral mixing results in a loss of char from the gasifier to the connected combustor. In CLC fuel reactors, in contrast to direct combustion, moderate levels of lateral mixing increase the fuel residence time, thereby minimizing losses of unconverted char to the air reactor [14]. In calcium looping applied for thermochemical energy storage, there are recent proposals about the introduction of separation units to increase the efficiency of closed CO₂ cycles for power generation [15–18]. In the present case, segregation phenomena need to be favored over mixing. Another relevant aspect is the characteristic mixing/segregation time of a batch of active solids in the dense fluidizing bed. The relationship between mixing/segregation and competing processes characteristic times determines the effectiveness of the overall process. For example, operational experience of FB-combustors of high-volatile biomasses has shown that fuel particles rapidly tend to segregate at the bed surface during the devolatilization stage, leading to "stratified" conversion patterns [6]. One can draw the conclusion that the success of any process involving a variety of different types of solids depends on a thorough understanding of the key factors impacting solids mixing dynamics. To properly design and operate fluidized beds, engineers need to predict the dynamics of polydisperse mixtures and anticipate how these respond to changes in operating conditions.

Processes involving fast heterogeneous chemical reactions are those mostly sensitive to bed hydrodynamics, as mixing and mass transfer phenomena become the controlling steps of the conversion [6]. This is the case, for instance, of fluidized bed combustion of biomass [19–21] or fossil solid fuels [22,23], performed at temperatures high enough for intrinsic kinetics not to be the rate-controlling step.

1.2Hydrodynamics and mass transfer in dense gas-fluidized beds

1.2.1 Literature review

The *two-phase theory of fluidization* postulated by Toomey and Johnstone [24] has been of fundamental importance to the comprehension of the concept of *aggregative* fluidization. In freely bubbling fluidization, the bed is composed of two main phases: solids-free bubbles and a dense *emulsion* phase, consisting of solids dispersed in the gas. All the gas exceeding the incipient fluidization velocity, U_{mf} , flows across the bed as bubbles, while the emulsion phase is kept at incipient fluidization. This theory applies to solids belonging to group A of Geldart classification [25], once the minimum bubbling velocity, U_{mb} , is attained, and to groups B and D, in which the minimum bubbling velocity coincides with U_{mf} . Nevertheless, it is a long-established fact that the two-phase theory seriously overestimates the visible bubble flow in most cases [26]. Two contrasting explanations have been advanced: some studies have attributed this deficit in visible bubble flow to an increase in interstitial gas velocity in the dense phase above that required for incipient fluidization [27–29]. In this case, the division of gas flow between phases would be more favorable for gas-solid reactions. Following studies have confirmed that the dense phase does not stay at minimum fluidization conditions as superficial gas velocity is increased. Departures of the voidage in the emulsion phase with respect to that at incipient fluidization conditions have been observed for Geldart A, AB [30], B [31] and D [32] groups solids. Cui et al. [33,34] underlined that both Geldart A and B solids exhibit a distribution of emulsion-phase voidages, the mean void fraction of the emulsion phase in a freely bubbling bed being remarkably different from that at incipient fluidization. Yates et al. [35] demonstrated, for groups A and B of Geldart classification, that voidage around gas bubbles decreases exponentially to that of the emulsion phase far from the bubble, and that there is no sharply defined boundary between bubble, cloud, and emulsion. Andreux and Chaouki [36] identified thresholds to separate the dense phase, the cloud and bubbles by adopting a statistically-based approach. However, a systematic modelling of the dense-phase expansion for the different groups of Geldart classification lacks. Other theories have ascribed the reduction in visible bubble flow mostly to throughflow inside bubbles [37], leading to the so-called modified two-phase theory [38]. Grace and Clift [26] considered this theory still oversimplified and proved it by collecting highly scattered results on throughflow contribution from several studies. In a more comprehensive view, Valenzuela and Glicksman [39] considered that the gas may cross the horizontal section of a conventional bubbling fluidized bed following all the mentioned mechanisms (Fig. 1.1):

- as bubble voids, contributing to the visible bubble flow,
- as flow through the bubbles, known as throughflow component,
- as interstitial flow relative to the particles in the dense phase (not necessarily at minimum fluidization conditions).

This can be traduced in the following gas balance on superficial gas velocity, U:

$$U = U_e(1 - \delta) + U_b \delta + U_{tf} \delta \tag{1}$$

where δ is the volume fraction of the bed in bubbles, U_e represents the superficial gas velocity in the dense phase, U_b the bubble velocity, U_{tf} the velocity of gas passing through the bubbles. All these quantities represent average values both in time and space.

For Darcy-type gas flow in the dense phase where constant voidage, ε_e , is considered, U_{tf} is dependent only on the pressure field in the bubbling fluidized bed and on densephase permeability. It is postulated that the pressure field is independent of whether the bubbles are in motion, but it depends only on bubble size, shape, and location, if constant bubble volumes are considered [40]. Dense-phase permeability is related to U_e , which is demonstrated to be only dependent on ε_e [39]. The interrelation between U_{tf} and U_e is, therefore, expressed through a proportionality coefficient, k_{tf} , resulting in:

$$U = U_e(1 - \delta) + U_b\delta + k_{tf}U_e\delta$$
⁽²⁾

For a single three-dimensional spherical bubble in an infinite bed, k_{tf} is 3. Deviations from this value occur in freely bubbling fluidized beds for bubbles having a shape different than the spherical one and following specific bubbles patterns. All these aspects would lead either to an increase or to a reduction in the throughflow coefficient with respect to 3 [39].



Figure 1.1 Schematic diagram of gas distribution on a horizontal section of the freely bubbling fluidized bed.

Glicksman and McAndrews [41] measured the throughflow coefficient for several bed widths, but considered the dense phase being at incipient fluidization conditions, even though fluidization numbers higher than unity were adopted. Olowson and Almstedt [42] measured the throughflow velocity of gas inside bubbles of a 3D cold large-fluidized bed using Pitot-static pressure probes at different pressure conditions. Other researchers [43,44] performed measurements in 2D fluidized beds of isolated bubbles operated at superficial velocity slightly higher than incipient. Lim et al. [45] measured a throughflow factor in a 2D fluidized bed of Geldart B solids using a gas balance where bubble, wake and dense phases were included, with the dense phase considered at minimum fluidization conditions. Wu et al. [46] tested the effect of bed temperature on the interphase mass transfer coefficient between the bubble and the dense phase for different materials by injecting single bubbles into an incipiently 3D fluidized bed. By modifying the Sit and Grace model [47] to reflect possible changes in the throughflow gas velocity, they identified a range of throughflow coefficients, which varied according to the operating temperature and the adopted material. Experiments to quantitatively assess gas mixing and hydrodynamic patterns associated with the rise of isolated bubbles in a 3D hot gasfluidized bed at incipient fluidization conditions were also performed by Solimene et al. [48]. In this context, local throughflow coefficients were derived from experimental results on Geldart B and D solids. Almendros-Ibáñez et al. [49] studied the effect of voidage distribution around endogenous bubbles on the throughflow component in 2D fluidized beds. Bakshi et al. [50] adopted computational fluid dynamics (CFD) to simulate bubbling fluidized beds representative of large-scale units. The authors statistically determined the gas-flow distribution in fluidized beds of three distinct Geldart B particles: the percentage of gas moving as/through bubbles or percolating in the dense phase was calculated for the three materials at several superficial gas velocities. Moreover, a throughflow factor, indicating the tendency for throughflow, was defined. Even though they did not account for the throughflow contribution using the coefficient k_{tf} , it could be probably deduced from their results. Villanueva-Chávez and Bizzo [51] developed a one-dimensional mathematical model of the fluid dynamics and the biomass combustion process in a bubbling fluidized bed. They included the throughflow component in the gas balance and, unlike in the classic approach, the emulsion phase was considered not to remain under minimum fluidization conditions. Results were validated with experimental and CFD studies from other authors [52,53].

The coefficient k_{tf} could be deduced from the gas balance expressed in Eq. 2, if all the other terms are known. Among them, U_e is of relevance as it could be significantly different from U_{mf} and, in turn affect the term associated to the throughflow. This would have consequences especially for those processes in which hydrodynamics play a crucial role on the overall gas-solid reaction conversion. In aggregative fluidization of Geldart B and D solids, U_e can be calculated from the relationship of Hilligardt and Werther [31], valid for three-dimensional beds:

$$\frac{U_e - U_{mf}}{U - U_{mf}} = \frac{1}{3}$$
(3)

Eq. 3 can be a powerful tool to predict the superficial velocity of gas percolating through the expanded emulsion phase of a bubbling fluidized bed, despite not accounting for differences between Geldart B and D solids and possible local differences inside the dense bed.

In homogeneous fluidization, a consolidated relationship links $U_e (\equiv U)$ with $\varepsilon_e (\equiv \varepsilon_f)$:

$$\frac{U_e}{U_{mf}} = \left(\frac{\varepsilon_e}{\varepsilon_{mf}}\right)^n \tag{4}$$

Eq. 4 derives from the original form of the Richardson-Zaki correlation [54]

$$\frac{d \log U}{d \log \varepsilon} = n = constant \tag{5}$$

integrated with the boundary condition $U = U_{mf}$ at which $\varepsilon = \varepsilon_{mf}$. In the most common formulation, Eq. 5 is, actually, integrated with the boundary condition $U = U_t$ at which $\varepsilon = 1$. The parameter *n* correlates with the Archimedes number through the relation of Khan and Richardson [55]. Eq. 5 originates from liquid fluidization and, as resumed by Di Felice, several authors have confirmed its applicability to the homogeneous expansion range of gas-solid beds [56,57]. In particular, it has been demonstrated that an analytical derivation of Eqs. 4 and 5 can be obtained starting from the important property of fluidized beds that any modification in the fluid flux gives rise to changes in the void fraction to keep the unrecoverable bed pressure loss constant [58]. Supposed improvements of the original Richardson-Zaki equation have been suggested afterwards, but in general the predictive capability does not change significantly in spite of increased complexity and the use of "non-justifiable factors" [56]. The idea of extending the relationship to liquid fluidized beds encountering the appearance of bubbles has been mentioned in the review of Di Felice. The fact that hydrodynamic modelling of gas-solid two-phase flow, where the phenomena are dominated in a chaotic manner by the presence of bubbles, would benefit from basic input from liquid-solid systems studies, was also suggested. Long before, Avidan and Yerusalemi [59] had studied the applicability of the Richardson-Zaki equation to Geldart A solids fluidized in the slugging and turbulent regimes. Afterwards, Olowson and Almstedt [32] adopted the Richardson-Zaki correlation to solids at the boundary between groups B and D, fluidized in the bubbling regime, to calculate the dense-phase expansion from U_e measurements.

Concerning mass transfer between the bulk of the fluidized bed and an active particle, it is typically expressed in terms of the Sherwood number:

$$Sh = \frac{k_g d_a}{\mathcal{D}_a} \tag{6}$$

where k_g is the gas mass transfer coefficient, d_a is the active particle diameter, \mathcal{D}_g is the gas diffusion coefficient. Sherwood number represents the average dimensionless gas concentration gradient of the transferring species at the active particle surface. In analogy with the mass transfer around isolated spheres in a gas flow, mass transfer data in the emulsion phase of a fluidized bed can be described according to a Frössling-type correlation [60]:

$$Sh = 2.0 + K \cdot Re^{1/2}Sc^{1/3} \tag{7}$$

 $Re = \frac{\rho_g U d_a}{\mu_g}$ and $Sc = \frac{\mu_g}{\mathcal{D}_g \rho_g}$ are the dimensionless Reynolds and Schmidt numbers and *K* is a constant. The most accurate value for *K* has been proposed by Rowe *et al.* [61] – who extended the results on mass transfer around isolated particles by Ranz and Marshall [62] to Reynolds numbers comprised between 20 and 2000 – and is equal to 0.69. In the version of the correlation applied to the dense phase of a fluidized bed, where active particles generally reside, the effect of bed particles, which leads to a decrease of the available volume for gas-particle mass transfer, must be considered. Accordingly, the Frössling-type correlation is modified as following:

$$Sh = 2.0 \cdot \varepsilon_e + K \cdot \left(\frac{Re_e}{\varepsilon_e}\right)^{1/2} Sc^{1/3}$$
(8)

The correlation, as expressed in Eq. 8, is a general form in which is highlighted that the Sherwood number refers to the emulsion-phase properties. Also in the Reynolds number, *U* refers to the superficial gas velocity in the emulsion phase. According to the *two-phase theory of fluidization*, Eq. 8 writes as following:

$$Sh = 2.0 \cdot \varepsilon_{mf} + K \cdot \left(\frac{Re_{mf}}{\varepsilon_{mf}}\right)^{1/2} Sc^{1/3}$$
⁽⁹⁾

Scala has proved the validity of Eq. 9 [63] and K = 0.70 resulted from the best fitting of data. The reference to properties of the bed at incipient fluidization arises from the assumption that active particles mostly reside in the emulsion phase, and by the additional hypothesis that, according to the two-phase theory, the emulsion-phase voidage is equal to the bed voidage at incipient fluidization. Accordingly, *Sh*, does not show any dependence on the fluidization velocity. The results obtained by the author can be justified in the light of the adopted experimental conditions. In all the experimental tests, the bed rapidly encounters the slugging regime as superficial gas velocity is increased, due to the small internal diameter of the column. It is reported that the two-phase theory is a better approximation for slugging than for bubbling beds [64]. These results suggest how interesting it would be to assess the mass transfer in a larger bubbling fluidized bed: herein deviations from simple theories as regards the split of fluidizing gas between the bubble and the emulsion phases could probably not be neglected.

1.2.2 Diagnostics

Very long-standing literature studies have highlighted that fluidization patterns of dense gas-FBs may largely depart from the basic two-phase theory. This has been stimulating a continuing effort over years in the development and application of a broad variety of experimental techniques aimed at pointwise characterization of bed voidage distribution, particle velocity, particle mass flux, gas velocity distribution and bubble features.

Below, the main experimental techniques developed to characterize FBs hydrodynamics have been grouped according to their intrusiveness in the dense bed.

Visual observation is a straightforward non-intrusive way to obtain information about bed voidage distribution, bubble shape and size, particles and gas velocity. However, its use is limited to transparent-wall units hosting very dilute systems, the outer layer of fluidized beds, and pseudo-2D beds [65]. Visual inspection of the bed may be accomplished at moderate-to-high temperature by infrared [66] or X-ray imaging [35,67]. The latter could be extended to 3D units, although visualization of multiple bubbles and 3D patterns is hampered by the 2D projection of 3D objects. High temporal resolution magnetic resonance imaging (MRI) has been employed to gather 2D images of particle concentration, bubbles and velocity fields in dense fluidized beds [68]. Limitations to the use of this otherwise promising technique are posed by operation at high temperatures, and by the need to develop engineered granular materials that may be considered representative of those fluidized in industrial applications. Tomography can be used as a non-invasive 3D imaging technique. Most electrical capacitance tomography (ECT) systems operate at up to 1000 frames/sec sampling rate. This is an advantage over radioactivity-based tomography, for which sampling frequency is an issue to the benefit of higher spatial resolution. On the other hand, application of ECT in industrial installations is often problematic in high-pressure and/or high-temperature applications in processes carried out in metallic vessels [65]. Radioactive particle tracking (RPT) is an option for investigating particle velocity and bed voidage [69], but an additional technique should be considered to study bubbles phenomenology. Moreover, RPT implementation entails the use of a tailored material resembling real bed properties. Positron emission particle tracking (PEPT) is a non-invasive technique similar to RPT [70].

Among intrusive diagnostics, fast response borescopic probes connected to high speed/resolution cameras can optically access the interior of the dense fluidized bed and provide time-resolved and local information on both bubble and emulsion phases [70]. Post-processing of borescope images may be somehow non-straightforward, entailing the choice of thresholds and imaging parameters that may introduce some bias in the results. Borescopic probes have been used in high temperature dense fluidized beds [71] as a non-invasive technique in pseudo-2D units. Thus, the technique has not been proved yet as intrusive technique in high temperature 3D dense fluidized beds. Instead, optical fiber pyrometry has been successfully used as an intrusive tool in dense fluidized beds operated at 850 °C [72]. Optical probes can be employed for measuring gas distribution, solids

velocity and bubble properties, including velocity, in fluidized beds. They have also been used in high temperature units [73]. They provide local measurements; thus, a sufficiently high number of probes must be adopted to gather a 3D description of the dense fluidized bed. Capacitance probes are similar to optical probes as they allow the investigation of several aspects of the dense fluidized bed, they can be easily implemented, and signals are not difficult to interpret. Small measuring volumes [74], fine temporal resolution, relatively low costs and possible applicability in the harsh environments of industrial units represent other positive features of this technique [65]. Needle-type capacitance probes [74] are usually utilized in fluidized beds since the miniaturized design causes very little disturbances of the flow. This aspect has been proved in the study of Tebianian et al. [75]: the use of a 4 mm OD probe produced slight qualitative variations on voidage distribution, and, quantitatively, the average voidage only changed within 2 % with reference to the condition where the probe was absent. A customized uncooled capacitance probe has been designed and manufactured for application to fluidized beds operated at high temperature [76]. The response of the probe can be fast enough to follow voidage fluctuations up to 2 kHz [65].

Diagnosis based on gas pressure measurements can be either intrusive or not. Pressure probes are cheap and relatively easy to manufacture, and therefore widely applied in fluidized beds. They can give an estimate of bed bulk density or average bed height. When pressure is sampled at sufficiently high frequency, the pressure fluctuation signal can yield much more information about bed hydrodynamics. Indeed, pressure signal is a combination of local bubble passage and non-local compression waves, which originates from bubble generation, bubble coalescence, bubble eruption, and gas flow fluctuations. Time-resolved measurements concern single-point absolute pressures or pressure differences between two points. Even when suitable sensors are used, measurements can easily be distorted due to resonance effects from the connection tubes, signal dampening caused by connection tubes small diameters, disturbances from purge flows, particles entering the probe, probe positioning relative to the bed. Moreover, interpretation of pressure signals is not straightforward [65]. Particle pressure can be measured separately from gas pressure by adding some bypass tubing to the chamber of the sensor covered by the diaphragm [77]. Acoustic measurements can be an alternative to pressure taps, especially in industrial units operated at high pressure. However, they are only used to obtain qualitative information about the state of fluidization [65].

The combined use of several diagnostics has greatly contributed to advance towards a more realistic description of the FBs, shedding light, among the others, on bubbling patterns: shape and size of bubbles, wake extension and associated flow [19], particle fingering and raining from the roof of the bubble, and associated bubbles splitting [2], formation of clouds, coalescence, bubble-induced large scale motion and solids mixing [78]. Concerning the emulsion-phase behavior, as reported in the literature review on hydrodynamics and mass transfer in dense gas-fluidized beds (sub-paragraph 1.2.1), several experimental techniques have revealed the presence of an expanded dense phase occurring when superficial gas velocity is increased above minimum fluidization conditions. Along a different pathway, other studies have confirmed the presence of gas flowing through bubbles. A systematic modelling of the dense-phase expansion for the different groups of Geldart classification is still lacking and throughflow coefficients have been measured mostly in incipiently fluidized and/or 2D beds, with single-bubble injections.

1.3 Mixing of polydisperse solids in dense gas-fluidized beds

1.3.1 Literature review

Many applications of fluidization technology regard processes in which dissimilar materials, i.e., particles of different density and/or size, are involved. Effective mixing conditions of different solids are typically necessary in most of the fluidized bed processes, although in some applications segregation is a phenomenon to be emphasized (see paragraph 1.1). Mechanisms of mixing and segregation in dense FBs mainly rely on the phenomenon of "bubbling". Along their upward motion, bubbles cause particle movement inside the fluidized bed. Solids are transported to the bed surface within the wake and the upward drift that generates around the vertical axis of the bubble (mechanisms of wake and drift [64]). These patterns, prevailingly active along the vertical direction, have their closure in the splash and grid zone, where solids motion has a horizontal character. The mechanism of lateral mixing by bubbles bursting at bed surface is dominant in shallow beds, and emphasized for solids undergoing axial segregation [66]. The bubble-induced gross solids circulation described above is known as gulf-streaming

motion and occurs at the scale of the bed height. Internal circulation of solids, instead, occurs at the scale of bubble diameter [79]. Internal circulation mechanisms include solids sinking in the emulsion phase to fill the gap created by the rising bubble and unstable circulation motion of particles within bubble wake (wake shedding mechanism). In this last mechanism, solids are laterally released in the surrounding emulsion phase and replaced. Local particle displacement within the bubble wake and between the wake and the emulsion can be attributed to the Brownian-type motion of particles [80]. Bubbles coalescence is another mechanism occurring at the bubble-diameter scale, which contributes to lateral solids mixing [79].

Literature on gas-fluidized bed units of polydisperse solids can be resumed into two major categories. In both cases, the presence of *flotsam* and *jetsam* components can be recognized. The terminology refers to *flotsam* the particles that tend to accumulate to the top of the bed and to jetsam those that sink down at the bottom of the bed [81]. The first category of FBs of polydisperse solids can be referred as mixtures of bed materials. The bed is characterized by the presence of two or more dissimilar solids in fairly equal or moderate proportion with one another. The solid species generally differ from each other in size and/or density in a limited extent. The inert bed of sand as adopted in industrial practices can be conceived as polydisperse bed in the light of the above definition: it is composed of a wide size range of fluidized particles having the same density. The second category of FBs polydisperse mixtures refer to solids species differing in size and density by orders of magnitude. The former solid species is present in small percentages with respect to bed material solids in a way that, in a perfectly mixed state, it is surrounded only by bed material solids. Referring to examples of practical interest, the solid species which is present in smaller amounts is generally larger and lighter than bed material solids. It is the case of biogenic large solid fuels [82], representing a small percentage of the bed inventory in a thermochemical process. The utilization of large particle sizes is fulfilled to compensate for the markedly lower density of the biomass solid if compared to bed inert particles. In this case study, the inference on the flotsam/jetsam component is accomplished by comparing bed particles bulk density with large solids particle density.

Most of the numerical and experimental literature studies are focused on the fluidization of binary systems of solids. Such systems are easier to investigate, and results can be extrapolated with some confidence to more complex cases. A fluidized bed of two dissimilar solids can be characterized by determining a series of properties. Among them, the initial fluidization velocity and the final fluidization velocity serve to identify the gas velocity interval along which fluidization of the binary mixture takes place [83]. Besides, the interest in most of the studies on binary mixtures lies in determining the equilibrium condition between the mixing and the segregating tendencies of particles under the fluidization state. Mixing and segregation occur concurrently, and their dynamic equilibrium yields axial/radial profiles of particle concentrations. The mixing or segregation index [84–87] represents the best way to assess such equilibrium based on solids properties and operating conditions. This approach can reveal the dominant property in the establishment of segregation patterns (size-segregating [88], density segregating [89]). As for the description of the dynamics of mixing/segregation patterns, some studies have addressed the unsteady state of fluidization that may establish at gas superficial velocity below the threshold for complete and uniform fluidization of solid mixtures and the dynamics of particle segregation expressed through the drift flux velocity of mixture components [86,90]. Among mathematical models, a completely predictive one [91], without adjustable parameters, is able to foresee the segregation tendency/direction of solid species in unconventional binary mixtures of dissimilar materials in which the role of jetsam and flotsam cannot be established a priori. The characterization methods above are applied to binary mixtures studied in small-scale units.

In the industrial field, where large-scale fluidized beds are operated, multiple mixing cells [78,92] establish along the vertical or transversal direction depending on whether deep or shallow beds are utilized. In this context, the dispersion model represents the most reliable and feasible option to assess mixing in the solid phase. The flux of particles is expressed as a solid dispersion coefficient, \mathfrak{D}_s , multiplied by the gradient of particle concentration and is referred only to the displacement of solids from one mixing cell to its neighbors. Solids dispersion coefficient does not give information on the mechanisms governing the mixing process. Instead, it is a useful design parameter, whence one can understand its relevance. Utilization of the macroscopic dispersion model to small apparatuses or units in which one or very few mixing cells can be identified is questionable. In this kind of apparatuses mixing can be addressed at a meso-to-micro scale level [93]. Given that the mechanisms of solids mixing along the horizontal direction result, overall, to be less

effective than those active on the vertical direction [2], research has been quite focused on the investigation of lateral dispersion of solids. Lateral dispersion coefficients evaluated in 3D medium-to-large scale units, in which bed aspect ratios were less than unity, span over a very broad range of four orders of magnitude $(10^{-4} - 10^{-1} \text{ m}^2/\text{s})$ [14,72,74,87–96]. These results have been interpreted over years in the light of the dependance of mixing phenomena on several operating parameters. The lowest values of solid lateral dispersion coefficients are likely to be observed in smaller units [80,98] due to significant wall effects. Higher \mathfrak{D}_s^r values result as superficial gas velocity is increased with respect to incipient fluidization, although this effect is limited in shallow beds [97]. The same tendency is shown as initial bed height increases [96]: bubbles become larger due to coalescence and inflow from the dense phase, with positive consequences for particle projection in the splashing zone. Lateral dispersion coefficient seems to be positively correlated with temperature [101,103]. Gas distributor can influence the dispersion of a tracer in the dense bed, as it is responsible for bubbles formation. The effect of tracer feed rate and location is not clear due to contrasting literature results [97,104]. The objective would be to develop a correlation equation able to predict the horizontal dispersion coefficient depending on the main fluidization features for, in turn, improving the design and operation of large-scale fluidized bed units. Correlations that have been proposed so far are comprehensively resumed in the review of Solimene [2].

1.3.2 Diagnostics

The main diagnostics employed in literature to characterize mixing and segregation of bidisperse solids in dense gas-fluidized beds are summarized as follows. Eulerian techniques locally measure a tracer concentration, not giving information on the trajectory of single tracer particles. In many cases such diagnostic techniques are intrusive, as the measuring probes have to access different points of the dense bed. When possible (see paragraph 1.3.1), tracer concentrations measured along the axial and/or radial coordinate of the dense bed can be fitted with a dispersion model to derive a solid dispersion coefficient. Lagrangian techniques track the patterns of a single or multiple tracers, and are mostly non-intrusive with respect to Eulerian methods. After measuring tracer particle

trajectories, a dispersion coefficient can be calculated using the Einstein's equation for Brownian motions [105].

Among Eulerian techniques, solid sampling is used to measure the local concentration of a tracer in the dense bed by withdrawing solid samples from it. It is a direct method as one can directly measure the concentration of the tracer in the retrieved sample. Tracer is distinguished from bed solids by size [106,107], density [103], color [108,109], or composition [98,100,102]. Solid sampling can be realized either on-line or after defluidization of the bed [106,110–112] to measure the tracer concentration at steady state conditions of the fluidized bed or in a transient phase of the mixing/segregation phenomenon. On-line samples collection out from the reactor is considered a drawback. Bed-collapse method can cause solids segregation and alter the measurement. Thermal tracing consists in assessing mixing by means of heated [113–115] or cooled tracers [13,97]. It is an indirect method as solid tracer concentration is gathered passing through the measurement of local temperature inside the system [99,116]. High-frequency fast sensors are required to obtain reliable measures in transient conditions. The method requires the bed material to be at a different temperature than the injected sample of tracer solids. The method loses its effectiveness when temperature gets uniform inside the bed. Therefore, it is important to understand which of the two mechanisms, solid mixing and heat transfer, is limiting in the operation of the fluidized bed. Thermal tracing could also be implemented non-intrusively by measuring temperature with an infrared camera [66]. In this case, the implementation of the technique would be limited to the surface of the dense fluidized bed or to 2D units. Gas sampling [101,104,117] enables the study of timeresolved solid mixing in dense beds. By sampling and analyzing the gas above the bed coming from tracer particles, it is possible to indirectly measure the gas-emitting tracer concentration in the bed. The non-intrusive usage of this Eulerian technique implies uncertainties for inferring the local tracer concentration from gas analysis, especially if evaporation, desorption, gasification or reaction rates are too low to have an accurate online measure. Moreover, inference on mixing/segregation mechanisms along the bed axial coordinate can hardly be accomplished. Thus, such a technique could be considered if coupled with other techniques, such as temperature measurements inside the bed when using frozen CO_2 tracers [13,97]. The use of gas emitting tracers can simulate the formation of endogenous bubbles inside the bed and the method allows low contamination of the bed if tracers are progressively worn out through evaporation or chemical reaction. When axial mixing/segregation is to be addressed in very deep beds, multiple pressure probes can be fitted to the column and bed-slices composition can be measured by determining the local minimum fluidization velocity of the mixture [118]. Capacitance probes can be used to indirectly measure the concentration of a tracer in a dense fluidized bed of bidisperse solids [119,120]. Time-resolved voltage signal associated with the emulsion phase of the bed depends on void fraction and on the relative amount of the two solids. Tracer relative dielectric constant must be sufficiently different from that of bed material solids. An assumption on the emulsion-phase voidage is required to postprocess the emulsion-phase signal. The technique has been tested only with bidisperse mixtures of solids having the same size. The method can be applied to high-temperature 3D large-scale systems, although this has not been tested yet.

Some Lagrangian techniques consist in video recording and subsequent digital image analysis of particle trajectories. A fast camera is put on the roof of the reactor or outside a transparent 2D apparatus. The tracer has to be clearly distinguishable from the bed material. Phosphorescent tracers [78,121] are preferred over pigmented particles although phosphorescence is a time-limited phenomenon. Hot tracers can also be adopted [94,122,123]. Single or multiple tracers can be used. The technique is non-intrusive and allows time-transient and steady-state studies. Data collection at the surface of dense beds is limited to the domain above the dense bed surface, i.e. does not allow for continuous tracking of individual tracer particles as tracers regularly immerse in the dense bed. Xrays, gamma-rays [124], and electrical capacitance [125] are tomography-tracking techniques more suited for 3D systems if compared to camera-based ones. The first two techniques require substantial safety measures. In magnetic particle tracing, magnetoresistive sensors track a single magnetic tracer particle, whose properties can be tuned to have the required particle density and diameter. Generally, there are limitations in the maximum operating temperature depending on the Curie point of the magnet. Moreover, the insulation and the heating system can represent an obstacle for the effectiveness of the method. The operation of the fluidized bed in fluid-dynamic scaled conditions represents the solution to the stated problem [103]. In this case, the use of large apparatuses is still advised if operation of large-scale units is to be represented, to avoid that measurements could be affected by wall effects [96].

1.4Scope of the thesis

The scope of this PhD thesis is to investigate fluidized beds hydrodynamics and mixing between bidisperse solids. In particular, the characterization of bubbling fluidized beds of monodisperse Geldart B/D solids at ambient and high temperature is of interest, as they are widely employed in industrial applications. Several aspects of the fluidized bed hydrodynamics must be addressed, particularly focusing on departures of the system from simplified models. Concerning mixing of dissimilar solids in gas fluidized beds, the aim is the assessment of the transient dispersion of one solid component into the other, and of the parameters affecting the establishment of the equilibrium between mixing and segregation mechanisms. For the mentioned purposes, a suitable diagnostics has to be chosen and developed, taking a cue from literature. The proposed diagnostic tool should combine lack of intrusiveness, good sensitivity and reproducibility, robustness with respect to a broad range of process conditions, such as high temperature environments, and large-scale three-dimensional units. Once set up, the diagnostic technique has to be tested in a purposely designed experimental apparatus through the implementation of experimental procedures of interest. Results should be correctly interpreted and validated, coherent with those proposed in literature and contribute to the further understanding of the mechanisms concerning fluidization of monodisperse and bidisperse solids.

2. CAPACITANCE PROBE DIAGNOSTICS

Capacitance probes have been chosen due to their favorable features as compared with alternative diagnostics in terms of ease of operation and signal interpretation, temporal resolution, cost, applicability in severe high temperature environments, and applicability in industrial units. The versatility of the diagnostic technique in investigating several aspects of dense gas-fluidized beds of monodisperse solids, and the potential in exploring the behavior of mixtures of two dissimilar solids is, also, a plus.

2.1 Capacitance probes: operation principle, design and applications to dense gas-fluidized beds

A capacitance probe is, basically, a capacitor. Accordingly, it is composed of two conductors, one of which is at the ground potential. The measuring volume of the probe is defined by the electric field which establishes between the sensing conductor and the ground conductor. The capacitance, C, depends on the relative dielectric constant, κ , of the medium placed between the two conductors and on the geometry of the measuring volume. A characteristic geometric parameter, Σ , can be defined for the measuring volume of the capacitance probe. In a parallel-plate capacitor, $\Sigma = A/h$, where A is the surface area of each conductor and h represents their distance. The conductors of the capacitance probe are connected to an amplifier. The ground conductor is connected to the amplifier for reference. The sensing conductor is separately connected to the amplifier, which rectifies the AC voltage of the sensor into a DC signal voltage, and amplifies it of a gain factor, Gain, generating the output voltage of the measuring instrument, V. The gain factor depends on the capacitance range to be measured and is generally adjusted to have an output voltage ranging from 0 to 10 V. The capacitance of the cable connecting the sensing conductor to the amplifier contributes to the overall measurement, considerably reducing the sensitivity of the system. This is the reason why a third element must be added to the design of the capacitance probe, called guard conductor. The guard technique has been first introduced by Riley and Louge [126] in a parallel-plate configuration. The sensing conductor is surrounded by the guard conductor, and both are connected to the amplifier through a coaxial cable. The amplifier imposes a voltage to the guard electrode that is identical in amplitude and phase to the sensing conductor voltage. This circuitry effectuates a voltage difference equal to zero between both electrodes, disabling the measurement of cable capacitance. The guard should also disable possible external disturbances ("stray capacitances"). The effectiveness of the guard technique depends on the parameters of the amplifier, set with reference to the specific capacitance probe design. In case of non-perfect parameters setting, or modification of the capacitance probe design, it is possible that the amplifier minimizes the contribution of cable capacitance but not undoes it. Nonetheless, cable capacitance is in parallel to the capacitance of the sensing volume (which earlier we referred to as "measuring"). If the left cable capacitance is known, the problem can be calibrated away by subtracting its contribution the overall capacitance.



Figure 2.1 Needle-type guarded capacitance probes designs: (a) uncooled one-channel probe; (b) water-cooled two-channel probe; (c) water-cooled combined capacitance/zirconia-cell probe. From [127].

Capacitance probe measurements in gas-fluidized beds rely on the intrinsic difference between the dielectric constants of solids and gases. The probe is inserted into the fluidized bed with the measuring volume located in the region of interest. Changes of void fraction in this zone affect the dielectric constant, which in turn alter the system capacitance. Miniaturized needle-type capacitance probes are used: a cylindrical design that should minimize disturbances to the flow (Fig. 2.1). In the configuration without the guard electrode, the central sensing conductor protrudes with respect to the ground external concentric tube. The measuring volume is comprised between the sensing needle and the ground tube, which are opportunely insulated one from the other. The sensing volume includes the probe body and the sensing-cable length. Werther and Molerus [128] were the first in using needle-type capacitance probes, before the introduction of the guard conductor. They successfully measured bubbles properties, such as mean size, distribution inside the bed, hold up and rise velocity; indeed, non-guarded probes can be used when gross changes in capacitance, such as those occurring at the passage of a bubble, are of interest. Lancia *et al.* [129] used non-guarded capacitance probes to assess the transition from slugging to turbulent flow regimes in fluidized beds. The fact that capacitance probes signal reflects a local phenomenology is beneficial for this type of applications. Indeed, in studies of the transition between flow regimes in gas-FBs with pressure probes, the presence of local and non-local components in pressure signals (see sub-paragraph 1.2.2) can undermine the correct interpretation of hydrodynamics, especially in large-scale units.

When the guard is added to the needle-type system, an intermediate cylindrical conductor is placed between the sensing conductor and the ground concentric tube (Fig. 2.1 (a)). The presence of the guard tube and of a coaxial cable connected to the sensing and the guard conductors reduces the sensing volume to the space having the length of the protruding part of the needle and the ground tube outer diameter as characteristic dimensions. An insulating material is used to avoid contacts between the three conductors. Ceramic tubes are adopted when the capacitance probe is designed for hightemperature environments. Both cooled and uncooled designs have been adopted in literature, which are well described by Wiesendorf and Werther [127] (Fig. 2.1). Uncooled designs are preferable over air/water cooled ones (Fig. 2.1 (b), (c)), which present drawbacks in terms of leakage risk, increased footprint and design complexity. The difficulty in designing uncooled capacitance probes is to deal with different thermal expansions of steel and ceramic tubes. During high-temperature operation, the metal parts expand relative to the ceramic tubes. The resulting gaps between the metal and the ceramic parts at the probe tip might fill with particles, which would influence the signal level and may cause damage to the probe during cooling. The problem was solved by Hage and Werther [76], who separated the insulator tubes into small front sections and long sections for the rest of the probe. The ceramic front sections were kept in place by folding the outer metal tube as well as the guard inner electrode. This design guaranteed flush outer probe surfaces and prevented particles from being deposited in the gaps (Fig. 2.1 (a)). The employment of uncooled capacitance probes capable of operation up to 900 °C has been demonstrated [130]. In these applications, dependence of reference voltages on temperature has to be checked [131]. Capacitance probes utilization in high pressure environments has also been successfully carried out [42,132,133].

Accurate quantitative measurements of voidage in gas-solid flows are possible only by guarded probes. Different correlations for the calculation of the solids concentration, f, from the measured voltages by capacitance probe have been proposed in literature [127]. The linear approach proposed by Hage and Werther [76], as expressed in Eq. 10, is the most used one.

$$f = f_{fb} \frac{V - V_0}{V_{fb} - V_0} \tag{10}$$

 f_{fb} is the solids concentration in fixed bed conditions, V_{fb} is the associated reference voltage, and V_0 is the reference voltage in absence of solids (usually air). It is worth mentioning that in the study of Hage and Werther, where the linear approach was first adopted, the measured voltage showed a direct proportionality with the capacitance, C. Two-channel probes (Fig. 2.1 (b), (c)) are specific for bubbles and particles velocity measurements in dense and lean systems, respectively. The cross-correlation method determines the mean transit time of specific signal structures between two neighboring capacitance sensors. Other bubble features (e. g., wake and cloud volume extent with respect to bubble size, voidage distribution around the bubble, bubble hold-up, bubble distribution) can be revealed combining a time-resolved analysis of voidage signals [130,134] with a statistically based approach [128]. Dead zones in dense gas-FBs and jetting in shallow beds were, also, investigated by capacitance probes [135]. Experiences with heterogeneous bulk solids were made in the bottom zone of a fluidized bed combustor containing significant amounts of char [127]. Qualitative investigation of time-resolved signals from capacitance probes has revealed the presence of char-rich zones, thanks to a significantly higher dielectric constant of char with respect to the rest of the ash consisting mostly of quartz sand, limestone and combustion residues. More recently, capacitance probes have been tested in a 2D cold bubbling FB of binary mixtures of solids belonging to groups B and D of Geldart classification and having the same particle diameter [119,120,136]. Tracer volume concentration was measured by opportunely filtering-out parts of the signal associated with the bubble phase. The mass balance in the emulsion phase was resolved by keeping voidage at minimum fluidization conditions. Tracer volume fraction, f_1 , was obtained through the following correlation:

$$f_1 = \frac{V - V_2}{V_1 - V_2} \tag{11}$$

with V_1 and V_2 being the emulsion-phase signals associated with $f_1 = 1$ and $f_1 = 0$, respectively.

Capacitance probes demonstrate to be a versatile diagnostic tool in the field of dense gasfluidized beds. Multiple measurements can be performed at the same time, reducing the number of required diagnostics for characterizing fluidized bed hydrodynamics. The intrusiveness of the technique is undoubtedly a negative; nevertheless, very tiny probes minimize the footprint. Another drawback is the necessity to use a high number of probes in large units. Lastly, postprocessing of signals of bidisperse mixtures may be anything but trivial if solids of different sizes are used and if deviations from the two-phase theory cannot be neglected.

2.2Development and setup of capacitance probe diagnostics for the thesis scope

In the present thesis work, the hydrodynamics and mixing of dissimilar solids in densegas fluidized beds have been characterized using a custom-made uncooled capacitance probe resistant to high temperatures. Fig. 2.2 shows the layout of the capacitance probe that is based on the typical needle-type cylindric design. Central sensor, guard and ground cylinders are made of stainless steel, while the electric insulation is obtained by using ceramic tubes in the probe section immersed in the hot bed, and Teflon tubes in the cold end of the probe. The centering of steel and ceramic tubes around the needle sensor is carried out via γ -alumina powder ($d_p = 200 \mu m$), which is gently poured between the tubes. The ground tube outer diameter is 6.75 mm, the needle length and diameter are 5.7 mm and 1.6 mm, respectively. The measuring volume can be estimated around 130 mm³, calculated as mean value of the volume associated to a cylinder and to a cone. To deal with different thermal expansions of steel and ceramic tubes, the tubes are connected with a suited glue (sealant for ceramic-steel bonding) close to the sensing volume. In this way they can freely expand to the side opposite to the probe tip without altering the sensing volume geometry at high temperature. The glue also prevents particles from entering between the cylinders. Fig. 2.3 resumes the stages of cylinders assembling.



Figure 2.2 Outline of the uncooled capacitance probe (needle-type cylindric design) electrically wired to the amplifier by a low-noise coaxial cable.



Figure 2.3 The capacitance probe. (A) From left to right: needle-type central sensor, inner ceramic tube, guard tube, outer ceramic tube, ground tube; (B) needle-type central sensor and ceramic tube assembly; (C) guard tube addition; (D) complete assembly; (E) refractory glue addition.
The connection of the central and guard electrodes to the customized amplifier (AccumeasureTM System 9000, MTI Instrument Inc.) via a low noise BNC cable limits any disturbances on the measured signal. The signal shows inverse proportionality with the capacitance, C, through the gain factor of the amplifier (Fig 2.4):

$$V = \frac{Gain}{C} = \frac{Gain}{\kappa \varepsilon_0 \Sigma}$$
(12)

where ε_0 is the void dielectric constant. Consequently, the equation to convert the timeresolved voltage into the bed voidage time series cannot be that expressed by Eq. 10, but must be adapted to the general linear relationship, analogous to that validated by Brereton [137]:

$$\varepsilon = \frac{\kappa - \kappa_s}{1 - \kappa_s} \tag{13}$$

where the time-resolved dielectric constant of the medium that passes through the measuring volume of the probe, κ , derives from Eq. 12. The dielectric constant of the solid, κ_s , is measured *in situ* under incipient fluidization conditions, at which the corresponding emulsion-phase voidage, ε_{mf} , is known, and Eq. 13 becomes:





Figure 2.4 Relationship between output voltage *V* and relative dielectric constant κ for the applied capacitance measuring instrument ($V_0 = 7.6$ V, $\Sigma = 0.3$ -, *Gain* = 21 pF V).

 κ_s measurement under incipient fluidization condition is preferable over fixed bed conditions. In this last case, solids could not-perfectly pack around the sensing volume of the probe, making the measurement less repeatable.



Figure 2.5 Characteristic curve of the capacitance measuring instrument (relationship between output voltage *V* and relative dielectric constant κ). Different effects of the same relative dielectric constant variation ($\Delta \kappa = 1$ -) on the measured voltage.

The relationship expressed by Eq. 13 can be further generalized to a system composed by gas and a mixture of two dissimilar solids:

$$\kappa = \left(\kappa_s^{tr} \cdot f_{tr} + \kappa_s^{bed} \cdot (1 - f_{tr})\right) \cdot (1 - \varepsilon) + \varepsilon \tag{15}$$

 κ_s^{tr} is the relative dielectric constant of the material chosen as tracer, κ_s^{bed} is the relative dielectric constant of the second material, f_{tr} represents tracer volume fraction, ε is the voidage of the medium. Validity of the present relationship is subject to verification that the dielectric constants of the two solids do not influence each other in mixture. The effectiveness of capacitance probe application to quantitatively characterize gas-fluidized beds of dissimilar solids strongly depends on the difference between the dielectric properties of the two materials and on the characteristic instrument curve, which, in the present case, is not linear, as represented in Fig. 2.4. Non-linearity of the measuring instrument curve has consequences on the instrument sensitivity, which will depend on where the relative dielectric constant of the medium is positioned on the curve. This can be better understood by the observation of Fig. 2.5, in which the characteristic curve of the instrument is re-proposed. The highest voltage value corresponds to the case in which

the sensing volume of the probe is immersed in free air (V_0). Measured voltage values decrease as the relative dielectric constant of the medium in the sensing volume increases. The same change in relative dielectric constant, as shown by the distance along the x-axis between the first pair of red and green points on the left and the second pair on the right, produces a completely different difference in the output voltage.

As for the custom-made capacitance probe, preliminary tests have been performed to assess signal stability and reliability. Small hits on the probe needle produce downward spikes in the capacitance probe signal, and the reference signal is immediately repristinated afterwards. When the probe is inserted in the empty stainless steel fluidization column with the measuring volume flush to the walls, the reference signal in air, V_0 , is slightly lowered, but its average value never goes under 96 % of the signal recorded in free air outside the column. The reference value in air at 500 °C is recorded after heating the probe with fluidized quartz sand and bed draining. The small variation of the signal from ambient temperature to 500 °C can be due to a small radial expansion of the ground tube, thus capacitance increase and voltage decrease. The impact of this variation on actual measurements is negligible.

3. EXPERIMENTAL

3.1 Experimental apparatus



Figure 3.1 Laboratory-scale experimental apparatus. (1) Windbox; (2) electrical furnaces; (3) ceramic insulation; (4) gas distributor; (5) column lateral accesses (schedule 40: ID 12.4 mm);
(6) thermocouple for oven PID controller; (7) bed solids; (8) fluidization column; (9) hood; PT: piezoresistive pressure transducer (operating range: 0-75 mbar); TC: K-type thermocouple.

The laboratory-scale apparatus is a stainless steel 3'' diameter (schedule 40: ID 77.92 mm) and 1300 mm high column (Fig. 3.1). The fluidization gas distributor belongs to the low pressure drop type. It is a 2 mm triangular pitch perforated plate placed under two stainless steel nets (mesh size of 40 μ m), which provide the major contribution to the distributor pressure drop. The average pressure drop across the gas distributor is 173 Pa, and its ratio to the pressure drop across bed solids ranges between 8 to 11 %, depending on gas superficial velocity. These data refer to a bed solids weight of 900 gr fluidized in the superficial gas velocity range of 0.17–0.80 m/s at 500 °C. The windbox is a 225 mm high stainless-steel column filled with ceramic rings to equalize the gas flow. The fluidization column is thermally insulated and heated by two semi-cylindrical 2.4 kW ceramic ovens, while the bed temperature is kept at the set point by a PID control unit.

Entrained dust, which results from the abrasion of dense bed particles during testing, is removed via a fume hood. The two ports located under and right above the gas distributor, respectively, are 4 mm ID tubes exclusively used for pressure and temperature measurement. The second pressure tap is located at 0.01 m above the grid. The column presents other six 3/8'' diameter (schedule 40: ID 12.4 mm) tubes, mounted flush to the column wall, that provide access to pressure/temperature and capacitance probes. These lateral accesses are placed at different vertical positions along the column, at distances above the distributor plate of 0.06, 0.1, 0.14, 0.18, 0.34 and 0.95 m.

3.2 Materials

Four different bed solids have been used in the experimental study of the present thesis: grey quartz sand, silicon carbide and two y-alumina samples. Material properties are listed in Table 1. Grey quartz sand and silicon carbide were conditioned at 800 °C and double sieved in a relatively narrow particle size range of 420–590 μ m. γ -alumina samples do not need any conditioning procedure due to their sphericity. For the first two solids, the mean diameter, \tilde{d}_p , derives from the arithmetic mean between the sieving range limits of 420 and 590 μ m. The γ -alumina samples are composed by mono-sized particles. ε_{mf} values at ambient temperature were considered equal to the loose bed voidages [138]. The loose bed voidage, as well as the packed bed voidage, ε_{pack} , was measured in a graduated cylinder of 500 ml so that wall effects could be minimized [139]. ε_{mf} at 500 °C for the four samples was calculated from Ergun equation [140] starting from the actual particles diameter, density and sphericity, the experimental U_{mf} and gas properties at 500 °C. This procedure, suggested by Knowlton [141], has been also adopted by Formisani et al. [142]. The sphericity of grey quartz sand and silicon carbide, ϕ , was obtained as an adjustable parameter from Ergun equation starting from solids and gas properties at ambient temperature. ϕ values seem to be reasonable in either case, as demonstrated by SEM images (Fig. 3.2) of the samples. The classification into Geldart groups [140] has been accomplished considering the emulsion-phase interstitial gas velocity referred to minimum fluidization conditions compared to the mean bubble velocity. Grey quartz sand material, as well as γ -alumina-0.6, exhibits bubble mean velocity which exceeds the interstitial gas velocity of the emulsion phase at minimum fluidization conditions both at room temperature and 500 °C. Thus, they are certainly classified as B-group particles. Silicon carbide bed presents slow bubbles at ambient temperature, but changes its behavior at 500 °C with fast bubbles if compared to the interstitial gas velocity in the dense phase. γ -Alumina–1 is undoubtedly a type-D material.

Material	Grey quartz sand	Silicon carbide	γ-Alumina–0.6	γ-Alumina–1
Sieve range, d_p [µm]	420-590	420-590	Monosize	Monosize
$ ilde{d}_p$ [µm]	505	505	610	1000
φ [-]	0.64	0.63	1	1
$\rho_p [\text{kg/m}^3]$	2650	3253	1187	1209
<i>ρ_{pack}</i> (20 °C) [kg/m ³]	1488	1764	774	779
Geldart group	В	B/D	В	D
$U_{mf}(20 \ ^{\circ}\text{C}) \ [\text{m/s}] \ (\text{experimental})$	0.207	0.305	0.191	0.411
$U_{mf}(500 \text{ °C}) \text{ [m/s]} \text{ (experimental)}$	0.119	0.190	0.106	0.300
$U_t(20 \text{ °C}) \text{ [m/s]}$ (Haider and Levenspiel, 1989)	2.44	2.72	3.14	4.72
U_t (500 °C) [m/s] (Haider and Levenspiel, 1989)	3.13	3.58	3.28	5.97
<i>ε_{pack}</i> (20 °C) [−]	0.44	0.46	0.35	0.33
<i>ε_{mf}</i> (20 °C) [−]	0.48	0.5	0.39	0.43
<i>ε_{mf}</i> (500 °C) [−] (Ergun, 1952)	0.49	0.52	0.43	0.43
$\kappa_s(20 \text{ °C}) [-] (experimental)$	3.5	12.7	3.0	3.3
$\kappa_s(500 \ ^\circ\text{C}) [-] (\text{experimental})$	6.2	11.8	2.6	2.7

Table 1. Properties of bed materials.



Figure 3.2 SEM images of three out of four bed materials. From left to right: grey quartz sand after conditioning, silicon carbide after conditioning, γ -alumina–1.

A $2\%_{w/w}$ Pt catalyst supported on spheres of γ -alumina has been used in some experiments. Properties of catalyst particles are described in Table 2. Each catalyst particle has been measured with a caliper and weighted by a precision balance. The catalyst has been selected among those tested by Scala [63].

Table 2. Hoperites of eatalyst particles.				
Mean particle size, \widetilde{d}_p [mm]	Mean particle density, $\widetilde{ ho}_p$ [kg/mm ³]	Description		
3.9 ±0.11	1128 ±109.4	2 % _{w/w} Pt on γ-alumina spheres provided by Süd-Chemie		

Table 2. Properties of catalyst particles

3.3 Experimental procedures and data analysis

3.3.1 Experiment 1: hydrodynamic characterization of gas-fluidized beds of monodisperse solids

Fig. 3.3 reports an outline of the laboratory-scale apparatus equipped for the experiments of hydrodynamic characterization of dense gas-FBs of monodisperse solids by capacitance probes. All four bed materials described in the paragraph 3.2 have been tested in this unit operated as atmospheric bubbling fluidized bed. Each material has been fluidized with air, at ambient temperature and at 500 °C, fed to the column via highprecision digital mass flowmeter/controller. The same excess gas superficial velocities with respect to incipient fluidization, in the range of 0.01–0.35 m/s, were applied for the two temperatures and for each bed material. Additional excess gas velocities were tested at 500 °C, up to $U - U_{mf} = 0.7$ m/s. The excess gas velocity, $U - U_{mf}$, has been chosen as operative variable for the experiments since it is a widely used parameter in fluidization contexts, deriving its origin from the two-phase theory. The packed bed aspect ratio, H/D, was in the range 1.6-1.7 for the four samples. The capacitance signal was recorded at three different axial positions inside the bed, H_1 , H_2 and H_3 , at a distance from the distributor plate of 0.06, 0.1 and 0.14 m (Fig. 3.3). At each bed height, capacitance probes were placed at three radial positions, namely bed center, mid-radius and wall, corresponding to r/R ratios of 0, 1/2 and 7/9, respectively. Capacitance probes, pressure probes and thermocouples were connected to data acquisition modules and signals were

acquired simultaneously, with a sampling frequency of 1 kHz, on a laboratory computer using LabVIEW software. Recording time lasted 180 s at each gas superficial velocity.

The dielectric constant of a material is a property which depends on several parameters; values reported in literature on the materials of interest could be different from relative dielectric constants of the adopted samples. Since accuracy in bed voidage measurement by capacitance probes is critically dependent on the knowledge of the correct material relative permittivity, it was worth to perform dedicated measurement tests. As mentioned in paragraph 2.2, the dielectric constant of each material could be measured *in situ* by recording the capacitance signal from the bed kept at minimum fluidization conditions. κ_s was obtained from Eq. 12 and 14. Resulting values for the four samples at room temperature and 500 °C are reported in Table 1.



Figure 3.3 Experimental apparatus equipped for experiments of hydrodynamic characterization of dense FBs. (1) Air compressor; (2) air flowmeter; (3) column lateral tubes for capacitance probes (CP) fitting. $H_1 = 0.06$ m, $H_2 = 0.1$ m, $H_3 = 0.14$ m represent the axial location of the capacitance probes in terms of distance from the distributor. PT: piezoresistive pressure transducer (operating range: 0-75 mbar); TC: K-type thermocouple.

During data analysis, the time-resolved local relative permittivity of the fluidized bed obtained from Eq. 12 was further worked out through Eq. 13 to obtain the time-series of local bed voidage. These time series have been further analyzed by a statistical method

to generate Probability Density Functions (PDF) of the local voidage, using the Matlab software. The Freedman-Diaconis rule [143] has been used to select the optimal bin width, so that the resulting PDFs were not affected by bed voidage values and acquisition time. The main features of the PDFs have been compared in terms of excess gas velocity with respect to minimum fluidization, axial/radial coordinate of capacitance probe sensing volume and temperature for each material. Results from the different materials were also compared to identify possible different distinctive behaviors.

Pointwise bed voidage measurements by capacitance probes, ε_f , obtained by averaging voidage signals over time, were validated through comparison with mean bed voidage values, $\tilde{\varepsilon}_f$, gathered from unrelated methods. The first, maybe rough but effective, comparative method is purely experimental. It consists in dipping a glue-greased tube into the fluidized bed and measuring the length of the portion of the tube densely covered by particles. The trait where the covering starts being less dense, which may be associated to the maximum bed expansion plus the splashing zone contribution, was discarded. The resulting fluidized bed mean voidage was calculated by Eq. 16:

$$\tilde{\varepsilon}_f = 1 - \frac{H_{mf}(1 - \varepsilon_{mf})}{\tilde{H}}$$
(16)

where \tilde{H} is the measured mean bed height. Another estimate of \tilde{H} was obtained by calculation of the volume fraction of the bed occupied by bubbles δ , as:

$$\frac{(\widetilde{H} - H_{mf})}{H_{mf}} = \frac{\delta}{(1 - \delta)}$$
(17)

The relationship expressed by Eq. 17 is valid for group B and D powders, under the assumption, from the *two-phase theory of fluidization*, that the dense phase voidage does not depart much from ε_{mf} and bed expansion is dominated by the hold-up of bubbles [64]. When the visible bubble flow and the mean bubble velocity are considered, Eq. 17 becomes

$$\frac{(\widetilde{H} - H_{mf})}{H_{mf}} = \frac{(U - U_{mf})}{\widetilde{U}_{b\infty}}$$
(18)

where $\tilde{U}_{b\infty}$, the mean bubble rise velocity with respect to the emulsion phase, is estimated for a characteristic bubble diameter, \tilde{d}_b , which, in the present case, was the bubble diameter at mid-height of the fluidized bed, estimated according to Darton *et al.* [144]. The local capacitance probe measurements were integrated first over the whole cross section under axisymmetric assumption and then over the bed height. The integration was performed by dividing the column section into three concentric subsections, S_i :

$$\langle \varepsilon \rangle_r = \frac{\sum_{i=1}^3 \varepsilon_{f,i} S_i}{S} \tag{19}$$

with *i* representing the subsection number. Values from Eq. 19 were averaged over height by the arithmetic mean.



Figure 3.4 Variation of the mean number of pulses per unit time in the voidage signal from grey quartz sand experiment run at ambient temperature and with an excess gas velocity $U - U_{mf} = 0.35$ m/s. Capacitance probe sensing volume located at H_2 and column center.

The last procedure was devoted to solving the gas velocity balance on an intermediate section of the fluidized bed (Eq. 2). To this end, data gathered at H_2 were chosen for the four samples. Three different methods have been adopted to calculate the superficial velocity of the gas passing through the emulsion phase, U_e , at each superficial gas velocity, U. In the first method, the equation of Hilligardt and Werther [31] has been implemented (Eq. 3). It does not require any measured quantity apart from the minimum fluidization velocity of the material at the temperature of interest. The second method involved the use of the Richardson-Zaki correlation [54] expressed according to Eq. 4. In this second case, more experimental values are required. ε_e is the characteristic voidage of the emulsion phase. The procedure to calculate it from measured data is the following:

the time-resolved voidage signal associated to the emulsion phase is extracted from the whole signal by selecting a threshold value, ε_{th} . The threshold identification at relatively high superficial gas velocities is carried out with the "method of pulses" proposed by Werther and Molerus [128]. Herein, the mean number of pulses per unit time in the time-resolved signal is obtained for different levels of voidage values (Fig. 3.4): the mean number of pulses per unit time rapidly increases as voidage rises from an initial value corresponding to packed conditions. After reaching a maximum, corresponding to the passage of all peaks due to porosity fluctuations in the emulsion phase and bubbles passage, the mean number of pulses per unit time decreases and the pulse count reaches a stationary value. This value should only refer to the pulses associated to bubbles passage. Thus, the first value associated to the plateau is chosen as the threshold between the emulsion phase and the bubble phase. When the method of pulses is not applicable due to less evident presence of bubbles or small ones, which results in the lack of a plateau in the plot of the mean number of pulses per unit time, a symmetry condition was adopted for the PDF associated to the emulsion phase, as shown in Fig. 3.5.



Figure 3.5 Probability Density Function (PDF) of time-resolved voidage signal from grey quartz sand experiment run at ambient temperature and with an excess gas velocity with respect to minimum fluidization conditions $U - U_{mf} = 0.005$ m/s. Capacitance probe sensing volume located at H_2 and column center.

Given ε_{th} , the emulsion-phase signal was extracted from the overall signal by filtering out the parts associated to the bubble phase. It is worth mentioning that the methodology used to obtain the emulsion-phase signal, as represented in Fig. 3.6, excludes voidage values lower than ε_{th} that immediately precede and follow the bubble peak. The voidage signal associated to the emulsion phase was, finally, averaged over time. In Eq. 4, ε_e is the time-averaged emulsion-phase voidage measured at the axial coordinate associated to H_2 (Fig. 3.3), which results from the integration, over the whole cross section, of the values measured at column center, mid-radius and wall, under axisymmetric assumption (Eq. 19). In the third method, a gas balance over the cross section of the fluidized bed was written according to Eq. 2. δ was derived from the mass balance on bed solids:

$$\varepsilon_f = \delta + (1 - \delta)\varepsilon_e \tag{20}$$

where the presence of small amounts of solids in bubbles was neglected. ε_f is the mean fluidized bed voidage referred to bed cross-section at the axial coordinate H_2 . The mean bubble rise velocity, U_b , could be derived by adopting the cross-correlation of signals from capacitance probes sensing volumes located at H_1 and H_2 and column center. The visible bubble flow, $U_b\delta$, has been compared with values obtained using the correlation of Fu *et al.* [145] valid for Geldart B and D solids. As for the throughflow velocity, U_{tf} , it has been expressed as proportional to the velocity of gas passing through the emulsion phase (Eq. 2), $k_{tf}U_e$, while varying the coefficient k_{tf} between 0 and 1 to identify a range of possible U_e values.



Figure 3.6 Emulsion-phase signal resolved over a fictitious time from grey quartz sand experiment run at ambient temperature and with an excess gas velocity $U - U_{mf} = 0.35$ m/s. Capacitance probe sensing volume located at H_2 and column center.

3.3.2 Experiment 2: characterization of mass transfer between an active particle and the fluidized bed

The oxidation reaction of CO with oxygen over a Pt catalyst has been chosen as a model reaction to be used for the determination of mass transfer between an active particle and a gas-fluidized bed in the bubbling regime. Venderbosch et al. [146] were the first to propose this method for packed and fluidized beds. It was shown, with experiments in a fixed bed and in a riser system, that this reaction is completely mass transfer controlled in the temperature range 450–500 °C, even for very small active particles (<100 µm) at low CO bulk concentrations. The authors highlighted a number of advantages for this technique like the easy preparation and stability of the catalyst particles and the absence of side reactions. Subsequently, Scala [63] successfully applied the technique to fluidized beds. In the present study, grey quartz sand particles have been used as inert bed material (Table 1) to disperse a batch of Pt catalyst supported on attrition-resistant spheres of γ alumina (Table 2). Given the catalyst particles properties with respect to bed material solids, the mixture falls into the second category, as defined in the sub-paragraph 1.3.1. Very low CO inlet concentrations (<1000 ppm_v) have been adopted. In these experimental conditions the following advantages over the other existing techniques on mass transfer measurement can be identified:

- 1. Only the heterogeneous oxidation reaction $CO + \frac{1}{2}O_2 = CO_2$ at the catalyst particle surface is active and no parallel homogeneous or side reactions are present.
- 2. The reaction is completely controlled by external mass transfer and no influence of intrinsic kinetics or intraparticle diffusion is present (infinitely fast reaction kinetics can be assumed).
- 3. At low CO concentrations heat effects are negligible and the catalyst particle temperature can be safely assumed to be equal to the bed one.
- 4. The CO conversion degree can be easily and accurately calculated by measuring the CO and/or the CO₂ concentrations at the reactor outlet.
- 5. CO and CO₂ are not adsorbed significantly by typical inert bed materials.
- At low CO concentrations, the true Sherwood number can be calculated without the need to account for high mass transfer rate and non-equimolar-counter diffusion corrections.

- 7. The catalyst can be easily prepared and is very stable with respect to the oxidation reaction.
- 8. The catalyst particle keeps a constant size during the experiments.
- 9. The catalyst particle attrition rate in the fluidized bed is negligible.
- 10. Properties of the different gaseous species and solid particles can be easily and accurately estimated.



Figure 3.7 Experimental apparatus for reactive experiments. (1) Gas cylinders; (2) gas flowmeters; (3) gas suction probe; (4) membrane pump; (5) gas analyzers. PT: piezoresistive pressure transducer (operating range: 0-75 mbar); TC: K-type thermocouple.

Fig. 3.7 shows the experimental apparatus equipped for the reaction experiments. The amount of bed material loaded in the column was the same as in the experiments described in the subparagraph 3.3.1. The first three lateral measurement ports, starting from the distributor, were equipped with gas pressure transducers to check the fluidization quality, and with K-type thermocouples to verify bed temperature uniformity. The fourth port was employed for the PID thermocouple. Ports from the fifth to the seventh hosted K-type thermocouples to measure the temperature in the splash zone and in the freeboard of the reactor. The gas feeding at the desired composition (CO 830 ppm_v, O₂ 5%_{v/v}, N₂) has been obtained by mixing three streams of gas supplied from cylinders containing high purity N₂, O₂, and a N₂-CO mixture ($30\%_{v/v}$ CO), respectively, metered by three gas flowmeters

calibrated with a bubble flowmeter. A stainless-steel L-shape probe was inserted from the top of the column in order to convey a known fraction (60 l/h) of the exit gas directly to the gas analyzers. Gas sampling has been performed at a distance from the top section of the bed of about 450 mm. The probe is a 4 mm ID tube, plugged at the end of the horizontal section inserted in the column. Gas was sampled through five 1 mm ID holes, uniformly distributed along the horizontal section of the tube so as to measure the mean gas composition over the column cross-section. The analyzers measured on-line O_2 , CO and CO_2 concentrations in the exhaust gases. The measuring ranges of the CO and CO_2 analyzers used in the experiments are 10000 and 2000 ppm_v, respectively. They were calibrated at the beginning of each lab-work day with specific calibration cylinders for CO (1000 ppm_v CO) and CO₂ (200.2 ppm_v CO₂). The analyzers were also employed to verify the composition of the gas mixture at the column feeding port, via a valve that deviates a small gas flowrate to the analyzers.

Experiments have been carried out at a bed temperature of 450 °C. A preliminary check was directed to verify that contributions to CO oxidation arising from homogeneous gas phase reactions and from sand or wall catalyzed reactions could be neglected at the selected temperature. Possible segregation of catalyst particles was ruled out after dedicated cold tests, at scaled operating conditions, in which the bed solids and the catalyst particles were fluidized in a Plexiglas column to allow visual inspection. External diffusion around the catalyst particle was considered as the only controlling resistance for CO oxidation at 450°C, as widely verified by Venderbosch et al. [146] and by Scala [63]. The gas superficial velocity was varied in the range 0.215-0.815 m/s, corresponding to fully established freely bubbling fluidization regime. A preliminary analysis of the pressure time series in the frequency domain highlighted a dominant characteristic frequency in the range 2–3 Hz, typical of bubbling conditions and far from slugging [147]. The tests were performed by injecting a batch of catalyst particles in the fluidized bed from the top of the column. The mass of the catalyst was selected so as to establish a conversion degree of carbon monoxide, x, of about 5 %, corresponding to nearly differential operation. Accordingly, uncertainties associated with detailed fluid-dynamics of the bed were minimized. The mass of catalyst particles increased with increasing flowrate due to the decrease of the gas residence time. After catalyst feeding, concentrations of CO, CO₂ and O₂ in the exhaust gases were measured by the analyzers

and signals acquired using the LabVIEW software at a sampling rate of 1 Hz during the transient and the steady-state condition.

Analysis of the experimental data was made under the assumption that the catalyst particles only reside in the dense phase of the fluidized bed. This assumption is based on the experimental evidence reported in the literature, considering that catalyst particles are coarser than the inert bed solids. Bed fluid dynamics was modelled according to the two-phase fluidization theory: gas in the bubble phase is in plug flow; gas and solids in the emulsion phase are well stirred. Gas perfect mixing in the emulsion phase is a direct consequence of the small conversion degree. The bubble-emulsion phase mass transfer coefficient was calculated according to Sit and Grace [47] and, consequently, the bubble-emulsion phase mass transfer index, *X*, was derived. Under external diffusion control (assuming a vanishing CO concentration at the surface of the active particle) the total reaction rate of CO in the dense phase of the fluidized bed, ξ_{CO} , can be expressed as:

$$\xi_{CO} = A_a \cdot k_g \cdot c_{CO}^e \tag{21}$$

 A_a being the total external surface of the spherical catalyst particles and k_g the emulsion gas-to-active particle mass transfer coefficient. Below, the material balances on CO in the bubble (Eq. 22) and dense phase (Eq. 23), and at the reactor outlet (Eq. 24) are reported under the above assumptions:

$$c_{CO}^{b} = c_{CO}^{e} + \left(c_{CO}^{in} - c_{CO}^{e}\right) \cdot e^{-X}$$
(22)

$$A_a \cdot k_g \cdot c^e_{CO} = Q \left(c^{in}_{CO} - c^{out}_{CO} \right)$$
⁽²³⁾

$$Q \cdot c_{CO}^{out} = Q_{mf} \cdot c_{CO}^e + \left(Q - Q_{mf}\right) \cdot c_{CO}^b \tag{24}$$

where the unknowns are represented by k_g , CO concentration in the bubble phase, c_{CO}^b , and in the emulsion phase, c_{CO}^e . Q represents the volumetric flowrate. By substituting Eq. 22 in Eq. 24, c_{CO}^e can be expressed as a function of CO concentration at the inlet, c_{CO}^{in} , and outlet, c_{CO}^{out} . $x_{CO} = \frac{c_{CO}^{in} - c_{CO}^{out}}{c_{CO}^{in}}$ is the overall CO conversion degree in the reactor, as measured in the experiments, and the Sherwood number is defined as in Eq. 6 in which \mathcal{D}_g is the diffusion coefficient of CO. By introducing these two terms in Eq. 23 and substituting the expression for c_{CO}^e previously derived, the equation for the calculation of *Sh* number can be finally written:

$$Sh = \frac{d_a S}{\mathcal{D}_{co} A_a} \cdot \frac{U_{mf} + (U - U_{mf}) \cdot (1 - e^{-X})}{(1 - x_{co}) - \frac{U - U_{mf}}{U} \cdot e^{-X}} \cdot x_{co}$$
(25)

where S is the reactor cross section.

3.3.3 Experiment 3: characterization of solids mixing in a fluidized bed of bidisperse granular solids

A new method, based on capacitance probe diagnostics, has been proposed for the characterization of solids mixing in a gas-fluidized bed of two dissimilar solids in the bubbling regime. First validation tests have been performed at 500°C in the laboratory-scale unit equipped as described in Fig. 3.3. Silicon carbide (SiC) and γ -alumina have been chosen as they present sufficiently different relative dielectric constants (Table 1). Thus, they can potentially be well distinguished one from the other by the capacitance probe method. The adopted samples of SiC and γ -alumina are dissimilar in size and density but not by orders of magnitude. γ -alumina–1 is lighter than SiC, with a particle density ratio of 0.37, and larger, with a particle diameter ratio of 2 (Table 1). In addition, γ -alumina–1 particles are perfectly spherical, whereas SiC has an irregular shape (Fig. 3.2).

The experiment consisted in the rapid injection of a batch of tracer particles in the fluidized bed of monodisperse solids to follow the transient phases of tracer penetration in the dense bed and establishment of the mixing/segregation equilibrium between the two materials, and to measure tracer concentration in the emulsion phase at steady-state conditions while varying the superficial gas velocity in the range 0.34–0.87 m/s. Two experiments have been performed: in a first test, SiC was used as bed material and γ -alumina–1 as tracer; in the second experiment, γ -alumina–1 has been used as bed material. The amount of bed material loaded in the column was the same as in the experiments described in the subparagraph 3.3.1. The batch of tracer solids corresponds to a volume concentration of 13 % – defined on a fluid-free basis as $f_{tr} = \frac{v_{tr}}{v_{tr}+v_{bed}}$, with v being the volume occupied by the particles – in perfectly mixed conditions of the bed. The choice of a 13 % volume fraction is the result of an optimization having as objectives the minimization of the injection time and of the increase in bed height, and maximization of

legibility of the capacitance probe signal. The tracer batch was preheated at 500 °C before being injected in the system. The capacitance signal was recorded at three different axial positions inside the bed, H_1 , H_2 and H_3 , at a distance from the distributor plate of 0.06, 0.1 and 0.14 m (Fig. 3.3). At each bed height, capacitance probes were placed at three radial positions, namely bed center, mid-radius and wall, corresponding to r/R ratios of 0, 1/2 and 7/9, respectively. Before recording capacitance probe signals at steady-state conditions and different superficial gas velocities, the system was given sufficient time to establish the mixing/segregation equilibrium between the two solids. Signal acquisition time was set at 300 s for all the experimental conditions. It is greater if compared to experiments on fluidized beds of monodisperse solids, depending on the increased complexity of the system characterized by bidisperse solids, which makes a higher number of experimental points required for reliable statistical evaluations.



Figure 3.8 Identification of signal *changepoints* based on the evaluation of signal mean within each section. Operating conditions: bed axis, H_1 , T = 500 °C, U = 0.44 m/s.

Data postprocessing in the transient phase of the experiment was mainly based on detailed time-resolved analysis of the voltage signals, aided by Matlab signal-processing tools able to detect signal *changepoints* with a parametric global method [148,149]. A *changepoint* is a sample or time instant at which some statistical property of a signal changes abruptly. In the present case, the property in question was the mean of the signal. The function:

- 1. Chooses a point and divides the signal into two or more sections.
- 2. Computes an empirical estimate of the mean for each section.

- 3. At each point within a section, measures how much the mean deviates from the empirical estimate and adds the deviations for all points.
- 4. Adds the deviations section-to-section to find the total residual error.
- 5. Varies the location of the division points until the total residual error attains a minimum.

A result of the implementation of the method presented above is shown in Fig. 3.8.

As for data analysis at steady-state condition, the volumetric fraction of tracer particles, f_{tr} , in the emulsion phase was calculated at each investigated axial/radial coordinate of the column and superficial gas velocity. This is possible when the emulsion phase crosses the sensing volume of the capacitance probe. Therefore, only parts of the signal associated with the dense phase have been considered. At steady-state conditions, the statistical approach based on the computation of the PDF of voltage signal led to the identification of the characteristic voltage of the mixture in the emulsion phase. Then, the characteristic relative permittivity of the mixture at steady-state condition has been derived from Eq. 12. Calculation of f_{tr} , as expressed in Eq. 15, depends on voidage of the mixture in the emulsion phase. ε_e cannot be kept constant with f_{tr} when solids having different size are considered. The assumption that ε_e remains equal to that of bed material emulsion phase (solid species present in larger amounts) would determine major errors in case of marked segregation of the tracer in one zone of the bed. Consequently, a calibration with mixtures of known composition, varying in the range of one solid species volume fraction f =0-1, has been done in a graduated cylinder of 500 ml. The two materials have been premixed in a dedicated vessel, and poured in the cylinder preventing any segregation and in a way that a loose fixed bed could be obtained. The mixture bed voidage was obtained with the relationship expressed as:

$$\varepsilon = v_{tot} - v_1 - v_2 \tag{26}$$

where v_{tot} is the total volume occupied by the batch in the graduated cylinder, v_1 and v_2 are the known values of volumes occupied by the two solids, easily calculated from the weight and the particle density of each material. It was assumed that the correlation obtained for the loose voidage of the mixtures SiC/ γ -alumina holds true in the emulsion phase of the bubbling fluidized bed even when simplifications from the two-phase theory cannot be applied.

4. CHARACTERIZATION OF HYDRODYNAMICS AND MASS TRANSFER IN FLUIDIZED BEDS OF MONODISPERSE SOLIDS

Part of the results included in this chapter have been published on *Fuel* journal: L. Molignano, M. Troiano, R. Solimene, S. Tebianian, F. Scala, P. Salatino, J.F. Joly, Hydrodynamics and mass transfer around active particles in dense gas-fluidized beds, Fuel. 341 (2023) 127590. https://doi.org/10.1016/j.fuel.2023.127590.

4.1 Experiment 1

4.1.1 Bed voidage measurements by capacitance probes

Results on hydrodynamic characterization of gas-fluidized beds of the four monodisperse solids (Table 1) are referred to the bubbling regime. This has also been verified *a posteriori* from the analysis of bed pressure signals in the frequency domain. The characteristic frequency of bed pressure signal recorded at the highest superficial gas velocities ranges from 2.1 to 3.7 for the four samples at the two investigated temperatures. Conversely, the characteristic frequency of a fully developed slugging regime would be around 0.8, as calculated from the relationship reported by Falkowsky and Brown [147]. The standard deviation of absolute pressure fluctuations, measured at different bed heights, has also been computed for all the adopted experimental conditions, revealing that the investigated gas-solid suspensions do not reach the transition to turbulent fluidization [150]. Therefore, as superficial gas velocity attains maximum values within the chosen operating range, bed material is fluidized in a rather vigorous bubbling regime.

Figs. 4.1 and 4.2 report selected time-series of local bed voidage recorded for the four samples at 500 °C, at two different excess gas superficial velocities, with the capacitance probe sensing volume located at the column axis and H_1 . At the lower excess gas superficial velocity with respect to minimum fluidization conditions (Fig. 4.1), a signal baseline representing the emulsion-phase is recognizable, whereas upward spikes mark

the passage of bubbles. It is evident that the characteristic value of the baseline signal already departs from the emulsion-phase voidage at minimum fluidization. This result witnesses an incipient expansion of the dense phase with respect to minimum fluidization conditions or lower superficial gas velocities, in which voidage oscillation around a dominant value corresponding to ε_{mf} is observed. As gas superficial velocity is increased (Fig. 4.2) the passage of bubbles becomes more frequent, and the signal becomes more chaotic. In this case, it is more difficult to identify the baseline signal.



Figure 4.1 Time-resolved voidage signals. Probe radial location: center, probe level: H_1 , T = 500 °C, $U - U_{mf} = 0.1$ m/s.

The general qualitative features of the voidage time-series at high temperature resemble those observed at room temperature. Time-resolved bed voidages corresponding to the gas velocities, temperatures, and radial/axial locations of the capacitance probe tested for each material sample indicate that:

• Local bed voidages, averaged over the entire acquisition time (ε_f), do not exhibit a repetitive trend with temperature if results on the different materials are compared, for any given axial/radial position of the sensing volume of the probe.

- The mean local bed voidage, ε_f , is greater at the top levels H_2 and H_3 both at room and at high temperature for all the samples.
- ε_f values averaged over the radial and axial coordinate and normalized with respect to ε_{mf} result in a higher expansion of γ -alumina samples, with reference to the starting voidage condition.
- Maxima in the voidage signals slightly decrease as temperature is increased, a feature that could be due to smaller bubbles or more solids occupying the bubble volume at 500 °C. Hilligardt and Werther [31] reported that an increase in bed temperature results in a decrease of bubble size.
- No noticeable differences arise for minimum, maximum and mean values of local bed voidage measured along the radial coordinate, for the tested materials. The experimental apparatus is, probably, too small to reveal significative differences along the radial coordinate. In agreement with Cui *et al.* [33], the growth of maximum value is exponential for low values of $U U_{mf}$ and the voidage remains nearly constant at higher gas velocities.



Figure 4.2 Time-resolved voidage signals. Probe radial location: center, probe level: H_1 , T = 500 °C, $U - U_{mf} = 0.4$ m/s.

Fig. 4.3 reports values of bed voidage as a function of the excess gas superficial velocity. The time- and spatially-averaged experimental data gathered from capacitance probes show rather good agreement with calculations based on the *two-phase theory* and direct bed height measurements, which have been performed only at room temperature. Departures of results obtained with capacitance probes from those referred to the other methods never exceed 10 %.



Figure 4.3 Estimate of bed expansion by unrelated methods. (a) Results at ambient temperature; (b) results at 500 °C.

Interpretation of the voidage time series is better accomplished by means of the statistical approach presented hereinafter. To this end, the time series of the local voidage have been worked out to yield the Probability Density Functions (PDF) of voidage signals, parametric in the excess gas superficial velocity with respect to minimum fluidization conditions. PDFs reported in Fig. 4.4, for ambient temperature, and in Fig. 4.5, for the data set at 500°C, at different locations in the bed refer to the grey quartz sand sample. Analysis of the PDF turns out to be helpful to infer key features of bed hydrodynamics [34,36,128]. As the bed is operated under nearly incipient fluidization conditions ($U \cong$ U_{mf}), the PDF displays a slightly skewed unimodal trend, with a voidage modal value around ε_{mf} . Indeed, the bed is mainly constituted by the emulsion phase, characterized by a fairly narrow distribution of local void fractions, with small and occasional bubbles contributing to the tail of the PDF corresponding to the larger values of ε . As the gas superficial velocity is increased, a pronounced peak, representative of the bubble phase, appears at $\varepsilon \approx 1$. The bubble-phase peak sharpens as $U - U_{mf}$ increases, keeping an almost constant voidage, as also observed in the study of Wytrwat et al. [151]. The contribution of the bubble phase to the PDF is larger at the upper level and along the axis of the bed under all the experimental conditions for grey quartz sand. This finding suggests that bubbles move toward the bed axis and coalesce during their uprise [152]. The contribution of the bubble phase to the PDF is larger at 500 °C than at room temperature.





Once gas superficial velocity starts being increased, the modal value associated to the emulsion phase shifts toward higher voidages, marking the expanded state of the emulsion phase. As velocity is further increased, the distribution of voidages associated to the emulsion phase reveals a composite nature. The convolution of two modes becomes evident as a shoulder at first, emphasized as the gas superficial velocity increases to the

point of displaying two distinct peaks. The comparison of the PDF of the voidage signals recorded at different locations suggests that all the features become sharper at the upper level, H_2 . PDFs of time-resolved local voidage signals recorded at the axial coordinate H_3 do not exhibit the composite feature of the emulsion phase, but only one modal component is present, which corresponds to the expanded state of the emulsion phase. The recognition of the composite, bimodal nature of the PDF component associated with the emulsion phase is very remarkable, and suggests that different phases with specific voidages co-exist in the emulsion phase: a lower voidage LV-phase and a higher voidage HV-phase. The same features can be associated to the fluidized bed of silicon carbide, which results are reported as supplementary material (Figs. S.1-S.2), although the larger contribution of the bubble phase to the PDF along the axis of the bed is less marked. The observation of Figs. 4.4 and 4.5 reveals that a zone of intermediate voidages, which separates the emulsion-phase distributions from those associated with the bubble phase, exists and exhibits a rather flat trend of low probability, if compared to those of the emulsion/bubble phase. In a literature study on the behavior of the bubble, cloud, and emulsion phases in a fluidized bed by bi-optical probes, Andreux and Chaouki [36] interpreted the same portion of the PDF as being representative of the bubble cloud. In the present study, intermediate voidages are also observed for cloudless [153] bed materials. This evidence suggests that the measurement of intermediate voidages probably occurs when the sensing volume of the probe is not fully covered by the dense/bubble phase. Thus, more than one phase is detected simultaneously, and an averaged concentration of the dense and bubble phases is measured.

In order to shed light on the physical nature of the HV- and LV-phases, the voidage timeseries of grey quartz sand material have been further analyzed to assess whether recurrent temporal patterns could be recognized. To this end, a closer scrutiny has been dedicated to events associated to the passage of bubbles. Fig. 4.6A reports a close-up sample of voidage time-series obtained in experiments carried out with the probe located at the bed axis, upper level, H_2 , at ambient temperature and excess gas superficial velocity of $U - U_{mf} = 0.2$ m/s. The selection of the probe location at the bed axis and at the upper level, H_2 , was intentionally made to increase the probability for the probe to be located along the uprise trajectory of individual bubbles. Data in Fig. 4.6A have been interpreted in the light of the representative pattern reported in Fig. 4.6B, where distinct stages typically associated with the bubble passage are represented. The PDF of the voidage time series

is reported in Fig. 4.6C. A statistical analysis has been performed on the time series of bed voidage, by analyzing patterns associated to more than 50 bubble passages. Values of characteristic times in Fig. 4.6B have been obtained by determining the timings t_{down}^{**} and t_{up}^{**} at which the signal crosses the voidage ε^{**} , assumed as the threshold between the bubble and the emulsion phase, and the timings t^*_{down} and t^*_{up} at which the signal crosses the voidage ε^* , assumed as the threshold between the LV- and the HV-phases. Values of ε^* and ε^{**} have been taken as the minima in the PDF of Fig. 4.6C. The results of the statistical analysis are reported in Table 3. The entire cycle associated with a bubble passage, t_{up}^{**} , lasts, in the average 0.37 s. The time intervals during which the probe is in contact with the bubble, the LV-phase and the HV-phase are, in the average, 0.083 s, 0.037 s and 0.13 s, respectively. It is noteworthy that, on a statistical basis, $(t_{down}^* - t_{down}^{**}) \ll (t_{up}^{**} - t_{up}^*)$, a feature that suggests that the passage of the bubble is immediately followed by the detection of the LV-phase, eventually followed by the detection of a progressively more expanded state of the emulsion phase that reaches a maximum just before the arrival of a new bubble. This finding is consistent with the qualitative pattern represented in Fig. 4.6B, that implies the phenomenology associated to the passage of a bubble is characterized by the sequence Bubble \rightarrow LV-phase \rightarrow HVphase.

These features represent the basis for a tentative inference of the physical nature of the LV- and HV-phases. It may be speculated that the HV-phase establishes in the emulsion phase as a consequence of shear flow induced by the passage of the bubble. The broad spectrum of voidages would reflect different values of the local shear rates, that reach a maximum as a rising bubble approaches the probe. Accordingly, expansion of the emulsion phase in the proximity of bubbles would reflect the well-established dilatancy of dense granular flows subject to shear [154]. In this framework, the LV-phase immediately trailing the bubble should correspond to solids located in the bubble wake, characterized by prevailingly coherent translational motion and no shear. Of course, at small excess gas superficial velocities, the emulsion phase would be predominantly undisturbed by the bubble passage and a fairly homogeneous range of local bed voidages – as observed in the monomodal distribution of the PDF associated with the emulsion phase, where characteristic voidages oscillate around ε_{mf} or slightly higher values – would establish throughout the bed. Altogether, it may be concluded bubble-induced

shear might be responsible for the establishment of an expanded state of the emulsion phase at voidages well exceeding ε_{mf} to an extent that increases with increasing excess gas superficial velocity, $U - U_{mf}$. The fact that bubbles might be responsible for perturbations in the dense phase has already been highlighted in literature with reference to dense-phase expansion induced by large bubbles splitting, not necessarily related to the transition from bubbling to turbulent fluidization [155].



Figure 4.5 Probability density functions of the local voidage of grey quartz sand fluidized bed at 500 °C for different excess gas superficial velocities and probe locations.



Figure 4.6 (A) Sample of the time-resolved voidage signal. (B) Schematic pattern of the time resolved voidage associated with the passage of a bubble. (C) PDF of the time series. Operating conditions: ambient temperature, $U - U_{mf} = 0.2$ m/s, probe location: bed axis, H_2 .

Time [s]	
t_{up}^{**}	0.374 ±0.077
$t_{up}^* - t_{down}^*$	0.083 ± 0.023
$t^*_{down} - t^{**}_{down}$	0.037 ± 0.042
$t_{up}^{**}-t_{up}^{*}$	0.131 ± 0.054
$t_{down}^{**} \cong t_b$	0.122 ± 0.044

Table 3. Characteristic times of the voidage time series. Operating conditions: ambient temperature, $U - U_{mf} = 0.2$ m/s, probe location: bed axis, H_2 .



Figure 4.7 Probability density functions of the local voidage of γ -alumina–1 fluidized bed at ambient temperature for different excess gas superficial velocities and probe locations.



Figure 4.8 Probability density functions of the local voidage of γ -alumina–1 fluidized bed at 500 °C for different excess gas superficial velocities and probe locations.

As for the other two tested samples, in Figs. 4.7 and 4.8, PDFs of local voidage signals recorded during fluidization of γ -alumina–1 at room temperature and 500 °C are presented. Also in this case, when superficial gas velocity approaches incipient fluidization conditions, the PDFs exhibit a slightly skewed unimodal trend, with a voidage modal value around ε_{mf} . As gas superficial velocity starts being increased, the modal value associated to the emulsion phase shifts toward higher voidages, marking the expanded state of the emulsion-phase. As for the bimodal character of the emulsion phase, it is less pronounced. In particular, the LV- and HV-phases are more recognizable as

column center and the axial coordinate H_2 are approached, whereas, in the non-mentioned cases, the bimodality is less marked or the single modal peak could make think of a merging of the two modal components. Another aspect which deserves to be mentioned is that, when the bimodality of the emulsion phase is more evident, the fraction of the LV-phase in the emulsion phase PDF of the γ -alumina–1 fluidized bed seems to be higher if compared to grey quartz sand and silicon carbide samples. In the reasoning to assess the origin of these differences in the γ -alumina–1 sample there are two hypotheses: an intrinsic different behavior due to Geldart classification of the material into group D, or to its sphericity. The second hypothesis results prevalent as the same PDFs features have been found in the spherical γ -alumina–0.6, which belongs to the group B of Geldart classification. In Fig. 4.9, some PDFs of local bed voidage are reported to appreciate similarities between the two samples of γ -alumina. Likewise, similarities between the emulsion phase behavior of grey quartz sand and silicon carbide materials must be ascribed to particle surface irregularities of both samples [154].



Figure 4.9 Probability density functions of the local voidage of γ-alumina–0.6 fluidized bed for different temperatures, excess gas superficial velocities and probe locations.



Figure 4.10 Plot of the normalized mode values in the PDFs of the emulsion-phase voidage for the four material samples, at 500°C, as function of $U - U_{mf}$.

The peak voidages corresponding to the LV-phase and HV-phase are plotted as function of $U - U_{mf}$ for the four bed materials in the graphs of Fig. 4.10. Data points are reported in a normalized form with respect to ε_{mf} of each material and for two measurement levels, H_1 and H_2 . Only results at 500 °C have been represented for the sake of brevity. Results at ambient temperature are reported as supplementary material (Fig. S.3). When the emulsion phase PDF preserves its monomodal shape, only one value has been plotted in light blue. This happens at relatively low superficial gas velocities for all the samples, and also at higher superficial gas velocities with γ -alumina samples when the capacitance probe sensing volume is located at mid-radius or at the column wall. As for the peaks associated to the LV- and HV-distributions, these have been reported in green and red, respectively, only when they could be distinctively recognized in the PDFs of local voidage signals. In the other cases – when, for example, the LV distribution appears like a "shoulder" in the overall PDF of voidage signal – the assessment of the two modal components and of the associated peak values would require deconvolution procedures of the PDF associated with the emulsion phase of the fluidized bed, that have not been accomplished yet. In these cases, only one clearly visible peak has been represented which is, mostly, the modal peak associated to the HV distribution. However, the red color points out that a corresponding LV distribution is expected. It is interesting to observe that ε_e^{mode} values for the four materials tend to collapse around characteristic values when divided by the corresponding ε_{mf} . In particular, mode values of the HV-phase aggregate around values higher than unity, whereas those of the LV-phase mostly reside in a region around unity, displaying only moderate departures from ε_{mf} throughout the range of excess gas superficial velocities investigated.

4.1.2 Balance of superficial gas velocity at bed cross-section

Results on voidage spatial distribution in bubbling fluidized beds of the four tested materials, as reported in the sub-paragraph 4.1.1, confirm that fluidization patterns of dense gas fluidized beds may largely depart from the *two-phase theory* as regards the voidage in the emulsion phase. Accordingly, the split of fluidizing gas between the bubble and the emulsion phase, and associated bubble flow patterns, must be investigated and correctly modelled.

Figs. 4.11 and 4.12 report mean superficial gas velocities in the emulsion phase calculated with three different procedures (see sub-paragraph 3.3.1) and normalized with respect to the minimum fluidization velocity of the samples at the temperature of interest. As already specified, U_e resulting from the correlation of Hilligardt and Werther [31] does not depend on any measured quantity of the present work apart from U_{mf} . U_e derived from the Richardson-Zaki correlation [54] depends on the measured mean emulsion-

phase voidage averaged over bed section at the axial coordinate H_2 . U_e resulting from gas balance at the column cross section and height H_2 is based on all measured variables except the throughflow coefficient, which has been varied between 0 and 1. Zero value indicates the absence of the throughflow component. Inspection of Figs. 4.11 and 4.12 reveals that values obtained from Eq. 3 of Hilligardt and Werther would be associated to fluidized beds where the throughflow component is contemplated, with throughflow coefficients around/slightly higher than unity, and largely far from the theoretical throughflow coefficient of 3 [39]. Most of the results from Eq. 4 are supported by the fact that they fall into a reasonable range of emulsion-phase superficial gas velocities, to which throughflow coefficients in the range 0-1 are associated. It is hypothesized that, if at room temperature results from the Richardson-Zaki correlation for y-alumina-0.6 apparently lead to "negative" throughflow coefficients, this is due to a non-negligible overestimation of the experimental visible bubble flow, that has been determined by cross-correlating capacitance probe signals at H_1 and H_2 along bed axis. Experimental estimation of the visible bubble flow by the signals cross-correlation method has been first validated by measuring several bubbles velocity directly from signals observation in few chosen experimental conditions. Results are consistent with those from crosscorrelations within a 6 %. Then, experimental values of the visible bubble flow have been compared with predictions from the correlation of Fu et al. [145] (Fig. 4.13) valid for Geldart B and D solids. Overall, a good agreement between experimental values and predictions is shown. Experimental points associated to results on γ -alumina-0.6 at room temperature in Fig. 4.13 are those that mostly deviate from the bisect in the upper zone of the graph. This may confirm that for the present material the error makes the results on U_e from Eq. 4 misleading.

From Figs. 4.11 and 4.12 it is possible to note that the ratio U_e/U_{mf} , evaluated at the same $U - U_{mf}$, is fairly constant with increasing temperature for all the bed materials. As a consequence, U_e calculated according to Eq. 4 (Richardson-Zaki correlation) is systematically lower at 500 °C with respect to results at ambient temperature at the same superficial gas velocity or same excess gas velocity with respect to minimum fluidization conditions. The trend of U_e , as obtained with Eq. 4 for the four samples at ambient temperature and 500 °C, would suggest that the throughflow coefficient varies according to the operating conditions of the dense fluidized bed, namely operating temperature, superficial gas velocity, and bed material. It is hard to derive a constant value of k_{tf} for

each material. This is in accordance with the results of Olowson and Almsted [42], who have found no constant quota between the bubble throughflow velocity, U_{tf} , and emulsion phase superficial gas velocity, U_e . This is one of very few studies on throughflow velocity relative to bubbles in 3D beds operated at gas superficial velocities higher than U_{mf} . With their experimental apparatus, they measured a rather constant throughflow velocity relative to bubbles over the bed cross-section. Values of U_{tf} were of the order of four to five times U_{mf} . In our experiments, a value of around 5 is reached for the same ratio U_{tf}/U_{mf} , even if rarely and at high temperature. Results from Glicksman and McAndrews [41] cannot be considered for reliable comparisons because they refer to shallow 3D beds and do not consider the expansion of the emulsion phase as superficial gas velocity is increased in the gas balance of Eq. 1.



Figure 4.11 Comparison of dimensionless emulsion-phase gas superficial velocities reported versus $U - U_{mf}$, obtained with the three different procedures, for the four bed materials. Room temperature.



Figure 4.12 Comparison of dimensionless emulsion-phase gas superficial velocities reported versus $U - U_{mf}$, obtained with the three different procedures, for the four bed materials. 500°C.

According to the results on U_e obtained with the Richardson-Zaki correlation and compared with those from the gas balance at the column cross-section, temperature increase results in higher values of the throughflow coefficient, k_{tf} . However, the dependence of gas tendency to interstitially pass through bubbles on temperature is to be established from the product $\delta k_{tf} U_e$. U_e from Eq. 4 increases non monotonically with the gas superficial velocity. Accordingly, in some cases, an increase of k_{tf} with increasing excess gas velocity is found. This could be due to bubbles vertical coalescence, which is reported to enhance the throughflow component [39]. As for the dependence of throughflow coefficient or U_e on particle size, no apparent trend has been revealed from Figs. 4.11 and 4.12.

The theoretical approach to the Richardson-Zaki correlation developed by Gibilaro [58] seem to support the idea that, even in aggregative fluidization, the emulsion phase could be treated on a par with a homogeneous fluidized bed. This is due to a crucial characteristic of fluidized beds: variations in the fluid flux result in changes in the void
fraction, which maintains constant the unrecoverable pressure loss associated to the whole bed. These reflections are found to be perfectly in line with study of Olowson and Almstedt [32] on bubbling fluidized beds of Geldart B/D solids. The expansion of the dense phase and the increase of U_e with respect to minimum fluidization conditions combine to keep the drag force acting on the individual particles equal to that at incipient fluidization conditions. In this perspective, the emulsion phase of a bubbling fluidized bed can be considered "detached" by bubbles – although it is speculated that mechanisms of emulsion-phase expansion are bubble-induced – and U_e reasonably estimated from the correlation given by Richardson and Zaki [54]. The presence of more trustworthy throughflow coefficients from literature, for the closure of the mass balance on the fluidized bed gas (Eq. 2), would further support these subjects.



Figure 4.13 Comparison between the measured visible bubble flow and the one predicted from the correlation of Fu *et al.* [145] valid for Geldart B and D solids and reported on the x-axis.

4.2 Experiment 2: mass transfer-limited reaction experiments

Results of experiments aimed at measurement of the mass transfer coefficient under reactive conditions are reported in Fig. 4.14. The values of the Sherwood number measured during catalytic oxidation of CO are plotted as a function of the excess gas superficial velocity, $U - U_{mf}$, referred to the bed material. For each operating condition, data points were averaged over three independent experiments. The experimental procedure closely reflects that adopted by Scala [63], but the larger inner diameter of the

present experimental apparatus prevents the onset of slugging, so that all the experiments were carried out under freely bubbling conditions. Values of Sh computed using the Frössling-type equation (see sub-paragraph 1.2.1), as expressed by Eq. 9, are plotted in Fig. 4.14 for comparison with experimental data. It is noteworthy that the Sherwood numbers obtained from the experiments increase with increasing fluidization velocity, whereas Sh calculated from Eq. 9 is fairly constant. This discrepancy can be explained considering the results obtained in the previous sections, in the light of the bubble-induced expansion of the emulsion phase. Consistently with results of Scala [63], the catalyst particles, whose size largely exceeds that of the inert bed particles, mostly reside in the emulsion phase of the fluidized bed. Correspondingly, computations of Sh must be based on the value of the voidage that is actually established in the emulsion phase. The expanded state of the emulsion phase as the excess gas superficial velocity increases, reported and discussed in the sub-paragraph 4.1.1, must be taken into account in the computations. Accordingly, the Frössling-type correlation has been reviewed in the light of the generalized form expressed by Eq. 8, where ε_e and U_e are the effective voidage, and gas velocity of the emulsion phase, respectively. The validity of Eq. 8 has been evaluated utilizing ε_e^{HV} values averaged over bed cross section and height. It is observed that, if the value of U_e is estimated from the correlation reported by Hilligardt and Werther for three-dimensional beds [31] (Eq. 3) a value of 0.84 for the parameter K results from the best fitting of data. The good agreement of values of Sh computed with Eq. 8 with the experimental data points confirms the validity of the assumption that the expanded state of the emulsion phase must be taken into account in the calculation of the effective Sherwood number, and provides additional confirmation of the expansion of the emulsion phase of the bed at increasing gas superficial velocity.

Sh, according to Eq. 8, is composed of two additive contributions associated with the diffusive (Sh_{diff}) and convective (Sh_{conv}) terms of mass transfer, respectively. Sh_{conv} represents the major contribution of Sh since, as matter of fact, Sh_{diff} is limited by the effective voidage of the emulsion phase, which does not exceed 0.69 in the results reported in the present experimental campaign. This aspect suggests that even slightly inaccurate values of U_e may lead to wrong estimations of Sh. Accordingly, the red curve is obtained from Eq. 8, in which U_e values are calculated using the Richardson-Zaki correlation (Eq. 4) with ε_e^{HV} (averaged over the column cross section at H_2) as representative emulsion-phase voidage value. The outcomes are remarkable.

importance of this result is also reasoned by the fact that in the red curve, K is not a fitting parameter; instead, it is equal to 0.69, a consolidated number in literature as it derives from the study of Rowe *et al.* [61], who extended the results on mass transfer around isolated particles by Ranz and Marshall [62] to Reynolds numbers comprised between 20 and 2000. The modified Frössling-type correlation proposed as Eq. 8 is similar to that reported in the study of La Nauze and Jung [157], although they adopted the superficial gas velocity U instead of U_e in the Reynolds number.



Figure 4.14 Sherwood number as a function of excess gas superficial velocity. T = 450 °C; bed material: grey quartz sand. Frössling-type correlations: black continuous line, K = 0.70, $U_e = U_{mf}$, $\varepsilon_e = \varepsilon_{mf}$ [63]; black dashed line, K = 0.84, U_e obtained from Eq. 3, $\varepsilon_e = \varepsilon_e^{HV}$ [156]; red continuous line, K = 0.69 not used as fitting parameter, U_e obtained from Eq. 4 applied to the HV-phase, $\varepsilon_e = \varepsilon_e^{HV}$.

In conclusion, the hydrodynamics of the investigated bubbling fluidized beds have demonstrated to impact mass transfer. Accordingly, consequences on heat transfer coefficients are expected for fluidized beds exhibiting such peculiar bed voidage distribution. The assumption of the two-phase theory may lead to incorrect modeling of heat transfer as well. This aspect has been addressed in the studies of Stefanova *et al.* [158,159], in which voidage distribution of fluidized beds near the transition to the turbulent fluidization flow regime and in the turbulent regime has been characterized. The presence of structures of intermediate voidage between dense phase at minimum fluidization conditions and a more diluted phase, typically known as voids, is observed.

In this context, taking into account the contributions of such structures of intermediate voidage is mandatory for the correct predictions of heat transfer coefficients.

5. CHARACTERIZATION OF PARTICLE MIXING IN BEDS OF BIDISPERSE GRANULAR SOLIDS

5.1 Experiment 3

5.1.1 Study of the transient phase of mixing

Experiments aimed at the assessment of the transient state of mixing between the batch of tracer solids and bed material have been performed at a superficial gas velocity of 0.44 m/s and 500 °C. Once injected, tracer solids arranged homogeneously along the column cross section in their downward motion toward the fluidized bed surface. The whole batch reached the bed at the same time, as demonstrated by the time-resolved pressure profile recorded 0.01 m above the gas distributor (Fig. 5.1). The representation of the moving average of pressure oscillations in Fig. 5.1 has been accomplished to allow better visualization of the signal. It can be observed that, as the batch reaches the bed at about 120 s, pressure signal exhibits a one-step shift at a pressure level corresponding to the increased weight of the bed.



Figure 5.1 Moving average, computed on a time interval of 1 s, of time-resolved pressure signal recorded at 0.01 m above gas distributor. Operating conditions: T = 500 °C, U = 0.44 m/s; fluidized bed of γ -alumina–1 solids (0.486 kg), tracer batch of SiC solids (0.196 kg). Injection performed at about 120 s.

The moment at which pressure signal instantly increases is taken as reference time for the starting of mixing between the two different solids. Concerning signals from capacitance probes recorded at different bed axial levels (Fig. 5.2), it can be clearly observed that the batch of tracer solids enters the bed by, first, crossing the sensing volume of the upper probes and, finally, reaching the sensing volume of the probe placed at H_1 . The described pattern is shown in Fig. 5.2, in which SiC has been injected in the bed of γ -alumina-1 solids. The instant at which the batch passes through the sensing volume of the probes can be easily identified as the signal baseline immediately deviates toward lower signal levels, given the higher dielectric constant of SiC with respect to γ -alumina-1. In the "complementary" experiment, in which γ -alumina-1 is used as tracer material, the passage of γ -alumina-1 is identified by an increase of the signal baseline characteristic value. However, signal modification is much smoother in this last case, and the reason will be discussed in more detail in the next section. Apart from differences due to instruments response times, t_{H3} basically coincides with the mixing on-time identified from the pressure signal. The difference between the time defined by the pressure probe and t_{H1} , derived from the capacitance probe placed at H_1 , can be considered as an axial macro-mixing time of the tracer, namely the time required for the batch to vertically cross the entire bed height without being truly mixed with the rest of the bed yet. Defined this characteristic time of the system, it is observed that it lasts, on average, less than $1 \pm (0.71)$ ±0.46 s).



Figure 5.2 Time-resolved voltage signals recorded at bed axis with the probes sensing volume placed at H_1 (bottom) and H_3 (top). Operating conditions: T = 500 °C, U = 0.44 m/s; bed of γ -

alumina–1 solids (0.486 kg), tracer batch of SiC solids (0.196 kg). Injection performed at about 120 s. t_{H1} and t_{H3} represent the times at which the batch crosses the sensing volume of the two probes, respectively. $t_{H1} > t_{H3}$.

Concerning the time required for the tracer to reach local steady-state concentrations in the dense bed, it is one or two orders of magnitude higher, being in the average range 7-12 s.

5.1.2 Steady-state profiles of solid tracer concentration in the dense phase of the fluidized bed

The concentration of a solid tracer in the emulsion phase of the gas-FB, measured by the capacitance probe, can be calculated from the proposed correlation expressed by Eq. 15, prior verification that the dielectric constants of the two solids do not influence each other in mixture (see paragraph 2.2). Calibration tests with mixtures of SiC and γ -alumina–1 and with mixtures of other two dissimilar solids have been performed in the graduated cylinder of 500 ml. The results, as showed in Figs. S.4 and S.5, which have been reported as supplementary material, demonstrate that the correlation expressed by Eq. 15 holds true, meaning that the dielectric constants of the two solids – at least for the two tested cases – do not vary in mixture.

Another aspect to consider for the implementation of Eq. 15 is how the emulsion-phase voidage varies with tracer volume fraction when two solids having different size are used, which is the case of the present study. Voidage in perfectly mixed batches of SiC and γ -alumina–1 in fixed bed conditions, measured with the procedure reported in the sub-paragraph 3.3.3, exhibits, with good approximation, a linear trend with mixture composition, as expressed by the following equation:

$$\varepsilon = \varepsilon_1 f_1 + \varepsilon_2 (1 - f_1) \tag{27}$$

where ε_1 and ε_2 refer to fixed beds of solids 1 and 2, respectively (e. g. 1: γ -alumina–1, 2: SiC). The linear trend is reasonable as the size ratio between the two adopted materials does not approaches 0, a condition that would lead small particles to fill the interstices of large ones [139], resulting in a concave voidage profile with a minimum voidage value at a certain mixture composition. Besides, as in the present case the large particles are spherical, the high level of packing of the spheres may probably prevent even more SiC

particles from filling the interstices created by γ -alumina–1. Results on bed voidage, as obtained from the mixtures γ -alumina–1/SiC in static conditions, have been applied to the emulsion phase of the fluidized bed. The hydrodynamic characterization of gas fluidized beds (sub-paragraph 4.1.1) has revealed a non-negligible expansion of the dense phase in the bubbling regime. Accordingly, Eq. 27 has been adapted to a mixture of the two solids in the emulsion phase of the gas-FB. Values of ε_1 and ε_2 are the characteristic dense-phase voidages of γ -alumina–1 and SiC, as obtained in the experiments with fluidized beds of monodisperse solids. Therefore, in Eq. 15, ε derives from the linear combination (Eq. 27) of the mean γ -alumina–1 and SiC emulsion-phase voidages, which were measured in the fluidized bed operated at the same experimental conditions of the mixing experiment.



Figure 5.3 PDFs of voltage signals recorded by capacitance probe with the sensing volume placed at bed axis and H_1 . Operating conditions: T = 500 °C, U = 0.44 m/s. f_{γ} is the local volume fraction of γ -alumina–1 in the emulsion phase of the fluidized bed.

At steady-state conditions, the comparison between capacitance probe signals associated with mixtures γ -alumina–1/SiC of different composition and with the two beds of monodisperse solids can be made by a statistical approach. PDFs of voltage signals corresponding to different local volume fractions of γ -alumina–1 in the emulsion phase, f_{γ} , recorded at steady-state conditions of the fluidized bed, are reported in Figs. 5.3–5.5. All the curves refer to systems operated at a superficial gas velocity of 0.44 m/s, corresponding to $U - U_{mf}$ values of 0.25 and 0.17 m/s with reference to SiC and γ alumina–1, respectively. The green curves correspond to the fluidized bed of γ -alumina– 1, the blue curves to bed of SiC particles. The yellow curves result from the injection of a batch of SiC in the γ -alumina–1 bed, the red curves result from the complementary experiment. It is interesting to note that the blue curves and red curves of each figure are very similar one from the other. In the red curves, the part of the PDF referred to the emulsion phase of the fluidized bed is slightly shifted toward higher voltage values, indicating the presence of small amounts of γ -alumina–1. By considering comparable amounts of SiC in the bed of γ -alumina–1 (yellow curves), the shift of the PDF with respect to that associated to the bed of monodisperse γ -alumina–1 (greed curves) is much marked. The reason for such different results depends on the non-linearity in the characteristic curve of the capacitance measuring instrument (capacitance probe + amplifier), which has been thoroughly discussed in the paragraph 2.2. Non-linearity between the relative dielectric constant of the medium and the output voltage penalizes measurements carried out in the bed of SiC, in which γ -alumina–1 is injected as tracer. The extent of the shift of the red curve from the blue one risks being of the same order of magnitude of experimental random errors. This aspect causes more repetitions of the measurement to be required for this type of system.



Figure 5.4 PDFs of voltage signals recorded by capacitance probe with the sensing volume placed at bed axis and H_2 . Operating conditions: T = 500 °C, U = 0.44 m/s. f_{γ} is the local volume fraction of γ -alumina–1 in the emulsion phase of the fluidized bed.

With reference to the nomenclature proposed by Rowe [81], the dependence of the gas drag force on the projected particle surface generally determines that larger/smaller solids tend to act as *jetsam/flotsam*, respectively. Denser solids tend to sink to the bottom while less dense solids are typically found segregated up to the bed surface. In this context, higher-velocity fluidized beds tend to reach a more uniform, mixed state. The properties

of the two materials adopted in the present study make the basic question of which one component does act as flotsam in the mixture not at all trivial. Indeed, it can happen that the combination of properties driving towards opposed tendencies leads to an unpredictable behavior. In Figs. 5.6 and 5.7, tracer concentration profiles are reported for the two complementary experiments. Tracer volume fraction is reported versus superficial gas velocity and parametric in the axial coordinate of the bed. Each graph refers to a different radial coordinate, namely column axis, mid-radius, and wall. A continuous black line at a tracer volume fraction, f_{tr} , of 13 % is reported as reference for perfectly mixed conditions. When the measurement has been repeated more than one time in independent experiments, the error bar has been reported in the graphs, having minimum and maximum measured values as ends.



Figure 5.5 PDFs of voltage signals recorded by capacitance probe with the sensing volume placed at bed axis and H_3 . Operating conditions: T = 500 °C, U = 0.44 m/s. f_{γ} is the local volume fraction of γ -alumina–1 in the emulsion phase of the fluidized bed.

In Fig. 5.6, the volume fraction of silicon carbide, acting as tracer in the fluidized bed, is reported on y-axis versus U. At a superficial gas velocity of 0.44 m/s the fluidized bed results well mixed along the axial coordinate. As superficial gas velocity is increased, the system exhibits a vertical segregation with silicon carbide moving towards the top of the bed, resulting in a progressive pauperization of silicon carbide in the lower and intermediate zone of the bed. These patterns are particularly evident at bed axis and midradius, whereas the bed seems to be exempt from segregation mechanisms at the column wall. The same concentration profiles have been represented parametric in the radial coordinate in Fig. S.6, reported as supplementary material. It is observed that, at a

superficial gas velocity of 0.44 m/s the fluidized bed results well mixed along the radial coordinate of the bed, as well. As superficial gas velocity is increased, radial segregation patterns develop especially at H_1 and H_2 . Silicon carbide tends to segregate towards bed walls. H_3 is less subject to segregation mechanisms, although the slight radial segregation drives silicon carbide to concentrate towards the axis of the column, as opposite to what observed at H_1 and H_2 . In summary, superficial gas velocity intensifies the axial and lateral segregation of the mixture. Vertical segregation with superficial gas velocity is more pronounced at bed axis becoming progressively less intense towards bed walls. Radial segregation with superficial gas velocity is much emphasized at H_1 and the slight tracer segregation identified at H_3 occurs in the opposite direction with respect to H_1 and H_2 . In Fig. 5.7, results from the complementary experiment, in which γ -alumina-1 has been used as tracer material, are presented. At a superficial gas velocity of 0.44 m/s the fluidized bed results moderately mixed along the axial coordinate. As superficial gas velocity is increased, the system exhibits a vertical segregation with γ -alumina-1 moving towards the bottom and the intermediate zone of the bed, resulting in a progressive pauperization of γ -alumina–1 at the top of the bed. These patterns are particularly evident at bed axis and mid-radius, whereas mechanisms at the column wall are not well understood. The same concentration profiles have been represented parametric in the radial coordinate in Fig. S.7, reported as supplementary material. It is observed that, at a superficial gas velocity of 0.44 m/s the fluidized bed results fairly mixed along the radial coordinate of the bed. As superficial gas velocity is increased, radial segregation patterns develop at H_1 and H_2 , where γ -alumina-1 tends to segregate towards bed axis. At H_3 , the radial segregation drives γ -alumina-1 to concentrate towards the walls of the column, although, from U = 0.49 m/s, f_{tr} at H_3 decreases independently from the radial coordinate. Also in these experiments, with silicon carbide as bed material, superficial gas velocity is found to emphasize the axial and lateral segregation of the binary mixture. Some mechanisms at bed walls and H_3 are less clear, but this could be also due to the increased difficulty in postprocessing data from this mixture, as mentioned above.

A validation of the adopted procedure comes from the balance on tracer volume fraction over the whole bed. Similarly to Eq. 19, tracer concentration has been first averaged over bed cross section, as following:



(28)

Figure 5.6 Concentration profiles of silicon carbide in the emulsion phase of the fluidized bed of γ -alumina–1. Tracer volume fraction is represented versus superficial gas velocity, and parametric in the axial coordinate.

Then, results at each axial coordinate have been averaged over bed height. Results for the two mixtures are shown in Fig. 5.8. A continuous black line at a tracer volume fraction, f_{tr} , of 13 % is reported as reference for perfectly mixed conditions. The balance on tracer volume fraction can be considered fulfilled in both cases. The mean tracer concentration in the graph (a), represented by the dotted line, is a bit lower that the reference value for perfectly mixed conditions. However, part of the batch of silicon carbide is hypothesized to be located in zones of the bed which have not been investigated by the capacitance

probes. For example, the trends in Fig. 5.6 suggest that SiC tends to move towards bed walls. The radial coordinate to which the terminology *wall* is associated, actually corresponds to 7/9 of the column radius, with 0 being the value for column axis. Therefore, it is expected that even higher tracer volume fractions can be found at the real walls of the column. Along the same path, as SiC tends to concentrate at the top of the bed, it is likely for a layer of silicon carbide to establish above the capacitance probe placed at H_3 . The discretization of the bed domain seems to be, instead, more favorable in the case (b), as demonstrated by the balance on tracer volume fraction.



Figure 5.7 Concentration profiles of γ-alumina–1 in the emulsion phase of the fluidized bed of silicon carbide. Tracer volume fraction is represented versus superficial gas velocity, and parametric in the axial coordinate.



Figure 5.8 Concentration profiles of silicon carbide (a) and γ -alumina–1 (b) in the emulsion phase of the fluidized bed measured in complementary experiments. Tracer volume fraction is averaged over bed cross section (Eq. 28) at H_1 (circles), H_2 (diamonds), and H_3 (squares), and finally, averaged over bed height (dotted line).

Overall, experiments on the two complementary mixtures seem really to show coherent results. Tracer concentration profiles represented versus superficial gas velocity for the two investigated mixtures at several locations in the fluidized bed, resemble what in liquid fluidization has been called layer inversion phenomenon. It occurs with mixtures of two particle species, species 1 being larger and lower in density than species 2. An idealized and over-simplified description of the layer inversion phenomenon can be given as follows: at very low liquid velocity, the two species form distinct layers, with the denser smaller particles (species 2) at the bottom, and the larger lower-density particles (species 1) at the top. At high velocities, two distinct layers are again visible, but the layers are inverted, species 1 and 2 being at the bottom and top, respectively. The liquid velocity at which the bed inverts corresponds to homogeneous mixing of the two species [160]. Layer inversion has been extensively studied in the field of liquid fluidization [56,160– 163]. Rasul et al. [164] have shown how the theory of layer inversion can also be applied to gas fluidized beds. The authors operated under constrained conditions, choosing small particles that could give inversion between U_{mf} and U_{mb} , to prevent bubbles from interfering with the observation of the phenomenon. Afterwards, van Wachem et al. [165] reproduced the layer inversion phenomenon through a CFD model developed for gassolid fluidized beds containing a mixture of two particle species. The results of the present study, with regard to the axial segregation behavior, seem very coherent with the described phenomenology. The superficial gas velocity of 0.44 m/s may represent the velocity at which the bed starts displaying axial inversion patterns from a homogeneously mixed condition. Further investigations at superficial gas velocities lower than 0.44 m/s could confirm the described phenomenology. At lower gas velocity, the gravity force and the upward drag force should lead to a much smaller upward force for the small and heavy particles (SiC). As for radial segregation, this may be probably related to bubble patterns, which selectively drive solids species towards different regions of the column, this mechanism being emphasized as superficial gas velocity is increased. This aspect deserves further investigations to assess whether this type of segregation is, instead, an effect of the laboratory-scale apparatus.

6. CONCLUSIONS

The hydrodynamics of Geldart-B/D solids dense fluidized beds operated at ambient and high temperature has been successfully characterized using capacitance probes. The custom-made probes have displayed excellent durability, working for more than 300 hours at 500°C, under the mechanical action of the fluidizing particles, without noticeable alteration of the capacitance signal.

Spatial maps of pointwise values of the bed voidage obtained from capacitance probe measurements were consistent with independently derived values of the overall bed voidage. Statistical analysis of the time-series of local bed voidage yields probability density functions that display multimodal patterns. A remarkable bimodal character is apparent in the portion of the spectrum that refers to the emulsion phase of the bed, more pronounced as the gas superficial velocity is increased. It is inferred that different phases at distinctively different voidage co-exist in the emulsion phase: a lower voidage LV-phase and a higher voidage HV-phase. A detailed analysis of selected voidage time-series was accomplished, with the aim of inferring the physical nature of the LV- and HV-phases. It is speculated that the LV-phase, which is detected by the probes immediately after the passage of the bubble, may be associated with the wake of the bubble, whereas the HV-phase may be representative of the bulk of the emulsion phase. It is further speculated that the expanded state of the HV-phase, above the voidage of the incipiently fluidized bed, may be the consequence of bed dilatancy associated with bubble-induced shear flow.

With reference to the composite nature of the emulsion phase in the dense gas-fluidized bed of monodisperse solids, irregular solids and spherical particles present some different peculiar features, as revealed from the statistical approach. This aspect demonstrates that surface properties could impact emulsion-phase dilatancy, which results from bubble-induced shear flow. In spite of the highlighted differences, the characteristic voidages associated with the emulsion phase of the four tested materials show similar trends with superficial gas velocity in excess with respect to minimum fluidization conditions. This aspect has been demonstrated by the representation of data normalized with respect to the voidage values at incipient fluidization. Although results obtained at 500°C qualitatively resemble those obtained at ambient temperature, quantitative differences are observed,

confirming the need for characterization of bed hydrodynamics at temperatures of interest in industrial applications.

A dedicated campaign consisting of fluidized bed catalytic oxidation of CO has been directed to the assessment of the mass transfer coefficient between the bulk of the bed and active particles, under the assumption of infinitely fast chemical kinetics. The outcomes of the experiment are fully consistent with the experimental findings obtained from the hydrodynamic characterization of the bed at comparable temperature. Results confirm the close relationship between mass transfer and expansion patterns of the emulsion phase, and the need for proper hydrodynamic characterization of the bed. A more accurate version of the Frössling-type equation, modified for the estimation of mass transfer in dense fluidized beds, has been proposed. It is shown that better estimates of the active particle Sherwood number are obtained if the Frössling-type equation is implemented using the actual voidage of the expanded emulsion phase, rather than the voidage corresponding to incipient fluidization, as well as the actual superficial gas velocity in the emulsion phase. In this way, there is no need to fit any of the parameters present in the correlation, which can keep consolidated literature values. This analysis is relevant to the assessment of bed-particle mass transfer coefficients controlling the apparent reaction rate in the fast-chemical reaction regime. This regime is frequently encountered in many fluidized bed processes aimed at thermochemical conversion of solid fuels.

Results on fluidized bed hydrodynamics by capacitance probes along with validation from experiments on mass transfer-limited reaction suggest, with a good confidence level, the validity of the Richardson-Zaki correlation in the field of aggregative fluidization. This subject also finds confirmation in some relevant literature studies, in which experimental evidence is supported by a theoretical approach.

Overall, results on hydrodynamic characterization of monodisperse fluidized beds find some confirmation in the literature and provide new insights about fundamentals of fluidization. Although results have been obtained on a relatively small unit, the proposed approach to the investigated phenomena constitutes a good starting point for studies in larger units. The outcomes of the present thesis could serve as reliable reference for those studies on comparable units, in which the interpretation of results could be better accomplished through a detailed knowledge of the fluidized bed hydrodynamics. Capacitance probes have been employed innovatively to characterize beds of bidisperse solids. Size and density ratios of the two adopted solid species were on opposite sides of unity. A correlation which predicts the relative dielectric constant of a binary mixture has been proposed and successfully validated. The implementation of the correlation to the dense fluidized bed of two dissimilar solids requires the voidage of the dense phase to be known at the operating conditions of interest. Results on local concentrations of solid tracers in the emulsion phase of the fluidized bed are satisfactory and encouraging. The adopted binary mixtures exhibit the *layer inversion* phenomenon, well known in liquid fluidized beds.

Some drawbacks about the employment of capacitance probes with binary mixtures of solids are found in the non-linearity of the measurement instrument curve, which can be easily overcome by using a different amplification system. More serious issues concern the difficulty in following the time-series of local tracer concentration due to the unknown evolution with time of the emulsion-phase voidage. The voltage signal from a bed of two dissimilar solids is composed, in fact, of two unknowns, namely bed voidage and solid composition. This is a consequence of the fact that deviations from the *two-phase theory of fluidization* can, in some cases, hardly be neglected. This is the reason why, in the present study, tracer concentration profiles have been gathered only at steady-state condition by a statistical approach and evaluation of transient phases have been accomplished only by evaluation of the voltage signal, which does not give any information on the evolution of tracer concentration with time.

Capacitance probes work well with mixtures of the first category, as defined in the literature paragraphs, but might be unable to assess mixing of particles which volume is larger than the probe miniaturized sensing volume.

7. ONGOING ACTIVITIES AND FUTURE PERSPECTIVES

In the present study, very successful results have been obtained, in a relatively small unit, on fluidized bed hydrodynamics for Geldart B/D solids both at ambient temperature and 500 °C, and on mixing between binary mixtures of dissimilar solids. It is of interest to assess the scale effect on the investigated phenomena. In this regard, ongoing studies in a pilot-scale unit have already been offering interesting insights.

The pilot-scale apparatus is constituted by a stainless steel (AISI 310) fluidization column, with a 370 mm ID for almost all its height (5.05 m), whereas the upper part of freeboard is characterized by ID of 700 mm and height of 1.85 m (total height of 6.9 m). The lower section of the column is equipped with a windbox split into two concentric sections: the core and the annulus section, corresponding to 30 % and 70 % of the fluidized column cross-section, respectively. The distributor plate is equipped with 55 bubble caps. The fluidization column is fitted with several access ports for temperature, pressure, and capacitance probes. In particular, two symmetric flanges provide direct access to the dense bed in the bottom part of the column. Two cyclones, having medium and high efficiency, respectively, are used for flue gas de-dusting. Operation of the system at high temperatures is possible thanks to a propane premixed burner, connected to the annulus section of the plenum. Hot diluted flue gases from the burner are directly fed to the reactor to heat up bed solids. In absence of exothermic chemical reaction occurring in the fluidized bed, the burner has to be operated continuously until the end of the experiment. The entire vessel is thermally insulated by a ceramic wool blanket in order to minimize heat losses and to ensure a safe temperature at the external surface. The system temperature is controlled thanks to water and air-cooled exchangers. Temperature, pressure, and flue gas concentrations are monitored on-line and recorded using a data control and acquisition system. The fluidized bed is equipped with two feeding systems: an over-bed free falling chute and a purposely designed in-bed pneumatic injection system.

An experimental campaign at ambient temperature has been carried out, using silicon carbide (Table 1) as bed material. For the hydrodynamic characterization of the fluidized bed of monodisperse solids, capacitance probe sensing volumes have been located at five

different radial coordinate of the bed, spanning from column center to the wall proximity. Simultaneously, high frequency pressure measurements have been performed inside the dense bed and in the plenum. Mixing experiments have been performed by injecting a batch of γ -alumina–1 tracer above the bed from the free-falling chute. The amount of tracer has been kept equal to that adopted during mixing experiments in the laboratory-scale unit. The injection time and the zone where tracer concentrates at falling on the surface of the fluidized bed have been monitored by an infrared camera, located at the top of the column and focused on bed surface. To better visualize tracer falling and the entrance inside the bed, tracer batch has been pre-heated up to 20–30 °C above room temperature. The same type of experiments are about to be run at 500 °C. Overall results will be compared with those obtained in the laboratory-scale unit, to identify the main differences on the investigated phenomena due to scale effects.

About future perspectives and recommendation, capacitance probes demonstrate to be highly versatile, but they would probably be not sufficient alone to have the full picture: coupling with other techniques to study heat transfer phenomena and how these are related to mixing is recommended, as well as the integration of a Lagrangian technique to have a comprehensive view on the mixing/segregation patterns under relevant operating conditions. As a proposal, thermal tracing with non-contact and contact measuring probes could allow to determine particle-particle and particle-gas heat transfer in experiments during which a stream of solids is injected at a different temperature than bed material. Pyrometers connected to fiberoptic probes could access the dense bed and be placed at the same location of fast-response thermocouples and capacitance probes.

It would be of interest to utilize experimental data on bed hydrodynamics and mixing between dissimilar solids to validate or propose CFD/CFD-DEM models for gas-fluidized beds. Experimental and modeling tools used in parallel could help to a better understanding of the physical behavior of monodisperse and bidisperse fluidized bed systems.

Nomenclature

A	surface area [m ²]		
С	gas concentration [kmol/m ³]		
С	capacitance [F]		
d	diameter [m]		
ã	mean diameter [m]		
D	column diameter [m]		
\mathcal{D}	diffusion coefficient [m ² /s]		
\mathfrak{D}	dispersion coefficient [m ² /s]		
f	solid volume fraction (fluid-free basis) [-]		
$\langle f \rangle$	spatially-averaged solid volume fraction (fluid-free basis) [-]		
Gain	gain factor of the amplifier for capacitance probes [pF V]		
h	distance between the conductors of the parallel-plate capacitor [m]		
Н	height [m]		
\widetilde{H}	mean height [m]		
k	mass transfer coefficient [m/s]		
Κ	fitting parameter in Frössling-type correlation [-]		
k _{tf}	throughflow coefficient [-]		
n	parameter in Richardson-Zaki correlation [-]		
Q	volume flowrate [m ³ /s]		
r	radius [m]		
R	column radius [m]		
S	column cross section [m ²]		
t	time [s]		
U	superficial gas velocity [m/s]		
$\widetilde{U}_{b\infty}$	terminal rise velocity of an isolated bubble [m/s]		
v	volume [m ³]		
V	voltage [V]		
x	reaction conversion degree [-]		
X	bubble-emulsion phase mass transfer index [-]		
Greek symbols			

- δ volume fraction of the bed in bubbles [-]
- ε voidage [-]
- $\tilde{\varepsilon}$ mean bed voidage [-]
- $\langle \varepsilon \rangle$ spatially averaged voidage [-]
- ε_0 void dielectric constant [pF/m]
- κ relative dielectric constant [-]
- μ viscosity [N s m⁻²]
- ξ reaction rate [kmol/s]

- ρ density [kg/m³]
- $\tilde{\rho}$ mean density [kg/m³]
- ϕ particle sphericity [-]
- Σ capacitance probe geometric characteristic [m]

Dimensionless numbers

Re	Reynolds number	[-]
----	-----------------	-----

- *Sh* Sherwood number [-]
- *Sc* Schmidt number [-]

Subscripts

a	octivo	portiala
u	active	particle

- b bubble
- bed bed
- *conv* convective
- diff diffusive

down corresponding to a decreasing trend of voidage

- *e* emulsion/dense phase
- f fluidized bed
- fb fixed bed
- g gas
- *LV* low-voidage phase
- *HV* high-voidage phase
- *i* subsection number
- loose loose
- *mf* minimum/incipient fluidization conditions
- *mb* minimum bubbling
- *p* particle
- pack packed
- r radius
- s solid
- t terminal
- *tf* throughflow
- th threshold
- *tot* total
- *tr* tracer material
- *up* corresponding to an increasing trend of voidage
- 0 air
- 1 solid 1 in a binary mixture
- 2 solid 2 in a binary mixture
- γ γ -alumina

Superscripts

- b bubblebed bed materiale emulsionHV high-voidage phase
- *in* reactor inlet
- *mode* mode
- *out* reactor outlet
- r radial
- *tr* tracer material
- * threshold between the LV- and the HV-phases
- ** threshold between the HV- and the bubble-phase

References

- [1] J.R. Grace, Gas-Solid and Other Two-Phase Suspensions, Can. J. Chem. Eng. 64 (1986) 353–363. https://doi.org//10.1002/cjce.5450640301.
- R. Solimene, Mixing and Segregation in Fluidized Beds, in: Ref. Modul. Chem. Mol. Sci. Chem. Eng., 2017: pp. 1–29. https://doi.org/10.1016/b978-0-12-409547-2.12186-9.
- [3] R. Girimonte, V. Vivacqua, Design criteria for homogeneous fluidization of Geldart's class B solids upward through a packed bed, Powder Technol. 249 (2013) 316–322. https://doi.org/10.1016/j.powtec.2013.08.041.
- [4] G. Schöny, F. Dietrich, J. Fuchs, T. Pröll, H. Hofbauer, A multi-stage fluidized bed system for continuous CO₂ capture by means of temperature swing adsorption -First results from bench scale experiments, Powder Technol. 316 (2017) 519–527. https://doi.org//10.1016/j.powtec.2016.11.066.
- [5] F. Scala, R. Chirone, P. Meloni, G. Carangiu, M. Manca, G. Mulas, A. Mulas, Fluidized bed desulfurization using lime obtained after slow calcination of limestone particles, Fuel. 114 (2013) 99–105. https://doi.org//10.1016/j.fuel.2012.11.072.
- [6] P. Salatino, R. Solimene, Mixing and segregation in fluidized bed thermochemical conversion of biomass, Powder Technol. 316 (2017) 29–40. https://doi.org/10.1016/j.powtec.2016.11.058.
- [7] A. Lyngfelt, Chemical looping combustion: status and development challenges, Energy and Fuels. 34 (2020) 9077–9093. https://doi.org//10.1021/acs.energyfuels.0c01454.
- [8] C. Tregambi, M. Troiano, F. Montagnaro, R. Solimene, P. Salatino, Fluidized Beds for Concentrated Solar Thermal Technologies—A Review, Front. Energy Res. 9 (2021) 1–26. https://doi.org/10.3389/fenrg.2021.618421.
- [9] L. Guo, Q. Bao, J. Gao, Q. Zhu, Z. Guo, A review on prevention of sticking during fluidized bed reduction of fine iron ore, ISIJ Int. 60 (2020) 1–17. https://doi.org/10.2355/isijinternational.ISIJINT-2019-392.
- B. Formisani, R. Girimonte, G. Pataro, The influence of operating temperature on the dense phase properties of bubbling fluidized beds of solids, Powder Technol. 125 (2002) 28–38. https://doi.org//10.1016/S0032-5910(01)00494-6.
- [11] H. Cui, J. Chaouki, Effects of temperature on local two-phase flow structure in bubbling and turbulent fluidized beds of FCC particles, Chem. Eng. Sci. 59 (2004) 3413–3422. https://doi.org/10.1016/j.ces.2004.05.006.
- [12] J. Shabanian, J. Chaouki, Effects of temperature, pressure, and interparticle forces on the hydrodynamics of a gas-solid fluidized bed, Chem. Eng. J. 313 (2017) 580–

590. https://doi.org/10.1016/j.cej.2016.12.061.

- [13] P. Schlichthaerle, J. Werther, Solids mixing in the bottom zone of a circulating fluidized bed, Powder Technol. 120 (2001) 21–33. https://doi.org/10.1016/S0032-5910(01)00342-4.
- [14] E. Sette, D. Pallarès, F. Johnsson, Experimental evaluation of lateral mixing of bulk solids in a fluid-dynamically down-scaled bubbling fluidized bed, Powder Technol. 263 (2014) 74–80. https://doi.org/10.1016/j.powtec.2014.04.091.
- [15] B. Sarrion, J.M. Valverde, A. Perejon, L. Perez-Maqueda, P.E. Sanchez-Jimenez, On the Multicycle Activity of Natural Limestone/Dolomite for Thermochemical Energy Storage of Concentrated Solar Power, Energy Technol. 4 (2016) 1013– 1019. https://doi.org/10.1002/ente.201600068.
- [16] B. Sarrión, A. Perejón, P.E. Sánchez-Jiménez, L.A. Pérez-Maqueda, J.M. Valverde, Role of calcium looping conditions on the performance of natural and synthetic Ca-based materials for energy storage, J. CO₂ Util. 28 (2018) 374–384. https://doi.org/10.1016/j.jcou.2018.10.018.
- [17] S. Pascual, P. Lisbona, M. Bailera, L.M. Romeo, Design and operational performance maps of calcium looping thermochemical energy storage for concentrating solar power plants, Energy. 220 (2021) 1–19. https://doi.org/10.1016/j.energy.2020.119715.
- [18] C. Tregambi, F. Di Lauro, S. Pascual, P. Lisbona, L.M. Romeo, R. Solimene, P. Salatino, F. Montagnaro, Solar-driven calcium looping in fluidized beds for thermochemical energy storage, Chem. Eng. J. 466 (2023) 142708. https://doi.org/https://doi.org/10.1016/j.cej.2023.142708.
- [19] T. Li, H. Thunman, H. Ström, A fast-solving particle model for thermochemical conversion of biomass, Combust. Flame. 213 (2020) 117–131. https://doi.org/10.1016/j.combustflame.2019.11.018.
- M. Troiano, A. Cammarota, C. Tregambi, R. Chirone, P. Salatino, R. Solimene, Fluidized bed combustion of solid lignin-rich residues from bioethanol production, Powder Technol. 371 (2020) 170–179. https://doi.org/10.1016/j.powtec.2020.05.070.
- [21] K.Y. Kwong, R. Mao, S.A. Scott, J.S. Dennis, E.J. Marek, Analysis of the rate of combustion of biomass char in a fluidised bed of CLOU particles, Chem. Eng. J. 417 (2021) 127942. https://doi.org/10.1016/j.cej.2020.127942.
- [22] A.N. Hayhurst, M.S. Parmar, Measurement of the mass transfer coefficient and Sherwood number for carbon spheres burning in a bubbling fluidized bed, Combust. Flame. 130 (2002) 361–375. https://doi.org/10.1016/S0010-2180(02)00387-5.
- [23] F. Scala, A new technique for the measurement of the product CO/CO₂ ratio at the surface of char particles burning in a fluidized bed, Proc. Combust. Inst. 32 II (2009) 2021–2027. https://doi.org/10.1016/j.proci.2008.06.047.

- [24] R. Toomey, H.F. Johnstone, Gas Fluidization of Solid Particles, Chem. Eng. Prog. 48 (1952) 220–226.
- [25] D. Geldart, Types of gas fluidization, Powder Technol. 7 (1973) 285–292. https://doi.org//10.1016/0032-5910(73)80037-3.
- [26] J.R. Grace, R. Clift, On the two-phase theory of fluidization, Chem. Eng. Sci. 29 (1974) 327–334. https://doi.org/10.1016/0009-2509(74)80039-4.
- [27] D.L. Pyle, D. Harrison, An experimental investigation of the two-phase theory of fluidization, Chem. Eng. Sci. 22 (1967) 1199–1207. https://doi.org/10.1016/0009-2509(67)80186-6.
- [28] P.N. Rowe, L. Santoro, J.G. Yates, The division of gas between bubble and interstitial phases in fluidised beds of fine powders, Chem. Eng. Sci. 33 (1978) 133–140. https://doi.org/https://doi.org/10.1016/0009-2509(78)85079-9.
- [29] I.A. Khattab, C. Kuroda, M. Ishida, Radial and vertical distributions of the interstitial gas velocity in a fluidized bed, J. Chem. Eng. Japan. 21 (1988) 282– 287. https://doi.org/10.1252/jcej.21.282.
- [30] A.R. Abrahamsen, D. Geldart, Behaviour of gas-fluidized beds of fine powders part I. Homogeneous expansion, Powder Technol. 26 (1980) 35–46. https://doi.org/10.1016/0032-5910(80)85005-4.
- [31] K. Hilligardt, J. Werther, Influence of temperature and properties of solids on the size and growth of bubbles in gas fluidized beds, Chem. Eng. Technol. 10 (1987) 272–280. https://doi.org/10.1002/ceat.270100133.
- [32] P.A. Olowson, A.E. Almstedt, Hydrodynamics of a bubbling fluidized bed: influence of pressure and fluidization velocity in terms of drag force, Chem. Eng. Sci. 47 (1992) 357–366. https://doi.org//10.1016/0009-2509(92)80026-9.
- [33] H. Cui, N. Mostoufi, J. Chaouki, Characterization of dynamic gas-solid distribution in fluidized beds, 2000. https://doi.org/https://doi.org/10.1016/S1385-8947(00)00178-9.
- [34] H. Cui, N. Mostoufi, J. Chaouki, Gas and solids between dynamic bubble and emulsion in gas-fluidized beds, Powder Technol. 120 (2001) 12–20. https://doi.org/10.1016/S0032-5910(01)00341-2.
- [35] J.G. Yates, D.J. Cheesman, P. Lettieri, D. Newton, X-ray analysis of fluidized beds and other multiphase systems, KONA Powder Part. J. (2002). https://doi.org/10.14356/kona.2002016.
- [36] R. Andreux, J. Chaouki, Behaviors of the bubble, cloud, and emulsion phases in a fluidized bed, AIChE J. 54 (2008) 406–414. https://doi.org/10.1002/aic.11390.
- [37] M.J. Lockett, J.F. Davidson, D. Harrison, On the two-phase theory of fluidization, Chem. Eng. Sci. 22 (1967) 1059–1066. https://doi.org/https://doi.org/10.1016/0009-2509(67)80170-2.

- [38] J.R. Grace, D. Harrison, The behaviour of freely bubbling fluidised beds, Chem. Eng. Sci. 24 (1969) 497–508. https://doi.org/10.1016/0009-2509(69)85021-9.
- [39] J.A. Valenzuela, L.R. Glicksman, Gas flow distribution in a bubbling fluidized bed, Powder Technol. 44 (1985) 103–113. https://doi.org/https://doi.org/10.1016/0032-5910(85)87016-9.
- [40] J.F. Davidson, D. Harrison, The behaviour of a continuously bubbling fluidised bed, Chem. Eng. Sci. 21 (1966) 731–738. https://doi.org/10.1016/0009-2509(66)87001-X.
- [41] L.R. Glicksman, G. McAndrews, The effect of bed width on the hydrodynamics of large particle fluidized beds, Powder Technol. 42 (1985) 159–167. https://doi.org/10.1016/0032-5910(85)80049-8.
- [42] P.A. Olowson, A.E. Almstedt, Influence of pressure and fluidization velocity on the bubble behaviour and gas flow distribution in a fluidized bed, Chem. Eng. Sci. 45 (1990) 1733–1741. https://doi.org/10.1016/0009-2509(90)87051-S.
- [43] L. Hailu, F. Plaka, R. Clift, J.F. Davidson, Measurement of gas flow through a twodimensional bubble in a fluidised bed, Chem. Eng. Res. Des. 71 (1993) 382–389.
- [44] M. Gautam, J.T. Jurewicz, S.R. Kale, An experimental investigation of throughflow velocities in two-dimensional fluidized bed bubbles: Laser doppler anemometer measurements, J. Fluids Eng. Trans. ASME. 116 (1994) 605–612. https://doi.org/10.1115/1.2910320.
- [45] K.S. Lim, V.S. Gururajan, P.K. Agarwal, Mixing of homogeneous solids in bubbling fluidized beds: Theoretical modelling and experimental investigation using digital image analysis, Chem. Eng. Sci. 48 (1993) 2251–2265. https://doi.org/10.1016/0009-2509(93)80241-H.
- [46] W. Wu, P.K. Agarwal, The effect of bed temperature on mass transfer between the bubble and emulsion phases in a fluidized bed, Can. J. Chem. Eng. 81 (2003) 940– 948. https://doi.org/10.1002/cjce.5450810503.
- [47] S.P. Sit, J.R. Grace, Effect of bubble interaction on interphase mass transfer in gas fluidized beds, Chem. Eng. Sci. 36 (1981) 327–335. https://doi.org/10.1016/0009-2509(81)85012-9.
- [48] R. Solimene, A. Marzocchella, G. Passarelli, P. Salatino, Assessment of gasfluidized beds mixing and hydrodynamics by zirconia sensors, AIChE J. 52 (2006) 185–198. https://doi.org/10.1002/aic.10592.
- [49] J.A. Almendros-Ibáñez, D. Pallarès, F. Johnsson, D. Santana, Voidage distribution around bubbles in a fluidized bed: Influence on throughflow, Powder Technol. 197 (2010) 73–82. https://doi.org/10.1016/j.powtec.2009.08.021.
- [50] A. Bakshi, A.F. Ghoniem, C. Altantzis, Mixing dynamics in bubbling fluidized beds, AIChE J. 63 (2017) 4316–4328. https://doi.org/10.1002/aic.15801.
- [51] J.G. Villanueva-Chávez, W.A. Bizzo, Fluid dynamic modeling of a large bubbling

fluidized bed for biomass combustion: Mass transfer in bubbles, Chem. Eng. Sci. 196 (2019) 414–424. https://doi.org/10.1016/j.ces.2018.11.023.

- [52] L. Shen, F. Johnsson, B. Leckner, Digital image analysis of hydrodynamics twodimensional bubbling fluidized beds, Chem. Eng. Sci. 59 (2004) 2607–2617. https://doi.org/10.1016/j.ces.2004.01.063.
- [53] A. Vepsäläinen, S. Shah, J. Ritvanen, T. Hyppänen, Interphase mass transfer coefficient in fluidized bed combustion by Eulerian CFD modeling, Chem. Eng. Sci. 106 (2014) 30–38. https://doi.org/10.1016/j.ces.2013.11.042.
- [54] J.F. Richardson, W.N. Zaki, The sedimentation of a suspension of uniform spheres under conditions of viscous flow, Chem. Eng. Sci. 3 (1954) 65–73. https://doi.org/https://doi.org/10.1016/0009-2509(54)85015-9.
- [55] A.R. Khan, J.F. Richardson, Fluid-particle interactions and flow characteristics of fluidized beds and settling suspensions of spherical particles, Chem. Eng. Commun. 78 (1989) 111–130. https://doi.org/10.1080/00986448908940189.
- [56] R. Di Felice, Hydrodynamics of liquid fluidisation, Chem. Eng. Sci. 50 (1995) 1213–1245. https://doi.org/10.1016/0009-2509(95)98838-6.
- [57] P. Lettieri, D. Newton, J.G. Yates, Homogeneous bed expansion of FCC catalysts, influence of temperature on the parameters of the Richardson-Zaki equation, Powder Technol. 123 (2002) 221–231. https://doi.org/10.1016/S0032-5910(01)00463-6.
- [58] L.G. Gibilaro, Homogeneous fluidization, in: Fluid. Dyn., 2001: pp. 31–41. https://doi.org/https://doi.org/10.1016/B978-075065003-8/50007-0.
- [59] A.A. Avidan, J. Yerushalmi, Bed expansion in high velocity fluidization, Powder Technol. 32 (1982) 223–232. https://doi.org/10.1016/0032-5910(82)85024-9.
- [60] N. Frössling, On the evaporation of falling drops, Gerlands Beitrage Zur Geophys. 52 (1938) 170.
- [61] P.N. Rowe, K.T. Claxton, J.B. Lewis, Heat and mass transfer from a single sphere in an extensive flowing fluid, Trans. Inst. Chem. Eng. 43 (1965) 14–31.
- [62] W.E. Ranz, W.R. Marshall Jr, Evaporation from drops, Chem. Eng. Prog. 48 (1952) 141–146 and 173–180.
- [63] F. Scala, Mass transfer around freely moving active particles in the dense phase of a gas fluidized bed of inert particles, Chem. Eng. Sci. 62 (2007) 4159–4176. https://doi.org/10.1016/j.ces.2007.04.040.
- [64] R. Clift, J.R. Grace, Continuous bubbling and slugging, in: Academic Press (Ed.), Fluidization, 2nd ed., London, 1985: pp. 73–132.
- [65] J.R. Van Ommen, R.F. Mudde, Measuring the gas-solids distribution in fluidized beds - A review, Int. J. Chem. React. Eng. 6 (2008) 1–29. https://doi.org/10.2202/1542-6580.1796.

- [66] G. Martinez Castilla, A. Larsson, L. Lundberg, F. Johnsson, D. Pallarès, A novel experimental method for determining lateral mixing of solids in fluidized beds – Quantification of the splash-zone contribution, Powder Technol. 370 (2020) 96– 103. https://doi.org/10.1016/j.powtec.2020.05.036.
- [67] P. Lettieri, J.G. Yates, New Generation X-ray Imaging for multiphase systems, 14th Int. Conf. Fluid. From Fundam. to Prod. (2013) 641–648. http://dc.engconfintl.org/fluidization_xiv/56%0A.
- [68] A. Penn, C.M. Boyce, T. Kovar, T. Tsuji, K.P. Pruessmann, C.R. Müller, Real-Time Magnetic Resonance Imaging of Bubble Behavior and Particle Velocity in Fluidized Beds, Ind. Eng. Chem. Res. 57 (2018) 9674–9682. https://doi.org/10.1021/acs.iecr.8b00932.
- [69] K. Dubrawski, S. Tebianian, H.T. Bi, J. Chaouki, N. Ellis, R. Gerspacher, R. Jafari, A. Kantzas, C. Lim, G.S. Patience, T. Pugsley, M.Z. Qi, J.X. Zhu, J.R. Grace, Traveling column for comparison of invasive and non-invasive fluidization voidage measurement techniques, Powder Technol. 235 (2013) 203–220. https://doi.org/10.1016/j.powtec.2012.10.031.
- [70] S. Tebianian, K. Dubrawski, N. Ellis, R.A. Cocco, R. Hays, S.B. Reddy Karri, T.W. Leadbeater, D.J. Parker, J. Chaouki, R. Jafari, P. Garcia-Trinanes, J.P.K. Seville, J.R. Grace, Investigation of particle velocity in FCC gas-fluidized beds based on different measurement techniques, Chem. Eng. Sci. 127 (2015) 310–322. https://doi.org/10.1016/j.ces.2015.01.049.
- [71] I.C. Velarde, F. Gallucci, M. van Sint Annaland, Development of an endoscopiclaser PIV/DIA technique for high-temperature gas-solid fluidized beds, Chem. Eng. Sci. 143 (2016) 351–363. https://doi.org/10.1016/j.ces.2016.01.002.
- [72] R. Hernberg, J. Stenberg, B. Zethræus, Simultaneous in situ measurement of temperature and size of burning char particles in a fluidized bed furnace by means of fiberoptic pyrometry, Combust. Flame. (1993). https://doi.org/10.1016/0010-2180(93)90061-7.
- [73] H. Johnsson, F. Johnsson, Measurements of local solids volume-fraction in fluidized bed boilers, Powder Technol. 115 (2001) 13–26. https://doi.org/10.1016/S0032-5910(00)00270-9.
- [74] V. Wiesendorf, J. Werther, Capacitance probes for solids volume concentration and velocity measurements in industrial fluidized bed reactors, in: Powder Technol., 2000. https://doi.org/10.1016/S0032-5910(99)00276-4.
- [75] S. Tebianian, N. Ellis, P. Lettieri, J.R. Grace, X-ray imaging for flow characterization and investigation of invasive probe interference in travelling fluidized bed, Chem. Eng. Res. Des. (2015). https://doi.org/10.1016/j.cherd.2015.08.006.
- [76] B. Hage, J. Werther, The guarded capacitance probe A tool for the measurement of solids flow patterns in laboratory and industrial fluidized bed combustors, Powder Technol. (1997). https://doi.org/10.1016/S0032-5910(97)03276-2.

- [77] C.S. Campbell, D.G. Wang, A particle pressure transducer suitable for use in gasfluidized beds, Meas. Sci. Technol. 1 (1990) 1275–1279. https://doi.org/10.1088/0957-0233/1/12/002.
- [78] J. Olsson, D. Pallarès, F. Johnsson, Lateral fuel dispersion in a large-scale bubbling fluidized bed, Chem. Eng. Sci. 74 (2012) 148–159. https://doi.org/10.1016/j.ces.2012.02.027.
- [79] H.R. Norouzi, N. Mostoufi, Z. Mansourpour, R. Sotudeh-Gharebagh, J. Chaouki, Characterization of solids mixing patterns in bubbling fluidized beds, Chem. Eng. Res. Des. 89 (2011) 817–826. https://doi.org/10.1016/j.cherd.2010.10.014.
- [80] N. Mostoufi, J. Chaouki, Local solid mixing in gas-solid fluidized beds, Powder Technol. 114 (2001) 23–31. https://doi.org//10.1016/S0032-5910(00)00258-8.
- [81] P.N. Rowe, A.W. Nienow, A.J. Agbim, The mechanisms by which particles segregate in gas fluidised beds – binary systems of near-spherical particles, Trans. Inst. Chem. Eng. 50 (1972) 310–323.
- [82] A. Köhler, E. Cano-Pleite, A. Soria-Verdugo, D. Pallarès, F. Johnsson, Modeling the motion of fuel particles in a fluidized bed, Fuel. 305 (2021) 121424. https://doi.org//10.1016/j.fuel.2021.121424.
- [83] B. Formisani, R. Girimonte, V. Vivacqua, Fluidization of mixtures of two solids differing in density or size, AIChE J. 57 (2011) 2325–2333. https://doi.org//10.1002/aic.12450.
- [84] P.N. Rowe, A.W. Nienow, A.J. Agbim, A preliminary quantitative study of particle segregation in a gas fluidized beds-binary systems of near spherical particles, Trans. Inst. Chem. Eng. 50 (1972) 324–333.
- [85] P.M.C. Lacey, Developments in the theory of particle mixing, J. Appl. Chem. 4 (1954) 257–268.
- [86] A. Marzocchella, P. Salatino, V. Di Pastena, L. Lirer, Transient fluidization and segregation of binary mixtures of particles, AIChE J. 46 (2000) 2175–2182. https://doi.org/10.1002/aic.690461110.
- [87] M.J.V. Goldschmidt, J.M. Link, S. Mellema, J.A.M. Kuipers, Digital image analysis measurements of bed expansion and segregation dynamics in dense gasfluidised beds, Powder Technol. 138 (2003) 135–159. https://doi.org/10.1016/j.powtec.2003.09.003.
- [88] B. Formisani, G. De Cristofaro, R. Girimonte, A fundamental approach to the phenomenology of fluidization of size segregating binary mixtures of solids, Chem. Eng. Sci. 56 (2001) 109–119. https://doi.org//10.1016/S0009-2509(00)00426-7.
- [89] B. Formisani, R. Girimonte, T. Longo, The fluidization pattern of densitysegregating binary mixtures, Chem. Eng. Res. Des. 86 (2008) 344–348. https://doi.org//10.1016/j.cherd.2007.11.004.

- [90] G. Olivieri, A. Marzocchella, P. Salatino, Segregation of fluidized binary mixtures of granular solids, AIChE J. 50 (2004) 3095–3106. https://doi.org/10.1002/aic.10340.
- [91] F.P. Di Maio, A. Di Renzo, V. Vivacqua, A particle segregation model for gasfluidization of binary mixtures, Powder Technol. 226 (2012) 180–188. https://doi.org/10.1016/j.powtec.2012.04.040.
- [92] D. Pallarès, P.A. Díez, F. Johnsson, Experimental analysis of fuel mixing patterns in a fluidized bed, 12th Int. Conf. Fluid. - New Horizons Fluid. Eng. (2007) 929– 936.
- [93] J.C. Abanades, G.S. Grasa, Modeling the axial and lateral mixing of solids in fluidized beds, Ind. Eng. Chem. Res. 40 (2001) 5656–5665. https://doi.org/10.1021/ie0009278.
- [94] E. Sette, T. Berdugo Vilches, D. Pallarès, F. Johnsson, Measuring fuel mixing under industrial fluidized-bed conditions - A camera-probe based fuel tracking system, Appl. Energy. 163 (2016) 304–312. https://doi.org//10.1016/j.apenergy.2015.11.024.
- [95] E. Sette, D. Pallarès, F. Johnsson, F. Ahrentorp, A. Ericsson, C. Johansson, Magnetic tracer-particle tracking in a fluid dynamically down-scaled bubbling fluidized bed, Fuel Process. Technol. 138 (2015) 368–377. https://doi.org/10.1016/j.fuproc.2015.06.016.
- [96] D.C. Guío-Pérez, F. Johnsson, D. Pallarès, Experimental investigation of the lateral mixing of large and light particles immersed in a fluidized bed, 346 (2023) 1–10. https://doi.org/10.1016/j.fuel.2023.128343.
- [97] D. Bellgardt, J. Werther, A novel method for the investigation of particle mixing in gas-solid systems, Powder Technol. 48 (1986) 173–180. https://doi.org//10.1016/0032-5910(86)80076-6.
- [98] F. Berruti, D.S. Scott, E. Rhodes, Measuring and modelling lateral solid mixing in a three-dimensional batch gas—solid fluidized bed reactor, Can. J. Chem. Eng. 64 (1986) 48–56. https://doi.org/10.1002/cjce.5450640107.
- [99] V.A. Borodulya, Y.G. Epanov, Y.S. Teplitskii, Horizontal particle mixing in a free fluidized bed, J. Eng. Phys. 42 (1982) 528–533. https://doi.org/10.1007/BF00824945.
- [100] J. Highley, D. Merrick, Effect of the spacing between solid feed points on the performance of a large fluidized bed reactor, AIChe Symp. Ser. 67 (1971) 219– 227.
- [101] F. Niklasson, H. Thunman, F. Johnsson, B. Leckner, Estimation of solids mixing in a fluidized-bed combustor, Ind. Eng. Chem. Res. 41 (2002) 4663–4673. https://doi.org/10.1021/ie020173s.
- [102] X. Qian, H. Guoquan, N. Mingjiang, C. Kefa, T. Tao, Lateral dispersion of large coal particles in an industrial-scale fluidised bed combustor, in: 9th Int. Conf.

Fluid. Bed Combust., 1987: pp. 546–553.

- [103] E. Sette, D. Pallarès, F. Johnsson, Experimental quantification of lateral mixing of fuels in fluid-dynamically down-scaled bubbling fluidized beds, Appl. Energy. 136 (2014) 671–681. https://doi.org/10.1016/j.apenergy.2014.09.075.
- [104] R. Chirone, F. Miccio, F. Scala, On the relevance of axial and transversal fuel segregation during the FB combustion of a biomass, Energy and Fuels. (2004). https://doi.org/10.1021/ef034084j.
- [105] A. Einstein, The elementary theory of the Brownian motion, in: I. Dover Publications (Ed.), Investig. Theory Brownian Mov., 1st ed., New York, 1956: pp. 68–85. https://doi.org/10.1038/scientificamerican10121918-230bsupp.
- [106] D. Liu, X. Chen, Experimental profiles of lateral mixing of feed particles in a threedimensional fluidized bed, AIChE J. 57 (2011) 1459–1469. https://doi.org/10.1002/aic.12376.
- [107] P. Xiao, G. Yan, D. Wang, Investigation on horizontal mixing of particles in dense bed in circulating fluidized bed (CFB), J. Therm. Sci. 7 (1998) 78–84. https://doi.org/10.1007/s11630-998-0002-4.
- [108] D.C. Chesonis, G.E. Klinzing, Y.T. Shah, C.G. Dassori, Y.T. Shah, C.G. Dassori, Hydrodynamics and mixing of solids in a recirculating fluidized bed, Ind. Eng. Chem. Res. 29 (1990) 1785–1792. https://doi.org/10.1021/ie00105a008.
- [109] L.T. Fan, Y.F. Shl, Lateral mixing of solids in batch gas-solids fluidized beds, Ind.
 Eng. Chem. Process Des. Dev. 23 (1984) 337–341. https://doi.org/10.1021/i200025a026.
- [110] G. Lardier, J. Kaknics, A. Dufour, R. Michel, B. Cluet, O. Authier, J. Poirier, G. Mauviel, Gas and bed axial composition in a bubbling fluidized bed gasifier: results with miscanthus and olivine, Energy and Fuels. 30 (2016) 8316–8326. https://doi.org/10.1021/acs.energyfuels.6b01816.
- [111] Y. Zhang, B. Jin, W. Zhong, Experimental investigation on mixing and segregation behavior of biomass particle in fluidized bed, Chem. Eng. Process. Process Intensif. 48 (2009) 745–754. https://doi.org/10.1016/j.cep.2008.09.004.
- [112] B. Jin, Y. Zhang, W. Zhong, R. Xiao, Experimental study of the effect of particle density on mixing behavior in a spout-fluid bed, Ind. Eng. Chem. Res. 48 (2009) 10055–10064. https://doi.org/10.1021/ie900689r.
- [113] D. Liu, X. Chen, Quantifying lateral solids mixing in a fluidized bed by modeling the thermal tracing method, AIChE J. 58 (2012) 745–755. https://doi.org/10.1002/aic.12627.
- [114] D. Westphalen, L. Glicksman, Lateral solid mixing measurements in circulating fluidized beds, Powder Technol. 82 (1995) 153–167. https://doi.org/10.1016/0032-5910(94)02909-8.
- [115] J.A. Valenzuela, L.R. Glicksman, An experimental study of solids mixing in a

freely bubbling two-dimensional fluidized bed, Powder Technol. 38 (1984) 63–72. https://doi.org/10.1016/0032-5910(84)80034-0.

- [116] T. Salam, Y. Ren, B. Gibbs, Lateral solid and thermal dispersion in fluidized bed combustors, in: 9th Int. Conf. Fluid. Bed Combust., 1987.
- [117] I.N.S. Winaya, T. Shimizu, D. Yamada, A new method to evaluate horizontal solid dispersion in a bubbling fluidized bed, Powder Technol. 178 (2007) 173–178. https://doi.org/10.1016/j.powtec.2007.05.005.
- [118] S. Turrado, J.R. Fernández, J.C. Abanades, Investigation of the segregation of binary mixtures with iron-based particles in a bubbling fluidized bed, ACS Omega. 4 (2019) 9065–9073. https://doi.org/10.1021/acsomega.9b00674.
- [119] Z. Wan, Y. Lu, H. Wang, Instantaneous mixing characteristics of binary mixtures differing in density in a gas-solid fluidised bed, Particuology. 53 (2020) 63–71. https://doi.org/10.1016/j.partic.2019.11.007.
- [120] J. Huang, Y. Lu, H. Wang, A new quantitative measurement method for mixing and segregation of binary-mixture fluidized bed by capacitance probe, Chem. Eng. J. 326 (2017) 99–108. https://doi.org/10.1016/j.cej.2017.05.126.
- [121] D. Pallarès, F. Johnsson, A novel technique for particle tracking in cold 2dimensional fluidized beds - Simulating fuel dispersion, Chem. Eng. Sci. 61 (2006) 2710–2720. https://doi.org/10.1016/j.ces.2005.11.030.
- [122] M. Errigo, M. Materazzi, P. Lettieri, Parametric analysis of factors affecting the thermal-hydraulic behavior of agglomerates in gas-solid fluidized-bed reactors, in: Fluid. Bed Convers. Conf., 2022.
- [123] M. Errigo, A. Sebastiani, S. Iannello, M. Materazzi, P. Lettieri, Application of imaging techniques for the characterization of lumps behaviour in gas – solid fluidized-bed reactors, Fuel. 349 (2023) 128634. https://doi.org/10.1016/j.fuel.2023.128634.
- [124] Y.C. Seo, D. Gidaspow, An X-ray—γ-Ray Method of Measurement of Binary Solids Concentrations and Voids in Fluidized Beds, Ind. Eng. Chem. Res. 26 (1987) 1622–1628. https://doi.org/10.1021/ie00068a021.
- [125] B. Du, F. Wei, Lateral solids mixing behavior of different particles in a riser with FCC particles as fluidized material, Chem. Eng. Process. Process Intensif. 41 (2002) 329–335. https://doi.org/10.1016/S0255-2701(01)00149-0.
- [126] C.A. Riley, M. Louge, Quantitative capacitive measurements of voidage in gassolid flows, Part. Sci. Technol. 7 (1989) 51–59. https://doi.org/10.1080/02726358908906523.
- [127] V. Wiesendorf, J. Werther, Capacitance probes for solids volume concentration and velocity measurements in industrial fluidized bed reactors, 2000. https://doi.org/10.1016/S0032-5910(99)00276-4.
- [128] J. Werther, O. Molerus, The local structure of gas fluidized beds I. A statistically

based measuring system, Int. J. Multiph. Flow. 1 (1973) 103–122. https://doi.org/10.1016/0301-9322(73)90007-4.

- [129] A. Lancia, R. Nigro, G. Volpicelli, L. Santoro, Transition from slugging to turbulent flow regimes in fluidized beds detected by means of capacitance probes, Powder Technol. 56 (1988) 49–56. https://doi.org/10.1016/0032-5910(88)80021-4.
- [130] C.R. Sutton, J.C. Chen, A local transient approach to monitoring fluidization quality in freely bubbling beds, Powder Technol. 180 (2008) 296–306. https://doi.org/10.1016/j.powtec.2007.02.022.
- [131] B. Hage, J. Werther, K. Narukawa, S. Mori, Capacitance probe measurement technique for local particle volume concentration in circulating fluidized bed combustors, J. Chem. Eng. Japan. 29 (1996) 594–602. https://doi.org/10.1252/jcej.29.594.
- [132] C. Vogt, R. Schreiber, G. Brunner, J. Werther, Fluid dynamics of the supercritical fluidized bed, Powder Technol. 158 (2005) 102–114. https://doi.org/10.1016/j.powtec.2005.04.022.
- [133] H. Wang, Y. Lu, Fluidization of particles in SCW fluidized bed: Voidage distribution of emulsion phase, Particuology. 63 (2022) 60–75. https://doi.org/10.1016/j.partic.2021.04.019.
- [134] J. Huang, Y. Lu, Characteristics of bubble, cloud and wake in jetting fluidised bed determined using a capacitance probe, Chem. Eng. Res. Des. 136 (2018) 687–697. https://doi.org/10.1016/j.cherd.2018.04.028.
- [135] N. Yutani, T.C. Ho, L.T. Fan, W.P. Walawender, J.C. Song, Statistical study of the grid zone behavior in a shallow gas-solid fluidized bed using a mini-capacitance probe, Chem. Eng. Sci. 38 (1983) 575–582. https://doi.org/10.1016/0009-2509(83)80117-1.
- [136] H. Li, J. Huang, Z. Liu, M. Lv, C. Ji, Experimental quantification of the lateral mixing of binary solids in bubbling fluidized beds, Energies. 14 (2021). https://doi.org/10.3390/en14227796.
- [137] C. Brereton, Fluid mechanics of high velocity fluidised beds, University of British Columbia, 1987. https://doi.org//10.14288/1.0058687.
- [138] J.R. Grace, Properties, Minimum Fluidization, and Geldart Groups, in: Essentials Fluid. Technol., 2020: pp. 11–32. https://doi.org/10.1002/9783527699483.ch2.
- [139] W.-C. Yang, Flow through fixed beds, in: Handb. Fluid. Fluid-Particle Syst., 2003: pp. 29–52. https://doi.org/10.1016/s1672-2515(07)60126-2.
- [140] D. Kunii, O. Levenspiel, Fluidization and Mapping of Regimes, in: Fluid. Eng., 1991: pp. 61–94. https://doi.org/10.1016/b978-0-08-050664-7.50009-3.
- [141] T.M. Knowlton, Pressure and temperature effects in fluid-particle systems, in: O.E. Potter, D.J. Nicklin (Eds.), Fluid. 7, Engineering Foundation, New York, 1992: pp.

27-46. https://doi.org/10.1016/B978-081551427-5.50004-1.

- [142] B. Formisani, R. Girimonte, L. Mancuso, Analysis of the fluidization process of particle beds at high temperature, 1998. https://doi.org/10.1016/S0009-2509(97)00370-9.
- [143] D.C. Montgomery, G.C. Runger, Applied Statistics and Probability for Engineers, 7° edition, New York, 2018.
- [144] R.C. Darton, R.D. La Nauze, J. Davidson, H. Harrison, Bubble growth due to coalescence in fluidised beds, T I Chem Eng-L. 55 (1977) 274 – 280.
- [145] Z. Fu, J. Zhu, S. Barghi, Y. Zhao, Z. Luo, C. Duan, On the two-phase theory of fluidization for Geldart B and D particles, Powder Technol. 354 (2019) 64–70. https://doi.org/10.1016/j.powtec.2019.05.051.
- [146] R.H. Venderbosch, W. Prins, W.P.M. Van Swaaij, Platinum catalyzed oxidation of carbon monoxide as a model reaction in mass transfer measurements, Chem. Eng. Sci. 53 (1998) 3355–3366. https://doi.org/10.1016/S0009-2509(98)00151-1.
- [147] D. Falkowski, R.C. Brown, Analysis of pressure fluctuations in fluidized beds, Ind. Eng. Chem. Res. 43 (2004) 5721–5729. https://doi.org/10.1021/ie030684u.
- [148] M. Lavielle, Using penalized contrasts for the change-point problem, Signal Processing. 85 (2005) 1501–1510. https://doi.org//10.1016/j.sigpro.2005.01.012.
- [149] R. Killick, P. Fearnhead, I.A. Eckley, Optimal detection of changepoints with a linear computational cost, J. Am. Stat. Assoc. 107 (2012) 1590–1598. https://doi.org/10.1080/01621459.2012.737745.
- [150] H.T. Bi, N. Ellis, I.A. Abba, J.R. Grace, A state-of-the-art review of gas-solid turbulent fluidization, Chem. Eng. Sci. 55 (2000) 4789–4825. https://doi.org/10.1016/S0009-2509(00)00107-X.
- [151] T. Wytrwat, M. Yazdanpanah, S. Heinrich, Bubble properties in bubbling and turbulent fluidized beds for particles of Geldart's group B, Processes. 8 (2020). https://doi.org/10.3390/pr8091098.
- [152] J. Werther, O. Molerus, The local structure of gas fluidized beds -II. The spatial distribution of bubbles, Int. J. Multiph. Flow. (1973). https://doi.org/10.1016/0301-9322(73)90008-6.
- [153] D. Kunii, O. Levenspiel, Bubbles in Dense Beds, in: Fluid. Eng., 1991: pp. 115–135. https://doi.org/10.1016/b978-0-08-050664-7.50011-1.
- [154] Y. Forterre, O. Pouliquen, Flows of dense granular media, Annu. Rev. Fluid Mech. 40 (2008) 1–24. https://doi.org/10.1146/annurev.fluid.40.111406.102142.
- [155] H.T. Bi, Local phase holdups in gas-solids fluidization and transport, AIChE J. 47 (2001) 2025–2031. https://doi.org/10.1002/aic.690470913.
- [156] L. Molignano, M. Troiano, R. Solimene, S. Tebianian, F. Scala, P. Salatino, J.F.

Joly, Hydrodynamics and mass transfer around active particles in dense gasfluidized beds, Fuel. 341 (2023) 127590. https://doi.org/10.1016/j.fuel.2023.127590.

- [157] R.D. La Nauze, K. Jung, The kinetics of combustion of petroleum coke particles in a fluidized-bed combustor, in: Proc. Combust. Inst., 1982: pp. 1087–1092. https://doi.org/https://doi.org/10.1016/S0082-0784(82)80284-1.
- [158] A. Stefanova, H.T. Bi, C.J. Lim, J.R. Grace, Heat transfer from immersed vertical tube in a fluidized bed of group A particles near the transition to the turbulent fluidization flow regime, Int. J. Heat Mass Transf. 51 (2008) 2020–2028. https://doi.org/10.1016/j.ijheatmasstransfer.2007.06.005.
- [159] A. Stefanova, X.T. Bi, C. Jim Lim, J.R. Grace, A probabilistic heat transfer model for turbulent fluidized beds, Powder Technol. 365 (2020) 163–171. https://doi.org/10.1016/j.powtec.2019.01.066.
- [160] N. Epstein, B.P. LeClair, Liquid fluidization of binary particle mixtures-II. Bed inversion, Chem. Eng. Sci. 40 (1985) 1517–1526. https://doi.org/10.1016/0009-2509(85)80093-2.
- [161] H. Moritomi, T. Iwase, T. Chiba, A comprehensive interpretation of solid layer inversion in liquid fluidised beds, Chem. Eng. Sci. 37 (1982) 1751–1757. https://doi.org/10.1016/0009-2509(82)80047-X.
- [162] L.G. Gibilaro, R. Di Felice, S.P. Waldram, P.U. Foscolo, A predictive model for the equilibrium composition and inversion of binary-solid liquid fluidized beds, Chem. Eng. Sci. 41 (1986) 379–387. https://doi.org/10.1016/0009-2509(86)87017-8.
- [163] R. Escudié, N. Epstein, J.R. Grace, H.T. Bi, Layer inversion phenomenon in binary-solid liquid-fluidized beds: Prediction of the inversion velocity, Chem. Eng. Sci. 61 (2006) 6667–6690. https://doi.org/10.1016/j.ces.2006.06.008.
- [164] M.G. Rasul, V. Rudolph, M. Carsky, Segregation potential in binary gas fluidized beds, Powder Technol. 103 (1999) 175–181. https://doi.org/10.1016/S0032-5910(98)00230-7.
- [165] B.G.M. Van Wachem, J.C. Schouten, C.M. Van den Bleek, R. Krishna, J.L. Sinclair, CFD modeling of gas-fluidized beds with a bimodal particle mixture, AIChE J. 47 (2001) 1292–1302. https://doi.org/10.1002/aic.690470607.
Supplementary material



Figure S.1 Probability density functions of the local voidage of SiC fluidized bed at ambient temperature for different excess gas superficial velocities and probe locations.



Figure S.2 Probability density functions of the local voidage of SiC fluidized bed at 500 °C for different excess gas superficial velocities and probe locations.



Figure S.3 Plot of the normalized mode values in the PDFs of the emulsion-phase voidage for the four material samples, at room temperature, as function of $U - U_{mf}$.



Figure S.4 Validation of the correlation expressed by Eq. 15 (paragraph 2.2), re-proposed in the present figure. Calibration performed with mixtures at known homogeneous composition of two different solids: lantanium-impregnated γ -alumina ($\tilde{d}_p = 125 \mu m$, $\rho_p = 1325 \text{ kg/m}^3$, $\kappa_s = 12.8$ -) and grey quartz sand ($\tilde{d}_p = 600 \mu m$, $\rho_p = 2600 \text{ kg/m}^3$, $\kappa_s = 3.6$ -). The experimental points represent voltages measured by the capacitance probe immersed in the mixture in fixed bed conditions. The dotted line represents the predicted voltage obtained from Eq. 12 after calculating the mixture relative dielectric constant from Eq. 15. Mixture voidage, ε , is measured in the same graduated cylinder (Eq. 26). *f* represents the volume fraction of lantanium-impregnated γ -alumina.



Figure S.5 Validation of the correlation expressed by Eq. 15 (paragraph 2.2), re-proposed in the present figure. Calibration performed with mixtures at known homogeneous composition of two different solids: γ-alumina–1 and silicon carbide (properties reported in Table 1). The experimental points represent voltages measured by the capacitance probe immersed in the mixture in fixed bed conditions. The dotted line represents the predicted voltage obtained from Eq. 12 after calculating the mixture relative dielectric constant from Eq. 15. Mixture voidage, ε, is measured in the same graduated cylinder (Eq. 26). *f* represents the volume fraction of γ-alumina–1.



Figure S.6 Concentration profiles of silicon carbide in the emulsion phase of the fluidized bed of γ -alumina–1. Tracer volume fraction is represented versus superficial gas velocity, and parametric in the radial coordinate.



Figure S.7 Concentration profiles of γ-alumina–1 in the emulsion phase of the fluidized bed of silicon carbide. Tracer volume fraction is represented versus superficial gas velocity, and parametric in the radial coordinate.