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# Towards solar iron metallurgy: Complete hydrogen reduction of iron ore pellets under a concentrated light flux

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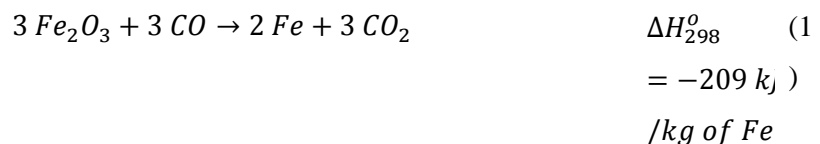
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## 32 I. Introduction:

33 Iron and steelmaking industry is responsible for large greenhouse gas emissions, representing  
 34 close to 6.7% of global anthropogenic CO<sub>2</sub> emissions [1]. Additionally, the ironmaking  
 35 process has a crucial importance in our society since steel is one of the most used materials  
 36 worldwide. To respect the +1.5 °C limit of Paris agreement, the emissions from the  
 37 steelmaking industry should drop from 1.85 t CO<sub>2</sub>/t steel to 0.6-0.3 t CO<sub>2</sub>/t steel by 2050 in a  
 38 perspective of a 38% production growth [2]. The most used route to produce steel is the  
 39 integrated route, which consists in transforming iron ore (mainly composed of hematite and  
 40 small amounts of magnetite and other mineral oxides) into liquid pig iron (iron-carbon alloy  
 41 containing up to 5% of carbon) using coal. Some carbon is then removed from pig iron in an  
 42 oxygen furnace, leading to steel. This route produces alone 71% of the total crude steel used  
 43 worldwide and emits approximately 2.2 tCO<sub>2</sub>/t steel [3]. Another well-known and largely  
 44 used way to produce iron is direct reduction, which consists in a solid-state reduction of iron  
 45 ore by different reducing gas (CO and/or H<sub>2</sub>) at a temperature around 950 °C. The reducing  
 46 gases mainly originate from coal and natural gas, but can also be produced by biomass  
 47 pyrolysis [4]. When the reducing agent is carbon monoxide, the reaction contributes to  
 48 greenhouse gas emissions as shown in Equation (1) [4]:



49 The direct reduced iron (DRI) is then melted with carbon in an electric arc furnace to form  
 50 steel. Globally, direct reduction route leads to lower emissions than the integrated one: 1.95  
 51 tCO<sub>2</sub> / t steel and 1.4 tCO<sub>2</sub>/ t steel for the coal-based and the gas-based route, respectively [3].

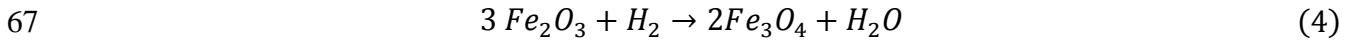
52 Industries and laboratories have investigated several routes to reduce the greenhouse gas  
 53 emissions of the ironmaking processes. For the integrated route, reduction of the amount of  
 54 coke used, optimization of the reducer/ore ratio, recycling of the exhaust gas, improvement of  
 55 the upstream process (coking, smelting) are pathways to diminish the ecological weight of the  
 56 process [5]. Additionally, Suopajarvi *et al.* have shown that coal consumption and  
 57 consequently CO<sub>2</sub> emissions could be significantly reduced when partly substituting coal with  
 58 charcoal, torrefied wood or bio-synthetic natural gas [6]. Unfortunately, they also noted that

59 the production cost of such reducers would be a drawback for this technology. Moreover, the  
60 availability of the biomass resource would also be a serious issue.

61 For the direct reduction route, the most studied alternative is based on the use of hydrogen as  
62 reducing agent, which forms water as by-product. The reaction goes through different  
63 intermediates according to temperature as shown by the Chaudron phase diagram (see  
64 Supplementary Information (S.I.) Figure A-1) [4]. For temperatures below 570 °C, magnetite  
65 (Fe<sub>3</sub>O<sub>4</sub>) is formed before reduced iron [7]:



66 For temperatures higher than 570 °C, both magnetite and wustite (FeO) are formed [7]:



68 The reduction of wustite [Equation (6)] is the limiting step of the overall kinetics of the  
69 reaction.

70 The use of hydrogen as a low-carbon reducer has already been studied, as reviewed by  
71 Heidari *et al.* [8]. Wagner *et al.* showed that the reduction rate rises with temperature [9].  
72 Choi and Sohn studied the high temperature (900-1500 °C) reduction of iron ore small  
73 particles (< 100 µm) and showed that at 1200 °C the particles were reduced over 90% in 1.6 s  
74 with around 1000% of H<sub>2</sub> excess. At 1300 °C, around 90% of the reduction was achieved in  
75 2.4 s with 240% of H<sub>2</sub> excess [10]. Hydrogen is also used as reducing agent by companies  
76 working with the DRI process (*e.g.* Midrex [11]) and is planned to be more and more used  
77 (Hybrit project [12]). Ammonia has also been studied as a carbon-free reducer [16, 17, 18].  
78 For instance, Hosokai *et al.* showed that 0.27 g of pure hematite could be reduced completely  
79 at 600°C and 700°C after respectively 2h and 1h.

80 However, the hydrogen route is intensive in electricity when green hydrogen – i.e. produced  
81 by electrolysis using low-carbon electricity – is used. Indeed, the energy consumption to  
82 produce iron from green hydrogen represents 3.5 MWh<sub>e</sub>/t steel, with approximately 70% due  
83 to the production of green hydrogen itself [14]. As comparison, the integrated route uses 356  
84 kWh<sub>e</sub>/t steel and the DRI route 1.2-1.3 MWh<sub>e</sub>/t steel [3]. Among the later, the melting of the

85 DRI in the EAF furnace is the main item of consumption : it has been estimated to 918 kWh/t  
86 of steel by Fan *et al.* [3] and to 753 kWh/t by Vogl *et al.* [14]. Provided that 1.9 Gt of steel  
87 were produced in 2023 [15], maintaining the current level of iron production with green  
88 hydrogen would require 6 622 TWh of low-carbon electricity. This value corresponds to 22%  
89 of the electricity produced worldwide the same year (29 471 TWh in 2023) [16]. Providing  
90 such an amount of low-carbon electricity in a few decades is a huge challenge, to say the  
91 least.

92 As already mentioned above, another way to reduce emissions in the integrated or DRI route  
93 would be to change the classically used coke to biochar or biogas. However, biomass  
94 resources – as low-carbon electricity – are also limited and should be shared with other  
95 industrial sectors. So decarbonating iron production at our current level of production in a few  
96 decades seems difficult; with a view to a sustainable future, it might even not be desirable to  
97 keep such a high level of production in reasons of the global upstream and downstream social  
98 and environmental impacts of iron (mining, artificialisation, infrastructures, ...). Thus, an  
99 approach based on a more efficient steel use, on reuse and on low contamination recycling  
100 would lead to a decreased level of production, complementary of any low-carbon process.  
101 Sufficiency and lifestyle changes are also additional ways to induce a significant production  
102 decrease [17].

103 To efficiently reduce the CO<sub>2</sub> emissions of the DRI process, the contributions originating of  
104 both heat production and chemical reaction should be tackled. In this work, it will be studied  
105 the use of concentrated light flux to provide heat and hydrogen as reducer.

106 In this perspective, the use of solar concentrated power as a heat source has been studied  
107 before. For instance, in 1991, Steinfeld and Fletcher studied direct carbothermic reduction  
108 (reduction of hematite with solid carbon) under concentrated solar flux and were able to reach  
109 78% of reduction yield at 2000 K [18]. In 1993, Steinfeld and Kuhn studied the reduction of  
110 magnetite (Fe<sub>3</sub>O<sub>4</sub>) under concentrated solar flux and methane atmosphere [19]. They were  
111 able to reach 68% of reduced iron from a dry mixture of magnetite and silica after heating it  
112 during 15 minutes at 1273 K in a solar oven. Fernández-González *et al.* studied the smelting  
113 reduction of hematite (Fe<sub>2</sub>O<sub>3</sub>) with carbon under solar flux and the one of sintered ore with  
114 coke breeze [20]. They were able to reach a maximum of 5.6% of reduced iron in the hematite  
115 sample at 1353 °C and 29.7% in the sintered oxide one, reaching a temperature high enough  
116 to melt the upper layer of the sample.

117 So far, only two studies of the combined use of hydrogen and solar energy for direct reduction  
118 has been recently published : Li *et al.* [21] and Abanades *et al.* [22]. First, Li *et al.* studied the  
119 reduction under hydrogen of hematite fine particles in an indirect solar heating reactor  
120 equipped with a vibrant fluidized bed and were able to reach 98% of reduction in 50 min. -  
121 Secondly, Abanades *et al.* studied the reduction of iron ore power (from 0.25 to 2 mm in  
122 diameter) in backed bed under solar irradiation. They showed a complete reduction after 15  
123 min at 1000 °C and showed that the quantity of powder in the backed bed had an influence on  
124 the reduction rate.

125 The experiments described hereafter differs from both studies. First, they were conducted on  
126 the exact same pellets as the one used in industrial processes whereas iron ore power or  
127 hematite powder was used in the previous studies. Secondly, here, the reduction was realized  
128 by exposing directly the sample to concentrated light flux (direct reactor) where Li *et al.* and  
129 Abanades *et al.* used an indirect reactor. Moreover, in this work, several experimental  
130 parameters of the reduction were varied in order to understand the reaction mechanisms and  
131 to reach high reduction yield in a short time.

132 This article is organised as follows. First, test bench, samples and methods are described.  
133 Second, the influence of various parameters (pressure, time, power) is shown. Third, results to  
134 optimize the reduction time and yield are presented, as well as an energy analysis. Finally, the  
135 results are discussed before providing a general conclusion.

## 136 II. Materials and methods:

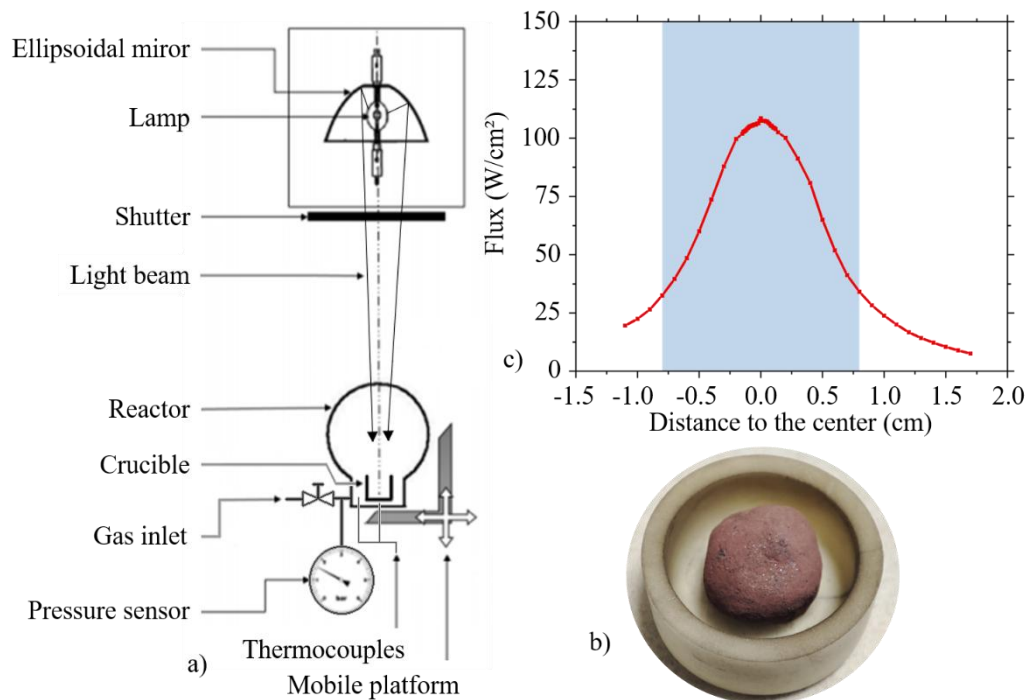


Figure 1: (a) Schematic of the solar simulator bench used for the experiments. (b) Detail picture of the crucible holding a typical iron ore pellet (crucible A). (c) Light flux measurement over the crucible radius.

137 Experiments were realised using the experimental set-up shown in Figure 1-a. The bench is  
 138 composed of a Xe lamp (electric power of 1600 W<sub>e</sub>, 9 mm long arc) placed at the focal point  
 139 of an ellipsoidal mirror (XE1600, Sciencetech). The total light power at the output of the  
 140 reflector was calculated by performing a series of flux measurements (flux meter TG1000-0,  
 141 Vatell) over the complete radius of the light spot (see Figure 1-c). The total power is then  
 142 obtained after an integration of the curve. An alumina crucible (diameter: 16 mm, Sceram  
 143 ceramics) is placed inside a 0.6 L borosilicate glass reactor resistant to 10 bars of gas  
 144 pressure. This reactor is placed on a mobile XY platform (Thorlabs – two XR25C mounted at  
 145 90°), the displacement over the Z axis being realised with a homemade rack and pinion. The  
 146 crucible was placed a few centimetres below the focal point to be more homogeneously  
 147 illuminated. At this position, a power of about 140 W was measured, corresponding to a mean  
 148 flux of 70 W/cm<sup>2</sup> (see Figure 1-c). The temperature is measured with two K-type  
 149 thermocouples: one placed right under the crucible and the other one in the atmosphere but  
 150 not directly under the light flux. The pressure inside the reactor is measured with a sensor  
 151 (type 520, Huba control). Both temperature and pressure are acquired in real-time using a  
 152 homemade Labview program. Before each experiment, the reactor is successively vacuumed  
 153 and refilled three times with the reducing gas before setting it at the required pressure; each

154 experiment was thus performed under a static atmosphere condition. The hydrogen is  
155 produced by water electrolysis using a H<sub>2</sub> generator (F-DGSi, model WM-H2, O<sub>2</sub> < 0.01 ppm  
156 and moisture < 1 ppm). After the experiment, samples are left to cool before being placed in  
157 the ambient atmosphere and analysed.

158 The samples used for the experiments were industrial grade iron ore pellets used in the DRI  
159 process, courtesy of the ironmaking company ArcelorMittal (Metz, France). They are mainly  
160 composed of iron oxide (> 97%) with a small amount of standard impurities (Si, Al, Ca,  
161 MgO). The composition provided by the furnisher can be found in S.I. Table B-1.

162 First, reduction experiments under different conditions were realised by placing the sample in  
163 a 2.0 cm<sup>2</sup> area crucible (crucible A, see Figure 1-b) under several pressures and exposure  
164 times. The pressure studied were 1, 2 and 4 bars to determine which minimal pressure was  
165 acceptable to ensure the sample reduction and to prevent its re-oxidation by the water vapor  
166 produced during reduction [19], [23]. The maximum of 4 bars allows to be far from the safety  
167 limit of our glass reactor even at the end of the experiments since pressure increases all along  
168 the reduction process. Additionally, the longest exposure time of 28 minutes was chosen after  
169 preliminary experiments showing a significant reduction yield of iron ore powder after this  
170 duration. For these series of experiments, only the quantitative advancement of the reduction  
171 was studied and not the reduction yield itself. To this end, the samples were dried before the  
172 experiments at least 1 week into a proofer at 110 °C and weighted before and after reduction.  
173 This allowed to access the oxygen loss value, which is a good indicator of the quantitative  
174 advancement of the reduction.

175 Other experiments were realized to observe specifically the way the reduction proceeds inside  
176 the samples. Firstly, the exposure time was varied from 0.5 min to 16 min under 60 W/cm<sup>2</sup>.  
177 Secondly, 4 min reductions under different mean light density flux values were performed  
178 (46 W/cm<sup>2</sup>, 54 W/cm<sup>2</sup>, 60 W/cm<sup>2</sup>, 65 W/cm<sup>2</sup> and 75 W/cm<sup>2</sup>). For each varied parameter,  
179 measurements were realised on two series of pellets. In each series, their masses differed by  
180 less than 5% (see Table 1). The pellets were cut in half vertically and observed using optical  
181 microscopy. The surface of the iron phase compared to the oxide one was measured using  
182 ImageJ software by contouring each surface. EDX mapping was also realised using a SAMx  
183 detector on a JEOL 6060-LA SEM.

184 *Table 1 : Conditions of the performed reduction experiments.*

Varied	Variation	Samples	Masses (g)	Mean	H <sub>2</sub>	Note
--------	-----------	---------	------------	------	----------------	------



parameter				diameter (cm)	pressure (bar)	
<b>Exposure time</b>	0.5 to 16 min	Serie 1	2.11 to 2.19	1.05	2	60 W/cm <sup>2</sup>
		Serie 2	2.29 to 2.38	1.14	2	
<b>Light power density</b>	46 to 75 W/cm <sup>2</sup>	Serie 3	2.18 to 2.25	1.13	2	4 min reductions
		Serie 4	2.33 to 2.38	1.13	2	

185

186 Finally, the reduction yield of the process was assessed and different ways were tested to  
187 reach high enough values with respect to industrial requirement (approx. 93-94% for the DRI  
188 process [24], [25]). To this end, the initial shape of the raw materials was changed into gravel  
189 or disks, by either grinding the pellet or by cutting it using a precision circular saw with  
190 diamond blade (Buehler IsoMet low speed saw; Buehler – n°114254). Experiments on disks  
191 were conducted using a specifically designed crucible (crucible B, see S.I. Figure E-3): it  
192 favours gas circulation by avoiding a direct contact between the bottom surface of the disk  
193 and the crucible; it also avoids shading the disk by the crucible walls.

194 To measure the reduction yield, samples were transformed in powder using mortar and pestle,  
195 and then analysed using an X-ray diffractometer (PANalytical Empyrean 45 mA 35 kV, Co).  
196 For experiments on pellets, the quantity of analysed powder represented between 1/4 and 1/3  
197 of the pellet. For experiments on gravels, all the gravels present in the crucible were  
198 transformed into a powder which was analysed. Afterwards, Highscore software was used to  
199 identify the phases within the sample; MAUD software was then used to realize Rietveld  
200 refinements on the diffractograms to access the mass percentage of each phase. When the  
201 refinements were used, the contribution of the residual peaks was less than 1%. Finally, the  
202 experimental reduction yield was calculated by dividing the mass of metallic iron after  
203 reduction by the mass of iron-containing phases in the sample before reduction, as shown by  
204 Equation (7).

$$Reduction\ yield = \frac{\%_{Fe(0)}}{\%_{Fe_2O_3} + \%_{Fe_3O_4} + \%_{FeO} + \%_{Fe(0)}} \# (7)$$

### 205 III. Results and discussion

206

207 III.1. Influence of pressure, exposure time and lamp power on reduction  
208 performances

209 Figure 2 presents the results of iron ore reduction under a solar simulated flux as a function of  
210 exposure time for different hydrogen pressures. The oxygen mass loss analysis was realised  
211 following the previously presented protocol. The interest of this analysis is to allow for a  
212 quick observation of the effect of experimental parameters on the reduction rate. At first sight,  
213 it can be observed in Figure 2 that the oxygen loss rises steeply during the first 4 min without  
214 significant influence of pressure. Afterwards and until 8 min the steepness of the curves  
215 lowers slightly but still without major influence of pressure. After 8 min, the curves split: the  
216 4-bar curve continues to rise with a decrease in the steepness; the 2-bar curve plateaus; the 1  
217 bar curve decreases. The splitting of the curves during the reaction is attributed to hydrogen  
218 consumption [26]; theoretically, to completely reduce one equivalent of  $\text{Fe}^{3+}$ , 1.5 equivalents  
219 of  $\text{H}_2$  are necessary. At the beginning of the reaction, the  $\text{H}_2$ :Fe ratios are 1.55:1, 2.35:1 and  
220 3.89:1 at 1, 2 and 4 bars respectively (the ratios were calculated using the iron oxide masses,  
221 the reactor volume and the stoichiometry of the reaction). Thus, at 1 bar pressure, there is only  
222 a small excess of hydrogen compared to the theoretical value. So, as the reduction progresses  
223 and because the experiments are realised in batch, the competition between the water vapor  
224 formed and the remaining hydrogen lowers the activity of the latter, as previously discussed in  
225 the literature [27]. The decrease after 8 min of the 1 bar curve is interpreted as a re-oxidation  
226 of the sample due to the presence of a large excess of water. This behaviour has previously  
227 been reported for magnetite at temperatures between 100 and 500 °C [18, 21].

228

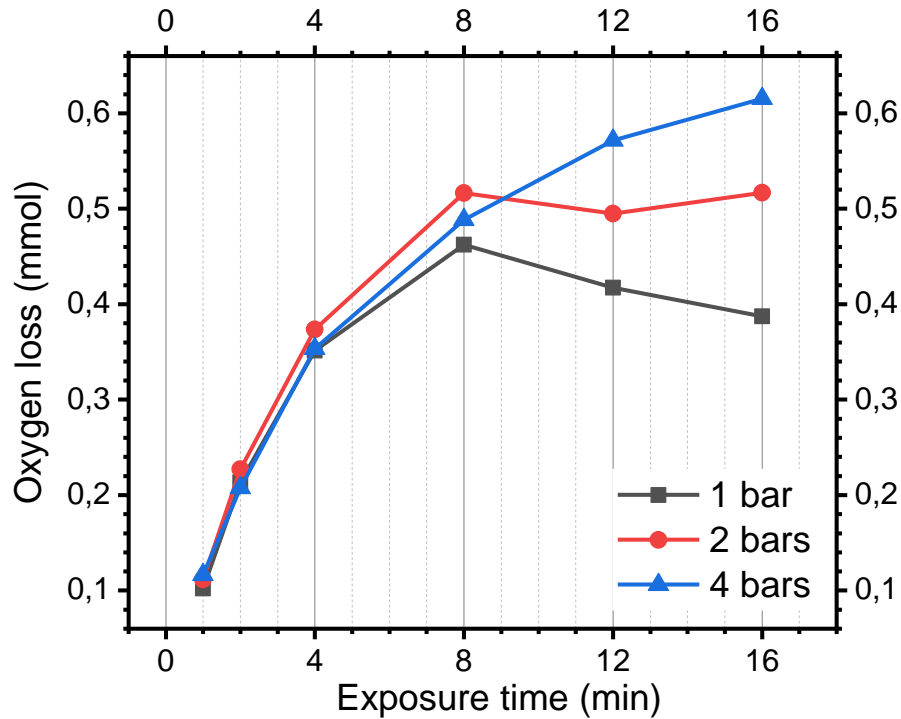


Figure 2: Oxygen loss as a function of the exposure time for various pressures of hydrogen (black: 1 bar; red: 2 bars; blue: 4 bars) after reduction of iron ore pellets under 60 W/cm<sup>2</sup>. Each point of the curves represents a complete experiment.

229 Since the light flux is concentrated onto the top of the sample, the conditions are drastically  
 230 different from a classic furnace. Therefore, it was decided to cut the reduced pellets in half (as  
 231 shown in Figure 3-a) to observe the progression of the reduction front. Figure 3-b and c show  
 232 the inside of two pellets exposed to the light flux during 2 and 7 min, respectively, the red line  
 233 representing the reduction front. In the pictures, two zones with very different colours are  
 234 observed. SEM observations coupled with EDX mapping show that the upper part (above the  
 235 red line) of the sample is iron whereas the lower one (under the red line) is iron oxide.  
 236 Quantitative analyses show that the transitions between the two materials occurs within ca.  
 237 0.5 mm (see S.I. Figures C-1). In a standard oven, the reduction of pellets is usually described  
 238 by the shrinking core model: the reduction starts from the external surface of the pellets and  
 239 goes towards the core of the pellets, thus creating an iron shell [28]. Here, the behaviour is  
 240 different: because of light irradiation, the reduction starts from the top of the pellet and grows  
 241 downwards, hence preserving the iron oxide in the shadowed side of the pellet. The reduction  
 242 being temperature dependent, this reveals the presence of a temperature gradient within the  
 243 pellet.

244

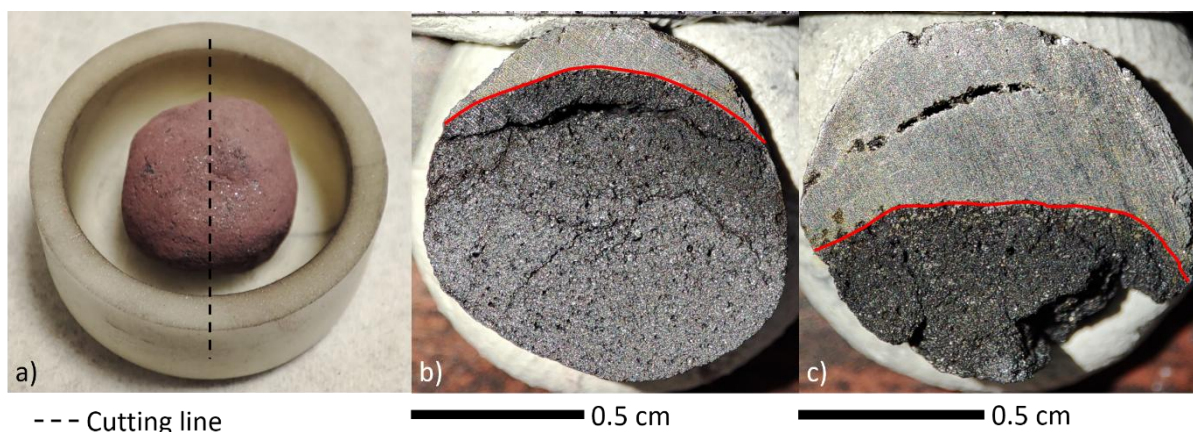


Figure 3: (a) Picture of a pellet in the crucible. The dotted line represents the profile on which the pellets were cut in half. Picture of a pellet after hydrogen reduction during (b) 2 min and (c) 7 min under 2 bars of hydrogen and 60 W/cm<sup>2</sup>. The pellet was cut in two after the experiments to perform this observation. The red line represents the reduction front with the reduced iron above and the iron oxides below. Samples were illuminated from the top.

245 To quantify this progression, the surface of reduced iron for an exposure time varying from  
 246 0.5 min to 16 min as well as the total surface of the pellets were measured (see Figure 4). The  
 247 surfaces were determined using the software ImageJ on images such as the ones shown in  
 248 Figure 3-b and Figure 3-c. The corresponding pictures are available in S.I. Figures C-2 and C-  
 249 3. Results show that the reaction rate follows an exponential decay tendency, plateauing or  
 250 strongly slowing down after 10 minutes, before the reduction is complete. These pictures can  
 251 also be used to estimate the reduced thickness per unit of time: it evolves from 2 mm/min at  
 252 the very beginning to 0.3 mm/min before the plateau (between 7 and 10 min of reaction).  
 253 Such a behaviour has previously been observed in the hydrogen reduction of pellets in an  
 254 oven, and was interpreted as due to the slower diffusion rate of hydrogen in the reduced iron  
 255 as opposed to the one in the porous oxide [29]. However, here, since the bottom of the pellet  
 256 is clearly not reduced, hydrogen keeps its capability to feed the reaction toward the reduction  
 257 front at the same rate. This result is therefore interpreted as resulting from a temperature  
 258 gradient appearing inside the pellet and will be discussed more thoroughly in section III.3.

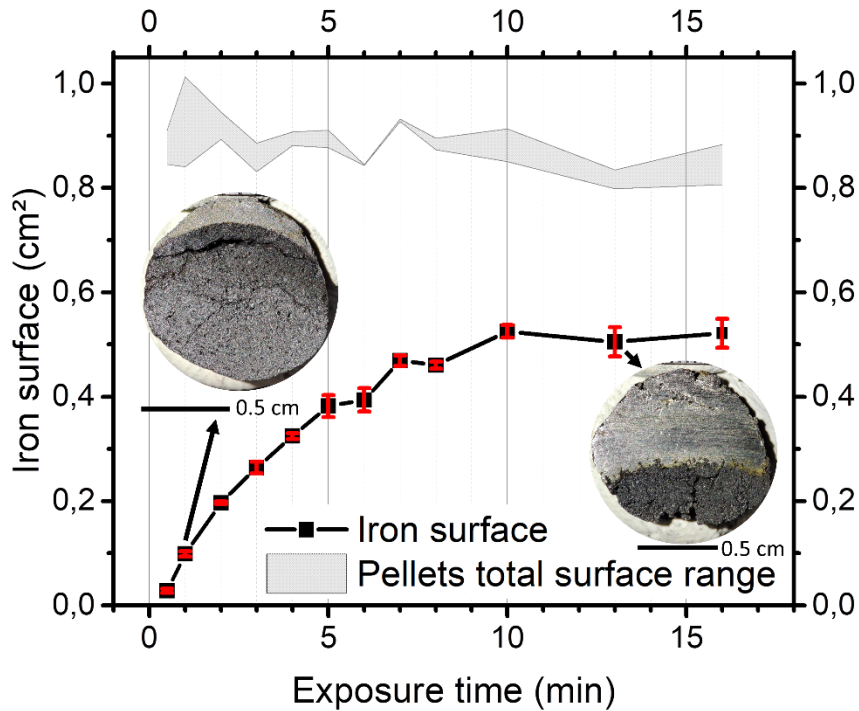


Figure 4: Iron surface evolution as a function of exposure time after the reduction of pellets under 2 bars of hydrogen and 60 W/cm<sup>2</sup> (square dots). The black line corresponds to the iron surface averaged over the two series, and the error bar to the standard deviation. The total surface of each of the two pellets used to measure one point is indicated as two grey-filled curves. Pictures of cut samples exposed for 2 min and 13 min are shown as insets.

259 Figure 5 shows the evolution of the iron surface as a function of the light flux density for 4  
 260 min of reduction under 2 bars as well as the total surface of the pellets. The later were cut as  
 261 shown in Figure 3-a and corresponding pictures are shown in S.I. Figures D-1 and D-2. The  
 262 surfaces were here again determined using the software ImageJ. As expected, the reduced  
 263 surface increases with lamp power, evidencing the influence of temperature on reduction rate.

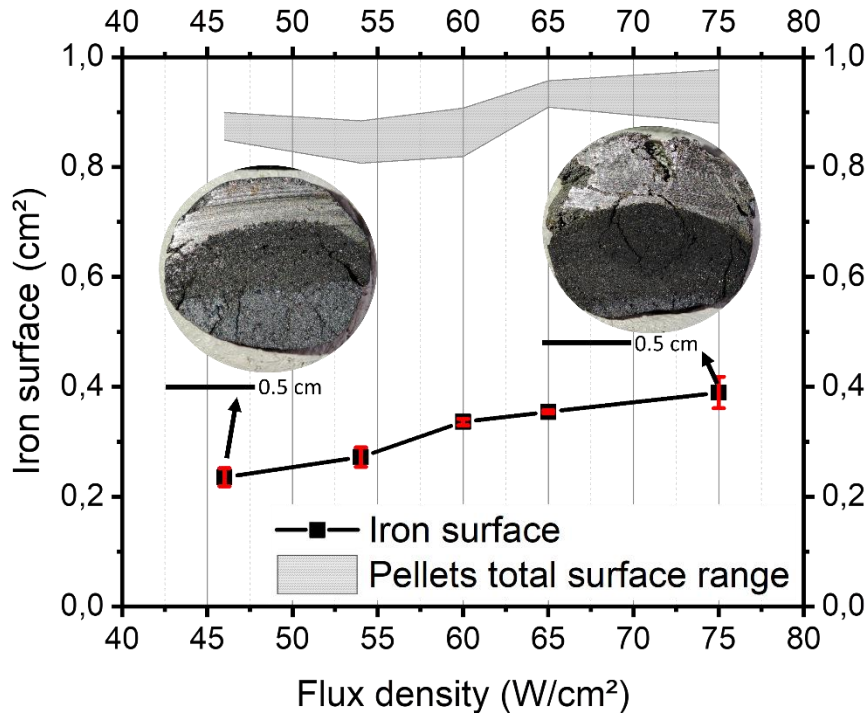


Figure 5: Iron surface after 4 min reduction under simulated solar flux and 2 bars of hydrogen for several light flux density: 46 W/cm<sup>2</sup>, 54 W/cm<sup>2</sup>, 60 W/cm<sup>2</sup>, 65 W/cm<sup>2</sup> and 75 W/cm<sup>2</sup>. The total surface of the pellets is indicated as two grey-filled curves. The black line corresponds to the iron surface averaged over the two series and the error bar to the standard deviation. Pictures of cut pellets for 46 W/cm<sup>2</sup> and 75 W/cm<sup>2</sup> are shown as insets.

### 264 III.2. Optimization of reduction yield and kinetics

265 The reduction rates observed in these experiments were of the same order of magnitude as the  
 266 one found in the literature on hydrogen reduction [30], [31]. Nonetheless, in order to try to  
 267 reduce exposure times, experiments consisting in turning over the pellets one or three times  
 268 by 180° or 90°, respectively, were conducted. Similar experiments were also conducted on  
 269 gravel. In the latter case, they were only shaken until a majority of them were turned. For  
 270 experiments on both pellets and gravel, crucible A was used and the samples were allowed to  
 271 cool down before being manually turned over radially or shaken.

272 Finally, optimization was attempted on three types of samples in order to study the impact of  
 273 sample shape on the reduction yield and kinetics: i) pellets, ii) a single-layer of gravel of ca.  
 274 2.0 mm and iii) 2.0 (± 0.11) mm thick disks with different mean radius (7.7 mm, 5.9 mm and  
 275 4.5 mm). Since their thicknesses are similar, the disks are listed as function of their radius.  
 276 Pictures of the gravel and the disks are available in S.I. Figures E-1 and Table E-1  
 277 respectively. Table 2 summarizes the structural properties of the various samples (pellets,  
 278 gravel and disks), the experimental conditions, as well as the main results.

279 *Table 2: Structural properties, experimental conditions and main results in the series of*  
 280 *experiments aiming at maximizing the reduction yield (XRD quantification) under hydrogen*  
 281 *atmosphere. The lamp flux density was 60 W/cm<sup>2</sup>. A reactor with a constant volume of 0.6 L*  
 282 *was used. For the temperature, the one of the disks are not informative because of the specific*  
 283 *configuration of the experiments (cf S.I. Figure E-3).*

<b>Sample</b>	<b>Sample type</b>	<b>Initial mass (g)</b>	<b>Pressure (bar)</b>	<b>Total exposure time (min)</b>	<b>Reduction yield (%)</b>	<b>Wustite percentage (%)</b>	<b>Temperature under the crucible (°C)</b>	<b>Note</b>
<b>S1</b>	<i>Gravel</i>	<i>0.37</i>	<i>2</i>	<i>28</i>	<i>88.4</i>	<i>11.6</i>	<i>412</i>	
<b>S2</b>	<i>Gravel</i>	<i>0.31</i>	<i>2</i>	<i>28</i>	<i>94.7</i>	<i>5.3</i>	<i>389</i>	<i>Turned over once by approx. 180°</i>
<b>S3</b>	<i>Pellet</i>	<i>1.70</i>	<i>3.5</i>	<i>28</i>	<i>83.8</i>	<i>14.5</i>	<i>371</i>	
<b>S4</b>	<i>Pellet</i>	<i>1.71</i>	<i>3.5</i>	<i>28</i>	<i>97.3</i>	<i>2.7</i>	<i>380</i>	<i>Turned over once by approx. 180°</i>
<b>S5</b>	<i>Pellet</i>	<i>1.90</i>	<i>2</i>	<i>16</i>	<i>95.1</i>	<i>4.9</i>	<i>371</i>	<i>Turned over once by approx. 180°</i>
<b>S6</b>	<i>Pellet</i>	<i>1.92</i>	<i>2.4</i>	<i>17</i>	<i>99.0</i>	<i>1.0</i>	<i>351</i>	<i>Turned over thrice by approx. 90°</i>
<b>S7</b>	<i>Pellet</i>	<i>1.94</i>	<i>2.4</i>	<i>12</i>	<i>95.1</i>	<i>4.9</i>	<i>323</i>	<i>Turned over thrice by approx. 90°</i>
<b>S8</b>	<i>Disk</i>	<i>1.24</i>	<i>2</i>	<i>2</i>	<i>73.5</i>	<i>23.5</i>	<i>-</i>	<i>Radius: 7.70 mm</i>
<b>S9</b>	<i>Disk</i>	<i>0.71</i>	<i>2</i>	<i>2</i>	<i>96.0</i>	<i>3.9</i>	<i>-</i>	<i>Radius: 5.90 mm</i>
<b>S10</b>	<i>Disk</i>	<i>0.45</i>	<i>2</i>	<i>2</i>	<i>92.7</i>	<i>6.3</i>	<i>-</i>	<i>Radius: 4.50 mm</i>

284

### 285 III.2.1. Pellet reduction

286 Sample S3 is considered as the reference sample: a non-turned pellet exposed to the light flux  
 287 during 28 min under 3.5 bars of hydrogen. The temperature profile measured by the  
 288 thermocouple under the crucible shows a maximum of 371 °C at the end of the experiment  
 289 (see S.I. Figure E-2). The XRD diffractogram of the reference sample after reduction is  
 290 provided in S.I. Figure D-3. The reduction yield deduced from the refinement of the curve is  
 291 84%, which is too low for an industrial application. In order to improve the efficiency of the

292 process, the pellet was turned upside down after 14 min of reduction (sample S4), increasing  
293 the yield up to 97%.

294 Then, the possibility i) to reduce the exposure time and ii) to lower the hydrogen pressure was  
295 tested to see if it could still lead to an acceptable yield. Provided that no re-oxidation was  
296 observed at 2 bars for a pellet of around 2.83 g (see Figure 2), the pressure value was kept at  
297 2 bars or 2.4 bars depending of the pellet mass. As shown in Figure 3, a 7 min reduction is  
298 expected to be sufficient to reduce half the pellet. Sample S5 was therefore reduced during  
299 two sets of 8 min and was rolled over in between, leading to a reduction yield of 95.1%. Here,  
300 a difference between the highest temperature before (357 °C) and after (371 °C) the rolling  
301 over is observed. This small difference is probably due to the higher thermal conductivity of  
302 metallic iron compared to magnetite.

303 Finally, it was tested to rotate the pellet 3 times by approx. 90° and to expose it 4 min only  
304 between rotations. Samples S6 and S7 show reduction yields of 99.0 % and 95.8% for a total  
305 exposure time of 17 min and 12 min, respectively. The XRD diffractogram of sample S6 is  
306 available in Figure S.I. D-4. This evidences that rotating pellets under the concentrated light  
307 flux remarkably increases reduction yield and/or decreases reduction time. With regards to  
308 temperatures, as for sample S5, a difference in the reached temperature was observed between  
309 each phase of the experiment. For S6 the maxima were 313 °C, 329 °C, 351 °C and 348 °C;  
310 for S7 they were 302 °C, 315 °C, 323 °C and 322 °C. Here again, the general trend observed  
311 is attributed to the higher conductivity of metallic iron. For both samples, the temperature  
312 reached during the last part of the reduction is close to the temperature reached during the  
313 previous one. This could mean that the reduction is mostly complete after the third phase of  
314 the experiment.

315 One should note that the temperatures measured under the crucible are relatively low  
316 compared to the one allowing a fast and complete reduction [32]. However, it is important to  
317 keep in mind that the top of the pellet is directly illuminated so it reaches much higher  
318 temperatures. As example, during preliminary experiments, a pyrometer was used to measure  
319 the surface temperature of powder samples; it was saturated, which indicated temperatures  
320 higher than 900 °C. This issue will be fully discussed in section III.3.

321 XRD analysis of all the samples indicates that, when the reduction is well advanced, the  
322 sample is composed of iron and wustite only. This is the case for samples S2, S4, S5, S6, S7,  
323 S9 and S10. Nevertheless, for less reduced sample (S1, S3 and S8) the sum of wustite and

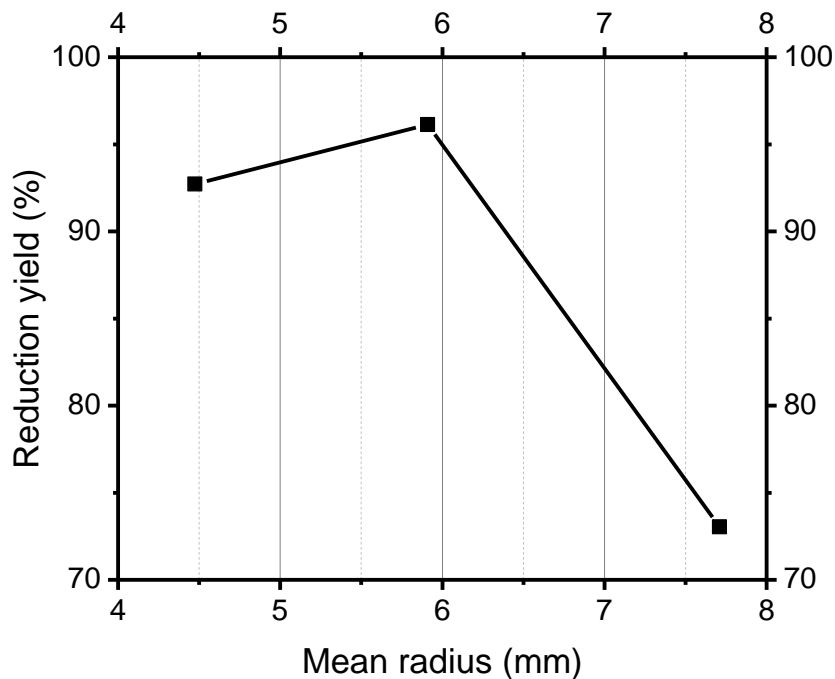


324 iron does not reach 100%, as shown in Table 2. The difference is the amount of magnetite in  
325 the sample. For these samples, the temperature was not high enough to fully reduce magnetite  
326 into wustite at the end of the experiment.

### 327 III.2.2. Gravel reduction

328 In order to lower the reduction time further, gravels were studied. A single layer of gravel was  
329 placed at the bottom of the crucible in order to ensure a complete exposition of the samples.  
330 The temperature profile during the experiment on non-turned gravels is available in S.I.  
331 Figure E-2. It can be observed that the highest temperature measured under the crucible was  
332 412 °C. XRD analysis evidences that the reduction yield was 88.4% after 28 min, the  
333 remaining oxide being wustite only (see Table 2). The second experiment was conducted with  
334 the same total exposure time but the gravels were shaken to turn them over after 14 min. A  
335 reduction yield of 95% was obtained, which fulfils industrial requirements but remains  
336 slightly lower than the one obtained on pellets. The relationship between the reduction yield  
337 and the measured temperature under the crucible will be discussed in section III.3.

### 338 III.2.3. Disk reduction



*Figure 6: Reduction yield of disks cut into industrial iron ore pellets as a function of their mean radius. The lamp flux density was 60 W/cm<sup>2</sup>, hydrogen pressure 2 bars and reduction time 2 min.*

339 Experiments conducted on pellets have shown that the reduction front has moved of ca. 2 mm  
340 after 2 min of exposure (see Figure 4). In order to optimize the process, disks with a thickness  
341 of 2 mm were cut and studied. The XRD diffractograms of samples S8, S9 and S10 after  
342 reduction are available in S.I. Figures E-4, E-5 and E-6, respectively. They show the presence  
343 of wustite and magnetite for S8 and S10, with more intense peaks in the case of S8. Figure 6  
344 shows the reduction yield of the disks after 2 min of exposure under 2 bars of hydrogen.

345 Large reduction yields of 92% and 96% were obtained for the disks with a radius of 4.75 mm  
346 and 5.90 mm, respectively, matching industrial requirements. However, a significant decrease  
347 down to 73% occurs for the sample with a radius of 7.70 mm. This decrease was assumed to  
348 be related to the non-homogeneity of the light flux in the disk plane. The area where the light  
349 flux is more intense is approximately 6 mm in diameter (see Figure 1-c) and can be identified  
350 as the whitest spot on the disk in S.I. Table E-1.

351 Overall, results from section III.2 show that the shape of the iron oxide materials significantly  
352 affects reduction time. It is possible to reach low reduction times and large reduction yields  
353 when the thickness is reduced. Here, the exposure time was divided by a factor of 14 when  
354 going from a 3D sample (single pellet exposed during 28 min) to a 2D one (disk exposed  
355 during 2 min). With respect to production rate, it increased by a factor 6 (0.06 g/min to  
356 0.36 g/min) when going from pellet to disk. This shows that the sample size and shape is a  
357 really important parameter in the performance of the process.

#### 358 III.2.4. Energetical efficiency

359 For the sake of comparison with future developments and other processes, the energy  
360 efficiency of the experiments was estimated. Efficiencies were calculated for the most  
361 representative cases: the pellet not turned over (S3), one of the pellets turned over (S7) and  
362 one of the disks (S9). The efficiency is defined as the theoretical energy required to heat and  
363 reduce the sample ( $E_{th}$ ) divided by the measured energy of the incoming light on the area of  
364 the crucible ( $E_l$ ), as explained in section II. Details on the calculations are provided in S.I.  
365 section G. Results are displayed in Table 3 for three temperatures ranging from 500 °C to  
366 1500 °C. The lower bound of this range corresponds to the lowest temperature allowing a  
367 complete reduction [33]. The upper bound is the fusion temperature of iron, which was never  
368 observed in any of our experiments. As expected for experiments performed on single objects  
369 in a non-thermally optimized reactor, the absolute efficiency values are quite low due to  
370 thermal losses by radiation and convection. However, the efficiency values increase by a

371 factor 6 (respectively 2.47) between S3 and S9 (respectively S7), evidencing quantitatively  
372 the interest in turning the pellets or using flat samples.

373 *Table 3 : Energy to heat and reduce the sample ( $E_{th}$ ), energy output of the simulator for each*  
374 *sample ( $E_l$ ) and energy efficiency as the ratio between the two values.*

Sample	$E_{th}$ (J)			$E_l$ (J)	Efficiency (%)		
	500 °C	1000 °C	1500 °C		500 °C	1000 °C	1500 °C
S3	971	1505	2039	201600	0.48	0.75	1.01
S7	1142	1751	2360	86400	1.32	2.03	2.73
S9	424	647	870	14400	2.95	4.49	6.04

375

### 376 III.3. Discussion

377 In the present section, three worthwhile points will be discussed: i) the temperature of the  
378 samples and its link with the reduction mechanism, ii) the scaling-up and potential  
379 industrialisation of such a process, and iii) the potential environmental interest of such  
380 process.

381 In the process studied here, the pictures of the cut pellets (see Figure 3-a and 3-b and S.I.  
382 Figures C-2, C-3, D-1 and D-2) show that the top of the pellet react first. One could think to  
383 two hypotheses to explain it, related to two different limiting factors: i) the temperature is  
384 larger at the top ii) the hydrogen does not reach easily the bottom of the pellet because it is  
385 sunk into the crucible. The second hypothesis has been excluded by performing an experiment  
386 where a pellet was hold onto the top of a small tripod, without any potential limit to hydrogen  
387 access. No change in the asymmetry of the reduction was observed, indicating that the  
388 limiting factor of the reduction process is temperature and not hydrogen diffusion around the  
389 pellet. The mechanism of diffusion of the hydrogen into the pellets is well known. It consists  
390 of a mass transfer of the gaseous hydrogen from the atmosphere to the surface of the pellet,  
391 followed by a diffusion of the gas through the macro- and micropores of the pellet to reach the  
392 active sites and reduce the oxide. The water vapor exits in the opposite way [32], [34].  
393 Additionally, when iron is formed around the sample, is it possible for hydrogen to diffuse  
394 through it [32], [34].

395 The clear frontier between the iron oxide phase and the iron(0) observable on all the pictures  
396 of cut pellets suggests the presence of an isotherm. The heat being provided by a direct  
397 illumination of the samples, having access to the temperature of this isotherm is not an easy

398 task as the temperature is expected to be strongly inhomogeneous. In experiments (not shown)  
399 where the top surface temperature of the sample has been measured using a pyrometer, values  
400 above the upper limit of our apparatus (900 °C) were obtained. Since the iron formed at the  
401 top of the pellet has not melt during any of the experiments, the temperature necessarily stays  
402 below 1500 °C (iron fusion temperature). On the other hand, the temperature measured just  
403 below the crucible (see Figure 1-a) after 28 min was 371 °C for the pellet (see S.I. Figure E-  
404 2). Thus, the temperature of the sample during the reaction lies between 1500 °C and this last  
405 value (371 °C). A rough estimate of the isotherm value is provided by combining the  
406 reduction front speed deduced from Figure 4 (2 mm/min at the beginning and 0.3 mm/min  
407 before reaction plateaus) and the experiments by Turkdogan et Vinters on the link between  
408 reaction temperature and size of pellets [35]. Using their data, it is estimated that the isotherm  
409 value varies from above 1000 °C at the beginning of the reaction to roughly 800 °C when the  
410 front speed equals 0.3 mm/min.

411 For the reduction of gravel, it might, at first sight, seems counter-intuitive that the temperature  
412 measured under the crucible was higher for the gravel than for the pellet (412 °C vs 371 °C; cf  
413 S.I. Figure E-2) whereas the reduction yield was smaller. This observation could be explained  
414 by several phenomena: i) a smaller temperature gradient due to the smaller size of the gravel,  
415 ii) an increase of thermal losses due to their larger surface-to-volume ratio, iii) an incomplete  
416 coverage of the crucible by the gravel so that parts of its bottom are directly exposed to the  
417 light flux, iv) a slow-down of the reduction rate for small samples as observed previously by  
418 Turkdogan et Vinters [35] and v) the heat stored by the gravel because of the smaller mass of  
419 the sample. Presently available experimental data are not sufficient to decide between these  
420 various hypotheses.

421 In term of scale-up, high concentration ratio technologies like dish or central receivers  
422 produce large enough temperature (> 800 °C) to allow hydrogen-based reduction. Given the  
423 results provided in the present article, it seems that two different types of reactors could be  
424 considered when working with a direct concentrated solar flux. Firstly, moving reactors like  
425 rotary kiln or rotating cylindrical reactor have already been studied for high temperature  
426 concentrated solar based thermochemical process [36], [37], [38]. This kind of reactor could  
427 allow for an advantageous random but continuous rotation of the pellets since it has been  
428 shown here that the slowing down of the reaction can be overcome when rotating the pellets.  
429 Secondly, in the view of the results with the disk samples, a new reactor in which a few  
430 millimetre-thick plates or chips of iron oxide would slide through the light flux on a conveyer

431 belt type reactor could potentially be interesting. These paths will be explored in future  
432 experiments.

433 Solar facilities only count on renewable energy during their use phase, which is a clear  
434 advantage compared to the fossil-fuel based equivalent processes. However, such solar  
435 facilities are generally much more material-intensive and therefore energy-intensive during  
436 their building phase than standard processes due to the necessity to produce and hold in place  
437 large areas of reflectors. The potential savings of CO<sub>2</sub> emissions and reduction of other  
438 environmental impacts of solar metallurgy should be studied using life cycle assessment. This  
439 will be the subject of future studies. As a preliminary study, our group has recently shown that  
440 cooking with parabolic solar cookers compared to standard devices strongly reduce  
441 impacts [39]. It is possible to provide a very rough range for the CO<sub>2</sub> emissions of a potential  
442 hydrogen-based solar process. As recalled in the introduction, a non-solar hydrogen-based  
443 electrically-produced steel consumes 3.5 MWh/t, among which 70% comes from the  
444 hydrogen production, the remaining being the energy to heat the ore and melt the DRI [14].  
445 With a low-carbon electricity mix such as the French one (86 gCO<sub>2eq</sub>/kWh [40]), the non-  
446 solar process would emit 301 kgCO<sub>2eq</sub>/t of steel. With a carbon intensive electricity mix such  
447 as the Australian one (943 gCO<sub>2eq</sub>/kWh [41]), the impact is more than ten times higher (3300  
448 kgCO<sub>2eq</sub>/t). These numbers have to be compared with the 522 kgCO<sub>2eq</sub>/t and 1048 kgCO<sub>2eq</sub>/t  
449 for the natural gas-based DRI and the coal-based, respectively. Concentrated solar power  
450 could replace the energy required to heat the ore and melt the DRI. The lower limit for the  
451 emissions is calculated by assuming that the solar concentrator would have zero emissions on  
452 its entire life cycle. This would drop the global emissions by 30%, reaching 210 kgCO<sub>2eq</sub>/t  
453 and 2300 kgCO<sub>2eq</sub>/t of steel for the French and the Australian electricity mix, respectively.  
454 These basic calculations show that combining concentrated solar power and green hydrogen  
455 production could drop the CO<sub>2</sub> emissions by at most a factor 5 compared to coal-based DRI. It  
456 also illustrates that using hydrogen with an electricity mix intensive in CO<sub>2</sub> is, on the contrary,  
457 of no interest.

## 458 IV. Conclusion

459 An alternative ironmaking process based on a concentrated light flux and hydrogen was  
460 studied using industrial iron ore pellets. It was first demonstrated that the hydrogen pressure  
461 does not have a strong impact on the dynamics of the process as long as the partial water  
462 vapor is kept well below the one of hydrogen. It is also shown that using direct light as the

463 heating source induces a reduction mechanism different from the shrinking core model  
464 describing standard processes: here, reduction starts from the illuminated surface towards the  
465 shadowed side, due to the large temperature gradient inside the sample. This naturally  
466 conducted us to perform experiments in which the pellets were rotated, consequently reducing  
467 exposure time. On single pellets, a reduction yield of 96% was reached in 12 min by turning  
468 them three times during the exposure. Other shapes of samples seem more suitable to a  
469 reduction under light flux than spherical pellets so gravels and flat disks were tested. If the  
470 former did not lead to significant improvement, results obtained on the latter were quite  
471 impressive: a 2 mm thick disk reached a 96% reduction yield after only 2 min of exposure.

472 **Our results show that, for an efficient process, two parameters need particular attention : i) the**  
473 **thickness of the sample (few millimetres depending on the power) and ii) the atmosphere**  
474 **pressure ( $H_2:Fe$  ratio needs to be at least 2.35:1) to avoid the re-oxydation. Additionally, it is**  
475 **also shown that energy efficiency increases with both pressure and power. With these**  
476 **considerations, for an optimized reactor, flat foils or chips of iron ore placed under the solar**  
477 **flux might be a path to envisage. Optimizing such a process requires further simulations of the**  
478 **gas diffusion as well as the temperature distribution into the sample. These points are**  
479 **currently being studied by collaborators [42].** Once the reactor set and the process optimized,  
480 it will be mandatory to perform life cycle assessments following several scenarios to study the  
481 potential ecological advantage of this process.

482 The scale at which such a process could be advantageously envisaged is hard to determine. In  
483 our view, such a solar process could only make sense in a society that seriously considers  
484 sufficiency as a way to preserve human life as we know it as long as possible on our planet.  
485 The “right” scale for this process should therefore be determined by considering the  
486 geographical distribution of the production units and the global production level.

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