



Project No: **764697** 

Project acronym:

# CHEERS

Project full title: Chinese-European Emission-Reducing Solutions

Type of Action: RIA

Call/Topic: European Horizon 2020 Work Programme 2016 – 2017, 10. 'Secure, Clean and Efficient Energy', under the low-carbon energy initiative LCE-29-2017: *CCS in Industry, including BioCCS* 

> Start-up: 2017-10-01 Duration: 72 months

## Deliverable D3.5: Oxygen-carrier development

Due submission date: 2023-08-31

### Actual delivery date: 2024-05-07

Organisation name of lead beneficiary for this deliverable: SINTEF AS (short name: SINTEF MK)

Project funded by the European Union's Horizon 2020 research and innovation programme under grant agreement No 764697, and co-funded by the Chinese Ministry of Science and Technology (MOST)		
Dissemination Level		
PU	Public	Х
CO	Confidential, only for members of the consortium (including the Commission Services and MOST)	

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Deliverable number:	D3.5
Deliverable title:	Oxygen-carrier development
Deliverable description:	Part of Task 3.1 on oxygen-carrier development
Work package:	WP3 Oxygen carriers and characterisation of fuel conversion phenomena
Lead participant:	SINTEF MK

Quality assurance, status of deliverable			
Action	Performed by	Date	
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Endorsed (Executive Board)	By e-mail	2024-06-28	
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## List of abbreviations

CLC	Chemical Looping Combustion
FR	Fuel Reactor
AR	Air Reactor
HP-TGA	High pressure – thermogravimetric analyser
MFB-TGA	Micro-fluidized bed thermogravimetric analyser
TGA	Thermogravimetric analyser
XRD	X-Ray Diffraction
EDX/EDS	Energy dispersive x-ray spectroscopy
SEM	Scanning Electron Microscopy
OCM	Oxygen Carrier Materials (metal-oxides, minerals)
OC	Oxygen Carrier
OTC	Oxygen Transfer Capacity
CMTF	Ca(Mn,Ti,Fe)O3
T1 and T2	Different size fraction of ilmenite delivered by Titania
IFPEN	IFP Energies Nouvelles
TEOT	TotalEnergies OneTech
DBC	Dongfang Boiler Group Co., LTD (DONGFANG)



### 0 PREFACE

CHEERS conforms to the European Horizon 2020 Work Programme 2016 – 2017, 10. 'Secure, Clean and Efficient Energy', under the low-carbon energy initiative (LCE-29-2017: CCS in Industry, including BioCCS). The ambition is to improve the efficacy of  $CO_2$  capture in industry, and help ensuring sustainable, secure, and affordable energy.

The action involves a 2<sup>nd</sup> generation chemical-looping technology. The 1<sup>st</sup> generation is tested and verified at laboratory scale / pilot scale (150 kWth). Within the framework of CHEERS, the core technology will be developed into a 3 MWth system prototype for demonstration in an operational environment - CHEERS demonstration unit. This constitutes a major step towards large-scale decarbonisation of industry, offering a considerable potential for retrofitting industrial combustion processes.

The system prototype is based on a fundamentally new fuel-conversion process acquired from previous research and development actions over more than a decade. The system will include heat recovery steam generation with  $CO_2$  separation and purification, and it will comply with industrial standards, specifications and safety regulations. Except for  $CO_2$  compression work, the innovative concept is capable of removing 96% of the  $CO_2$  while eliminating capture losses to almost zero.

The CHEERS project is financed by the European Union's Horizon 2020 research and innovation programme under grant agreement No 764697, and co-funded by the Chinese Ministry of Science and Technology (MOST). CHEERS started from 1 October 2017 and was scheduled to end by September 2023. The total cost amounts to approximately 25 million EUR.

WP3 of the CHEERS project is about oxygen carrier materials and fuel conversion. A main objective of this WP is to ensure that proper oxygen carriers will be available for demonstration of petcoke conversion by Chemical Looping Combustion in the CHEERS demonstration unit to be developed within the project.

There is a close coupling between the oxygen carrier properties and the design and sizing of the CHEERS demonstration unit. Oxygen carrier materials need to be developed and evaluated for the selected window of operation for the particular chemical looping configuration system to be designed. In this project, the aim is to have a high air utilization giving lean air with less than  $2\% O_2$  out of the air reactor, to ensure high energetic efficiency. The fuel reactor will be a bubbling bed with high residence time due to the slow gasification of petcoke. To prevent the residence time from being exceedingly high, the average temperature in the fuel reactor will be at least around  $950^{\circ}$ C.

If the selected oxygen carrier material causes an endothermic reaction in the fuel reactor, the oxygen carrier will also have to provide sufficient heat to ensure 950°C in the fuel reactor. Consequently, the outlet temperature of the air reactor might go up to 1050 - 1100°C. In case of oxygen carrier materials with exothermic reaction in the fuel reactor, the air reactor temperature can be reduced. Furthermore, the selection of oxygen carrier will also affect the nominal power of the pilot plant since this is related to the circulated amount of oxygen carrier material and its oxygen capacity.

Deliverable 3.5 is the summary report for Task 3.1 on oxygen carrier development and selection. It summarizes the development and laboratory scale testing and evaluation of oxygen carrier materials that could be relevant for application in the CHEERS demonstration unit. Special emphasis has been put on the oxygen carriers that were selected as the most relevant candidates. These have been ilmenite T1 chosen as the first candidate, LY Mn - a manganese ore from China as the second candidate, ilmenite T2 as the third.

Perovskites based on CMTF were not selected as candidate oxygen carrier due to deactivation in the presence of the high sulphur content in petcoke but was successfully upscaled at Tsinghua University to 1 tonne based on its lifetime perspective in fuel with low sulphur content.



The oxygen carrier materials have been evaluated based on their suitability for the process, considering parameters such as oxygen capacity and oxygen release, temperature of operation, reaction kinetics, availability, sulphur tolerance, etc. The development process has been coordinated by SINTEF MK in close collaboration with, Tsinghua University, IFPEN, and SINTEF ER. Ilmenite T2 was finally selected, and 250 tonnes of T2 were delivered to China for the testing campaigns in the CHEERS demonstration unit.

Deliverable 3.5 was moved to the end of the project to also cover the post-characterisation of the bed materials sampled before, during and after operation. Post-characterisation was mainly performed for investigation of material strength and activation/degradation under operation in CHEERS demonstration unit.



## **1 EXECUTIVE SUMMARY**

Deliverable 3.5 is the summary report for the selected oxygen carrier material system, including the laboratory and pilot scale testing and evaluation of selected oxygen carrier material to be applied in the CHEERS demonstration unit.

SINTEF MK and IFPEN collaborated with Tsinghua University to acquire two resources of ilmenites from Vietnam and Mozambique, and Fe ores from Guangxi province, and Mn ores from Hunan province China. In addition, ilmenite from Titania AS in Norway has been tested. After sieving, the materials have been evaluated at both SINTEF MK and IFPEN by means of various techniques including TGA, SEM, micro-reactor, and reactor testing (100  $W_{th}$  screening in batch fluidized bed reactor). The materials have been evaluated based on their suitability for the process, considering parameters such as oxygen transfer capacity and oxygen release, temperature of operation, reaction kinetics, availability, and sulphur tolerance. From the four ilmenites tested, the two from Norway had much higher performance and were selected firstly as candidates for pilot tests.

Fe minerals from Guangxi province have shown high oxygen capacity and fast kinetics. However, further applications have been hindered due to stability issue such as Fe outwards diffusion leading to swelling of the materials, and loss of the strength during redox cycles. Suitable amount of Mn inside the Fe mineral can increase its stability if they are intermixed with each other. Thermal treatment of such minerals at high temperature can cause the inter-diffusion between Fe and Mn rich phases, which may increase the structure stability of minerals, but such thermal treatment also results in higher cost. Based on fast degradation and higher cost, we did not further study such minerals for potential pilot testing.

Three Mn ores from Hunan province China with different ratios of Fe and Mn have also been studied and tested. Redox cycling experiments have found that the higher the Fe concentration inside the ores, the higher the oxygen transfer capacity. However, post-characterizations by SEM have found significant degradation of Mn ores with high content of Fe after redox cycling, while only a slight degradation in the LY Mn ore (Mn-ore with relatively low content of Fe). The heat-treated LY Mn ore also showed no degradation in the presence of petcoke and was therefore selected as the second candidate for pilot testing.

For the pilot testing in SINTEF ER and IFPEN in 150kW and 10kW rigs, respectively, about **one tonne of** ilmenite was delivered for the first pilot test. Furthermore, **four tonnes** of the LY Mn-ore from Hunan province, China were purchased, pretreated, crushed and sieved. Afterwards, 530 kg and 1368 kg were sent to IFPEN and SINTEF ER for the second pilot scale testing, respectively. The material degradation of the LY Mn-ore was found to be high compared to ilmenite. Therefore, ilmenite was selected for the demonstration campaign in China for both the European and the Chinese configuration.

Titania could deliver two different versions of ilmenite, where the most important difference between them was the particle size distribution and the cost. We have named the two versions T1 and T2.

Ilmenite T2 had a more suitable size distribution giving lower cost than T1 and was selected for the CHEERS demonstration unit at Dongfang Boiler (Deyang, Sichuan Province). The mass needed was based on filling and lifetime prediction for the two different configurations of the CHEERS demonstration unit; ca. **160 tonnes** of oxygen carrier material (OCM) were needed for the European test campaign and **90 tonnes** for the Chinese design. (Previously, **28 tonne** of ilmenite T1 was also purchased for use in the cold mock-up design testing in China.)

Several synthetic material compositions including the Fe-Mn-Ti (Mg) system and Ca(Mn,Ti,Fe)O<sub>3</sub> system have been developed and tested in this project. For the spinel of Fe-Mn-Ti (Mg) system, homogeneous phases were hard to achieve for the granulates although good redox performance was obtained. Therefore, we did not go further in upscaling for this material system. For perovskite Ca(Mn,Ti,Fe)O<sub>3</sub> system, the most stable composition was found to be CaMn<sub>0.375</sub>Ti<sub>0.5</sub>Fe<sub>0.125</sub>O<sub>3</sub> (CMTF8341), but a better performing



CaMn<sub>0.5</sub>Ti<sub>0.375</sub>Fe<sub>0.125</sub>O<sub>3</sub> (CMTF8431) [1,2,3,4,5,6] was selected for testing in 100 kW pilot plant at Tsinghua University in China and **1 tonne** of this composition was produced in China by means of spray drying method. But this material was not selected for the CHEERS demonstration unit with petcoke since the high amount of sulphur in petcoke was found to have a detrimental effect on the material. These materials have been reported in detail in an internal project deliverable and will not be the focus in this public deliverable.

This deliverable also highlights the main findings from the post characterization of the OC after use in the CHEERS demonstration unit, showing that the material strength is as good as expected, and that precalcination gives the required oxidation of the particles before they are used in the unit. Samling from the CHEEERS demonstration unit shows expected distribution of fully and not so activated (fresher) particles, due to constant fresh samples added to the unit. The relatively high content of fresh particles in the end of the campaign was also as expected based on operation issues with the fuel.



## 2 JOINT EFFORTS AND MATERIALS EXCHANGE DURING THE DEVELOPMENT

To develop the oxygen carriers with required properties in CHEERS, it needs to combine the strengths of all institutes, e.g. fundamental studies of oxygen carriers at SINTEF MK, and testing in lab- and pilot-scale reactor systems at IFPEN and SINTEF ER. Moreover, since this is a joint project between EU and China, and the final demonstration stage will be carried out at Dongfang Boiler test site close to Chengdu in China, it would be necessary to have materials exchange from China.

### 2.1 SINTEF MK and IFPEN

For the oxygen carriers to be used in pilot testing and final in the CHEERS demonstration unit in China, the oxygen carriers were first screened and developed at SINTEF MK to evaluate their performance at high temperature such as oxygen transfer capacities and redox kinetics, together with post-characterization by SEM to understand mechanisms related to materials stability. Considering that TGA is a very harsh testing for materials (small amounts of materials being constantly flushed with reducing/oxidizing gases), the promising oxygen carriers which show good OTC and reactivity, should also be evaluated in a relatively mild condition such as lower temperatures in the reactor by co-feeding petcoke at IFPEN. According to the need of this project, all the materials have been crushed and sieved in fraction between 210-300 µm and 180-300 µm (later stage) before delivered to IFPEN, which include ilmenites from Titania (T1 and T2), ilmenites from Tsinghua (Vietnam and Mozambique), Mn ore (LY Mn), and CMTF perovskites.

### 2.2 SINTEF MK and Tsinghua University

Since the project final demonstration stage will be held in China, SINTEF MK also searched for some original batches of Fe-rich ores from Guangxi, China. The research group of Zhenshan Li in Tsinghua University helped to purchase 4 kg of ores for each composition and deliver them to Oslo, Norway. Besides, two bags of Ilmenite from China (around 1-2 kg each) were also sent for testing. In the end of 2019, 3 batches of Mn ores with different Fe contents in the amount of 100 g to a few kg were sent from Tsinghua to SINTEF MK for evaluation. Meanwhile, SINTEF also sent a series of CMTFs to Tsinghua university for testing, from which some fruitful results have been jointly published in 4 peer-reviewed journals [1,2,3,4], where upscaling of CMTF perovskites production has been successfully achieved with 1 tonne of granulates [4].

### 2.3 SINTEF MK and Dongfang Boiler Group

28 tonnes of ilmenite T1 were shipped from Norway to China for use in the cold flow model. Later in the project when ilmenite T2 was selected for the demonstration test, 250 tonnes of this material were shipped to China to be used in the CHEERS demonstration unit.



#### 2.4 Material systems

The investigated oxygen carriers are summarized in the table below.

Table 3-1: Investigated oxygen carriers and their origins.

Materials	Origin	Form
Ilmenite-Nor	Norway	Mineral
Ilmenite-Viet.	Vietnam	Mineral
Ilmenite-Moz.	Mozambique	Mineral
Fe-rich ore	Guangxi, China	Mineral
Fe-Mn ore	Guangxi, China	Mineral
CMTF8440	Lab, SINTEF	Synthetic
CMTF8341	Lab, SINTEF	Synthetic
CMTF8431	Lab, SINTEF	Synthetic
FeMnTi(Mg) syn.	Lab, SINTEF	Synthetic
GT Mn ore	Hunan, China	Mineral
MG Mn ore	Hunan, China	Mineral
LY Mn ore	Hunan, China	Mineral

### 2.5 Methodologies

To evaluate the different oxygen carriers, we have utilized various advanced instruments and test units available within the consortium of this WP, which will give a comprehensive assessment beginning with the fundamental knowledge of materials to the final application in CLC with petcock. Reduction-oxidation (redox) cycles testing of the materials were performed as a screening test to select the most promising materials for CLC purposes in the project CHEERS. This was performed in a Setsys Evolution (Setaram) thermogravimetric analyser apparatus coupled with a fully automated in-house gas mixing system (Figure 4-1). Constant total flow of 200 mL/min was used in all experiments. The materials were first heated up to 900 °C in air, then 20 redox cycles between wet (80% saturated at room temperature, see below) 20%  $O_2$  and wet 5%  $H_2$  for activation. Thereafter, 19 redox cycles between 10 %  $H_2 \leftrightarrow$  20%  $O_2$ , 10 %  $H_2 \leftrightarrow$  10%  $O_2$ , 10 %  $H_2 \leftrightarrow 5\%$   $O_2$ , 5 %  $H_2 \leftrightarrow 20\%$   $O_2$ , 5 %  $H_2 \leftrightarrow 10\%$   $O_2$ , and 5 %  $H_2 \leftrightarrow 5\%$   $O_2$  were performed at 950, 1000 and 1050 °C. A mix of 25% CO<sub>2</sub> plus inert N<sub>2</sub> or Ar were used for conditioning in all the gas mixtures. The humidity of the reactive gases was stabilized to 80% of the saturation humidity at room temperature via bubbling the gas through saturated KBr solution. During each redox cycle, samples were kept for 2 minutes in reducing and 2 minutes in oxidizing atmosphere with an inert period of 2 minutes in between (visualised in Figure 4-2). These conditions were chosen to estimate the maximum oxygen capacity for each candidate material and give an indication of reversibility after each cycle, effect of activation, and redox reaction rate. The chosen residence time, gas compositions and temperatures are comparable with the actual operational condition in



the circulating fluidized bed CLC process in the presence of petcoke. The mixtures of wet 20%  $O_2 + 25\%$   $CO_2$ and 5%  $O_2 + 25\%$   $CO_2$  simulate the conditions close to the inlet and outlet of the air reactor. The wet  $H_2/CO_2$ buffer results in a shift reaction, giving milder reducing condition and weaker driving force for the reaction, simulating the inlet of the fuel reactor. The buoyancy effect during TG measurements is dependent on the molar weight of the gas in the instrument. Separate experiments have been performed on the system without oxygen carriers, showing the effect of buoyancy is negligible for these test conditions. It should also be mentioned here that redox cycles under such conditions are very harsh, and more degradation of oxygen carriers can be expected as compared to real reactor testing, according to literature. In addition, various fuels such as CO, CH<sub>4</sub>, H<sub>2</sub> were also used for evaluation.



Figure 4-1: Thermogravimetric analyser (TGA) with automatically gas exchange system.



Figure 4-2: A typical TGA curve shows mass change vs. time under various redox conditions. Ilmenite T1 is used here.



Rubotherm thermogravimetric analyzer equipped with a magnetic suspension balance (termed as HP-TGA) was used to evaluate sulphur tolerance of oxygen carriers. To evaluate microstructure stability, pre- and postcharacterisations were performed on the samples prior to and after the redox cycling by means of scanning electron microscopy (SEM). The mechanical strength was evaluated by cold attrition test following ASTM E728 standard protocol.

At Tsinghua University, micro-fluidized bed thermogravimetric (MFB-TGA) experiments were performed to measure the redox reaction kinetics under the fluidization state with enhanced heat and mass transfer, and the obtained experimental data at different temperatures were fitted by a fluidized-bed reactor model coupled with a semi-empirical kinetic model.



Figure 4-3: Schematic diagram of the MFB-TGA.

At IFPEN, the batch fluidized bed reactor facility in Figure 4-4 was used to measure reactivity of oxygen carriers for fuel conversion, ageing test for redox cycle stability, and petcoke influence on the reactivity.



Figure 4-4: Batch fluidized bed unit.



Moreover, it is also a challenge to upscale the oxygen carriers from the lab level to the industry application in the field of CLC, especially to maintain their physical and chemical properties comparable with the lab powders. In this project, spray granulation has been developed at both SINTEF MK and Tsinghua University to upscale the production of the developed perovskite oxygen carriers.





## **3** A SHORT SUMMARY OF DEVELOPED/SELECTED OXYGEN CARRIERS

#### 3.1 Synthetic oxides

#### 3.1.1 Fe-Ti-Mn (Mg) spinnels

Four different compositions were produced and tested. They had all reasonable and fast kinetics and two of them also good oxygen transfer capacity. (Rec 3 and Rec 4 in Figure 5.1-1). But during testing they had phase separation giving Fe rich and MgTiO<sub>3</sub> rich phases and showed degradation similar to ilmenite (Fe<sub>2</sub>O<sub>3</sub> on surface while Ti-Mg in the inner part). The performance was rather equal to ilmenite but slightly less OTC than ilmenite and comparable lifetime to ilmenite. These findings plus additional cost, without giving necessary benefit, eliminated these materials for further advancement as candidate materials.



Figure 5.1-1: Redox cycles of 4 compositions of Fe-Ti-Mn (Mg) spinel.

### 3.1.2 Ca-Mn-Ti-Fe based perovskites

As ceramic materials with well-defined structure and high redox and thermal stability, perovskite-type complex oxides (ABO<sub>3</sub>, radius atom A>B) have been widely studied in some applied and fundamental areas of solid-state chemistry and catalysis. The perovskite phase is normally stable over a very large range of oxygen partial pressures and known for its low cation diffusion compared to oxygen ionic diffusion. These properties of good oxygen diffusion and exchange without undergoing crystal phase changes are not possessed to an appreciable degree by other oxides containing transition metals. Different cations on A and



B sites can be compositionally tuned to regulate the oxygen vacancies concentration, i.e. oxygen transfer capacity (OTC) and stability of OCMs. In this project, perovskites based on  $Ca(Mn_xTi_yFe_{1-x-y})O_3$  (CMTF) compositions have been designed. By tailoring the cation ratios on the B site, various redox performance has been achieved, e.g., a high amount of Mn for a fast reactivity, a high Ti for a good stability.

Based on the know-how on functional ceramic oxides at SINTEF MK, three different compositions were initially compared: Ca<sub>8</sub>Mn<sub>4</sub>Ti<sub>3</sub>FeO<sub>24</sub> (CMTF8431), Ca<sub>8</sub>Mn<sub>3</sub>Ti<sub>4</sub>FeO<sub>24</sub> (CMTF8341), and Ca<sub>8</sub>Mn<sub>4</sub>Ti<sub>4</sub>O<sub>24</sub> (CMTF8440). Two compositions of CMTFs have been developed and designed for more detailed investigation. One has less Mn but more Ti, i.e., CMTF8341, and another one has more Mn but less Ti, i.e., CMTF8431. It is expected that CMTF8341 should be more stable while CMTF8431 more reactive according to the concentration of Mn and Ti on the B-site.

The CMTF8431 showed faster kinetics than CMTF8341 [2,6] and had also higher oxygen transition capacity based on the higher content of Mn and therefore selected for upscaling to one tonne by partner Tsinghua University [4], for testing with fuels with low sulphur content. The CMTF8431 have also higher reactivity with CH<sub>4</sub> than CMTF8341. CMTF8341 is the most stable composition – no pores formed after deep redox cycles at high temperatures and also with homogeneous composition. For CMTF8431, we can see that the materials become more porous especially at the centre of the particles, but the compositions of the materials are mostly homogeneous, which explains the high OTC during redox cycles.

Granulates of CMTF8341 and CMTF8431 fabricated by spray granulation at SINTEF MK show reproducible and comparable performance under redox cycles with the powders synthesized in the lab, even though they have inhomogeneous compositions before redox cycling. These granulates were further used to evaluate the mechanical strength of the materials, as well as checking petcoke influence in reactor tests at IFPEN.

The mechanical strength of the OCM used in the CLC process is an essential property that strongly influences the lifetime of the material. The lifetime expectancy, which is only limited to mechanical attrition, was in the present work estimated by comparing the results of the cold attrition test to those of a Ni/NiAl<sub>2</sub>O<sub>4</sub> reference recorded by VITO (Flemish Institute for Technological Research) in Belgium. Linderholm et al. [7] estimated the lifetime of this reference material to be about 33000 hours. From the attrition behaviour in Figure 5.1-2, it is clear that CMTF8341 granulates have higher mechanical strength and estimated lifetime as compared to CMTF8431 due to higher sintering temperature (1350 vs. 1300 °C). CMTF8431-China, which was fabricated in tonne-scale in China with a similar protocol as in this work, has shown even higher lifetime than the reference material Ni/NiAl<sub>2</sub>O<sub>4</sub>, indicating high potential for industrial applications of the investigated granules in this work.





Figure 5.1-2: Mechanical stability from attrition test for granulates of CMTF8341 and CMTF8431 as compared to other types of manufactured OCMs.

In the presence of petcoke, CMTF shows a fast deactivation from the reactor test at IFPEN.

- Only one petcoke injection was enough to partially deactivate perovskite (even lower CO<sub>2</sub> production),
- More petcoke injections worsened the deactivation.

In the presence of  $H_2S$ , the isothermal cycling at 900 °C for CMTF8341 was performed at SINTEF MK's  $H_2S$  lab and presented in Figure 5.1-3. As noted in the figure caption, the purple line in this graph represents the cycles in which  $H_2S$  is added to the reducing gas (800 ppm  $H_2S$ ). No mass increase due to sulfide formation has been observed from the purple line (reducing condition with  $H_2S$ ). From the reproducibility point of view, CMTF8341 keeps its redox capacity in the 15 steps of study with a full oxygen capacity of ~ 3-4 wt%, which is similar to that measured with ambient pressure TGA.



Figure 5.1-3: Redox cycle of CMTF8341 at 900°C under CLC condition. The purple line is performed in the presence of 800 ppm H<sub>2</sub>S.

The discrepancy between these observations is mainly related to the degree of reduction which is important for regeneration of the OCM since the CaSO<sub>4</sub> formed on the surface of CMTF in the air reactor, will be



decomposed and release as SO<sub>2</sub> during deep reduction as described by Pishahang et al. [8]. But under real CLC operation with mild reducing condition given by petcoke the sulphur will be accumulated on the surface. The CMTF is therefore not suitable for CLC with fuels with high H<sub>2</sub>S concentration and mild reducing condition in the fuel reactor. The sulphur issues with petcoke prevented the CMTF materials from coming on the candidate list for testing in CHEERS demonstration unit.

## 3.2 Fe and Mn minerals from China

Since the final stage CHEERS demonstration unit will be at Dongfang boiler, China, possible local suitable, cheap mineral oxygen carrier candidate containing Fe and Mn were searched. These selected mineral ores from China were purchased and tested without and with pretreatment, to see if pretreatment could homogenize the sample and increase the OCM lifetime. The ideal scenarios for such ores are that even distribution of Fe and Mn can prevent the diffusion of the majority cation Fe or Mn, thereby increasing its stability. Minerals have most cases very uneven distribution of Fe and Mn and contain different silicates and aluminates etc. Homogenisation by thermal treatment was attempted to increase stability of oxygen carriers by sintering the minerals at high temperatures.

#### 3.2.1 Fe-rich Ore

A typical TGA curve for long redox cycles has been plotted in Figure 5.2-1 using Fe-rich ore as an example for showing test condition of various cycles. The mass change corresponding to change in OTC was recorded as a function of time and redox cycles. By comparing the TGA curves between sintered and fresh Fe-rich ores, it is clearly shown that both can fulfil the basic requirement of 2 wt% OTC in this project at temperature lower than 1050°C as shown in Figure 5.2-2, but the materials lose the reactivity as temperature increases to 1050°C, especially under less reducing condition (5% H<sub>2</sub>), i.e. less driving force. After sintering at 1200 °C for 12 h, the mineral seems to have a better performance at 1050 °C than the fresh one. SEM images of fresh Fe-rich ore (c.f. Figure 5.2-3 (left)) show that Fe and Mn are dissociated without intermixing prior to redox cycles, and the particles are fragmented and become more porous in Fe-rich areas after redox testing. After thermal treatment at 1200 °C, Mn and Fe are more intermixed and present as small grains embedded in the glassy phase, as shown from the top of Figure 5.2-3 (right). However, de-mixing of Fe and Mn still occurs after redox cycling, with Fe enrichment towards the outer surfaces, as shown from the bottom of Figure 5.2-3. Considering the weak stability of Fe-rich ore even after thermal treatment, we did not make further investigations on it.



Figure 5.2-1: A typical TGA curve shows long redox cycles using H<sub>2</sub> fuel at 950°C. Fe-rich ore is used here.





Figure 5.2-2: Comparison of redox cycles between fresh and sintered Fe-rich ore at 950, 1000 and 1050 °C.



Figure 5.2-3: Comparison of microstructure changes of fresh (left) and sintered (right) Fe-rich ore prior to and after redox cycles. The increased homogeneity of the particles can clearly be seen on the pre-sintered samples.

#### 3.2.2 Fe-Mn ore

For Fe-Mn ore purchased in 2019, we used CO and CH<sub>4</sub> as fuel for screening tests. A typical TGA curve of redox cycles at 900 °C is plotted in Figure 5.2-4 showing a relatively higher OTC with CO as fuel than that of CH<sub>4</sub>. Figure 5.2-5 (top) shows that the original ore has a higher activity during redox cycling at low temperatures than at high temperatures, which is probably due to materials degradation or deactivation through formation of stable inactive Mn and Fe silicates. However, the thermal treated (sintered) one has a lower activity at low temperatures than at high temperatures as shown in Figure 5.2-5 (bottom). Comparing SEM images in Figure 5.2-6, it can be found that Fe and Mn are mostly intermixed with each other after annealing at 1200 °C for 12h. Nonetheless, due to formation of glass phases between Fe/Mn and Si, we did not notice any enhancement in OTC although the stability is increased. Considering too low OTC, we did not put more efforts on this batch of minerals.





Figure 5.2-4: Redox cycles of Fe-Mn ore using CO and CH<sub>4</sub> as fuel at 900°C.



Figure 5.2-5: Comparison of redox cycles between original ore (top) and sintered (bottom) Fe-Mn ore.





Figure 5.2-6: Comparison of microstructure changes of original ore (left) and sintered (right) Fe-Mn ore prior to (top) and after (bottom) redox cycles. In this case less effect of the pre-sintering is found.

#### 3.3 Mn ore from China

Hydrogen fuel was used to screen the performance of Mn ores at high temperatures. It is clear from Figure 5.3-1 that a more reducing condition would yield a higher oxygen transfer capacity > 2 wt% for all Mn ores, which is a threshold for oxygen carriers in this project. It is also quite evident that the higher the amount of Fe, the higher the OTC, i.e. GT Mn > MG Mn > LY Mn, and GT Mn ore has comparable OTC with the ilmenite (c.f. Figure 5.3-2).



Figure 5.3-1: Comparison of deep redox cycles of Mn ores from China series at 950, 1000 and 1050°C.





Figure 5.3-2: Comparison of oxygen transfer capacities of Mn ores from China with ilmenite from Titania.

SEM images have been performed prior to and after redox cycling of all three Mn ore as shown in Figure 5.3-3. For the fresh GT Mn and MG Mn ores (c.f. Figure 5.3-3 (a) and (b)), Mn and Fe are not intermixed with each other and Si appears as both separate particles and mixture with other particles; after redox cycling at high temperatures, the materials become highly porous, and Mn and Fe are still separate. For the fresh LY Mn ore (c.f. Figure 5.3-3 (c)), it is mainly Mn with small amount of Fe, and Si is often intermixed with other particles; more porous structures appear after redox cycling using hydrogen (Figure 5.3-3 (d)).

In summary for all three Mn ores from China, GT Mn and MG Mn have shown serious degradation after redox cycling at high temperatures, although they have shown good oxygen transfer capacity, and cannot be selected as oxygen carrier for pilot testing. LY Mn shows a rather stable structure after redox cycling at SINTEF and IFPEN although its OTC is relatively lower than the other two Mn ores. The higher stability demonstrated in LY Mn ore is probably due to the Si phase being intermixed with other phases, preventing cations such as Mn from fast diffusion towards outer layer, and yielding a longer lifetime.

LY Mn - ore from Hunan province in China was therefore selected for pilot testing at both IFPEN and SINTEF ER. Four tonnes were bought, pretreated at 1100  $^{\circ}$ C, crushed and sieved. Afterwards, 530 kg and 1368 kg were sent to IFPEN and SINTEF ER for the pilot scale testing, respectively.





Figure 5.3-3: Comparison of microstructure change prior to and after redox cycles for a) GT Mn, b) MG Mn, c) LY Mn, and d) LY Mn after testing at IFPEN.

#### 3.4 Ilmenite minerals

Ilmenite (Fe-Ti-O) from Vietnam and Mozambique acquired by Tsinghua University were evaluated. Meanwhile, two types of ilmenites from Titania AS, Norway, were evaluated and tested thoroughly. One is the standard ilmenite (Ilmenite T1) including a lot of small particles and only 20% larger than 180 $\mu$ m, which were sieved through meshes between 210 and 300  $\mu$ m. The other one is a new batch of ilmenite (Ilmenite T2) which has larger particle sizes. Ilmenite T2 was tested directly without sieving.

Ilmenite is well known from literature for CLC systems operating up to 950 °C, in this project the aim was to use the ilmenite at higher temperatures up to 1020 °C for improved petcoke conversion, under more severe condition than given in normal CLC. By comparing the TGA curves in Figure 5.4-1, it is clearly shown that Ilmenite T1 can fulfil the basic requirement of 2 wt-% oxygen transfer capacity (OTC) in this project at all tested redox conditions and temperatures as shown. One should also note that ilmenite from Titania is also oxidized more fully between cycles when the residence time on stream is longer. Regarding the other two materials, Ilmenite Vietnam is very hard to be activated at all tested conditions, while Ilmenite Mozambique only functions at low temperatures such as 950 and 1000 °C and higher reducing conditions. SEM images (c.f. Figure 5.4-2) show that Ilmenite T1 has angular fresh particle shape, while the other two have more rounded or closed shapes. After redox cycles all the materials exhibit microstructure degradation, e.g. becoming more porous and dissociated, which is expected considering harsh redox conditions used in TGA.





Figure 5.4-1: Comparison of redox cycles between ilmenite T1, Vietnam and Mozambique at 950, 1000 and 1050 °C.



Figure 5.4-2: Comparison of microstructure changes between 3 ilmenites: fresh ilmenites (upper) and those after redox cycles (bottom).



Although ilmenite T2 has not been sieved, it shows similar redox behaviour as T1 at all testing conditions and temperatures, as shown in Figure 5.4-3. Therefore, these two batches of ilmenites are sent to IFPEN for further reactor and stability tests in 100W reactor.



Figure 5.4-3: Comparison of redox cycles between ilmenite T1 and T2.

## 3.4.1 Ageing tests results

In order to quickly provide a first oxygen carrier candidate, three ilmenites have been aged with methane as reducing gas at 900°C. The first one, proposed by Tsinghua University, comes from Vietnam. The other two ilmenites, proposed by SINTEF, come from Titania, a Norwegian mining company. Titania 1 (T1) is produced with a wide particle size distribution and needs to be sieved to reach the target oxygen carrier particle size distribution, which is the case for Titania 1 used in the experiments presented below. Titania 2 (T2) is directly produced with a proper particle size distribution which induces great reduction in its overall production costs for the CHEERS project.

#### a. Reactivity comparison

It has been observed that ilmenite material consumes a high amount of oxygen during its heating under air. Figure 5.4-4a presents the evolution of methane conversion as a function of the number of cycles for the 12 tests performed on the three ilmenites. Figure 5.4-4b shows the evolution of the oxygen carrier's  $r_0\Delta X$  as a function of the cycle number. The  $r_0\Delta X$  value is the mass of oxygen supplied by the material for fuel combustion over oxygen carrier mass.





Figure 5.4-4: Experimental results of the ageing tests performed on ilmenite materials. (a) evolution of the methane conversion with the number of cycles, (b) evolution of the oxygen carrier's  $r_0\Delta X$  value over the cycle number for the 12 tests performed with ilmenite oxygen carriers.

According to Figure 5.4-4, the ilmenite materials show a very strong activation over the first 50 cycles. Indeed, for similar cycle operating conditions, the methane conversion increases from 20% to between 45 and 70%. Besides, the  $r_0\Delta X$  value increases from 0.5% to between 1 and 2%. There is a disparity between the test results of a same material (e.g. Titania 2), this is mostly due to a level of experimental uncertainties and in some cases to reactor pollution from previous tests which led to Cu deposition within the reactor. Nevertheless, the conclusion on the results presented in Figure 5.4-4 is that ilmenite from Titania is more reactive than ilmenite from Vietnam. Besides, it seems that ilmenite from Vietnam's reactivity is decreasing slightly faster than for the other materials. On the basis of these results, ilmenite from Titania shall thus be preferred over ilmenite from Vietnam.

#### b. Agglomeration

Tests have been performed to determine if there are differences in terms of reactivity or stability between Titania 1 and Titania 2. It appears that Titania 2 has a greater tendency to agglomerate than Titania 1. For all the tests performed with Titania 2, a ring of agglomerated particles has formed at the bottom of the reactor (see Figure 5.4-5). At this stage, the reason of this ring formation has not been elucidated since Titania 1 and 2 have almost exactly the same properties.

Due to that problem, Titania 1 would be preferred over Titania 2 to reduce as much as possible the agglomeration occurrence in low fluidization zones of the bigger units (L-valves and loop seals in the IFPEN 10 kW<sub>th</sub> pilot and CHEERS demonstration unit).

At later stage, the agglomeration issue of T2 was reduced after modifying the test protocols, so it was selected as the 3<sup>rd</sup> candidate oxygen carrier for the pilot scale testing.





*Figure 5.4-5: Agglomerated ring of ilmenite.* 

#### c. Ilmenite morphological evolution

The three ilmenite samples have been characterized before and after the 250 cycles ageing tests with methane fuel, with a special focus on morphological evolution.



*Figure 5.4-6: Particle size distribution of fresh Titania 1 (sieved) and Titania 2, measured by laser granulometry.* 

Titania 1 and 2 come from the same mine, and as such, do not differ much, except Titania 2 has been dried, and sieved at a slightly larger particle size, as measured by laser granulometry (Figure 5.4-6). The mean particle size ( $D_v^{50}$ ) of sieved Titania 1 is 252 µm, and that of Titania 2 is 267 µm.

XRD analysis confirms that there is little difference between both samples,  $FeTiO_3$  (ilmenite) and  $Fe_2O_3$  (hematite) being the predominant detected phases, along with silicate-based impurities. The particles are very angular (Figure 5.4-7 and Figure 5.4-8), and literally non porous (0 ml/g porous volume, as measured by Hg porosimetry).





Figure 5.4-7: SEM pictures of fresh Titania 1 particles (left: direct observation; right: polished cross-section).



Figure 5.4-8: SEM pictures on polished cross-section of fresh Titania 2 particles.

The brighter areas in the polished cross-section pictures in Figure 5.4-7 and Figure 5.4-8 are constituted mainly of Fe and Ti oxides, while the darker areas are made of Si oxide mixed with other impurities. Based on the available characterization data, it is not possible to differentiate the sieved Titania 1 from Titania 2, except for the (very) small difference in particles size distribution. It is hence difficult to understand their different behaviour with regards to agglomeration during the ageing tests.





Figure 5.4-9: SEM pictures of Titania 1 after 250 redox cycles (left: direct observation; right: polished cross-section).



Figure 5.4-10: SEM pictures of Titania 2 after 250 redox cycles (left: direct observation; right: polished cross-section).

After 250 redox cycles in batch fluidized bed, the morphological evolution of Titania 1 and 2 is similar (Figure 5.4-9, Figure 5.4-10): in both samples, a large porosity increase of the particles is observed, which probably accounts for the reactivity increase observed during the first 50 cycles. EDS cartography of the aged particles (Figure 5.4-11) shows that Fe and Ti are segregated within the particles, with iron forming round shaped nodules both inside and at the surface of the particles.





Figure 5.4-11: SEM (left) and EDS (right) pictures of Titania 1 after 250 redox cycles, showing Fe and Ti distribution.

The morphological evolution of the Vietnamese ilmenite particles upon ageing (Figure 5.4-12, Figure 5.4-13) is very similar to that of Titania particles, in spite of a slightly different initial composition (35% TiO<sub>2</sub>, 22% Fe + Si based impurities).



Figure 5.4-12: SEM pictures of Vietnamese ilmenite particles (left: direct observation; right: polished cross-section).



Figure 5.4-13: SEM pictures of Vietnamese particles after 250 redox cycles (left: direct observation; right: polished cross-section)



#### 3.4.2 Kinetic screening

After 50 redox cycles pre-ageing of samples with methane, petcoke is injected in the oxygen carrier bed. In the presented study, a petcoke from TEOT noted petcoke T3 has been used since no Chinese one had been selected yet. Figure 5.4-14 shows the gaseous components profiles at the reactor outlet during the petcoke conversion stage. This particular curve has been obtained at 940°C with 50% of steam in the inlet gas.



Figure 5.4-14: CO<sub>2</sub> and CO concentration evolution at the reactor outlet during petcoke conversion in the batch fluidized bed reactor (at 940°C with 50% of steam in the inlet gas).



Figure 5.4-15: Impact of temperature and steam concentration on petcoke conversion in the batch fluidized bed unit. Test on petcoke from TEOT with Ilmenite Titania 2 as oxygen carrier.

When petcoke is injected in the reactor, volatiles are instantly released and burnt. After that, the gasification reaction takes place within several minutes. From these results, it is clearly visible that the limiting step of petcoke conversion is its gasification rate. It does not change when one ilmenite or another is used as oxygen carrier. However, unlike Titania ilmenites, the ilmenite from Vietnam does not fully convert carbon monoxide into carbon dioxide. No differences have been observed between T1 and T2 except agglomeration has been



observed in T2 (c.f. Figure 5.4-5). Due to that problem, Titania 1 would be preferred over Titania 2 to reduce as much as possible the agglomeration occurrence in low fluidization zones of the bigger units (L-valves and loop seals in the IFPEN 10 kW<sub>th</sub> pilot and CHEERS demonstration unit). At later stage, the agglomeration issue of T2 was reduced after modifying the test protocols, so it was selected as the 3<sup>rd</sup> candidate oxygen carrier for the pilot scale testing.

Ilmenites T1 and T2 from Titania was, based on results above, selected for pilot testing. The materials were delivered in tonne scale to the partners SINTEF ER and IFPEN.



## 4 TESTING AT PILOT SCALE

The public deliverable D3.3 [9] summarizes the pilot unit testing performed, being the last validation step before choosing a suitable oxygen carrier for use in the CHEERS demonstration unit. Three different OCs have been tested in the pilot units. They were chosen among many candidates that were evaluated and summarized in this deliverable.

The first candidate was a Norwegian ilmenite, a relatively cheap natural mineral that is well-known as OC in CLC, however, not so much with petcoke as fuel. The second candidate was a synthetic perovskite material, i.e., a material made from the bottom based on raw materials containing calcium, manganese, titanium, and iron, hence the short name CMTF. This will be much more costly and should show better performance to be competitive. The third material was a manganese ore from China, LY Mn-ore, that was delivered as small stones which were calcined and thereafter crushed, milled, and sieved.

During testing in a batch fluidised bed unit with petcoke, it showed up that the CMTF material became deactivated by fuel sulphur, even though it is a low-sulphur petcoke (~ 0.8 wt-% dry). For the CHEERS demonstration unit operation on petcoke it was concluded it could not be used. A second ilmenite material was then chosen as the final candidate for pilot testing.

The CHEERS project has two pilot units available: The 10 kW<sub>th</sub> unit at IFPEN and the 150 kW<sub>th</sub> unit at SINTEF ER, both being able to operate on solid fuels such as petcoke and biomass. They are quite different in design and way of operation, but together they cover the needed window of operating conditions.

Studies at IFPEN of the performance of oxygen carrier (OC) materials were done in two different reactors: a batch fluidised unit and the 10 kW pilot unit. Combustible conversion performances have been determined for each OC, and their structural evolution was monitored. Studies at IFPEN have shown that agglomeration issues observed during tests with the second ilmenite could be limited by adding steam throughout the test.

Results from SINTEF ER 150 kW pilot show equal performance of the two ilmenites for both biomass and petcoke fuels. LY Mn gives a slightly higher petcoke conversion than the ilmenites, but the fuel reactor gas conversion efficiency is generally lower.

Hot attrition testing by SINTEF MK shows that LY Mn has higher attrition rate and fines production than the ilmenites. i.e., lifetime will be shorter. This is also confirmed from the 10 kW pilot tests at IFPEN.

Due to their performance and interesting price, the ilmenites have been selected as the most promising candidates to be used in the CHEERS demonstration unit in China. The first ilmenite, T1, requires an additional sieving step to be in the correct particle size range, which is not the case with the second ilmenite, T2. Finally, as long as the agglomeration issues can be controlled by steam addition and careful fluidization of low-velocity and dense zones, the second ilmenite, T2, is the best candidate to be used in the CHEERS demonstration unit.



## 5 DELIVERY OF SELECTED MATERIAL FOR TESTING IN CHEERS DEMONSTRATION UNIT

250 tonnes of ilmenite T2 were delivered to China for sieving and testing in the European design configuration.



Figure 7-1: The transportation and product delivered at the CHEERS demonstration unit at Dongfang Boiler (Deyang, Sichuan Province).

Ilmenite T2 had a more suitable size distribution than T1 and was selected for CHEERS demonstration unit at Dongfang Boiler (Deyang, Sichuan Province). The mass needed was based on filling and lifetime prediction for two different configurations for the demonstration plant; ca. 160 tonnes of oxygen carrier material (OCM) were needed for the European test campaign in their design and 90 tonnes for the Chinese design. Availability, size fraction and cost were also crucial for the selection.



## 6 POST-CHARACTERISATIONS OF ILMENITE FROM CHEERS DEMONSTRATION UNIT

#### 6.1 Solid sampling

To monitor the evolution of the activity of the ilmenite along the different tests and to be able to measure the  $R_0\Delta X$ , several sampling points were installed at various positions in the unit.

One sampling point was installed in the DFB dense phase to monitor the effectiveness of the oxidation of the ilmenite at the AR outlet (DFB Sample). At this position, the ilmenite is in its most oxidized state. Two other sampling points were installed in the FR bottom dense phase (FR Sample) and in the Carbon Stripper to sample ilmenite in reduced state.

For the march 2024 operational test, ilmenite sampling was made using the sampling device described below. In the left part of Figure 8.1-1, we can see the sampling probe constantly inserted, up to the flange, in the process and constantly flushed with  $CO_2$  to prevent any plugging. In the right part of Figure 8.1-1, and Figure 8.1-2, the collecting part of the sampling system is presented. After a flush of  $CO_2$  to clean the sampling system and with the use of a vacuum pump at the end, the system under vacuum allows sampling around 300 g each time. The hot sample collected at the bottom of the sampling cyclone is then cool down in a  $CO_2$  atmosphere. This is done before it comes in contact with air to avoid reoxidation. Once cold, the ilmenite sample can be extracted and analysed with a muffle furnace test.



Figure 8.1-1: Sampling device schematic description.





Figure 8.1-2: Sampling device picture

## 6.2 Characterization of samples from the CHEERS demonstration unit

Five samples have been delivered to SINTEF MK for post-characterisations (Figure 8.2-1).

- 1) Sample No 1: Fresh ilmenite delivered and sieved.
- 2) Sample No 2: Pre-oxidized OCM loaded into reactor
- 3) Sample No 3: FR
- 4) Sample No 4: DFB
- 5) Sample No 5: OCM unloaded from reactor

05/03/24 17:00 19/03/24 14:20 19/03/24 15:00 02/04/24 (end of run from FR)





Figure 8.2-1: Ilmenite samples at different time slot during operation.

T2 has been sieved to obtain particles in the fraction 180-300 $\mu$ m, "as delivered" is this a dense particle (see Figure 8.2-2 below for optical view and Figure 8.2-3 for SEM-EDS). Most particles have similar colour and an angular shape. The EDS shows also that the FeTiO<sub>3</sub> phase is homogeneous.



Figure 8.2-2: Dense ilmenite (No 1) particles as delivered.

Figure 8.2-3 shows fresh ilmenite as it is; dense and rough shapes after crushing and sieving. Figure 8.2-4 shows the pre-oxidized samples before loaded into the reactor. The pre-oxidation step only get the particles into a full oxidized inventory, activation will not occur during this phase and findings are as expected. Figure 8.2-5 shows activated ilmenite (No 3) running in the fuel reactor (FR). Ilmenite particles in various states of "activation/degradation", from homogeneous particles (green arrows) to activated Ti-oxide core (Blue) – Feoxide shell (Red). One should note that no detrimental activation resulting in collapse of particles has been observed. Less degradation is expected based on earlier experience by comparing laboratory test and reactor tests, showing less degradation in reactor test, which is related to less deep and detrimental reduction of materials in a CLC reactor. No ash particles have been observed in the OC extracted from this location in the



fuel reactor. Figure 8.2-6 shows similar extraction of ilmenite (No 4) from the air reactor (AR), with also a broad range of particles from fresh to activated, related to new materials added continuously to replace loss of oxygen carrier in the cyclones. But the amount of activated particles is dominating which is important for the performance of the reactor. Figure 8.2-7 shows sample No 5 OC unloaded after the testing in the CHEERS demonstration unit. Similar to the one harvested during the test campaign, but with higher degree of particles with different residence time in the reactor, based on the continuous replacement of lost mass with fresh particles, The high degree of fresh samples in No 5 is expected and coherent with experience on site. The last feedstock used was "grinded petcoke" with a very low PSD (more than half of the particles below 45  $\mu$ m). This PSD did not allow high residence time in FR (particles easily entrained) and furthermore, high loss at the cyclone which were not designed for such low PSD. Consequently, this impacted the reduction degree in FR which was low as well. With the dilution of the make-up, the overall activation degree of the inventory is low.

optical image, bright field



SEM, atomic mass contrast (BSE)





EDS: Ti, Fe oxides

EDS: Al, Si, Mg, Ca oxides



Figure 8.2-3: Shows cross section of fresh ilmenite (No 1), and reveal that it has some small fractions of separate secondary phases of silicates and aluminates.





Figure 8.2-4: Shows the pre-oxidized ilmenite (No 2) loaded into the reactor (surface oxidized to avoid agglomeration).



Figure 8.2-5: Shows the activated ilmenite (No 3) running in the fuel reactor (FR). Ilmenite particles in various states of "activation/degradation", from homogeneous particles (green arrows) to activated Ti-oxide core(Blue) – Fe-oxide shell (Red). No ash particles seen in the OC extracted from this location in the fuel reactor.



Figure 8.2-6: Shows similar extraction of ilmenite (No 4) from the air reactor (AR). Same colour legend and explanation as in the figure above is the case also here.





Figure 8.2-7: Shows sample No 5 OC unloaded after the testing in the CHEERS demonstration unit. Similar to the one harvested during the test campaign, but with higher degree of particles with different residence time in the reactor, based on the continuous replacement of lost mass with fresh particles.

#### Summarizing the findings from CHEERS demonstration plant concerning the OCM:

- Post-characterisation of ilmenite from the CHEERS demonstration unit shows no contamination from petcoke during the test campaign.
- Regular redox degradation/activation is seen as expected and needed for having a sufficiently active oxygen carrier material
- The bed contain low amount of very activated materials, which might be due to limited test campaign period and the high make-up flow used.
- No agglomeration has been observed in the samples.
- The particles are well activated but the bed contains an even distribution of fresh to activated particles, since new mass is continuously added to replace the particles lost in the cyclone.
- The level of attrition is as expected (round shape of those particles that are more activated, i.e., have been longer in operation in the unit than those that are recently added).
- No critical degradation of the ilmenite is observed
- The injection system of the ilmenite (Bucket elevator, screws, rotary valve) works as intended as long as the ilmenite is dry.

Post-characterisations of the selected ilmenite T2 verify that it survived under the test conditions without notable influence of sulphur and ash.



## 7 CONCLUSIONS

Based on the performance in the lab testing and all the evaluation criteria, three main candidates have been selected and fabricated, for a larger scale testing in pilot units at IFPEN and SINTEF ER.

Candidate 1: Ilmenite T1 (standard product  $d_{50}$ =110 µm) from Titania has shown good performance at high temperatures from TGA measurements and relatively good stability. In addition, it is also easy for larger amount testing in later stages, since it is easily available and can be delivered in fraction 180-300 µm after sieving, but have less than 25 % of the particles in this range. Ilmenite from Titania AS was selected as the first candidate state of the art material for design purpose.

Candidate 2: LY Mn ore also passed the testing in the presence of petcoke. The minerals were purchased from China, thermal treated, crushed, sieved (Figure 9-1) and delivered to IFPEN and SINTEF ER.



Figure 9-1: Sieving equipment in Luoyang, Henan province.

Candidate 3: Ilmenite T2 (a sieved product with  $d_{50}$ =217 µm) from Titania had some initial agglomeration problems but was found to be caused by the test protocol used. After a change in the protocol, this material works well and was selected as the third candidate, since T2 also have a more suitable  $d_{50}$  than T1, having 85 % of the particles in the size range 180-300 µm, meaning less waste during sieving. This material was finally selected as the material for CHEERS demonstration in China unit and 250 tonnes of T2 was delivered from Titania AS in Norway. This material was successfully tested in the CHEERS demonstration unit, after some initial issues with the rig.

Post-characterisation of ilmenite from the CHEERS demonstration unit shows no side effect related to contamination from petcoke during the test campaign, except from regular redox degradation. No agglomeration was seen in the samples. The particles are well activated but the bed contains an even distribution of fresh to activated particles, since new mass is continuously added to replace the particles lost in the cyclone.



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