Fluidized bed sintering in TiO₂ and coke systems

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ABSTRACT

This paper reports on experimental tests aimed at studying the influence of operating conditions on the fluidization behaviour of petroleum coke mixed with different titanium ores industrial reactive powders.

The fluidization behaviour of several mixtures have been studied at process temperatures ranging from ambient up to 950 °C in a specially designed heated fluid-bed reactor, where the early stages of the sintering process were experimentally simulated.

Fundamental fluidization tests were performed using a unique high power pulsed x-ray imaging facility available at UCL, which enabled to visualise the internal flow pattern inside the metallic reactor and to obtain quantitative information about the fluidization behaviour of the systems investigated. Simultaneous measurements of local temperatures and pressure drops across the bed were carried out in order to detect possible agglomeration and sintering phenomena. The tests showed that operating conditions and coke characteristics combined can play a significant role on the formation of agglomerates and their properties. The resulting lumps of agglomerated particles were collected and systematically characterized to determine their properties and the chemical compositions of the sintered bonds formed.

KEYWORDS

Fluidization at high temperature; Sintering processes in industrial reactors; Industrial reactive powders; Agglomerates' characterization

1 INTRODUCTION

Fluidized beds are widely applied in industry for their ability to provide a high heat transfer rate and rapid solids mixing which lead to isothermal conditions in the particle bed, and high heat and mass transfer rates between gas and particles. Whenever a chemical reaction employing a particulate solid as a reactant or as a catalyst requires reliable

temperature control, a fluidized bed reactor is often the choice for ensuring nearly isothermal conditions by a suitable selection of the operating conditions.

Achieving a good knowledge of the hydrodynamics inside the bed is of great importance not only for the safety and the control of the process but also for its economics, as well as for achieving optimal operating conditions and avoiding unscheduled shutdowns. For example, gas-solid fluidized beds operating at elevated temperatures are prone to agglomerate, that can be a major operational problem [1].

Different phenomena, e.g. sintering, capillary interparticle forces, crystallization, chemical reaction, deposition of colloidal material and solidification of a binder, can increase the adhesiveness and stickiness of particles, causing the onset of permanent solid bridges between the colliding particles [2]. Among them, sintering has been identified as one the main causes for the formation of strong agglomerates in many industrial fluidized bed processes [3]. Examples include the production of polyolefin [4], combustion and gasification of biomass [5–8], the production of titanium tetrachloride [9], coal conversion, ores reduction and cement manufacture [10] and many others.

There are many aspects that need to be considered when dealing with particles' sintering. The term sintering is used for a variety of applications, but in the present work it refers to the formation of a continuous solid connection that forms when particles come into contact at temperatures high enough to cause the softening of the particle surface and formation of interparticle bonds. The temperature at which softening occurs is called minimum sintering temperature (T_s) and this is often lower than the fusion temperature of the bulk of the material. Many materials, such as metal ores that contain a variety of impurities, may form low-melting-point eutectics at the surface of particles, resulting in much lower minimum sintering temperature. The sintering process is traditionally classified into two main stages, i.e. the early and final stages of sintering, according to the ratio between the actual density of the agglomerate and the density of the fully compacted material. Some authors reported that the transition from early to final stage occurs when such a ration is greater than about 0.9 [11–13].

Both material properties (i.e. particle size, flowability, yield stress etc.) and operating conditions, such as temperature and fluidization regime, may influence the agglomeration of particles due to sintering [14,15].

This work examines the early stages of the sintering process occurring during the fluidization of mixtures of petroleum coke and different titanium ores, using a laboratory scale fluid bed system operating on air.

The goal of this paper is to identify the effect of the operating conditions on the agglomeration of particles and the consequent defluidization of the system. The materials investigated in this work are used in the production of titanium tetrachloride, TiCl_4 . The carbo-chlorination process is one in which the particles employed have a range of sizes and densities which fluidize over a range of fluidization velocities. Chlorinators for the production of TiCl_4 normally operate with chlorine as fluidising gas, but it is also fluidised on air for periods when the reactor requires purging for maintenance, and air is also used to reheat the fluid bed to a safe start-up temperature following a shutdown in order to avoid the incomplete conversion of chlorine, which is detrimental to operation. Heat generation while fluidising on air is still significant, with a similar specific energy generated. Fluidization operations on air are run at lower gas rates (typically at or close to minimum fluidization conditions) than on chlorine (typically 2-3 times the minimum fluidization conditions).

These initial sintering tests were therefore carried out using the combustion of air as the source of the heat, as industrial experience is that it is at these lower fluidisation conditions that particle agglomeration occurs. This in turn leads the particle to transition from free-flowing to a coherent solid, which segregates at the bottom of the bed causing the reactor to clog and eventually defluidize. For example, the pressure drops across the fluidized bed immediately after an interruption to fluidizing gas flow is often higher than just before the reactor was shut-down. However, it often recovers to normal values after several hours after the more aggressive fluidisation on chlorine is re-introduced.

The clog of the reactor represents a significant cost for the chlorinator's operation, as it requires lengthy reactor outages for cooling, unclogging and replacement of the damaged reactor. It is therefore important to gain a better understanding of the fluidization and defluidization behaviour of these industrial reactive systems.

To this end, the fluidization behaviour of several mixtures with different properties has been systematically studied at process temperatures ranging from ambient up to 950 °C in a specially designed heated fluid-bed reactor. In addition, the resulting agglomerates were collected and systematically characterized to investigate their properties and, in particular, the chemical compositions of the sintered bonds formed.

2 EXPERIMENTAL SETUP

2.1 Materials and mixtures properties

The main physical properties of all the materials investigated are reported in Table 1. This includes particle densities (ρ_p), bulk densities (ρ_b), Sauter mean diameters (d_{sv}), particle size distributions (PSD) and relative diameter spread ($RDS = (d_{84} - d_{16})/(2 d_{50})$). RDS is defined according to Geldart [16] by using the 16th, the 50th and the 84th percentile sizes (d_{16} , d_{50} and d_{84} respectively) obtained from sieve analysis. It is used to compare the width of the size distribution of the powders provided for this work. The minimum fluidization velocities (u_{mf}) measured for all the components at both ambient and high temperature (500 °C) are also reported (see [17] for further details). Details on the bulk flow properties of the materials can be found at the following references: [18,19].

Table 1 – Main physical properties of the investigated materials

Sample	ρ_p [kg/m ³]	ρ_b (25 °C) [kg/m ³]	d_{16} [μm]	d_{50} [μm]	d_{84} [μm]	d_{sv} [μm]	RDS [-]	u_{mf} (25 °C) [cm/s]	u_{mf} (500 °C) [cm/s]
Synthetic Rutile (SR)	3800	1500	122	162	212	145	0.28	2.3	0.6
Natural Rutile (NR)	4200	2320	117	202	379	155	0.65	2.7	0.9
Titania Slag (TS)	4200	2160	169	356	686	234	0.73	5.3	2.0
Small Pet Coke (SPC)	2060	870	322	620	1205	520	0.71	19	9
Medium Pet Coke (MPC)	2060	760	1840	2290	2720	2290	0.19	120	80
Large Pet Coke (LPC)	2060	650	2920	3440	4240	3690	0.19	150	115

The chemical and mineralogy analysis of the titanium based materials has been performed by the supplier (Venator) and shared with University College London for the aim of this research. The results are reported in Table 2.

The composition of the petroleum coke is 96.7 %wt. of free carbon, 3%wt. of ash, 0.2% of moisture and 0.1% of volatiles and according to the safety data sheet attached to the material it consists of granules of calcined petroleum coke (CPC) identified by EC number 265-210-9 [21].

Table 3 reports the compositions, the main physical properties and the nomenclature adopted for the different ternary mixtures that have been investigated.

The research work focused on two mixtures which differ in the type of rutile used: mixtures containing synthetic rutile and titania slag (ST systems) and mixtures containing natural rutile and titania slag (NT systems). Each mixture was investigated for various sizes of pet coke: three distinct subsystems were then considered using small (SPC), medium (MPC) and large size (LPC) coke (see Coke subsystems in Table 3). A fixed composition was

used (i.e. 45% wt. rutile, 30% slag material and 25% pet coke) in order to mimic the composition used in the industrial process. The behaviour of every single mixture was investigated systematically at three different fluidization conditions, close to and well above the complete fluidization conditions, as reported in Table 4.

Table 2 – Chemical analysis of the titanium based materials and relative melting temperature (T_M)

Component	%wt.			T_M (°C) [22]
	SR	NR	TS	
TiO ₂ (Ti ₂ O ₃)	96.7 (-)	97.2 (-)	88.6 (25.8)	1750 (2130)
FeO (Fe ₂ O ₃)	4.6 (-)	- (1.2)	5.8 (-)	1400 (1560)
Al ₂ O ₃	1.3	0.1	1.9	2000
MnO	1.1	0.01	0.5	1650
MgO	0.4	0.04	1.2	2800
CaO	0.1	0.01	0.1	2570
SiO ₂	-	0.4	1.0	1700
Cr ₂ O ₃	-	0.3	0.1	1900
V ₂ O ₅	-	0.6	0.3	800
Nb ₂ O ₅	-	0.2	0.3	1500
ZrO ₂	-	0.8	0.1	2700
S	0.4	0.3	-	120 (amorphous)

Table 3 – Ternary mixtures and nomenclature used in the analysis.

System	Coke subsystem	General Ref.	Component composition		
			45 %wt.	30 %wt.	25 %wt.
ST	S	STS	SR	TS	SPC
	M	STM	SR	TS	MPC
	L	STL	SR	TS	LPC
NT	S	NTS	NR	TS	SPC
	M	NTM	NR	TS	MPC
	L	NTL	NR	TS	LPC

Table 4 – General nomenclature for systems identification

Condition	Suffix
Fresh mixtures	-0
<ul style="list-style-type: none"> see Table 3 for composition 	
Spent mixture after test with air flowrate below fluidization conditions	-1
<ul style="list-style-type: none"> $u_{air} = 0.5x u_{cf}$ 	
Spent mixture after test with air flowrate close to incipient fluidization conditions	-2
<ul style="list-style-type: none"> $u_{air} = 0.5x (u_{mf} + u_{cf})$ 	
Spent mixture after test with air flowrate in bubbling bed conditions	-3
<ul style="list-style-type: none"> $u_{air} = 2x u_{cf}$ 	

2.2 Experimental facility

The experimental rig and the X-ray facility used are shown in Figure 1 and they are available in the Department of Chemical Engineering at University College London.

A 14.6 cm diameter x 100 cm tall inconel vessel with a wall thickness of 3mm is used for testing the powders at ambient pressure and for temperatures up to 950°C. The vessel is fitted with a very fine (i.e. pore size of 20µm) stainless steel sintered distributor plate to ensure a high pressure drop and therefore a good and even fluidization in the bed. The inconel plenum chamber below the distributor plate (windbox) has a height of 150 mm and it is packed with 10mm ceramic balls to uniform gas distribution. A 2.5 kW powered preheater (10 cm diameter x 30.5 cm length) is installed on the gas feeding line; it is able to provide an operating temperature up to 500 °C.

Figure 1 – Experimental Rig and X-ray facility (rear view on the right side and front view on the left side). The X-ray tube (1), the image intensifier (2) and the suspension unit (3) are shown as well.

The upper disengaging section fitted on top of the vessel is made of stainless steel, 50 cm height with a freeboard diameter of 25 cm. A stainless steel pipeline is connected to the top centre of the disengaging section, through flanges, to vent the fluidizing gas out of the bed. To reduce the loss of any elutriated fine material, a removable stainless steel filter is installed

on the vent line inside the disengaging section. The filter is a cylinder having 5mm diameter holes on the surface, around which a 45 μm stainless steel mesh is wrapped twice. Any fine material which escaped from the system was eventually recovered in a filter bag fitted at the other end of the vent line. A second stainless steel pipeline is connected to the disengaging section on the side and acted as a pressure relief valve. Any pressure built up in the fluidized bed is released, through this pipeline, into a stainless steel cylindrical tank (170 cm tall x 13 cm diameter) containing water. A schematic drawing of the system is presented in Figure 2, for a detail flow and control diagram please refer to [23].

Figure 2 – Schematic layout of the fluidization rig

Fluidizing gas, air or nitrogen, is measured with rotameters before being preheated then passed through the preheater and the windbox section, which is wrapped with 800 W heating tape. High temperatures in the vessel are achieved and maintained by means of two flexible ceramic heaters wrapped around it, and capable of providing operating temperatures up to 1250°C. The two ceramic heaters cover 90 cm of the vessel height. Since this material is not transparent to X-rays, they are fitted to leave a vertical window, 7 cm wide, on both sides of

the vessel, to let X-rays through. The hot surfaces are well-insulated using two layers of 1.5cm thick super-wool, covered by a 7cm thick layer of rockwool wrapped with silver tape.

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

A new high power pulsed X-ray generation facility has been employed to record the images of the fluidized bed [24,25]. The system is made of an X-ray tube (1) and an image intensifier (2) mounted on a twin column ceiling suspension unit (3), see Figure 1. It is able to provide X-ray pulses down to 200 μ s with an intensity of up to 450 mA at a voltage variable from 50 kV to 150 kV.

X-rays are detected on a 30 cm industrial X-ray Image Intensifier, optically coupled to a 1024x1024 pixels high-speed charge coupled device camera. The camera is triggered by the control software, which itself is triggered by the x-ray generator at frame rates from 24 to 72 frames per second (fps). 8-bit digital images are captured by the video camera and they are displayed and stored on a workstation using a custom version of the *SPS iX-Control* software. The software allows the acquisition, the display and the general handling of the frames, as well as the images post-processing and images play back up to 72 fps in either real time or frame by frame. It comes with an extensive set of analysis tools that allows also the off-line data analysis and measurements. Furthermore, several algorithms for image analysis were developed and implemented within MATLAB environment. In particular, the collected raw images need to be post-processed in order to be able to perform any quantitative fluid-dynamic analysis.

2.3 *Experimental procedures*

Early stages of the sintering process were experimentally simulated in the small pilot scale fluidization rig described in the previous section. The effect of high temperature and air flowrate was investigated systematically at different fluidization regimes, ranging from conditions far below the incipient fluidization to bubbling bed conditions.

For each fluidization regime, the bed was firstly filled with 3 kg of mixture and then fluidized at a superficial gas velocity higher than three times the minimum fluidization one for 15 minutes in order to ensure it was well mixed. Afterwards, the fluidizing gas was shutoff and fundamental parameters were determined, including the pressure drop across the bed, the complete fluidization velocity and the bed expansion profile by means of the X-ray images analysis.

2.3.1 Fundamental fluidization tests

Because of the complexity of the mixtures analysed, the standard procedure for determining the minimum fluidization velocity from pressure drop measurements [26] was found not to be reliable. When a multi-components mixture is fluidized, the species have in general different values of u_{mf} and thus the pressure drop curve of the whole mixtures presents more than one slope describing the packed bed regime [27–29]. This prevented finding the intersection between the horizontal line (i.e. constant pressure drop) describing a fully fluidized bed and the slope describing the packed bed. In order to overcome this problem, x-rays were used for estimating u_{mf} by means of visual analysis: x-ray images were analysed on a frame by frame basis to find the velocity at which the first bubble was seen to break the bed surface.

The complete fluidization velocity, u_{cf} , was obtained from the diagrams of the pressure drop across the bed over the fluidizing gas velocity, u . The pressure drop profiles were determined by firstly increasing the gas flow rate until the bed was entirely fluidized and then by decreasing the flow rate until the bed was completely settled down: the so-called “fluidization” and “defluidization” curves were then plotted. The experimental value of u_{cf} was determined from the “defluidization” curve as the first velocity value at which the plateau in the pressure drop is reached. Measurements were repeated at least three times in order to verify the reproducibility and the consistency of the outcomes.

Bed expansion profiles were obtained from the images recorded with the X-rays facility. The bed height H was recorded for both fluidization and defluidization stages and plots of H versus u were therefore produced for increasing and decreasing gas velocities.

An example of the raw x-ray images used for determining the minimum fluidization velocity and the bed height is reported in Figure 3.

Figure 3 – Example of raw X-ray images used for the analysis

2.3.2 Combustion and sintering tests

At first, the bed was heated up to 500 °C using nitrogen as fluidizing agent (gas velocity two times greater than the complete fluidization velocity) in order to avoid any combustion reaction during the heating step. Such a temperature value was chosen because it is above the small and medium coke ignition temperature and close to the large coke one, according to the experimental outcomes proposed by Mi et al. [30].

At this point, the gas feed was switched to air and the flowrate adjusted to the desired testing value. After 50 minutes, the air flow was shutoff and the system allowed to cool to ambient conditions. Time evolutions of pressure drop and temperatures were monitored and recorded. In particular, the temperatures inside the bed, outside the reactor and below the disengaging area were recorded as illustrated in Figure 2. A typical temperature profile recorded inside the bed during the entire experimental test is reported in Figure 4.

Fundamental fluidization tests were also carried out on the spent systems (i.e. after combustion and cooling stages) and compared to the fresh ones. The reactor was then emptied and the agglomerates collected for characterization and further examinations.

It is important to note that, in the present work, the term agglomerate has been used to denote large lumps (i.e. size greater than 2 cm) formed by sintering of a large amount of particles. Smaller and friable agglomerates that might have formed in the bed were not captured as the collection method enabled to extract only sufficiently strong agglomerates.

The collection method consisted in using a vacuum cleaner to extract the powder and then the segregated lumps were removed from the reactor by means of a custom built scoop.

The presence, the size and the chemical composition of the sintered bridges between the particles were inspected by Scanning Electron Microscope (SEM Hitachi SU 70) and Energy Dispersion X-ray (EDX Bruker xFlash 6130) analysis. In this work, SEM/EDX magnification and analysis on the agglomerates have been performed during a placement at Venator R&D group in Duisburg, Germany.

Figure 4 - Typical schematic temperature profile inside the bed during sintering test

3 RESULTS AND DISCUSSION

3.1 Fundamental fluidization tests on the fresh mixtures

The minimum and complete fluidization velocities measured for all the fresh mixtures at ambient temperature are reported in Table 6. These two parameters have been experimentally determined also at 500 °C, since this was the starting temperature for the combustion tests. Knowledge of u_{mf} and u_{cf} at 500 °C was crucial to determine the operative conditions for the tests, as reported in Table 3.

Figure 6 shows the pressure drop profiles, as well as the values of u_{mf} and u_{cf} , for each fresh mixture for both 25 and 500 °C. The former are plotted as the $\Delta P_m / \Delta P_c$ ratio, where ΔP_m is the experimentally measured pressure drop and ΔP_c is the pressure drop calculated when full bed support is achieved, to Eqn (1):

$$\Delta P_c = \frac{M g}{XSA} \quad (1)$$

where M is the bed material weight, g is the gravitational acceleration and XSA is the cross-section area occupied by the material.

As stated before, the pressure drop curve of a multi-components mixture presents more than one slope describing the packed bed regime, because of the different u_{mf} of each single component [27–29]. In order to support this, Table 5 and Figure 5 highlight the discrepancies observed between the values calculated from the pressure drop profiles and the ones observed using x-ray images analysis for the fresh mixtures at ambient temperature.

Figure 5 – Comparison between methodologies for evaluating the minimum fluidization velocity of multi-components mixtures: slopes-method (intersection between the horizontal line describing the fully fluidized bed and the sloped line describing the packed bed) vs. X-ray images investigation.

Table 5 - Comparison between the values of u_{mf} of the multi-components fresh mixtures obtained at ambient temperature using different methodologies

Mixture	u_{mf} (cm/s)		
	X-ray Images	Slope 1	Slope 2
STS-0	7.1	7.0	-
STM-0	10.6	11.4	9.9
STL-0	14.1	16.9	14.6
NTS-0	10.8	16.5	18.1
NTM-0	13.0	20.4	13.8
NTL-0	13.8	13.6	14.1

As expected, both the minimum and the complete fluidization velocities decreased with increasing temperature, as is expected due to the changes in gas density and viscosity. Significant hysteresis was observed when fluidizing and defluidizing the bed both at ambient temperature and at 500 °C. In particular, values of the pressure drop in the packed bed region showed significant fluctuation, indicating a certain difficulty of the mixtures to achieve complete fluidization. However, full bed support (i.e. $\Delta P_m/\Delta P_c = 0.95-1$) was eventually reached for both temperatures.

Bed expansion was investigated at ambient temperature for all the fresh mixtures. Figure 7 reports the absolute bed heights for ST and NT fresh mixtures at different superficial gas velocities; measurements were performed by decreasing the gas velocity from well-fluidized conditions to a complete settled bed. In all the cases, the bed expansion profiles do not level

off to an exact height and the maximum expansion registered is strongly dependent on the particle size of the coke present in the mixture. This decreases with increasing coke size whether synthetic or natural rutile is used. A maximum increase equal to or greater than 20% is observed when small and medium coke is used, whereas it drops drastically when large particles of coke are used, namely to 11% for the STL mixture and to 14% for the NTL mixture.

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

Figure 6 – Pressure drops profiles for the fresh mixtures at ambient and high temperature

Figure 7 – Bed expansion profiles of the fresh mixtures at ambient temperature

3.2 Combustion tests

The early stages of the sintering process were experimentally simulated according to the procedure reported above and for the operating conditions reported in Table 4.

The temperature and pressure drop profiles recorded inside the bed during the combustion of coke are reported in Figure 8 for ST mixtures with coke having different particle size distribution: small (STS), medium (STM) and large (STL) respectively. The operating time was set to 50 minutes in order to keep the temperature within the rig below the maximum temperature allowed for safe operations (950 °C). The temperature reached within the bed is strongly dependent on the air flowrate as this determines the amount of oxygen present in the reaction environment. In all the cases, the value of the final temperature reached increases as the air flowrate is increased. Conversely, the final temperature seems weakly dependent on the coke particle size, apart from the case where the gas velocity is close to incipient fluidization. When the temperature increases, the minimum fluidization velocity decreases; hence, for the same gas flow, the bed may become more evenly fluidized at higher temperature, with better oxygen transfer across the bed. Such a change is strongly related to the PSD of the mixtures and it can lead to higher final temperature in the bed.

It is worth mentioning that whilst recording the temperature and the pressure drop during the combustion stage, it was not possible to detect local hot spots inside the bed, which can initiate sintering. The tests were therefore carried out three times to ensure the reliability of the measurements. The pressure drop profiles obtained during the coke combustion stage showed little variation, which suggests that the agglomerates did not form during this specific stage.

Similar outcomes were observed for the NT mixtures with coke with different particle size distribution: small (NTS), medium (NTM) and large (NTL) respectively, see Figure 9. Also for these mixtures the operating time was set to 50 minutes, but in most of the cases the maximum safe temperature (950 °C) was reached in a shorter time frame compared with the ST mixtures. This dictated an earlier shutdown of the gas inlet.

Some important differences were observed for the bed pressure drop profiles obtained for the NTM and NTL mixtures compared with the ST cases, when the superficial gas velocity is close to incipient fluidization. In these two cases, there is a sudden and sharp decrease in the bed pressure drop towards the end of the test. This coincides with the onset of a sharp temperature increase, corresponding to a peak in the combustion rate, which triggers a greater consumption of the coke material, leading in turn to a reduction of the overall bed weight. This observation is further enhanced when larger particles of coke are used (darker blue lines in Figure 9).

After combustion, the systems were let to cool down to ambient temperature without any external aid (e.g. without injecting any cold airflow). The temperature profiles during the cooling stage showed a typical natural cooling profile in all the tested cases, confirming that the cooling conditions do not differ from case to case (more details can be found in the supplementary material).

Samples of the cooled systems were collected in order to perform composition and chemical analysis on the spent mixtures. Results on the amount of coke contained in the samples are reported in Figure 10.

Figure 8 – Temperature and pressure profiles inside the bed during combustion stage for ST mixtures at different fluidization conditions (see Table 4 for details).

Figure 9 – Temperature and pressure profiles inside the bed during combustion stage for NT mixtures at different fluidization conditions (see Table 4 for details).

Figure 10 - Coke material weight reduction due to combustion. The dashed line represents the initial percentage of coke in the fresh mixtures.

3.3 Fundamental fluidization tests on the spent mixtures

The parameters determined from the pressure drop measurements and from inspection of the bed height obtained with the X-rays for the spent mixtures at ambient conditions are reported in Table 6.

The pressure drops profiles are reported in Figure 11 for both the ST and the NT mixtures. $\Delta P_m/\Delta P_c$ values against the superficial gas velocity are compared to the results obtained for the fresh mixtures. ΔP_c values are calculated according to Eqn. (1) by taking into account the reduction of the weight of bed material due to coke combustion (see Figure 10).

Changes in both u_{mf} and u_{cf} were observed for the spent mixtures when comparing these with the results obtained for the fresh mixtures. The minimum fluidization velocity of the spent mixtures decreased in all the cases investigated and this was emphasized when larger particles of coke were used. As supported by the results shown in Figure 10, this might be due to the combustion of the coke, which reduces the size of the largest fraction, hence affecting u_{mf} and u_{cf} .

Significant hysteresis was observed between the “fluidization” and the “defluidization” curves for all the spent mixtures. The pressure drop in the packed bed region showed a fluctuating trend, indicating a certain difficulty of the mixtures to achieve complete fluidization. Moreover, the pressure drop measured in the packed bed of the spent mixtures was found to be greater than the measured one for the fresh mixtures in most of the cases. This indicates that the upward-flowing gas encounters more difficulty when passing through

the bed, due to the presence of agglomerates. These obstruct the gas flow, causing possible channelling and an increase in the pressure drop, due to the more drag caused by the agglomerates. As soon as the complete fluidization velocity is reached, only the loose particles are suspended. This is substantiated by the observation of the experimental pressure drop at complete fluidization conditions, as it does not equal the predicted one: final values of $\Delta P_m/\Delta P_c$ are always less than 1. This indicated that parts of the bed were not fully fluidised, suggesting the presence of agglomerates within the bed.

Table 6 – Main experimental results for fresh and spent mixtures

Mixture	Condition	u_{mf} (cm/s)	u_{cf} (cm/s)	Hs (cm)	ΔH_{MAX} (%)	% of agglomerates
STS	STS-0	7.1	8.0	11.0	20.5	-
	STS-1	6.0	8.0	11.4	14.2	4.8
	STS-2	5.7	9.0	10.7	15.4	5.5
	STS-3	4.5	7.0	11.3	21.4	-
STM	STM-0	10.6	12.0	11.3	20.0	-
	STM-1	9.6	12.0	11.6	17.9	0.8
	STM-2	7.7	10.0	11.0	11.2	1.3
	STM-3	5.5	6.5	11.4	20.4	-
STL	STL-0	14.1	17.0	12.1	11.0	-
	STL-1	11.5	13.0	12.4	13.8	1.0
	STL-2	10.9	12.0	12.6	9.5	1.9
	STL-3	7.2	8.5	12.0	13.1	2.8
NTS	NTS-0	10.8	15.5	10.9	27.0	-
	NTS-1	10.0	10.0	10.5	24.2	9.0
	NTS-2	8.5	11.0	10.2	22.0	-
	NTS-3	8.7	10.0	10.3	22.3	-
NTM	NTM-0	13.0	16.5	10.0	23.0	-
	NTM-1	12.0	14.0	10.7	13.5	6.1
	NTM-2	11.0	15.0	10.7	11.2	7.5
	NTM-3	10.0	16.4	10.3	11.8	-
NTL	NTL-0	13.8	16.0	10.9	13.5	-
	NTL-1	11.0	14.5	10.5	15.2	6.6
	NTL-2	10.5	17.0	10.5	16.0	5.0
	NTL-3	9.8	12.0	10.0	18.8	-

Only for the spent NTM mixtures, the trend of the pressure drop in the packed bed region is the reverse: the values found for the spent mixtures are all lower than the values for fresh mixtures.

Figure 11 – Comparison between pressure drops profiles for ST and NT spent mixtures and fresh ones

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

On the other hand, the complete fluidization condition is reached at lower gas velocity for most of the spent NT mixtures when compared to the fresh ones. This suggests that the combustion of coke particles is better promoted in the systems with natural rutile (NT mixtures) rather than in the ones with synthetic rutile (ST mixtures); this leads to a considerable reduction of the overall bed weight, due to the burning and shrinking of the coke particles, which in turn enables achieving complete fluidization at a lower gas velocity. Such outcomes are confirmed by the test performed to evaluate the coke weight reduction during combustion and reported in Figure 10. The only exception is the NTL-2 mixture, which has a complete fluidization velocity higher than the fresh one. This indicates that less coke has

been consumed in this case This observation is confirmed by the pressure drop measured at complete fluidization velocity: in this case, the value of $\Delta P_m/\Delta P_c$ is very close to the one obtained for the fresh mixture.

Bed expansion profiles for both ST and NT mixtures were also investigated by using the x-ray facility, as described above. The normalised deviation profiles from the settled bed height, as function of the gas velocity, are reported in Figure 12. The spent mixtures after combustion in well-fluidized conditions ($2 \times u_{cf}$) show, in most of the cases, higher bed height (see the yellow curves in the figures). In the other two cases, namely for the spent mixtures obtained after combustion with gas flowrates below and at incipient minimum fluidization (blue and red curves in the figures), the bed height is lower than the fresh mixtures' one when small or medium coke is used, while it is higher when large particles of coke are used.

Figure 12 – Comparison between bed expansion profiles for spent mixtures and fresh ones

3.4 Agglomerates investigations

The percentage of agglomerate materials found in the spent bed after the combustion tests is reported in Table 6 for all the cases investigated. Some photographs of the agglomerated particles found are reported in the supplementary material. The bond structures among the agglomerated particles were inspected by means of SEM analysis coupled with EDX that

permitted the assessment of the chemical composition of the sintered material. SEM images and EDX spectra are extensively discussed in [17] and some examples can be found in the supplementary material.

In order to aid the investigation of the bond, each sample was embedded in a special resin and part of its surface was grinded away. Such a technique allowed visualising the internal cross section of the interparticles' bonds. Figure 13 reports a typical SEM picture of one of the bonds obtained after resin embedding and surface grinding. The EDX spectra reported at the bottom of the figure belong to the different marked areas in the SEM picture. In particular, the areas A and B refer to the internal body of the particle and the area C refers to the bond between the two particles. EDX spectra on areas A and B reveal high amounts of titanium and iron, whereas in the area C, silicon, aluminium and calcium are present in higher proportions. More specific details on the elemental composition of the areas marked in Figure 13 are reported in Table 7. These reveal that only the synthetic rutile and slag give place to the formation of the sintered neck, with a particular enrichment of Al-Si phase in the bond.

Similar outcomes were observed in the other cases (see supplementary material for details) and the possibility of bonds involving coke particles was explored as well.

Figure 14 shows the details of the investigation on some coke embedded in the STL-2 samples. SEM/EDX pictures of some typical interparticles contact areas have been magnified and they are shown in contrast of topography and composition to enable getting information regarding the physic-chemical structure of the bond. It can be observed that no relevant bonding structures involving the coke particles could be found. It is worth mentioning that the EDX analysis was performed on the areas marked by the yellow arrows, showing small ore-type particles scattered around the large coke particle. However, no obvious bond structures could be identified.

Table 7 – Elements composition from EDX spectra of the marked areas in Figure 13

Element	Composition [wt.%]		
	Area A	Area B	Area C
O	35.33	40.20	47.65
Mg	1.16	-	-
Al	0.72	-	6.06
Si	-	-	30.34
Ca	-	-	7.31
Ti	29.88	58.33	4.25
Mn	4.84	-	2.02
Fe	28.07	1.48	2.37

Figure 13 – EDX analysis and spectra on STM-2 sample neck.

Figure 14 – SEM pictures around coke particles in STL-2 sample

4 CONCLUSIONS

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

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

The fluid-dynamic characteristic of the spent systems were assessed by means of pressure drop measurements and bed height inspections. Changes in u_{mf} and u_{cf} were compared with the fresh mixtures' results: they all decreased in the spent cases and this reduction was enhanced when larger particles of coke were used. The systems with synthetic rutile presented some differences from the systems with natural rutile, with respect to the complete fluidization velocity. In the former, the complete fluidization condition was reached at lower gas velocity for the spent mixtures than for the fresh ones only when high gas flowrates were used during the combustion stage. In the latter, u_{cf} was reached at lower gas velocity for most of the spent mixtures compared to the fresh ones, regardless of the fluidization regime of combustion stage. This suggested that the combustion of coke particles was better promoted in the systems with natural rutile (NT mixtures) than in the ones with synthetic rutile (ST mixtures). One possible explanation could be the high level of impurities contained in the natural rutile, which can significantly affect the combustion behaviour of the mixtures investigated.

The inspections on the bed expansion of the spent mixtures also showed a number of differences between the systems with synthetic rutile and the ones with natural rutile, and between the different spent conditions. However, it was observed that the spent mixtures with large coke particles after combustion in well-fluidized conditions expanded more than the fresh ones. A possible reason could be the higher change in size and mass observed when operating at high gas flowrate with medium and large particles of coke, which in turn cause a modification of the drag force exerted by the fluidizing gas on the bed of particles.

Finally, SEM/EDX analysis was performed with the aim of analysing the properties of the agglomerates. This allowed investigating the structure of the bridges among particles and the assessment of the chemical composition of the sintered material. The results suggested that only particles of rutile and slag were involved in the formation of the sintered bridge (with a particular enrichment of Al-Si phase in the bond) and no relevant bonding structures involving coke particles were found. Therefore, we can conclude that the coke particles do not affect particles agglomeration per se, but they are only responsible for local increase in temperature due to exothermic combustion. However, this may in turn favour the sintering phenomena observed for the rutile and slag particles.

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