

1 **Titanium Substituted Manganese-Ferrite as an Oxygen Carrier with Permanent Magnetic Properties**
2 **for Chemical Looping Combustion of Solid Fuels**

3 María Abián, Alberto Abad*, María T. Izquierdo, Pilar Gayán, Luis F. de Diego, Francisco García-Labiano,
4 Juan Adánez

5 Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán, 4, Zaragoza, E-50018, Spain.

6 Corresponding author: *Phone: + 34 976 733 977. Fax: +34 976 733 318. E-mail: abad@icb.csic.es

7 **Abstract**

8 Mixed oxides of Mn-Fe have been identified as suitable materials for Chemical Looping Combustion (CLC)
9 with solid fuels both via *in-situ* Gasification Chemical Looping Combustion (*iG*-CLC) and Chemical Looping
10 with Oxygen Uncoupling (CLOU) processes. These materials show the property of react with gaseous fuels as
11 well as release oxygen under given conditions, while cheap metals are used. In addition, these materials can
12 show magnetic properties that can be used for an easy separation from ash in CLC with solid fuels. Thus,
13 losses of oxygen carrier material in the ash drain stream would be reduced. Different cations have been
14 proposed for improving the magnetic properties of manganese ferrites, including Ti^{4+} . In this context, the
15 present work accomplishes a screening of $(Mn_xFe_{1-x})_2O_3$ doped with 7 wt.% TiO_2 , with x ranging from 0 to 1.
16 The influence of Mn:Fe ratio on their physical and chemical properties was evaluated. In general, particles
17 with high crushing strength values (>4 N) were obtained, and magnetic characteristics were highlighted when
18 $x \leq 0.66$. The oxygen uncoupling capability depended on the Mn:Fe ratio and the oxidation conditions, i.e.
19 temperature and oxygen partial pressure. Broader oxidation conditions to take advantage of the oxygen
20 uncoupling capability were found for materials with low Mn content. On contrary, the reactivity with fuel
21 gases (CH_4 , H_2 and CO) increased with the Mn content. Thus, oxygen carriers with Mn/(Mn+Fe) molar ratio
22 in the 0.5-0.9 interval showed interesting properties at suitable temperatures for the *iG*-CLC and CLOU
23 processes (i.e. 850-980 °C). The material with Mn/(Mn+Fe) = 0.55 was preferred considering a trade-off
24 between reactivity and magnetic properties.

25

26 **Keywords:** CO_2 capture, Chemical Looping Combustion, Oxygen carrier, Manganese oxide, Iron oxide.

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28

29 1. Introduction

30 Nowadays, research involving the reduction of net CO₂ emissions to the atmosphere from combustion systems
31 is still a challenge. Emerging combustion processes with intrinsic CO₂ capture, such as Chemical Looping
32 Combustion (CLC), are of increasing interest since no energy or equipment is needed for gas separation as
33 compared with the classic CO₂ capture systems (pre, post and oxyfuel combustion) [1]. Chemical Looping
34 Combustion (CLC) implies the use of an oxygen carrier, generally a metal oxide, to transfer the oxygen from
35 the air to the fuel. A CLC system basically consists of two interconnected fluidized beds, namely fuel and air
36 reactors, with a particulate oxygen carrier continuously circulating between them [2]. In the fuel reactor, the
37 fuel is combusted taken oxygen from the oxygen carrier, while the oxygen carrier is re-oxidized with air in the
38 air reactor. Thus, the direct contact between fuel and air is avoided and, the CO₂ capture is inherent to the
39 CLC process.

40 Mainly, the use of solid fuels in CLC is being developed by two different approaches: *in-situ* Gasification
41 Chemical Looping Combustion (*iG*-CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) [3]. In
42 *iG*-CLC, the solid fuel is gasified by steam and/or carbon dioxide; then the generated gaseous products
43 (mainly CO, H₂ and CH₄) react with the oxygen carrier to produce the combustion products (CO₂ and H₂O).
44 When coal is considered the fuel, loss of oxygen carrier particles is expected in the drainage flow of ash.
45 Thus, low cost materials such as ilmenite [4-6], iron ore [7-9], manganese ore [10] or waste materials [11]
46 have been mostly evaluated for *iG*-CLC in pilot units up to 1 MW_{th}. In these cases, high CO₂ capture was
47 achieved, but complete combustion was not reached [12]. In CLOU, the oxygen carrier is able to evolve
48 gaseous oxygen in the fuel reactor, thus allowing the combustion of the solid fuel with O₂. The CLOU process
49 was proposed by Mattisson et al. [13] to improve the combustion of solid fuels. Then, the proof of the concept
50 was performed in a 1.5 kW CLOU unit by Abad et al. [14]. High CO₂ capture rates with complete combustion
51 of different solid fuels (coal, lignite, biomass) was achieved by using a Cu-based oxygen carrier [14-16].

52 Alternatively to Cu-based materials, Mn-Fe mixed oxides have been identified as suitable materials for
53 CLOU, while cheap and environmental friendly metals are used [17]. Bixbyite phase, (Mn_xFe_{1-x})₂O₃, must be
54 formed during oxidation in order to show oxygen uncoupling capability during reduction to spinel phase,

55 $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ [18]. Thus, coal combustion was improved by taking advantage of the oxygen uncoupling
56 capability of bixbyite when oxidation in the air reactor was optimized [19]. In addition, spinel phase $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$
57 can be reduced by fuel gases (e.g. H_2 , CO , CH_4) to manganowüstite $(\text{Mn}_x\text{Fe}_{1-x})\text{O}$, thus being active for
58 iG-CLC [20-23].

59 The influence of the Mn:Fe ratio on the suitability of Mn-Fe mixed oxides for CLOU have been evaluated in
60 the literature [21-25]. In general, oxygen carriers with Mn:Fe ratios higher than 0.6 show better fuel gas
61 conversion and oxygen uncoupling capability at lower temperature (850 °C) than oxygen carriers with lower
62 Mn:Fe ratios. But the potential for the oxidation to bixbyite improved as the Mn:Fe ratio was decreased [23].
63 i.e. they can be oxidized at higher temperatures, e.g. 950 °C, than materials with high Mn:Fe ratio.

64 Although manganese and iron can be considered as cheap materials, Mn-Fe mixed oxide materials must be
65 synthesized, thus increasing its prize compared to low-cost materials such as natural ores. Therefore, it would
66 be very interesting the recovering of lost oxygen carrier particles with the ash. In this sense, Mn-Fe mixed
67 oxides show magnetic properties in the spinel phase [26, 27], which could be used for a magnetic separation
68 from ash. In addition, different cations have been proposed for improving the magnetic properties of
69 manganese ferrites, e.g. by dopping Mn-Fe mixed oxides with Ti^{4+} [28]. However, the magnetic properties of
70 Mn-Fe mixed oxides in oxygen carriers for chemical looping applications have been not studied.

71 An oxygen carrier should accomplish the following characteristics: sufficient oxygen capacity, favorable
72 thermodynamics regarding the fuel conversion to CO_2 and H_2O , high reactivity for reduction and oxidation
73 reactions maintaining it during many successive redox cycles, resistance to attrition, negligible carbon
74 deposition, good fluidization properties and environmental friendly characteristics [3]. In a previous work, Fe-
75 Mn mixed oxides particles were obtained by mechanical mixing of Mn_3O_4 and Fe_2O_3 powders (Mn:Fe molar
76 ratio of 0.77:0.33), which showed relatively high reactivity and crushing strength values ($> 1\text{N}$) [29]. Also,
77 particles were prepared by doping with TiO_2 a material prepared by spray drying with Mn:Fe molar ratio of
78 0.66:0.34. These particles were successfully tested in a continuously operated CLC unit burning coal [19].

79 In this context, in the present work a screening of the performance of Mn-Fe-Ti based oxygen carriers,
80 prepared with different Mn:Fe molar ratios and a fixed TiO_2 concentration, is performed. The characterization
81 of the oxygen carriers has been based on the evaluation of their mechanical strength, the reduction and

82 oxidation rates through TGA experiments at temperatures suitable for the *i*G-CLC and CLOU processes (i.e.
 83 850-950 °C), and the determination of the magnetic susceptibility of the particles as a reference value to
 84 evaluate the applicability of the magnetic separation from ash.

85 2. Experimental

86 2.1. Oxygen Carriers

87 The oxygen carrier particles were prepared using as raw materials Mn₃O₄ (Strem Chemical, Inc), Fe₂O₃
 88 (Panreac, Prs), and TiO₂ (Panreac, Prs), all of them in powder. The mass fraction of TiO₂ was fixed to 7 wt.%,
 89 which was the fraction used in a previous tested material [19], but the Mn:Fe molar ratio was varied in a broad
 90 interval; see Table 1. To prepare the oxygen carriers, the reactants, in their respective mass fractions, were
 91 firstly ball-milled for 30 min and subsequently pelletized by pressure in a hydraulic press at 160 bar for 60 s,
 92 obtaining cylindrical pellets of about 1 cm in diameter and 3 cm in length. The pellets were further calcined at
 93 1200 °C in a muffle furnace during 2 hours both, to increase the mechanical strength of the particles and to
 94 provide the material with permanent magnetic properties, considering results showed in [30]. In some cases,
 95 calcination at higher temperatures was required to provide magnetic properties. After calcination, materials
 96 with a general formula Mn_xFe_{1-x}Ti_yO_z were obtained. Finally, the pellets were crushed and sieved to obtain
 97 particles with a particle diameter of 100-300 μm.

98

99 **Table 1.** Chemical composition, calcination temperature, crushing strength, magnetic permeability and main
 100 phases (XRD) of the oxygen carriers.

Oxygen carrier*	Mn/(Mn+Fe) molar ratio	Mass fraction Mn ₃ O ₄ :Fe ₂ O ₃ :TiO ₂	T _{calc} (°C)	Crushing strength (N)	Magnetic permeability (-)	Main phases
FeTi7	0.00	0:93:7	1200	3.8	1.0	Fe ₂ O ₃ Fe ₂ TiO ₄
Mn28FeTi7	0.28	25:68:7	1200	5.8	5.8	Mn _{1.03} Fe _{1.97} O ₄ Mn ₂ FeO ₄ Fe ₂ O ₃ Fe _{1.5} Ti _{0.5} O ₃
Mn55FeTi7	0.55	50:43:7	1200	4.3	8.3	Mn ₂ FeO ₄ Mn ₃ Fe ₃ O ₈ Fe ₂ TiO ₄
Mn66FeTi7	0.66	60:33:7	1200	3.8	7.8	Mn ₂ FeO ₄ Mn _{1.58} Fe _{1.42} O ₄ Fe ₂ TiO ₄
Mn87FeTi7	0.87	80:13:7	1200 1300 1350 1400	4.7 4.4 4.5 5.4	1.0 1.2 1.2 1.2	Mn ₂ FeO ₄ Mn ₃ O ₄ FeTiO ₄

MnTi7	1.00	93:0:7	1200 1400	5.1 4.8	1.0 1.0	Mn ₂ O ₃ Mn ₃ O ₄ MnTiO ₃
* The nomenclature shows the stoichiometric coefficient x and y in the general formula Mn _x Fe _{1-x} Ti _y O _z						

101

102 The crushing strength of the particles was measured using a Shimpo FGN-5X crushing strength apparatus.

103 The value reported for each oxygen carrier is the average value of 20 measurements of the force needed to

104 fracture a particle. The magnetic permeability was measured using a Bartington single frequency MS2G

105 sensor connected to a magnetic susceptibility MS3 meter. Additional information about the determination of

106 magnetic permeability is shown in the Supplementary material S1.

107 The main phases of the Mn-Fe-Ti system were identified through characterization by X-ray diffraction

108 (XRD). The XRD analysis was performed using a Bruker D8 Advance X-ray powder diffractometer equipped

109 with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-

110 dimensional detector. In particular, the diffraction pattern was obtained with a scanning rate of 0.019° over the

111 2θ range of 10° to 80°, and the assignation and quantification of crystalline phases was performed through the

112 use of the DIFFRAC.EVA and TOPAS software, on base of Joint Committee on Powder Diffraction

113 Standards. The XRD results correspond to the analysis of the oxygen carrier particles obtained after the

114 calcination of the pellets at 1200 °C.

115 The oxidation state of Fe, Mn and Ti was studied by XPS in an ESCAPlus Omicron spectrometer equipped

116 with a non-monochromatized MgKα radiation (1253.6 eV). The hemispherical electron energy analyzer was

117 operated at pass energy of 50 eV for surveys, and 20 eV for high-resolution spectra. Binding energies (BE)

118 were referenced to the C1s peak (284.5 eV) from adventitious carbon contamination. Current region sweeps

119 for O1s, Fe 2p, Ti2p, Mn2p and Mn3s were obtained. The CASA data processing software allowed

120 smoothing, background subtraction, peak fitting and quantification.

121 2.2. Thermogravimetric analyzer (TGA) and procedure

122 The experiments were performed in a thermogravimetric analyzer (TGA CI Electronics). The detailed

123 description of the TGA and procedure can be found elsewhere [31] and therefore only a brief description is

124 given here. The oxygen carrier mass and gas flow used in the TGA experiments were chosen to avoid

125 limitations in the external film mass-transfer and/or inter particle diffusion. For each test, around 50 mg of

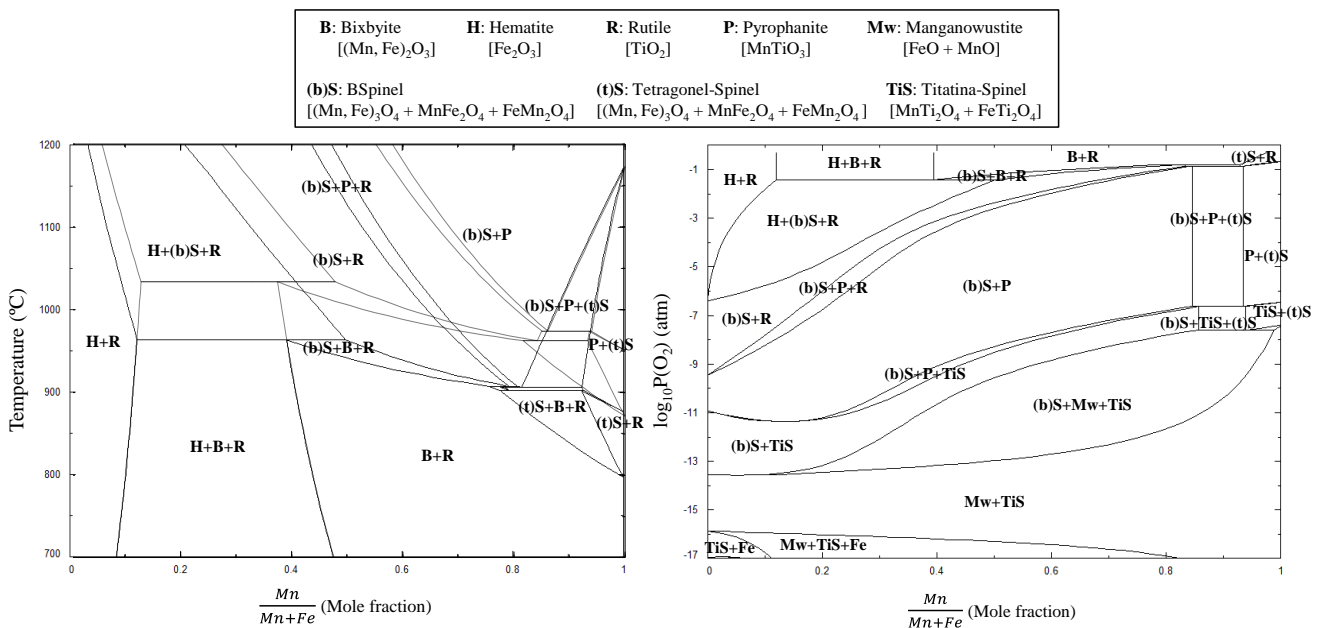
126 oxygen carrier particles were loaded in a platinum wired mesh basket and heated up to the desired temperature

127 (850, 900 or 950°C) in an air atmosphere. After stabilization, the oxygen carrier particles were exposed to five
 128 successive reduction-oxidation cycles. Both, reduction and oxidation periods were, respectively, 30 minutes.
 129 Reduction was carried out with H₂ (5 % H₂ + 40 % H₂O), CO (15 % CO + 20 % CO₂) or CH₄ (15 % CH₄ + 20
 130 % H₂O). A lower concentration was used with H₂ in order to avoid reduction of iron oxide to metallic iron,
 131 which is not interesting for CLC [32]. In addition, the oxygen uncoupling capability was evaluated by
 132 exposing the solid sample to an inert environment (100 % N₂). The oxidation was carried out either in air or 5
 133 vol.% O₂. A gas flow of 25 L/h (STP) was used in all cases. In general, except for the first cycle, no
 134 significant changes in the reactivity to the fuel gases, neither in the oxygen carrier regeneration, were
 135 observed through the successive redox cycles. All the results shown in the present work correspond to the
 136 third redox cycle.

137 3. Results

138 3.1. Phase diagram of the Mn-Fe-Ti-O system

139 The phase diagrams for different Mn:Fe ratio in the Mn-Fe-Ti-O system as function of the temperature and
 140 oxygen partial pressure are shown in Figures 1(a) and 1(b), respectively. FToxid database from the FactSage
 141 software was used [33]. According to the phase diagrams shown in Figure 1, seven phases in the (Mn_xFe_{1-x})
 142 Ti_{0.15}O_z system are thermodynamically stable, which are distributed in different regions depending upon the
 143 given oxygen partial pressure, temperature and the Mn:Fe ratio.



144

145 **Figure 1.** Phase diagram of the (Mn_yFe_{1-y})Ti_{0.07}O_x system as function of the Mn-Fe composition and (a)

146 temperature in either 0.05 (solid lines) or 0.21 atm O₂ (dot lines), and (b) partial pressure of O₂ at 950 °C.

147

148 Focused in the oxidation of Mn-Fe mixed oxides, equilibrium conditions at the air reactor exit are evaluated in
149 Figure 1(a); that is in 5 vol.% O₂ assuming 25 vol.% of air excess, similar to the excess used in conventional
150 combustion. In general, low temperature regions are dominated by bixbyite phases, while spinel phase appear
151 in the upper temperature region. The temperature for the bixbyite to spinel transformation monotonically
152 decreases from the transformation temperature for Fe₂O₃/Fe₃O₄ (1600 °C) to Mn₂O₃/Mn₃O₄ (800 °C) as the
153 Mn:Fe ratio increases. In the lower temperature regions, the hematite Fe₂O₃ and rutile TiO₂ phases coexist for
154 Mn contents lower than about 0.1. At increased Mn ratios bixbyite phase appears separated from Ti-
155 containing phases at the expense of the hematite phase; eventually bixbyite and rutile coexist as separated
156 phases for Mn/(Mn+Fe) ratios higher than 0.4-0.48. At higher temperatures, bixbyite or hematite is
157 completely transformed to spinel. Rutile and β-spinel dominates the regions with lower Mn content, while
158 pyrophanite (i.e. the manganese rich ilmenite MnTiO₃) and tetragonal spinel appear as the Mn content
159 increases.

160 **3.2. Crushing strength, XRD and magnetic permeability evaluation**

161 The crushing strength of all the particles prepared in the present work are around 4-5 N; see Table 1. A
162 minimum of 3.8 N was obtained for Mn₆₆FeTi₇, and the crushing strength was monotonically increased as
163 the Mn content either increased or decreased, excepting for FeTi₇ that showed a crushing strength of 3.8 N.
164 Similar results were obtained by Azimi et al. [24], but higher crushing strength values are here obtained.
165 Different preparation method, calcining temperature or the presence/avoidance of Ti can be argued to justify
166 the different crushing strength here obtained. However, similar particles but without Ti showed crushing
167 strength values around 2-3 N [29], suggesting that the improvement here shown could be mainly attributed to
168 the presence of Ti. Usually, oxygen carriers with a crushing strength above 1-2 N [34,35] have been identified
169 in previous works to be more likely resistant to attrition in continuous operation, which points to the potential
170 of these Mn-Fe-Ti based oxygen carriers for providing a good mechanical stability for CLC applications. This
171 is an interesting result since the material screening will not be conditioned by the mechanical strength of the
172 particles, but to the analysis of the effect of Mn:Fe ratio on the redox kinetics and the magnetic properties.

173 The revealed phases by XRD and magnetic permeability values resulted a function of the Mn-Fe relation and
174 the calcination temperature. Thus, only the oxygen carriers with Mn/(Mn+Fe) molar ratios between 0.28 and
175 0.66 showed magnetic properties when they were calcined for 2 h at 1200 °C, with magnetic permeability
176 values in the 5.5-8.5 interval. These particles were characterized by the presence of Mn-Fe mixed oxides in
177 the spinel form, i.e. $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$. Calcination conditions promoted the formation of the spinel phase (see
178 Figure 1), which was not oxidized to bixbyite phase, $(\text{Mn}_x\text{Fe}_{1-x})_2\text{O}_3$, during the cooling stage after calcination
179 of the pellets in air. It is well known the magnetism showed by the Mn-Fe spinel [27-29], which justify this
180 result. Nevertheless, the oxygen carrier particles are partially oxidized to bixbyite phase during the oxidation
181 tests in TGA. Rutile, TiO_2 , was not detected by XRD, but rather Fe-Ti mixed oxides were formed.

182 For the Mn87FeTi7 material, limited formation of spinel phase was observed because of the low iron content
183 regardless the calcination temperature, but in any case bixbyite was not detected. However, magnetic
184 permeability was raised from 1.0 to 1.2 when calcining temperature was increasing from 1200 to 1400 °C.
185 Therefore, the existence of magnetic properties is not only guaranteed by the presence of spinel phase, but
186 also another factor should be considered. The reason for the effect of calcining temperature on the magnetic
187 permeability could be found in the shifting of the following equilibrium:



189 In a Mn-rich spinel, the spinel structure would show the following general distribution of cations:
190 $[\text{Mn}_{1-x}^{3+}\text{Fe}_x^{2+}]_A [\text{Mn}_{1+x}^{3+}\text{Fe}_{1-x}^{2+}]_B \text{O}_4$; where subscripts "A" and "B" denote tetrahedral and octahedral sites,
191 respectively [CITA??]. In fact, XPS results revealed that Mn is in the Mn^{3+} oxidation state for the Mn87FeTi7
192 material when the calcining temperature is 1200 °C. However, XPS analysis revealed the presence of both
193 Mn^{3+} and Mn^{2+} in the samples calcined at higher temperatures (i.e. 1300, 1350 and 1400 °C), which means
194 that part of the Mn^{3+} is transformed to Mn^{2+} . Consequently, some Fe^{2+} should be transformed into Fe^{3+} ,
195 according to equilibrium (R1). The variation in the oxidation state of Mn and Fe modifies their disposition in
196 the crystal structure, which also modifies the magnetic permeability of the material [28].

197 Taking into account XRD, XPS and magnetic permeability results, the following theory is postulated to
198 address the magnetic behavior of Mn87FeTi7 material as function of the calcining temperature. Mn87FeTi7
199 calcined at 1200 °C would show the $[\text{Mn}_{1-x}^{3+}\text{Fe}_x^{2+}]_A [\text{Mn}_{1+x}^{3+}\text{Fe}_{1-x}^{2+}]_B \text{O}_4$ spinel structure, which does not show

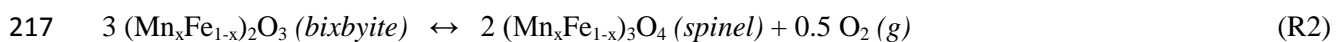
200 magnetic properties. The calcination at a higher temperature promoted the presence of Mn^{2+} and Fe^{3+} at the
201 expense of Mn^{3+} and Fe^{2+} both in the tetrahedral and octahedral sites leading to the formation of
202 $[Mn_{1-x-y}^{3+}Mn_y^{2+}Fe_{x-y}^{2+}Fe_y^{3+}]_A[Mn_{1+x-z}^{3+}Mn_z^{2+}Fe_{1-x-z}^{2+}Fe_z^{3+}]_B O_4$. The presence of Fe^{3+} ions both in the tetrahedral and
203 octahedral sites provides magnetic properties to the spinel structure [CITAS]. Thus, a higher calcining
204 temperature could result in higher magnetic properties.

205 On the contrary, neither the ilmenite surrogate ($FeTi_7$) nor the Mn-Ti based oxygen carrier ($MnTi_7$) showed
206 magnetic behavior independently on the calcination temperature (1200 to 1400 °C). In these cases, the
207 presence of Mn_2O_3 and/or Mn_3O_4 is highlighted. In addition, pyrophanite, $MnTiO_3$, was detected by XRD,
208 according to the phase diagram in Figure 1.

209 As a conclusion, high values of the magnetic permeability correspond to a ferrimagnetic behavior, and thus
210 would allow an easy separation of these carriers from the ashes. This property can be exploited for particles
211 with Mn/(Mn+Fe) ratios between 0.28 and 0.66. Particles calcined at 1200 °C were selected for further testing
212 and characterization, with the exception of $Mn_{87}FeTi_7$ which was calcined at 1300 °C.

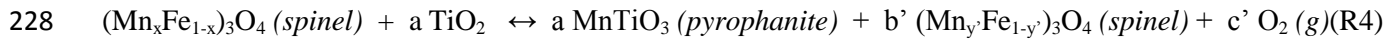
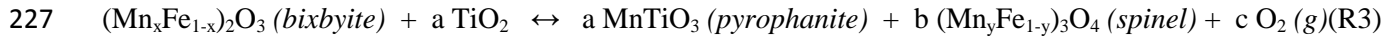
213 3.3. Oxygen transport capacity

214 The typical reaction involving the oxygen release for CLOU in these materials is the decomposition of
215 bixbyite ($Mn_xFe_{1-x}O_3$) to spinel ($Mn_xFe_{1-x}O_4$). Thus, bixbyite should be formed to take advantage of the
216 oxygen uncoupling capability of these materials; see reaction R1.



218 Between bixbyite and spinel phases there is a miscibility gap where bixbyite and spinel phases co-exist; see
219 Figure 1. This region is especially relevant for $Mn/(Mn+Fe) < 0.5$. However, the miscibility gap is
220 characterized by a low temperature difference for $Mn/(Mn+Fe)$ ratios in the 0.5-0.8 interval.

221 It is very interesting to note that a fraction of the Mn can also evolve oxygen via the formation of pyrophanite,
222 $MnTiO_3$, in the presence of Ti; see reactions R3 and R4 –additional information about the determination of
223 coefficients b, c and y in reactions R3 and R4 is shown in the Supplementary material S2–. This fact is
224 especially relevant for $Mn/(Mn+Fe) > 0.8$, when this transformation can occur at the vicinity of 900 °C.
225 However, for materials with high Mn content, bixtyite in the form of Mn_2O_3 only would be formed at a
226 temperature lower than 800 °C, which is not a temperature of interest for CLC with solid fuels.



229 In addition, Mn-Fe mixed oxides can be highly reduced to manganowüstite, $\text{Mn}_x\text{Fe}_{1-x}\text{O}$, in the presence of a
230 fuel gas, e.g. H_2 , CO or CH_4 [21]. To evaluate this issue, the phase diagram as a function of the oxygen partial
231 pressure is presented; see Figure 1(b). Regions in the upper oxygen pressure values are characterized by
232 bixbyite rich phases. As the oxygen partial pressure decreases, spinel rich phases are formed, following
233 reaction R2. As well, pyrophanite is formed for highly Mn-rich material following reactions R3 or R4. In
234 these cases, the oxygen uncoupling capability can be used due to these reactions take place spontaneously in
235 the fuel reactor where oxygen partial pressure is low. But manganowüstite, i.e. the more reduced phase
236 $\text{Mn}_x\text{Fe}_{1-x}\text{O}$, is formed at lower oxygen partial pressures. For practical purposes, this phase would be formed in
237 the presence of a reducing gas.

238 Considering re-oxidation in the air reactor, spinel phase can be easily formed at the air reactor conditions.
239 However, to take advantage of the oxygen uncoupling potential during successive cycles in the CLC system,
240 bixbyite needs to be effectively formed at the conditions of the air reactor via reverse of reaction R2. At the
241 relatively low partial pressure (5 vol.% O_2) the bixbyite regeneration is allowed for Mn/(Mn+Fe) molar ratios
242 lower than 0.5 at 950 °C. For higher Mn/(Mn+Fe) ratios a higher oxygen partial pressure or lower temperature
243 would be required to form bixbyite; see Figure 1.

244 From the above analysis it is concluded that oxygen carrier can be oxidized to bixbyite at suitable O_2 partial
245 pressure and temperature conditions. Then, bixbyite can transfer oxygen via oxygen uncoupling by reduction
246 to spinel, and a further reduction to manganowüstite can be exploited by reaction with a fuel gas. To evaluate
247 the fraction of available oxygen for every redox system, the oxygen transport capacity for a reaction i , R_{OC}^i , is
248 defined as the mass fraction of the oxygen carrier being transferable as oxygen:

249
$$R_{OC}^i = \frac{m_o^i - m_r^i}{m_{oxid}^i} \quad (1)$$

250 m_o^i being the initial mass of the sample, m_r^i the mass of the reduced sample and m_{oxid}^i the sample mass
251 assuming oxidation under a determined condition. Distinction among m_o^i and m_{oxid}^i was done to consider
252 uncomplete oxidation of the oxygen carrier particles after calcination or oxidation stages, i.e. $m_o^i < m_{oxid}^i$. In

253 addition, the maximum oxygen transport capacity, $R_{OC,max}^i$, was calculated assuming that all material was
 254 oxidized to bixbyite.

255 By knowing the theoretical oxygen transport capacity, the oxygen carrier conversion was calculated using
 256 Eqs. 2 and 3 for reduction and oxidation, respectively.

$$257 \quad X_{red}^i = \frac{m_o - m}{R_{OC,th}^i m_{oxid}} \quad (2)$$

$$258 \quad X_{ox}^i = \frac{m - m_r}{R_{OC,th}^i m_{oxid}} \quad (3)$$

259 For the oxygen uncoupling reaction, R_{OC}^{ou} is defined for reduction of bixbyite to spinel. When required, the
 260 presence of pyrophanite was also considered for the calculation of R_{OC}^{ou} . But for reduction with a fuel gas, R_{OC}^g
 261 is defined for reduction of the spinel phase to manganowüstite. The accumulated or total mass loss from
 262 bixbyite to manganowüstite is defined by $R_{OC}^t = R_{OC}^{ou} + R_{OC}^g$. Table 2 summarizes the theoretical and maximum
 263 values of these parameters, R_{OC}^{ou} and R_{OC}^t , for every oxygen carrier prepared in this work. The specific Mn-Fe
 264 composition of the different materials prepared in this work has been established to cover a wide range of
 265 Mn/(Mn+Fe) ratios on the basis of the phase diagram results shown in Figure 1. Theoretically, all the Ti
 266 substituted Mn-Fe mixed oxides materials show oxygen uncoupling, but FeTi7 does not show any interesting
 267 phase transformation unless a reducing gas was present.

268 **Table 2.** Oxygen transport capacity for gas-solid reactions, R_{OC}^t , and oxygen uncoupling, R_{OC}^{ou} at 950 °C; the
 269 subscripts “*max*”, “*th*” and “*exp*” denote maximum, theoretical and experimental values, respectively.

	FeTi7	Mn28FeTi7	Mn55FeTi7	Mn66FeTi7	Mn87FeTi7	MnTi7
$R_{OC,max}^{ou}$	0	3.1	3.1	3.6	3.6	3.6
$R_{OC,th}^{ou}$	0	3.1	3.1	3.6	2.8	0.47
$R_{OC,exp}^{ou}$	0	0.47	1.5	1.3	1.9	0.38
$X_{ou,exp}$	-	0.15	0.47	0.36	0.67	0.81
$R_{OC,max}^t$	9.3	9.4	9.4	9.4	9.4	9.4
$R_{OC,th}^t$	9.3	9.4	9.4	9.4	8.7	6.5
$R_{OC,exp}^t$	4.0	4.8	7.3	7.4	7.8	6.2
$X_{t,exp}$	0.49	0.51	0.78	0.80	0.90	0.96

270

271 For all the cases, the maximum oxygen uncoupling capacities are within the 3.1-3.6 interval, and the

272 maximum oxygen transport capacities for gas-solid reaction are within the 9.3-9.4. The maximum oxygen
273 carrier capacity achievement requires a suitable selection of the oxidation conditions in the air reactor, as
274 shown in Figures 1(a) and 1(b). Thus, according to this Figure, decreasing the Mn content of the carrier will
275 allow its fully oxidation to bixbyite at higher temperatures and/or lower partial pressure of O₂.
276 To evaluate the oxygen transport capability of prepared materials in this work, TGA experiments were carried
277 out by oxidizing the samples at 950 °C in air. Thus, the $R_{OC,th}^{ou}$ values are calculated by considering the stable
278 phase after oxidation at 950 °C in air. Under these conditions, Mn₂₈FeTi₇, Mn₅₅FeTi₇ and Mn₆₆FeTi₇ can
279 be fully oxidized to bixbyite with 3.7, 7.4 and 12.6 vol.% O₂, respectively. Thus, both the maximum and
280 theoretical ($R_{OC,th}^{ou}$ and $R_{OC,th}^{ou}$) were calculated to be 3.1 for Mn₂₈FeTi₇ and Mn₅₅FeTi₇, and 3.6 wt.% for
281 Mn₆₆FeTi₇. The higher $R_{OC,max}^{ou}$ and $R_{OC,th}^{ou}$ values for Mn₆₆FeTi₇ was due to the higher utilization of the
282 oxygen in the formation of some pyrophanite, MnTiO₃, with respect to the spinel. This was the case also for
283 $R_{OC,max}^{ou}$ in Mn₈₇FeTi₇. But in this case, only a partial oxidation to bixbyite would be only possible in air at
284 950 °C due to the miscibility gap observed for this material, and $R_{OC,th}^{ou}$ was correspondingly decreased to 2.8
285 wt.%. For MnTi₇, bixbyite is not formed in any extension at 950 °C in air. However, oxygen uncoupling was
286 associated to the appearance of pyrophanite, MnTiO₃, which allows a certain capability of oxygen uncoupling
287 for the spinel phase; see reaction R4.
288 Experimentally, any of the oxygen carriers reach their respective theoretical oxygen transport capability. The
289 differences between $R_{OC,exp}^{ou}$ and $R_{OC,th}^{ou}$ are in general increased as the Fe content is increased. Thus, the
290 maximum conversion of Mn₂₈FeTi₇ is 0.15 and that of MnTi₇ is 0.81. The oxygen carriers with intermediate
291 Mn/(Mn+Fe) molar ratios (0.55-0.87 interval) showed intermediate conversion values.
292 The differences found in the $R_{OC,th}^f$ values, depending upon the Mn/(Mn+Fe) ratio, are also related to the
293 phase transformations shown in Figure 1 when the oxygen partial pressure is varied. For the oxygen carriers
294 with a Mn/(Mn+Fe) ratio between 0.66 and 1, the $R_{OC,th}^f$ values shows a decreased tendency as the
295 Mn/(Mn+Fe) ratio is increased, whereas the $R_{OC,max}^f$ values are kept unaltered. This issue is related to a
296 progressive transformation of some of the mass in the oxidized state to spinel structures, with a more
297 pronounced degree of conversion as the Mn content is increased, due to the specific oxidation conditions

298 considered in the air reactor (i.e. 950 °C in air). This transformation counteracts the utilization of oxygen in
299 the system and consequently the $R'_{OC,th}$ decreases with increased Mn/(Mn+Fe) ratios.

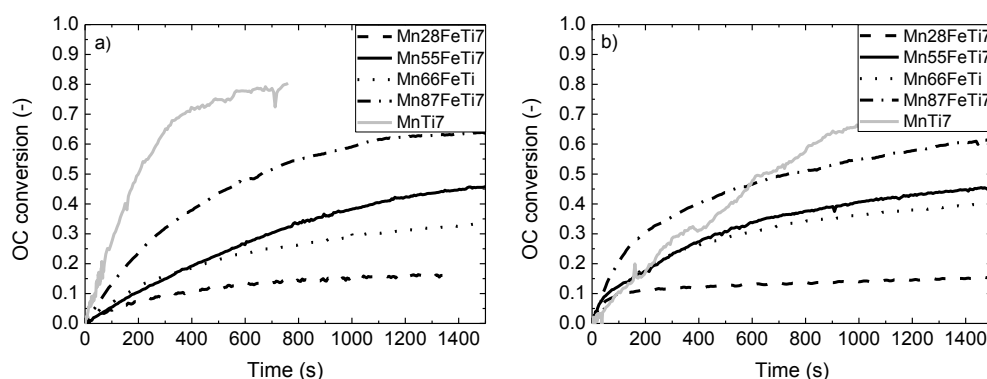
300 The experimental oxygen transport capacity for each oxygen carrier and operating condition was obtained
301 from reduction with H₂ in TGA; see Table 2. Only for MnTi7 the experimental $R'_{OC,exp}$ value lay within the
302 theoretical one, i.e. the solid conversion $X_{t,max}$ was close to unity; for the other carriers, the $R'_{OC,exp}$ values are
303 lower than the corresponding theoretical ones, with increased differences in $X_{t,max}$ as the Fe content in the
304 carrier is increased. This fact was related to the low degree of oxidation to bixbyite observed for these
305 materials; see $X_{ou,max}$ in Table 2. Nevertheless, the oxygen carriers with Mn/(Mn+Fe) molar ratios in the 55-87
306 interval showed the maximum experimental oxygen transport capacities.

307 3.4. Reactivity results

308 The evaluation of the oxygen carrier reactivity towards H₂, CO and CH₄, as well as its potential for oxygen
309 release have been done through isothermal redox cycles at 950 °C in TGA. Also, the regeneration with
310 different partial pressures of oxygen is analyzed.

311 3.4.1. Reactivity towards oxygen uncoupling

312 To analyze the oxygen release, Figure 2 shows normalized conversion vs. time curves for the different oxygen
313 carriers when decomposed in N₂ and oxidized with air at 950 °C. In general, the oxygen release rate is
314 increased as the Mn content in the oxygen carrier is increased; see Figure 2(a). Also the maximum oxygen
315 carrier conversion increased with the Mn content.



316 **Figure 2.** Solids conversion vs. time during (a) oxygen uncoupling in N₂, and (b) oxidation in air at 950 °C.
317

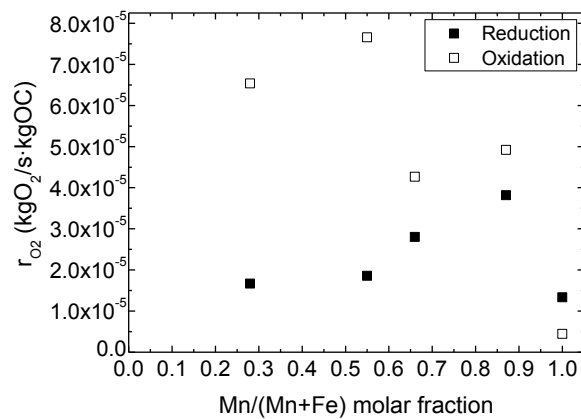
318

319 However, the oxygen carrier conversion was limited by the conversion reached during the oxidation stage; see

320 Figure 2(b). For screening purposes, the oxidation was carried out at 950 °C in air to force the formation of
321 bixbyite as much as possible. The oxidation rate considerably slowed with the reaction progress, not achieving
322 the full transport oxygen capacity at this temperature (950 °C) for each redox system, in accordance with
323 results shown in Table 2. The rate of oxygen transference per unit of mass, r_{O_2} , was a function of both the
324 conversion-based reaction rate and the oxygen transport capacity:

$$325 \quad r_{O_2} \left(\frac{kgO_2}{s \cdot kgOC} \right) = R_{OC,th}^{ou} \cdot \frac{dX_{ou}}{dt} \quad (4)$$

326 Figure 3 shows that the oxygen transference rate was higher for oxidation than for reduction, excepting for
327 MnTi7. The oxygen transference rate during reduction, i.e. oxygen release, is in the $1 \cdot 10^{-5}$ to $4 \cdot 10^{-5}$ kgO₂/s per
328 kg of oxygen carrier, with Mn87FeTi7 showing the highest reaction rate. These values can be compared to the
329 oxygen transference rate values of about $1 \cdot 10^{-3}$ kgO₂/s per kg of highly reactive Cu-based materials [36,37]
330 and about $3.5 \cdot 10^{-4}$ kgO₂/s per kg of promising CaMnO₃ based materials [31,38].



331

332 **Figure 3.** Instantaneous oxygen generation rate, r_{O_2} , for the different oxygen carriers at 950 °C.

333 3.4.2. Reactivity towards reduction with H₂, CO and CH₄

334 Figure 4(a)-4(c) shows the conversion vs. time curves for the different oxygen carriers when reduced with
335 CH₄, CO and H₂. All the oxygen carriers analyzed react faster with H₂ than with CO and CH₄, in spite of the
336 concentration of H₂ is 3 times lower than the one corresponding to CO or CH₄. In addition, the reduction
337 degree depended on the given Mn/(Mn+Fe) ratio and the reducing gas considered. Thus, decreasing the Mn
338 content results into lower conversions, except for the FeTi7 carrier due to further reduction of magnetite to
339 wüstite. Nevertheless, further reduction of magnetite is not of interest for CLC system based on

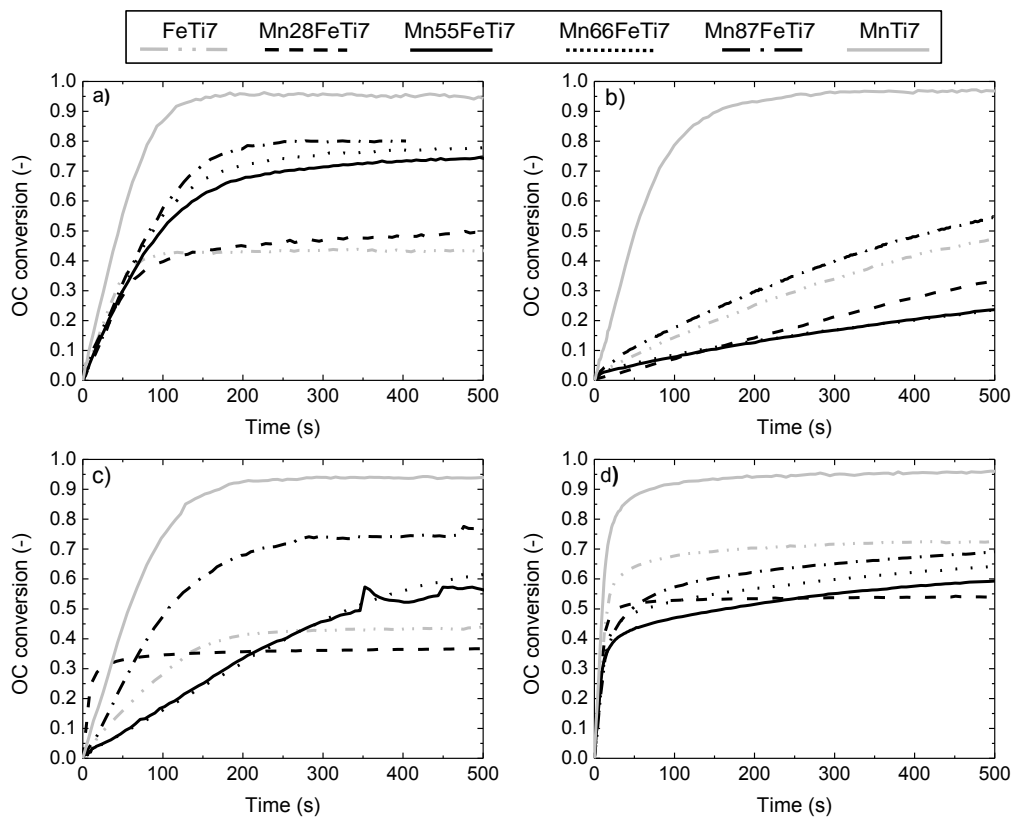
340 interconnected fluidized bed reactors [32], and only the part of the curve corresponding to reduction to Fe_3O_4 ,
 341 i.e. $X_{red} < 1$ for FeTi7, was here considered.

342 To go further into the evaluation of both reduction and oxidation reaction rates, the normalized rate index was
 343 calculated as [39]:

$$344 \text{ Rate index } \left(\frac{\%}{\text{min}} \right) = 60 \cdot 100 \cdot R_{OC,th}^t \cdot \left(\frac{dX_i}{dt} \right)_{norm} \quad (5)$$

345 $\left(\frac{dX_i}{dt} \right)_{norm}$ being the normalized rate calculated for a partial pressure of 0.15 atm for fuel gases and 0.10 atm

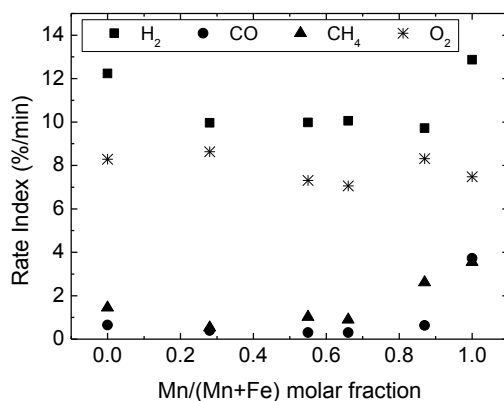
346 for oxygen.



347
 348 **Figure 4.** Oxygen carrier conversion with time during reduction with: a) H₂ (5% H₂ + 40% H₂O), b) CO (15%
 349 CO + 20% CO₂) and c) CH₄ (15% CH₄ + 20% H₂O), and oxidation with: d) air, at 950 °C.

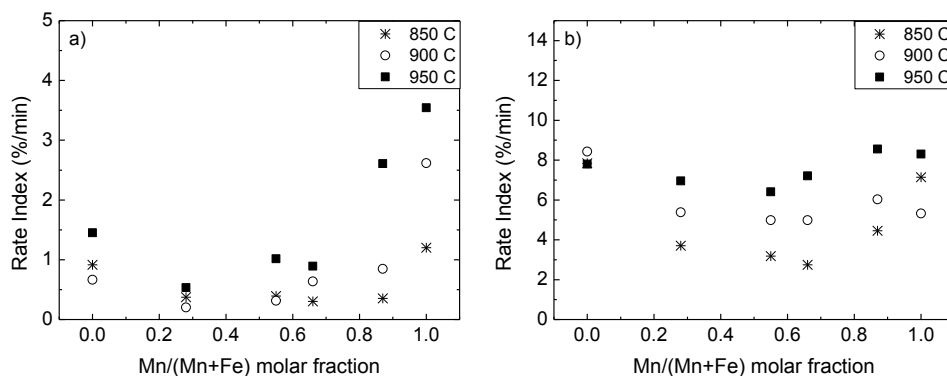
350
 351 Rate index values obtained for reduction reactions are shown in Figure 5. Independently of the Mn/(Mn+Fe)
 352 ratio considered, the normalized rate index is considerably higher for reduction with H₂ than with CO or CH₄,
 353 as already noticed from the results shown in Figure 4. Considering the influence of the Mn/(Mn+Fe) ratio, the
 354 highest rate index values were found in the extremes, i.e. for Mn- or Fe-rich materials. In general, lower

355 values of rate index were found for materials with Mn/(Mn+Fe) ratios between 0.2 and 0.9, but interestingly
356 these materials showed magnetic properties, In any case, rate index values for H₂ were similar to those of
357 promising low cost materials for iG-CLC, e.g. ilmenite, Fe-ESF and Tierga Fe-ore [40,41], but lower rate
358 index values were found for Mn-Fe mixed oxides with CH₄ and CO.



359 **Figure 5.** Normalized rate index for the reduction reactions of the different oxygen carriers with CH₄, CO and
360 H₂, and their subsequent oxidation with air. T = 950 °C, P_{ref} = 0.15 for reduction gases and P_{ref} = 0.10 for air.
361

362
363 The reaction kinetics and thermodynamic restrictions are very dependent on temperature. In order to analyze
364 to what extent the reactivity are affected by the temperature, Figure 6(a) shows the normalized rate index
365 during reduction with CH₄ at 850, 900 and 950 °C. The effect of temperature on the reduction rate is low for
366 the oxygen carriers with low Mn conten (Mn/(Mn+Fe)=0.28-0.66), and increases as the Mn concentration is
367 increased (Mn/(Mn+Fe)≥0.87), with a promoted rate of reduction by increasing the reaction temperature. At
368 850 °C the rate of reduction is considerably low for all the oxygen carriers studied and therefore higher
369 temperatures (≥900 °C) would be needed in the fuel reactor for a good performance of these redox systems.



370

371 **Figure 6.** Normalized rate index for the (a) reduction and (b) oxidation reactions of the different oxygen
372 carriers with CH₄ and air, respectively, at 850, 900 and 950 °C. P_{ref} = 0.15 for CH₄ and P_{ref} = 0.10 for O₂.

373

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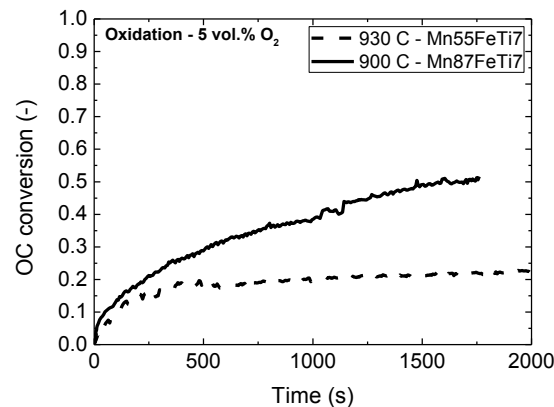
375 **3.4.3. Reactivity towards oxidation**

376 The oxidation of manganowustite to spinel phase is not problematic, and shows fast reaction kinetics for all
377 the cases analyzed; see Figures 4(d) and 5. The most pronounced oxygen carrier regeneration is produced
378 within the first 20 seconds. Eventually, the conversion reaches the value attained in the previous reduction
379 cycle indicating the potential of these carriers for regeneration in the air reactor under these conditions. In
380 addition, the oxidation rates are considerably high in the 850-950 °C temperature range; see Figure 6(b). The
381 rate index values for the oxidation of Mn-Fe mixed oxides are higher than those showed by other materials
382 tested, such as ilmenite or Fe-ore [40,41]. Therefore, this step is not a determining factor when deciding the
383 optimal composition of the oxygen carrier selected.

384 The oxidation of spinel to bixbyite phase following reverse of reaction R1, which is of interest in CLOU, is
385 highly dependent on the reacting temperature and the oxygen concentration [29]. A preliminary evaluation
386 was done using air for oxidation. Thus, oxidation in air was relatively high during the first 100 seconds and
387 are almost independent of the Mn:Fe ratio considered; see Figure 2(b). In this case, the instantaneous oxygen
388 generation rate (see Figure 3) shows the highest values for Mn/(Mn+Fe) ratios in the 0.28-0.55 interval and a
389 minimum for the Mn rich material. However, the complete oxidation to bixbyite was not allowed in air at 950
390 °C; see $X_{ou,exp}$ values in Table 2. Remarkable effect of the Mn:Fe ratio was found on conversion achieved, with
391 higher maximum conversion values as the Mn content is increased. For the oxygen carrier with the highest
392 Mn conten (MnTi7) the oxygen uncoupling observed is due to the spinel to pyrophanite transformation
393 (reaction R3). Thus, these results indicate that after pyrophanite formation, the regeneration to spinel is
394 possible.

395 Considering the effect of the oxygen concentration on the bixbyite regeneration, the phase diagram in Figure 1
396 shows that materials with Mn/(Mn+Fe) ratios higher than 0.55 are not able to oxidize to bixbyite with a 5
397 vol.% O₂ at 950 °C. Thus, the air reactor should operate at lower temperatures for these materials. Thus, for

398 Mn55FeTi7 a temperature of 930 °C is required to be completely oxidized to bixbyite, and a theoretical
399 oxygen transport capacity of $R_{OC,th}^{ou} = 3.13$ wt.% is exploitable for CLOU. But a temperature lower than 850
400 °C is required to allow complete oxidation to bixbyite for Mn87FeTi7, while a temperature between 850 and
401 900 °C would allow a partial oxidation of spinel to bixbyite due to the existence of a relevant miscibility gap.
402 In this case, the usable oxygen transport capacity for CLOU, $R_{OC,th}^{ou}$, are 1.77 and 3.60 wt.% at 900 and 850 °C,
403 respectively. However, despite the favorable thermodynamics shown at 850 °C, the regeneration of
404 Mn87FeTi7 was not possible at this temperature due to slow kinetics. In this context, Figure 7 shows the
405 conversion vs. time curves during oxidation in 5 vol.% O₂ at 930 °C for Mn55FeTi7 and at 900 °C for
406 Mn87FeTi7. Mn87FeTi7 achieved higher conversion values for longer periods. But during the first seconds of
407 the oxidation period (< 300 s), the oxidation rate of both carriers was almost similar. Considering that the
408 mean residence time in the air reactor would be lower than 300 s, both Mn87FeTi7 and Mn55FeTi7 would be
409 able to be oxidized in the air reactor with a similar behavior at their respective optimal temperatures.



410

411 **Figure 7.** Conversion with time during oxidation with 5 vol.% O₂ at 900 °C with Mn87FeTi7 and
412 Mn55FeTi7.

413 4. Discussion

414 A comprehensive evaluation of physical and chemical properties of the materials prepared with different
415 Mn:Fe ratios is done regarding their capability to be used in *i*G-CLC and CLOU processes. All particles
416 showed high enough crushing strength values (above 4 N in most of cases) to be used as oxygen carrier in the
417 fluidized bed reactors of a CLC unit.

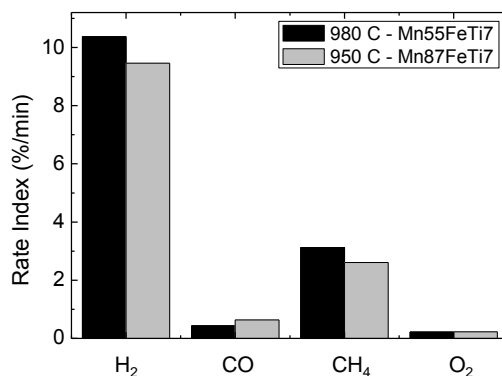
418 On the one hand, Mn28FeTi7, Mn55FeTi7 and Mn66FeTi7 showed high magnetic permeability values when

419 calcined at 1200 °C. In addition, similar reactivity with fuel gases was found for these materials. If the oxygen
420 uncoupling property is considered as well, bixbyite formation is favored for the Mn₅₅FeTi₇ material
421 regarding results on oxygen transport capacity and regeneration reactivity. Therefore, under the same
422 conditions for the rest of parameters, Mn₅₅FeTi₇ would be preferred among these materials to be used in the
423 CLOU process.

424 On the other hand, oxygen carriers with Mn/(Mn+Fe) molar ratios in the 0.87-1 interval showed better
425 reactivity towards CH₄, CO and H₂. However, only the Mn₈₇FeTi₇ showed soft magnetic properties after
426 calcination at 1300 °C; the MnTi₇ carrier is not magnetic. The oxygen uncoupling property of this material is
427 highly restricted by the oxidation conditions, as bixbyite formation requires a relatively high oxygen partial
428 pressure and/or low oxidizing temperature. Therefore, the Mn₈₇FeTi₇ would be selected to be used in coal
429 combustion in *i*G-CLC mode.

430 Following, the capabilities of selected materials, i.e. Mn₅₅FeTi₇ and Mn₈₇FeTi₇, to be used in *i*G-CLC
431 and/or CLOU is assessed. The optimal conditions in the *i*G-CLC process would include the operation of the
432 fuel reactor at the highest temperature possible. Considering the reactivity with fuel gases, Mn₈₇FeTi₇ shows
433 a clear advantage compared to Mn₅₅FeTi₇ to be used in the *i*G-CLC mode. Mn₈₇FeTi₇ shows also higher
434 reactivity and oxygen transport capacity for CLOU; see Table 2 and Figure 3. But some difficulties could be
435 expected for the bixbyite regeneration in the air reactor compared to Mn₅₅FeTi₇, which is mandatory to take
436 advantage of the oxygen uncoupling effect. Thus, more restricted conditions and lower temperature in the air
437 reactor would be required for Mn₈₇FeTi₇ (see Figure 7), which would have also influence on a lower
438 temperature in the fuel reactor due to the heat management of a CLC unit [42]. Considering the global
439 reaction in the fuel reactor is exothermic when bixbyite-spinel redox system is considered for CLOU [17,43],
440 the fuel reactor can operate at higher temperatures than the air reactor. Considering the optimal temperatures
441 for the air reactor showed above, fuel reactor temperatures of 950 °C for Mn₈₇FeTi₇ and at 980 °C for
442 Mn₅₅FeTi₇ seem reasonable. This option sacrifices the reaction rate with gases in order to exploit the oxygen
443 uncoupling capability. To evaluate the performance of these oxygen carriers at these fuel reactor temperatures,
444 Figure 8 shows the normalized rate index for the reduction with CH₄, H₂ and CO, as well as the instantaneous
445 oxygen generation rate, for Mn₈₇FeTi₇ and Mn₅₅FeTi₇ at 950 °C and 980 °C, respectively. At their

446 respective optimal temperatures, both carriers exhibit similar reactivity towards reduction with H₂, CH₄, CO
447 and oxygen uncoupling.



448 **Figure 8.** Normalized rate index (%/min) for the reduction of Mn55FeTi7 and Mn87FeTi7 with CH₄, H₂ and
449 CO, and the instantaneous oxygen generation rate (%/min), at 980°C and 950°C, respectively.
450

451

452 As a consequence of the results here shown, Mn55FeTi7 and Mn87FeTi7 materials are basically oxygen
453 carriers to be operated in *i*G-CLC mode. Note that reaction rate of oxygen generation by oxygen uncoupling
454 ($3.7 \cdot 10^{-5} \text{ s}^{-1}$ for Mn55FeTi7 at 980°C) are much lower than purely CLOU oxygen carriers such as Cu-based
455 materials [36,37]. However, even in this case, exploitation of the oxygen uncoupling capability would be very
456 beneficial, improving the performance of the CLC process via oxygen uncoupling in the so-called Chemical
457 Looping assisted by Oxygen Uncoupling (CLaOU) [19]. In addition, the Mn55FeTi7 oxygen carrier shows a
458 high magnetic permeability, $\mu = 8.3$. Therefore, the ferromagnetic behavior showed by Mn55FeTi7 would
459 allow an easy separation from ashes in the CLC process with coal. In this context, the results of this study
460 settle Mn55FeTi7 as the most promising oxygen carrier for coal combustion via CLOU. Another option to be
461 considered is to operate the air reactor with a higher air excess, which would allow an increase of both fuel
462 and air reactors temperature. The adequacy of the utilization of oxygen uncoupling will take place in future
463 work on continuous plant operation.

464 5. Conclusions

465 The present work accomplishes a screening of the performance of Mn-Fe-Ti based oxygen carriers, prepared
466 with a fixed 7 % wt. TiO₂ and different Mn/(Mn+Fe) molar ratios, ranging from 0 to 1. Materials were
467 prepared through physical mixing following by pelletizing by pressure, calcining, crushing and sieving in the

468 100-300 particle size interval. The potential of the resultant oxygen carrier particles for the Chemical Looping
469 Combustion process was determined theoretically through the prediction of the stable phases by
470 thermodynamics and calculation of the oxygen transport capacity, and the subsequent comparison to solid
471 phases found after characterization by XRD; and, experimentally through crushing strength, magnetic
472 properties and redox reactivity analysis at suitable temperatures for the iG-CLC and CLOU process, using a
473 thermogravimetric analyzer.

474 All the oxygen carriers prepared showed crushing strength values around 4-5 N. The magnetic permeability of
475 the oxygen carriers increased as the Mn content decreased, but neither the FeTi7 carrier nor the MnTi7
476 showed any magnetic property.

477 The oxygen carriers with Mn/(Mn+Fe) molar ratios in the 0.55-0.87 interval showed the maximum values of
478 either the oxygen uncoupling capacity and the oxygen transport capacity for gas-solid reactions. However, to
479 take advantage of the oxygen uncoupling capability, the oxidation conditions should allow the formation of
480 bixbyite in the air reactor. For highly Mn-rich materials, where this oxidation is very limited due to
481 temperature limitations, oxygen uncoupling was also observed via the formation of pyrophanite in the
482 presence of Ti.

483 Oxygen carriers with Mn/(Mn+Fe) molar ratios ≥ 0.87 showed the highest reactivity towards reduction gases
484 (CH_4 , CO and H_2) at 950°C. However, oxygen carriers with lower Mn content (i.e. Mn/(Mn+Fe) = 0.55)
485 showed similar reactivity during reduction at its optimal temperature, 980°C.

486 Therefore, considering the balance between reactivity and magnetic properties, the oxygen carrier with
487 Mn/(Mn+Fe) molar ratio of 0.55 would be very interesting for CLC with solids. In addition, regardless of
488 MnTi7 did not show neither magnetic properties nor significant O_2 release, the good reactivity exhibited by
489 this carrier with CO and H_2 would make it suitable for syngas combustion.

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